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The Phosphorescence Spectra of 9,10-Anthraquinone β- and β,β'-Sulfonates in an Aqueous Solution at 77 K

Akira KUBOYAMA* and Sanae Y. MATSUZAKI
National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki 305
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The nπ* phosphorescence spectra, and their excitation spectra and lifetimes of 9,10-anthraquinone-2-sulfonate, and -2,6- and -2,7-disulfonates in water–ethylene glycol 1:1 mixture at 77 K have been obtained. These phosphorescence spectra shift to the red with increases in the concentration of the solutions, and show an excitation-wavelength dependence. From the results obtained it is concluded that in the glassy solutions at 77 K an association of these quinones occurs, and that the phosphorescence state of the associates corresponds to the nπ* triplet excimer state, similar to that of the *p*-quinone aggregates in polycrystalline solutions at 77 K, previously studied.

Heretofore, we have studied the nπ* phosphorescence spectra of quinones in organic solvents at 77 K.[1] In this work, we examine the phosphorescence spectra of 9,10-anthraquinone β- and β,β'-sulfonates (9,10-anthraquinone is abbreviated as AQ in the following) in a glassy aqueous solution at 77 K. Investigations of the complex formation of these quinones with enzymes and cyclodextrins using these spectra are now in progress. These quinones have the following features favorable to the above studies. They are water-soluble and stable in the dark, have a large hydrophobic quinone moiety, and their phosphorescence spectra in a glassy aqueous solution at 77 K are relatively strong. Sodium AQ-2-sulfonate has been used in many photochemical[2] and biochemical[3] studies. However, few studies of the emission spectra of these quinones have been reported.

Experimental

Measurements. The phosphorescence spectra, and their excitation spectra and lifetimes in solutions were obtained at 77 K using an Aminco SPF-500 spectrofluorometer equipped with a photon counter (PM tube 1P28).[1] The energy distribution of the exciting radiation (a 250 W xenon arc lamp) and the spectral transmittance of the monochromator have not been taken into account. In the measurements, the sample solutions were rapidly cooled to 77 K. In some cases the results obtained using fast and slow cooling-speeds were compared. Water–ethylene glycol 1:1 mixture (H_2O–EG) which forms a glassy solution at 77 K was mainly used as a solvent. The pH value of this solvent was 6.8 at 26.0 °C. Methanol–ethanol 1:4 mixture which forms a glassy solution at 77 K was also used. The electronic absorption spectra in solution were obtained at room temperature using a Cary 17D self-recording spectrophotometer. In the measurements of high concentration solutions of the quinones, a 0.1 mm quartz cell of Gaskuro Kogyo Co. was used. Since the quinones are easily reduced in aqueous solutions by irradiation, especially at room temperature, care was taken to shield the sample solutions of the quinones from light.

Materials. Sodium AQ-2-sulfonate (AQ-2S) and disodium AQ-2,6-disulfonate (AQ-26S) of Tokyo Kasei Kogyo Co. were purified by recrystallization from water. Disodium AQ-2,7-disulfonate (AQ-27S) was purified by alumina column chromatography (eluent H_2O–EG). Their purity was checked by TLC (silica gel, developer water–propanol (3:7) mixture). Non-fluorescent water from Wako Junyaku Kogyo Co. was used. Ethylene glycol of Nakarai Kagaku Yakuhin Co. specially prepared for chromatography was used. No fluorescent impurity was detected in H_2O–EG. Spectrograde methanol and analytical-grade ethanol from Wako Junyaku Kogyo Co. were used without further purification.

Results and Discussion

In Fig. 1, the phosphorescence spectrum of AQ-2S in H_2O–EG shows a red-shift with increase in the concentration of the solutions, and an excitation-wavelength dependence, especially in the two medium concentrations (those in the spectra b and c). The spectra obtained with the 365 nm excitation are at longer wavelengths than those obtained with the 330 nm excitation. This excitation-wavelength dependence is very small in the low and high concentrations (those in the spectra a and d). These results suggest that the quinone molecules associate. The spectra in the low concentration (6.6×10^{-5} mol dm^{-3}) at the 330 nm excitation and in the high concentration (2.0×10^{-2} mol dm^{-3}) at the 365 nm excitation may be thought to be close to those of the quinone monomer and associate, respectively. The distance between these two spectra is *ca.* 600 cm^{-1}. Similar results were also observed in AQ-26S and -27S, as is seen in Figs. 2 and 3, but in these two quinones such a high concentration where the same spectra were obtained at the 330 and 365 nm excitations in the case of AQ-2S (the spectra d in Fig. 1) can not be realized because of the low solubility of these quinones in H_2O–EG.

The shapes of the spectra b and c of AQ-2S in the medium concentrations in Fig. 1 are similar to those of the spectra a and d in the low and high concentrations in Fig. 1. They are different from those of the simulation spectra in Fig. 4. The latter are composed of the two above-mentioned spectra which are thought to be close to those of the monomer and the associate. In Fig.

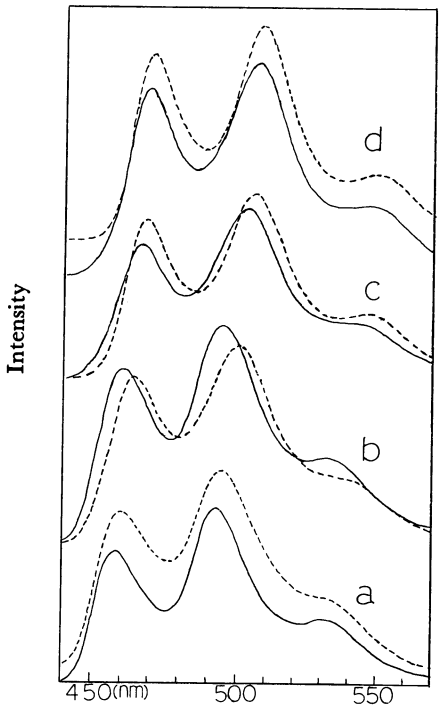

Fig. 1. Phosphorescence spectra of sodium 9,10-anthraquinone-2-sulfonate in the water–ethylene glycol mixture solution at 77 K, obtained without the rotating sector.
a: 6.6×10^{-5} M, b: 6.6×10^{-4} M, c: 6.6×10^{-3} M, d: 2.0×10^{-2} M, ——: 330 nm ex., ----: 365 nm ex. (In Figs. 1—8, M denotes the unit of mol dm^{-3}, and ex. does excitation.)

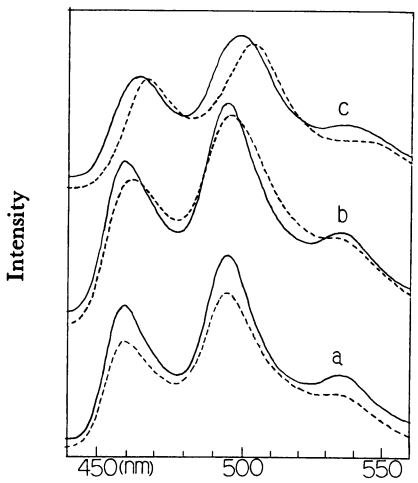

Fig. 2. Phosphorescence spectra of disodium 9,10-anthraquinone-2,6-disulfonate in the water–ethylene glycol mixture solution at 77 K, obtained without the rotating sector.
a: 6.0×10^{-5} M, b: 1.45×10^{-3} M, c: 1.2×10^{-2} M, ——: 330 nm ex., ----: 365 nm ex.

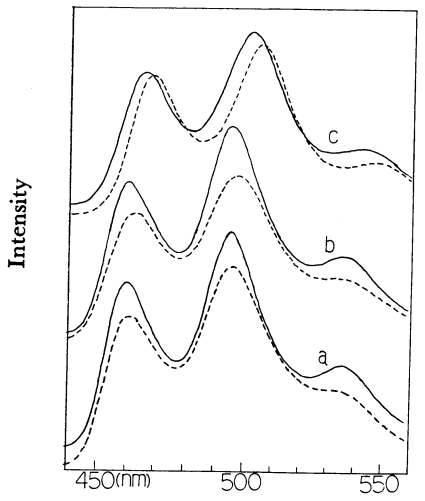

Fig. 3. Phosphorescence spectra of disodium 9,10-anthraquinone-2,7-disulfonate in the water–ethylene glycol mixture solution at 77 K, obtained without the rotating sector.
a: 6.5×10^{-5} M, b: 3.6×10^{-4} M, c: 7.9×10^{-3} M, ——: 330 nm ex., ----: 365 nm ex.

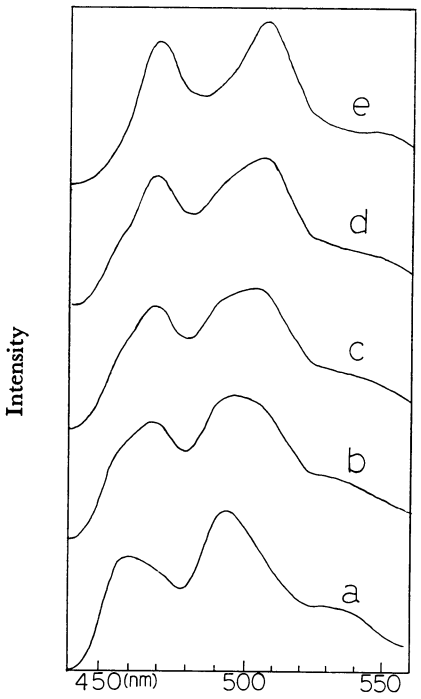

Fig. 4. Simulation spectra of sodium 9,10-anthraquinone-2-sulfonate composed of the spectra a (330 nm ex.) and d (365 nm ex.) in Fig. 1. The ratios of these two spectra in the spectra a—e are 4 : 1, 3 : 2, 1 : 1, 2 : 3, and 1 : 4, respectively.

l the peaks in the observed spectra are symmetrical, while in Fig. 4 most peaks in the simulation spectra are asymmetrical. Therefore, it is thought that there are more than one species in the number of the component molecules of the quinone associates, and consequently that in the high concentration solution the number of component molecules of the main part of the associates is greater than two, though its estimation is difficult at this stage. The spectra in the medium concentrations may be composed of the monomer and associates having various number of component molecules.

As is seen in AQ-2S (Fig. 5), the low-energy $\pi\pi^*$ absorption spectra[4] of these quinones in H_2O-EG at room temperature are broad and show only a small red-shift with increases in the concentration of the solutions. In Fig. 5, the peak wavelengths of the spectra 1 and 2 are 330 and 331 nm, respectively. The λ_{max} and molar absorption coefficients of the solutions of the concentrations lower than 1.8×10^{-3} mol dm^{-3} are almost constant.

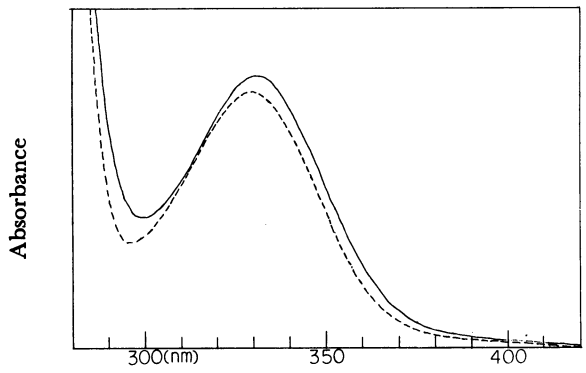

Fig. 5. Electronic absorption spectra of sodium 9,10-anthraquinone-2-sulfonate in the water–ethylene glycol solution at room temperature.
——: 2.0×10^{-2} M (spectrum 1), ----: 1.8×10^{-3} M (spectrum 2).
(The ordinate is arbitrary.)

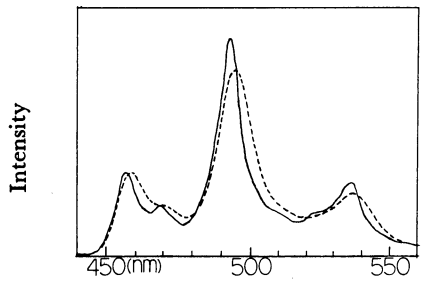

Fig. 6. Phosphorescence spectra of 9,10-anthraquinone (I) and sodium 9,10-anthraquinone-2-sulfonate (II) in the methanol–ethanol mixture solution at 77 K.
——: I 3.8×10^{-5} M, ----: II 6.1×10^{-5} M.

These phosphorescence spectra show a clear CO stretching vibrational structure and the phosphorescence lifetimes are around 2 ms, as is seen in Table 2. Since the phosphorescence spectra are similar to the $n\pi^*$ phosphorescence spectra of AQ[1b,1g] in organic solvents in position, vibrational structure, and lifetime, they also may be safely assigned to the $n\pi^*$ phosphorescence spectrum. As the electronic transition in the $n\pi^*$ phosphorescence spectra of AQ is orbitally forbidden,[5,6] the relative height of the shortest wavelength peak, 0–0 peak, in the phosphorescence spectrum of AQ-2S is also low in organic solvents, as is seen in Fig. 6,[7] while those in H_2O-EG in Fig. 1 are considerably larger. This may result from the symmetry-degradation of the quinone π-electronic system due to the strong, random hydrogen-bond formation between AQ-2S and water.

Table 1. Peak wavelengths, λ, of the phosphorescence spectra at 77 K

	Solvent	λ/nm			
AQ	M-E[b]	456.5	492	534.5	Fig. 6
AQ-2S[a]	M-E	458	493.5	535.5	Fig. 6
AQ-2S	H_2O-EG	456	491		Fig. 1[c]
AQ-2S	H_2O-EG	468.5	506		Fig. 1[d]
AQ-26S[a]	H_2O-EG	457	492.5		Fig. 2[c]
AQ-26S	H_2O-EG	465	501		Fig. 2[d]
AQ-27S[a]	H_2O-EG	459.5	495		Fig. 3[c]
AQ-27S	H_2O-EG	467.5	504.5		Fig. 3[d]

a) AQ-2S, -26S, and -27S denote sodium AQ-2-sulfonate and disodium AQ-26- and -27-disulfonates, respectively. b) M-E denotes the methanol-ethanol mixture solution. c) The values are for the low-concentration solutions (330 nm ex.). d) The values are for the high-concentration solutions (365 nm ex.).

Table 2. Observed phosphorescence lifetimes, τ, at 77 K

	Solvent	τ/ms	
AQ	M-E[b]	3.3	Fig. 6
AQ-2S[a]	M-E	2.3	Fig. 6
AQ-26S[a]	M-E	2.1	Ref. 10
AQ-2S	H_2O-EG	2.0	Fig. 1[c]
AQ-2S	H_2O-EG	2.3	Fig. 1[d]
AQ-26S	H_2O-EG	1.8	Fig. 2[e]
AQ-27S[a]	H_2O-EG	1.7	Fig. 3[e]

a) AQ-2S, -26S, and -27S denote sodium AQ-2-sulfonate and disodium AQ-26- and -27-disulfonates, respectively. b) M-E denotes the methanol-ethanol mixture solution. c) The value is for the low-concentration solution (330 nm ex.). d) The value is for the high-concentration solution (365 nm ex.). e) The values for the low-concentration solution (330 nm ex.) and the high-concentration solution (365 nm ex.) are almost the same.

As is seen in Fig. 7, the phosphorescence spectrum obtained with the slow rotating sector is far broader than that obtained with the fast rotating sector. In the spectra of the methanol–ethanol mixture solution of AQ-2S in Fig. 6, no such a sector-speed dependence of the phosphorescence spectra can be observed. In our previous work[1g] on methyl-substituted AQ's, results similar to the above sector-speed dependence of the phosphorescence spectra were obtained in non-saturated-hydrocarbon solutions. This may be due to there being a T_1 $n\pi^*$ level and a close-lying T_2 $\pi\pi^*$ level in AQ-2S in H_2O–EG, resulting from the strong hydrogen-bond formation between AQ-2S and water. There is a T_1 $\pi\pi^*$ level in the strongly solvated species. Consequently, in the spectra obtained with the slow rotating sector the sharp $n\pi^*$ and broad $\pi\pi^*$ spectra with different lifetimes overlap, as in the case of methyl-substituted AQ's.[1g] Since above-mentioned broad spectrum is observed only weakly, the phosphorescence spectrum obtained with the fast rotating sector contains the $\pi\pi^*$ spectrum as a very small contribution. The results similar to the above results are also observed in AQ-26S and -27S.

The phosphorescence excitation spectra of the low and high concentration solutions of AQ-2S are shown with that of a low-concentration solution of AQ-27S in Fig. 8. In these spectra, the weak long-wavelength part with a structure,[8] and the strong, broad short-wavelength part correspond to the S–S $n\pi^*$ and $\pi\pi^*$ absorption spectra, respectively.[9] In Fig. 8, the short-wavelength part of the excitation spectrum b of the high-concentration solution of AQ-2S is omitted, because the absorption in this wavelength region is very strong. The long-wavelength part of the excitation spectra in AQ-2S is almost the same in position and shape in the low- and high-concentration solutions. Similar results were obtained for AQ-26S and -27S. Therefore, the $n\pi^*$ absorption spectra of the monomer and associates of these quinones are at almost the same position. However, as mentioned before, the $n\pi^*$ phosphorescence spectra of these quinones shift considerably to the red with increases in the concentration. These circumstances are similar to those in the $n\pi^*$ phosphorescence spectra of the aggregates of the *p*-quinones, 1,4-naphthoquinone and 5,14:7,12-pentacenediquinone, in polycrystalline solutions at 77 K, previously studied.[1h] According to our previous work,[1h] the phosphorescence states of the quinone associates discussed here are also thought to correspond to the $n\pi^*$ excimer state. In these quinones, the $n\pi^*$ absorption spectra of the quinone monomer and associates are at almost the same position, as is mentioned above, while in the polycrystalline solutions the $n\pi^*$ absorption spectra of the aggregates are at shorter wavelengths than those of the corresponding quinone monomer, though the $n\pi^*$ phosphorescence spectra of these *p*-quinone aggregates appear at considerably longer wavelengths than those of the corresponding monomers.[10] This may indicate that the interaction between the quinone molecules in these associates is weaker than those in the *p*-quinone aggregates in the polycrystalline solutions.

With regards to the phosphorescence lifetimes shown in Table 2, the phosphorescence lifetimes of AQ-2S and -26S[11] in the methanol–ethanol mixture solution are considerably shorter than that of AQ

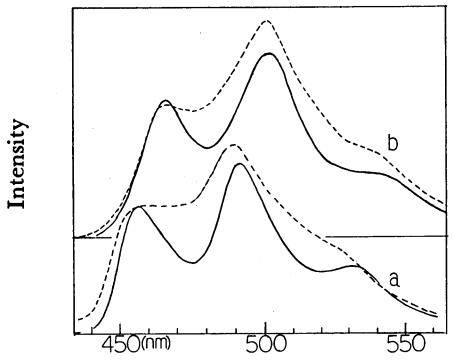

Fig. 7. Effect of the sector-speed on the phosphorescence spectra of sodium 9,10-anthraquinone-2-sulfonate in the water–ethylene glycol mixture solution at 77 K.
a: 6.6×10^{-5} M, 330 nm ex., b: 6.6×10^{-3} M, 330 nm ex., —— with the fast-rotating sector (11500 min^{-1}), ---- with the slow-rotating sector (2070 min^{-1}).

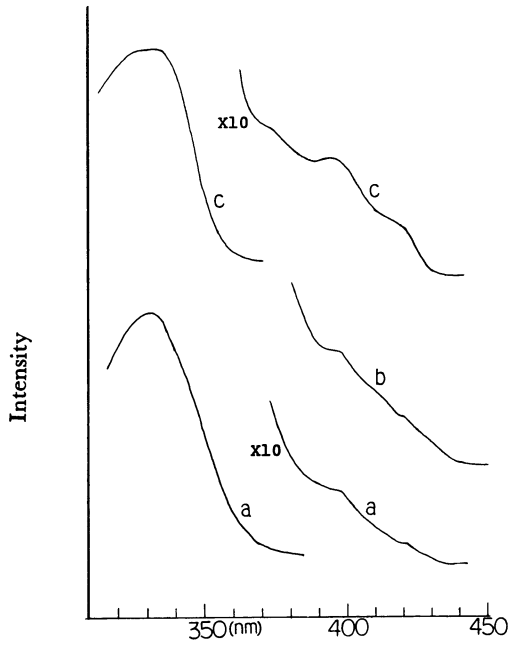

Fig. 8. Phosphorescence excitation spectra of sodium 9,10-anthraquinone-2-sulfonate (a,b) and disodium 9,10-anthraquinone-2,7-disulfonates (c) in the water–ethylene glycol mixture solution at 77 K.
a: 6.6×10^{-5} M, b: 6.6×10^{-3} M, c: 3.3×10^{-5} M.

and only slightly longer than the corresponding ones in H_2O–EG, in spite of the relative height of the 0–0 peak in the phosphorescence spectrum of AQ–2S in these two solutions being considerably different, as is seen in Figs. 1 and 6. In AQ also, the phosphorescence lifetimes of the methylcyclohexane and methanol–ethanol mixture solutions are both 3.3 ms, in spite of the relative height of the 0–0 peak in the latter solution being considerably larger than that in the former solution.[1g] In AQ–2S, the phosphorescence lifetime in the high-concentration solution is slightly longer than that in the low-concentration solution.

The association of these quinones is thought to be due to their having both a large hydrophobic quinone moiety and hydrophilic sulfonato anion groups. In the associates, the quinone molecules are thought to orient themselves, avoiding the strong steric hindrance of the sulfonato anion groups and overlapping their planar quinone moiety. The detailed structures of the associates can not be discussed at this stage.[1h]

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4) The $n\pi^*$ absorption spectra are observed as broad shoulders on the long-wavelength side.

5) The 0–0 peak in the $n\pi^*$ phosphorescence spectra of AQ in the normal paraffine Shpol'skii matrices is very weak.[1b]

6) K. E. Drabe, H. Veenvliet, and D. A. Wiersma, *Chem. Phys. Lett.*, **35**, 469 (1975); J. P. Galaup, J. Megel, and H. P. Trommsdorff, *ibid.*, **41**, 397 (1976); O. S. Khalil and L. Goodman, *J. Phys. Chem.*, **80**, 2170 (1976); N. S. Strokach and D. N. Shigorin, *Opt. Spectrosk.*, **43**, 34 (1977); E. Kanezaki, N. Nishi, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **52**, 2836 (1979).

7) These spectra show no quinone-concentration and excitation-wavelength dependences.

8) In both the spectra a and b, two shoulders are observed at 420 and 397.5 nm.

9) The long-wavelength part of the excitation spectra in AQ–26S is close to that in AQ–27S in Fig. 8 in position and shape.

10) Similar long-wavelength $n\pi^*$ phosphorescence spectra have also been observed in polycrystalline solutions of *p*-benzoquinone and 2-methyl-AQ.[1h]

11) The phosphorescence spectrum of AQ–26S in the methanol–ethanol mixture solution is close to that of AQ–2S in position and shape.