THE CYCLODEXTRIN-QUINONE INCLUSION COMPOUNDS IN AN AQUEOUS SOLUTION AT 77 K. I. 9,10-ANTHRAQUINONE SULFONATES AND 1,4-NAPHTHOQUINONES

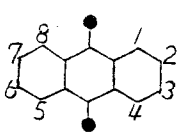
A. Kuboyama and S. Y. Matsuzaki
National Chemical Laboratory for Industry
Tsukuba Research Center
Yatabe, Ibaraki 305
Japan

ABSTRACT. The complex formation between cyclodextrins (α-,β-,γ-CD's and dimethyl-β-CD) and quinones (three 9,10-anthraquinone sulphonates and two 1,4-naphthoquinones) in the water-ethylene glycol 1:1 mixture solution at 77 K was investigated using the nπ* phosphorescence spectra and their excitation spectra and lifetimes of the quinones. It was concluded on the basis of the experimental results that the complexes have various structures according to the CD-quinone combination used. Vitamin K_3 was found to form the photodimer very efficiently in the presence of γ-CD. The assumed CD:quinone ratios of the complexes are given.

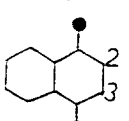
1. Introduction

Heretofore, few studies on the cyclodextrin-quinone inclusion compounds have been reported [1,2]. Previously, we studied the nπ* phosphorescence spectra of various p- and o-quinones in organic solvents at 77 K [3], and recently those of 9,10-anthraquinone (AQ) sulfonates in an aqueous solution at 77 K [4]. In this work, the complex formation between CD and AQ sulfonates and 1,4-naphthoquinones in an aqueous solution at 77 K was investigated using the nπ* phosphorescence spectra of the quinones.

2. Materials and Methods



(AQ)



(NQ)

All the quinones used were purchased from Tokyo Kasei Kogyo Co. Sodium AQ-2-sulfonate (AQ-2S) and disodium AQ-2,6-disulfonate (AQ-26S) were purified by recrystallization from water. Disodium AQ-2,7-disulfonate (AQ-27S) was purified by liquid chromatography (alumina column). Their purity was checked by the TLC method (silica-gel, developer H_2O-propanol 3:7 mixture). 1,4-Naphthoquinone (NQ) was purified by recrystallization from cyclohexane using active charcoal, and 2-methyl NQ (Vitamin K_3) by the zone-melting method. Their mp agreed with the literature

Journal of Inclusion Phenomena **2**, 755–764. 0167-7861/84.15.

values. α-, β-, and γ-CD's of Tokyo Kasei Kogyo Co. and dimethyl-o-β-CD of Toshin Chemical Co. were used as they are. Non-fluorescent water of Wako Junyaku Kogyo Co. and ethylene glycol specially prepared for chromatography by Nakarai Chemical Co. were also used as they are.

The phosphorescence spectra and their excitation spectra and lifetimes were obtained using an Aminco 500 spectrofluorophotometer equipped with a phosphorimeter and a photon counter [3,4]. Water-ethylene glycol 1:1 mixture (H_2O-EG) was used as a glassy solvent at 77 K. The CD's were usually used in concentrations near 2.0×10^{-3} mol dm^{-3}. The inner diameters of α-, β-, and γ-CD's were taken as about 5.0, 7.0, and 8.5-9.0 Å, respectively.

3. Results and Discussion

The dimensions of AQ-2S [5] and NQ [6] obtained using the v.d.W. radii are shown in Fig. 1. All the phosphorescence spectra of the p-quinones

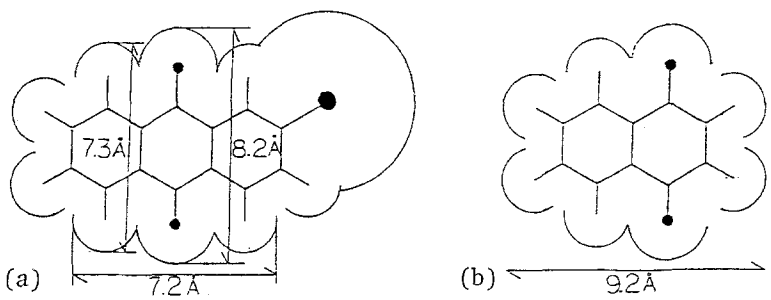


Fig. 1. Dimensions of the quinones (Å).
(a) Sodium AQ-2-sulfonate, (b) 1,4-naphthoquinone.

used in H_2O-EG at 77 K can be safely assigned to the $n\pi^*$ spectra except that of 2-methyl NQ about which a discussion will be given later, because of their short lifetimes and clear CO stretching vibrational structure. In all the p-quinones used, almost no change of the phosphorescence spectrum can be observed in the presence of α-CD.

Two points about the $n\pi^*$ phosphorescence spectra of the AQ sulfonates should be mentioned first. Firstly, as the corresponding $T\text{-}S_0$ transition [7] is substantially orbitally forbidden, the relative intensity of the 0-0 peak to the second main peak is stronger and the spectrum is broader in the aqueous solution than in organic solvents [3,4], resulting from the symmetry-degradation of the AQ π-electronic system accompanying the strong, random hydrogen-bond formation between water and the quinones. The $n\pi^*$ transition occurs at the carbonyl groups. Therefore, the relative intensity of the 0-0 peak should become weaker and the spectrum sharper, when the carbonyl groups of the AQ sulfonates are included in the hydrophobic cavity of the CD's in the aqueous solution. Secondly the phosphorescence spectra of the AQ sulfonates in the aqueous solution show red-shifts with increases in the concentration of the solutions, resulting from the formation of the quinone associates [4], as is seen in the spectra 1-3 in Fig. 2a.

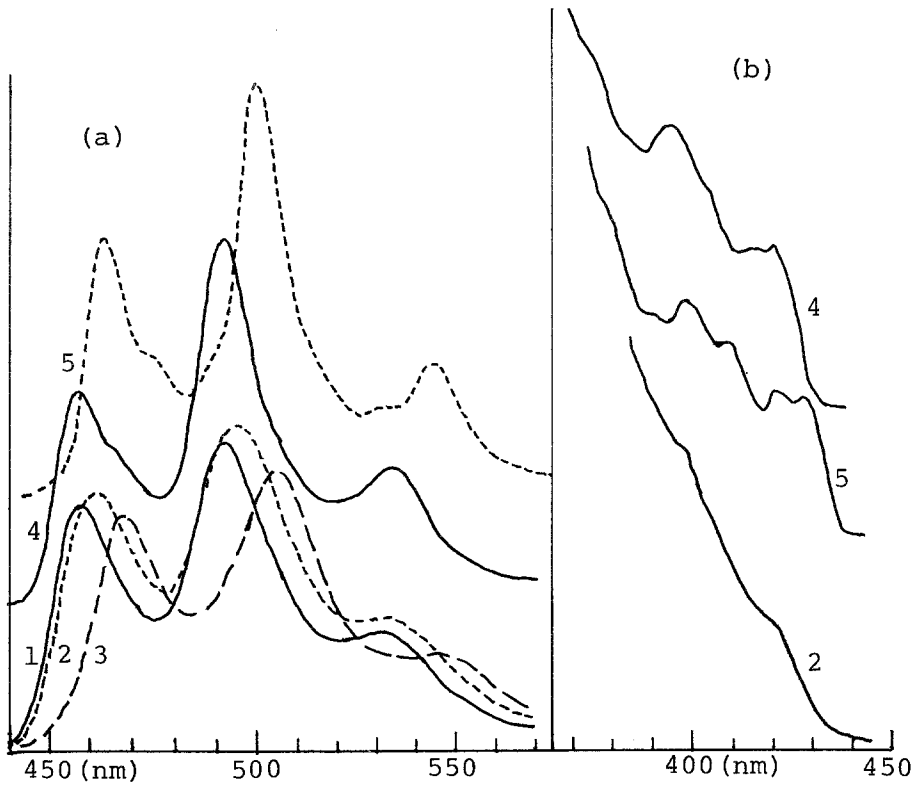


Fig. 2. Phosphorescence spectra (a) of sodium AQ-2-sulfonate in H_2O-EG at 77 K at the 330nm ex. and their excitation spectra (b).
1; 2.8×10^{-5}M, 2: 8.2×10^{-4}M, 3: 1.8×10^{-2}M, 4: 2+β-CD(2.0×10^{-3} M), 5: 2+γ-CD(2.0×10^{-3}M). (In all the figures, ex. and M denote excitation and mol dm^{-3}, respectively.)

In the phosphorescence spectra of AQ-2S in Fig. 2a, the spectra 4 and 5 are different from the spectrum 2 in the above-mentioned relative intensity of the 0-0 peak and sharpness. The spectrum 5 is at longer wavelengths by 320 cm^{-1} and a little sharper than the spectrum 4 which is at almost the same position as the spectrum 1. The excitation spectra in Fig. 2b correspond to the $n\pi^*$ absorption spectra. In Fig. 2b the spectra 4 and 5 are sharper than the spectrum 2,and the spectrum 5 is at longer wavelengths by 420 cm^{-1} and sharper than the spectrum 4 which is at almost the same position as the spectrum 2. The spectrum 2 is at almost the same position as that corresponding to the spectrum 1 in Fig. 2a. From these results, AQ-2S is concluded to form complexes with β- and γ-CD's, and is in surroundings more hydrophobic in the γ-CD complex than in the β-CD complex. The structures of the CD-AQ-2S complexes shown in Fig. 3 are thought to be most probable, in consideration of the quinone dimensions in Fig. 1a, the inner diameters of the CD's, and the results obtained by other authors [2,8].

In the phosphorescence spectra of AQ-26S in Fig. 4a, in the pres-

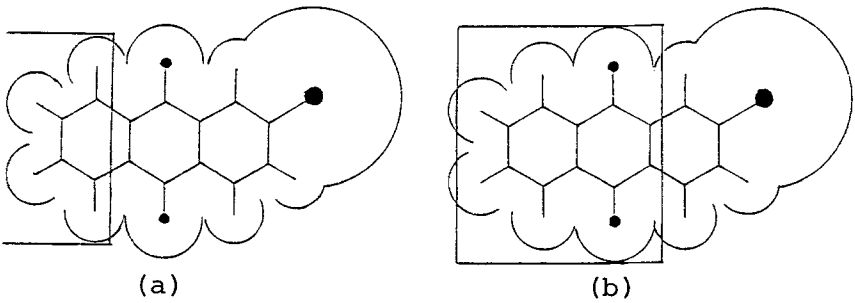


Fig. 3. Assumed structures of the CD-sodium AQ-2-sulfonate complexes.
(a) the β-CD complex, (b) the γ-CD complex.

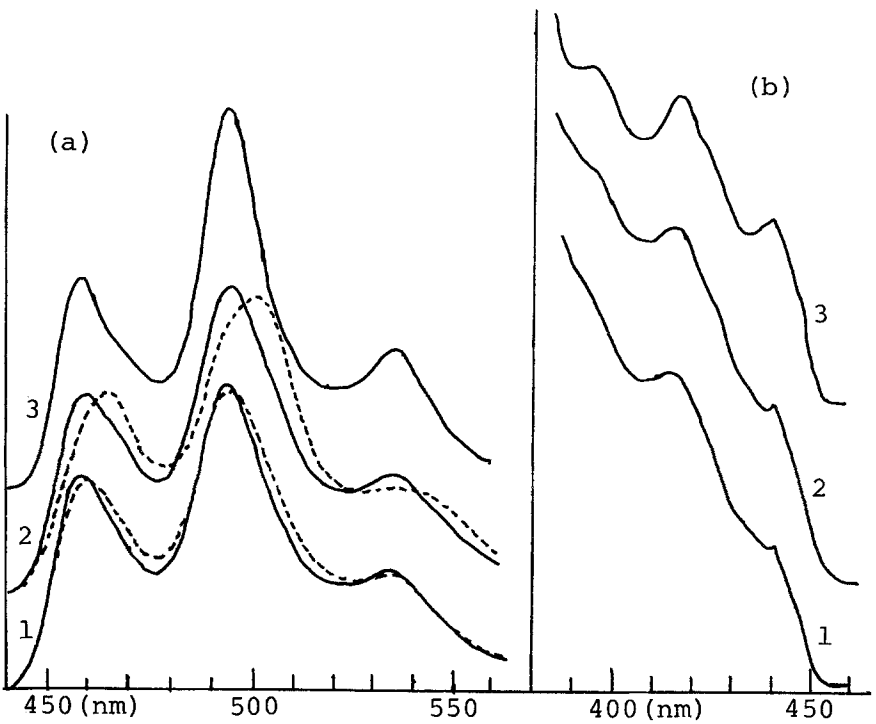


Fig. 4. Phosphorescence spectra (a) of disodium AQ-2,6-disulfonate in H_2O-EG at 77 K and their excitation spectra (b). 1: 1.5×10^{-3}M, 2: 1+γ-CD(3.2×10^{-3}M), 3: 1+β-CD(3.3×10^{-3}M), —— 330nm ex., ---- 365nm ex.

ence of β-CD a spectral change similar to that in AQ-2S is observed, and in the presence of γ-CD the long-wavelength peak observed at the 365nm excitation is assigned to the quinone associate [4]. The three excitation nπ* spectra in Fig. 4b are at almost the same position, and the spectrum 3 is a little sharper than the others. The β-CD complex is highly probable to be the 2(CD):1(quinone) complex, considering the dimensions of AQ-2S in Fig. 1 and that AQ-26S has the C_{2h} symmetry.

On the other hand, the γ-CD complex is highly probable to be not the 1:2 but the 2:2 complex [9] in which the dimer association of the 1:1 complex occurs, considering AQ-26S having two bulky sulfonato anion groups, and that in AQ-2S no quinone association occurs in the presence of γ-CD. The structures of the complexes shown in Figs. 5a and 5b seem to be most probable.

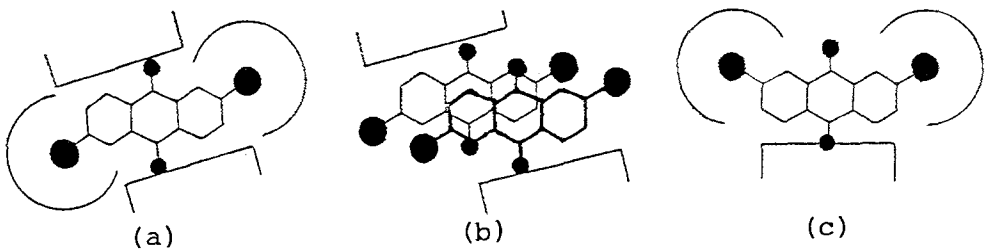


Fig. 5. Assumed structures of the CD-disodium AQ-2,6- and -2,7-disulfonates.
(a) the β-CD complex, (b) the γ-CD complex, (c) the β-CD complex.

AQ-27S shows a spectral change only in the presence of β-CD. In Fig. 6a, the relative intensity of the 0-0 peak of the spectrum 2 is slightly weaker than that of the spectrum 1. In Fig. 6b, the spectrum 2 is a little sharper than the spectrum 1. The structure of the β-CD complex is thought to be that shown in Fig. 5c, in view of AQ-27S having two bulky sulfonato anion groups and the dimensions of AQ-2S in Fig. 1.

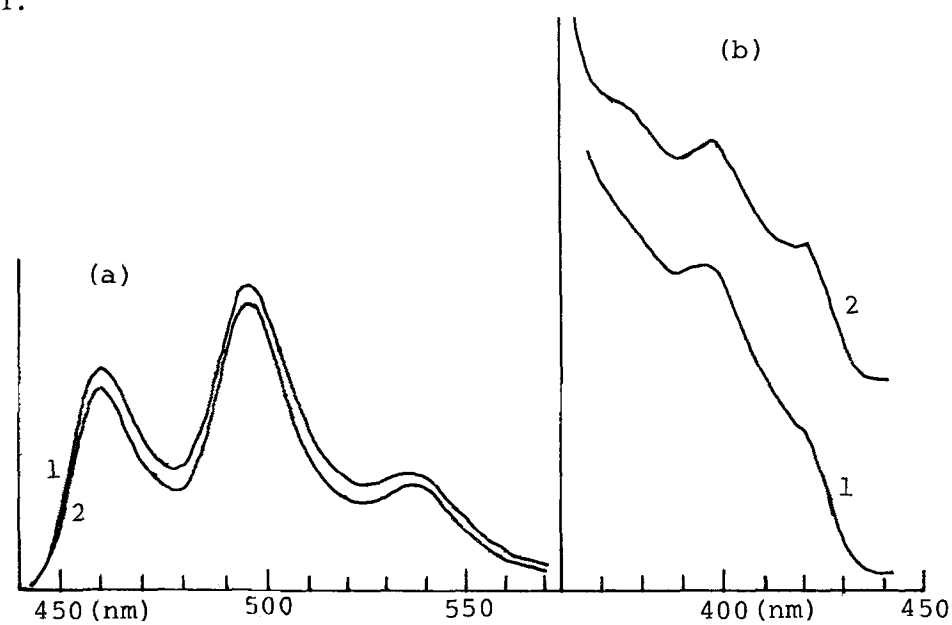


Fig. 6. Phosphorescence spectra (a) of disodium AQ-2,7-disulfonate in H_2O-EG at 77 K and their excitation spectra (b).
1: 3.6×10^{-4}M, 2: 1+β-CD(2.0×10^{-3}M).

As is seen in Fig. 7, in the three AQ sulfonates, the phosphorescence spectra are sharper and the relative intensities of the 0-0 peak are weaker in the presence of dimethyl β-CD than in the presence of β-CD, but the phosphorescence spectra are at almost the same position in both cases. From these results the structures of the dimethyl β-CD complexes are thought to be similar to those of the corresponding β-CD complexes in the three AQ sulfonates.

As is seen in Table I, the phosphorescence lifetimes of the AQ sulfonates become longer with the complex formation with the CD's. The result that the lifetime in the dimethyl β-CD-AQ-2S complex is shorter than that in the β-CD-AQ-2S complex is noticeable in view of the above-mentioned spectral change in the complex formation.

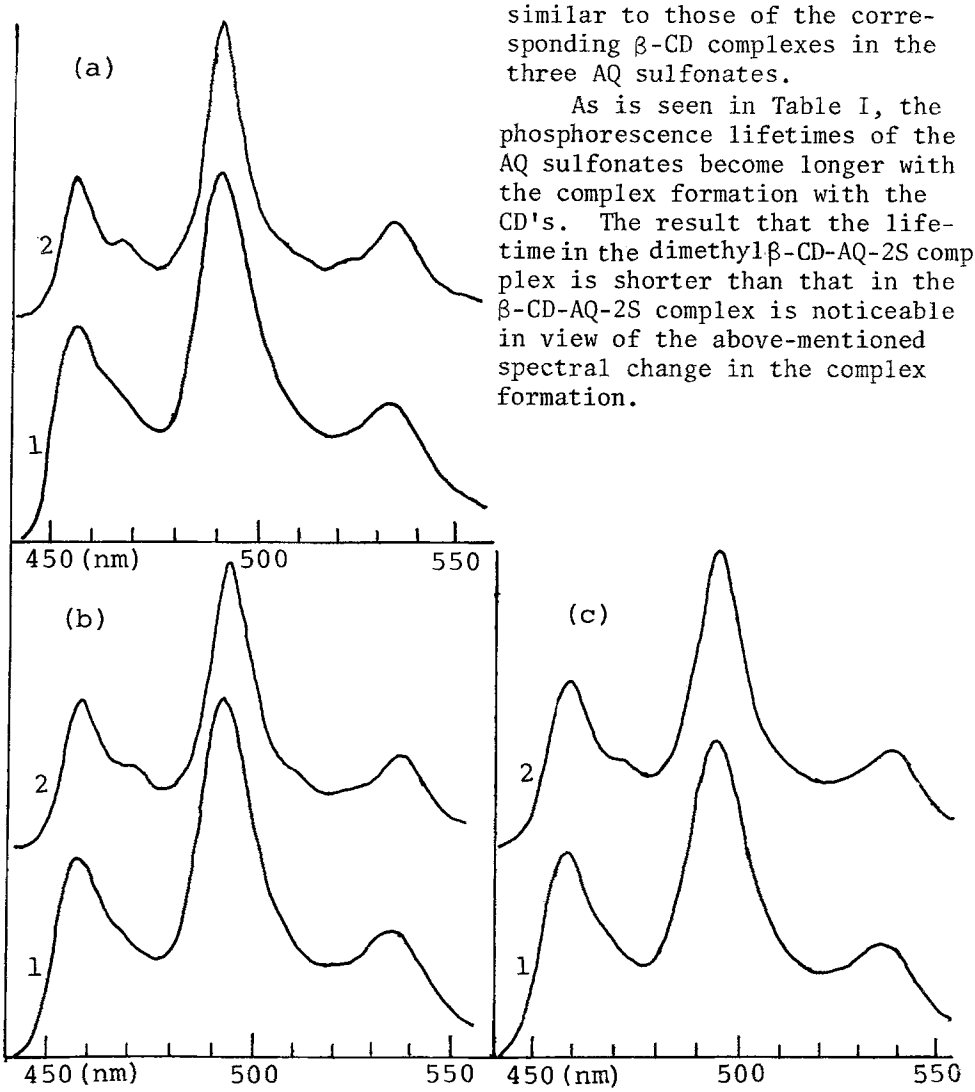


Fig. 7. Phosphorescence spectra of sodium AQ-2-sulfonate (a) and disodium AQ-2,6- and -2,7-disulfonates (b),(c) in H_2O-EG at 77 K at the 330nm ex.
(a) 1: 8.2×10^{-4}M+β-CD(2.0×10^{-3}M), 2: 1.4×10^{-4}M+dimethyl β-CD (2.7×10^{-3}M), (b) 1: 3.3×10^{-4}M+β-CD(2.0×10^{-3}M), 2: 3.3×10^{-4}M+dimethyl β-CD(2.7×10^{-3}M), (c) 1: 3.6×10^{-4}M+β-CD(2.0×10^{-3}M), 2: 3.6×10^{-4}M+dimethyl β-CD(2.7×10^{-3}M).

Table I. Observed phosphorescence lifetimes (ms)[a)]

		(β)	(γ)	(DMβ)
AQ-2-SO_3Na	2.0[b)] 2.3[b)]	2.7	2.7	2.45
AQ-2,6-diSO_3Na	1.8	2.1		2.1
AQ-2,7-diSO_3Na	1.7	1.95		2.0

a) β, γ, and DMβ denote β-, γ-, and dimethyl β-CD's, respectively.
b) These two values are those in the low and high concentration solutions, respectively [4].

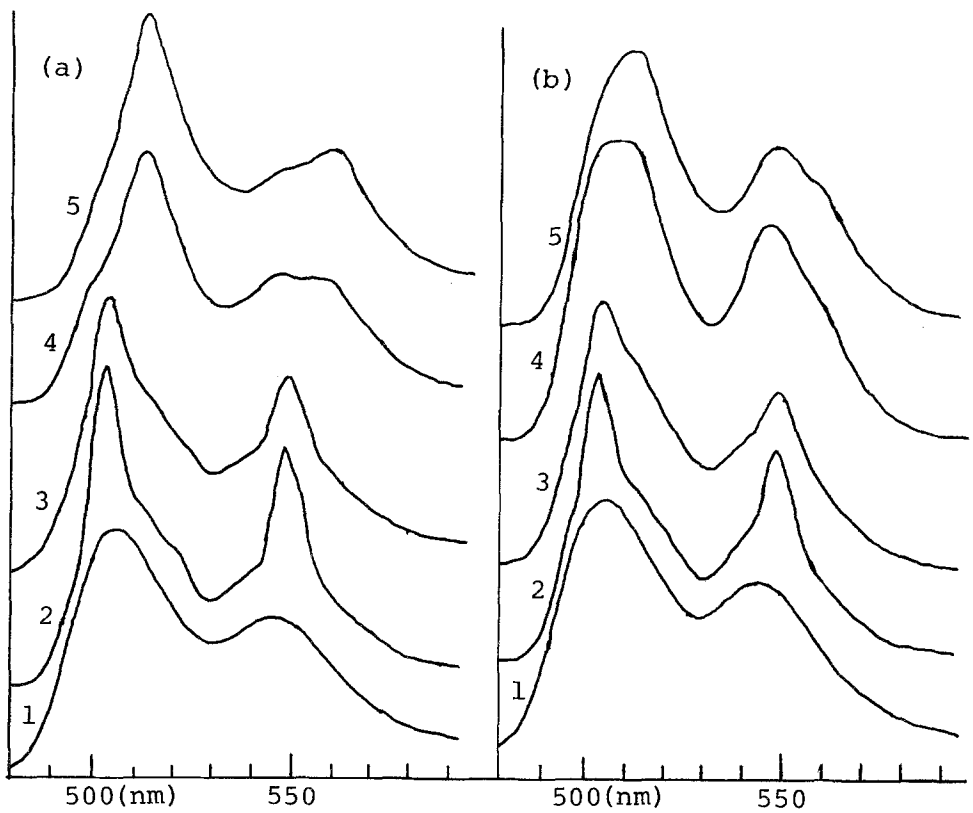


Fig. 8. Phosphorescence spectra of 1,4-naphthoquinone in H_2O-EG at 77 K.
(a) 1: 5.0×10^{-3}M, 365nm ex., 2: 1+β-CD(3.9×10^{-3}M), 330nm ex., 3: the same as 2, 365nm ex., 4: 1+γ-CD(3.8×10^{-3}M), 330nm ex., 5: the same as 4, 365nm ex. (b) 1: 1.3×10^{-3}M, 365nm ex., 2: 1+β-CD(1.9×10^{-3}M), 330nm ex., 3: the same as 2, 365nm ex., 4: 1+γ-CD(1.9×10^{-3}M), 330nm ex., 5: the same as 4, 365nm ex.

In NQ, as is seen in Fig. 8, in the presence of β-CD a sharp and a broad phosphorescence spectrum overlap each other, and they are at almost the same position as the spectrum obtained in the absence of β-CD. The relative intensity of the sharp spectrum to the broad spectrum decreases in the 365nm excitation in comparison with that in the 330nm excitation, and with the decreases in the concentration of NQ. On the other hand, two relatively sharp phosphorescence spectra the distance of which is about 480 cm^{-1} are observed in the presence of γ-CD. Their relative intensity changes with the excitation wavelengths and the concentrations of NQ. Since the relative intensity of the longer wavelength spectrum to the shorter wavelength spectrum becomes stronger at the longer wavelength excitation and with the increases in the concentration of NQ, the longer wavelength spectrum may be assigned to that of the quinone associates [4]. The shorter wavelength spectrum is at slightly shorter wavelengths than the sharp spectrum observed in the presence of β-CD.

The β-CD complex which shows the sharp spectrum probably takes the axial structure [2,8] similar to that of the β-CD-AQ-2S complex in Fig. 3. The sharp spectrum is probably that of the complex in the crystalline state in view of its sharpness and the concentration dependence of its relative intensity. The γ-CD complex which shows the longer wavelength spectrum is probably the 1:2 complex [10] in which the orientation of the quinone molecule is axial, in consideration of the dimensions of AQ-2S and NQ in Fig. 1. On the other hand, the γ-CD complex which shows the shorter wavelength spectrum is tentatively assigned to the 1:1 complex in which the orientation of the quinone molecule is equatorial [8], and consequently in which the quinone may form the hydrogen-bond with the solvent.

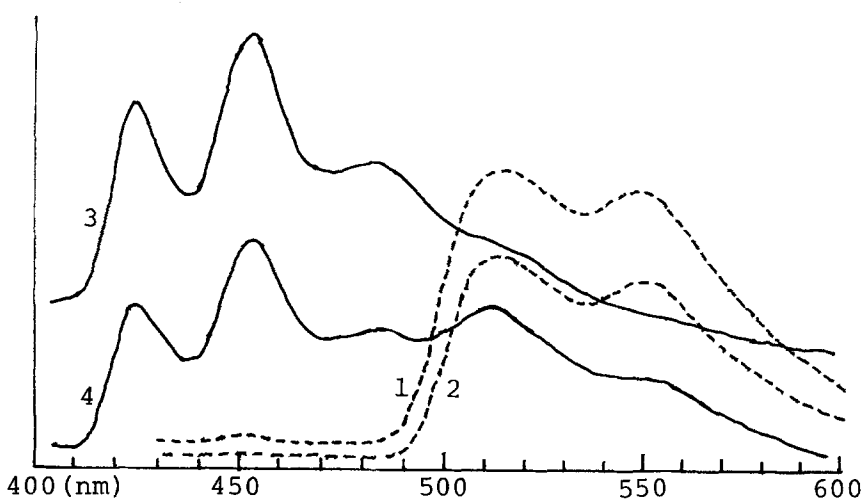


Fig. 9. Phosphorescence spectra of 2-methyl-1,4-naphthoquinone in H_2O-EG at 77 K.
1: 1.1×10^{-3}M, 365nm ex., 2: 5.5×10^{-4}M+β-CD(2.0×10^{-3}M), 365nm ex.
3: 1+γ-CD(1.9×10^{-3}M), 330nm ex., 4: the same as 3, 365nm ex.

As is seen in Fig. 9, 2-methyl NQ shows only a very small red-shift and almost no change of the spectral shape of the phosphorescence spectrum in the presence of β-CD, while in the presence of γ-CD it shows a phosphorescence spectrum completely different from that in the absence of γ-CD. Since 2-methyl NQ is thought to form a complex with β-CD which has a structure similar to that of the β-CD-NQ complex, the above very small spectral change seems to be puzzling, in comparison with those observed in the β-CD-AQ-2S and -NQ complexes. This may be explained as follows. The result that the phosphorescence spectrum of 2-methyl NQ in Fig. 9 is very broad may indicate that the phosphorescent lowest triplet state of 2-methyl NQ in H_2O-EG at 77 K is not the $n\pi^*$ but the $\pi\pi^*$ state which mixes with the close-lying $n\pi^*$ state [3]. Consequently the phosphorescence spectrum of the β-CD complex may be insensitive to the complex formation.

In the presence of γ-CD, the color of the emission of the sample solution very rapidly changes under the irradiation of the exciting light. As is seen in Fig. 9, the phosphorescence spectra obtained in the presence of γ-CD are at far shorter wavelengths than that obtained in the absence of γ-CD which shows almost no excitation-wavelength dependence, and the shapes of the former spectra are completely different from that of the latter. In Fig. 9, the spectrum 4 seems to contain the spectrum 1 as a small contribution in addition to the spectrum 3 which is the main contribution. From these results, the spectrum 3 is assigned to that of a photochemical reaction product. The spectrum 3 may be assigned to the $n\pi^*$ spectrum of an aromatic carbonyl compound because of its position, its clear vibrational structure, the vibrational frequency of which corresponds to that of the CO stretching vibration, and its short lifetimes (3.2 ms). 2-Methyl NQ is well known to give the photodimer [11] which has a cyclobutane ring, under the irradiation of sunlight a long time. Since the spectrum 3 is similar to that of this photodimer, it is thought that in this case the γ-CD-2-methyl NQ 1:2 complex formed in the beginning gives the photodimer very efficiently under the irradiation of the exciting light [12]. Studies on this problem are now in progress. The phosphorescence lifetimes of the NQ's are too short to be measured using the phosphorimeter [3c].

The CD:quinone ratios of the complexes assumed on the basis of the experimental results in this work are shown in Table II.

Table II. Assumed CD:quinone ratio's of the complexes[a)]

	(β)	(γ)	(DMβ)
AQ-2-SO_3Na	1:1	1:1	1:1
AQ-2,6-diSO_3Na	2:1	2:2	2:1
AQ-2,7-diSO_3Na	1:1	—	1:1
NQ	1:1	1:1,1:2	
2-Methyl NQ	1:1	(1:2)	

a) The same as ref. a) in Table I.

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