THE EFFECT OF WATER ON PHOTOCHEMICAL AND PHOTOPHYSICAL BEHAVIOR OF ANTHRAQUINONE DERIVATIVES

1988

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THE EFFECT OF WATER ON PHOTOCHEMICAL AND PHOTOPHYSICAL BEHAVIOR OF ANTHRAQUINONE DERIVATIVES

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Thesis
Submitted to the Graduate Faculty
in partial fulfillment of the requirements
for the degree of

DOCTOR OF SCIENCE

University of Tsukuba

1988

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Preface

The present thesis is a collection of studies which heve been carried out under the guidance of Professor Katsumi Tokumaru at University of Tsukuba during my graduate course from 1983 to 1988. The main subject of this thesis is the investigation of photochemical and photophysical behaviors of anthraquinone derivatives in aqueous organic solvents. A new aspect of the solvent effect is presented here.

My deep gratitude is expressed to Professor Katsumi Tokumaru for guidance and encouragement throughout the course of this study. I am grateful to Dr. Hirochika Sakuragi and Dr. Thomas W. Ebbesen for constant guidance, encouragement, discussion and advice. I wish to thank Dr. Tatsuo Arai, Dr. Ryoichi Akaba and Dr. Hiroaki Misawa. Thanks are also due to all the graduate and undergraduate members of Tokumaru's research group for kind cooperation during the course.

Akihiro Wakisaka

February, 1988

General Introduction

Quinones play a variety of roles in the life cycles of living organisms.[1,2] In this thesis a particular interest is taken in the roles of quinones in the electron-transfer systems in natural photosynthetic organisms. The function of plastoquinone (PQ) in photosynthesis has been well understood for many years. It transfers electrons accompanied with protons between electron-transfer sites located at opposite sides of thylakoid membrane. PQ accepts an electron from excited chlorophyll a through an unknown component Q on outer surface of thylakoid membrance. The reduced PQ ($PQ^{-}\cdot$) combines with a proton to form plastosemiquinone ($PQH\cdot$). The resulting $PQH\cdot$ shifts from the outer to inner surface of the membrane and reduces cytochrome b_{559} accompanied with deprotonation. As a result, PQ transfers an electron and a proton from the outer surface of the thylakoid membrane to its inner surface.

If quinones are reduced photochemically to their semiquinone radicals or semiquinone radical anions, it is much interesting as a model of the artificial photosynthetic systems. It is described in chapter 1 that eosin Y, a xanthene dye, sensitized the reduction of duroquinone and anthraquinone-2-sulfonate without photobleaching of eosin Y and that the resulting radical anions were persistently alive. In chapter 2 the electron transfer through the anthrasemiquinone radical anion produced photochemically as an intermediate is described.

The photochemical electron-transfer reactions studied in chapter 1 and 2 take place in aqueous organic solvent mixtures, and the efficiency of these electron transfer systems was influenced by the water content. This water content effect is not explained by the change of solvent polarity and is related with the preferential solvation by organic solvent component.

In chapter 3 and 4 the effects of water content on the photochemical and photophysical processes of anthraquinone derivatives in aqueous organic solvents are described and discussed in terms of preferential solvation by organic components. The photochemical hydrogen abstraction reaction of anthraquinone derivatives were extensively studied[3-7] in relation to the fact that photodegradation of cellulosic materials is accelerated by certain anthraquinone vat dyes. So photosensitized oxidation of alcohols and hydrocarbons and laser flash photolyses[4] were examined for some anthraquinone derivatives as sensitizer, especially for anthraquinone and its sulfonated derivatives. Furthermore, the photochemical reactions of sulfonated derivatives in aqueous solution were studied recently,[8-12] and a few mechanisms on photohydroxylation of sulfonated anthraquinones were presented. In those studies much attention was paid to the assignment of reaction intermediates. In this thesis, it will be indicated that the photochemical hydrogen abstraction by triplet-state anthraquinones and interaction of triplet-state anthraquinones with water are influenced by the solvation.

Many chemical reactions taking place in solution are influenced by solvent used since charged species are usually formed, disappeared, dispersed, separated or recombined during the course of reactions. The solvent effects are generally interpreted in terms of dipolar interactions of the medium with reactants, intermediates, and even transition states.

For example, the nucleophilic substitution reactions proceeding through S_N1 mechanism are more favorable in polar solvents because formation of a carbocation is the rate-determining step. The rate constant of solvolysis of tert-butyl chloride, k_s, in water is more than a hundred thousand times larger than that in ethanol.[13] This indicates that the ionization of tert-butyl chloride occurs in water more efficiently.

However, when water-ethanol mixtures are used as solvent for this reaction,[13] dependence of k_s on the water content in the mixed solvent cannot be explained by the change of solvent polarity. As shown in Figure 1-a, k_s is almost constant at water mole fraction in the mixed solvent lower than 0.7, but rapidly increases at water mole fractions higher than 0.7. Similar water content dependence is observed in binary mixtures of water with acetone and dioxane also as depicted in Figure 1-b and c.[13]

From these results Grunwald and Winstein suggested a quantitative correlation of the rates of solvolysis reaction in several solvents and assigned the Y values, which represent the "ionizing power" for several solvents and their mixtures using the value of k_s in 20:80 water-ethanol mixed solvent as a reference.[13,14] Brown and Hudson suggested that the ionization will occur when the transition state is surrounded by a critical number of water molecules in aqueous organic solvents.[15]

It is supposed that the observed water content effect as shown in Figure 1 may be attributable to the preferential solvation of tert-butyl chloride by organic components in aqueous mixtures. At water mole fractions lower than 0.7, since tert-butyl chloride will be preferentially solvated by organic component, water molecules cannot effectively interact with tert-butyl chloride molecules. On the other hand, at water mole fractions higher than 0.7 the number of water molecules in the solvation shell of tert-butyl chloride will increase with increasing water content, and so k_s rapidly increases. It should be noted that this kind of solvent effect cannot be understood only by the change of solvent polarity. When the substrate molecule is preferentially solvated by an inert solvent component in the mixed solvent, the influence of the solvation should be considered. It can be said that the effect of solvation corresponds to more microscopic solvent effect.

The importance of this "microscopic solvent effect" is presented through the investigation of photochemical and photophysical processes of anthraquinone derivatives in aqueous organic solvents.

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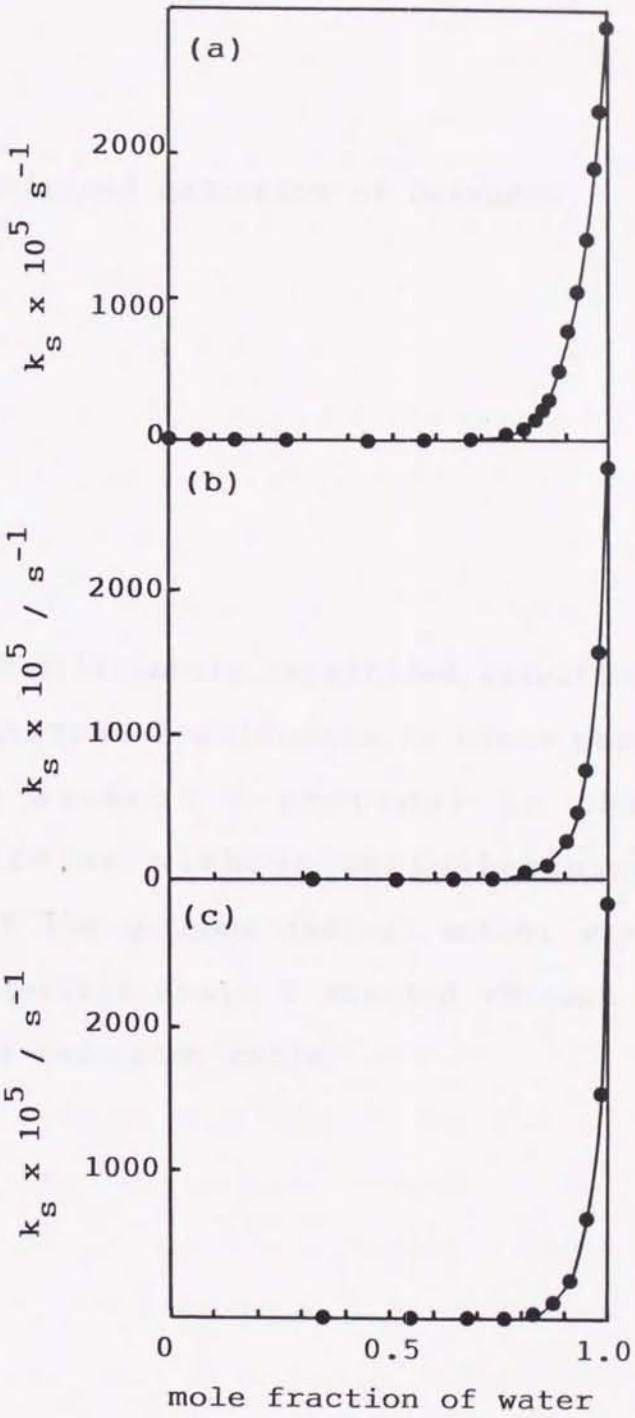

Figure 1. The first-order rate constants of solvolysis for tert-butyl chloride at 25 °C in water-ethanol (a), water-acetone (b), and water-dioxane (c) as a function of water mole fraction in mixed solvents.
(A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2770 (1956))

Chapter 1

Eosin Y Sensitized Reduction of Quinones

Abstract

Eosin Y efficiently sensitized reduction of duroquinone and anthraquinone-2-sulfonate to their persistent radical anions in aqueous 2-propanol in the presence of triethanolamine without photobleaching of Eosin Y. Formation of the quinone radical anions was more efficient when triplet-state Eosin Y reacted through oxidation cycle than through reduction cycle.

Introduction

Many attempts have been made to construct photochemical electron transfer systems to reduce quinones through excitation of dyes by mimicking natural photosynthetic systems[1-5] in which photoexcitation of chlorophyll induces electron transfer to plastoquinone followed by regeneration of chlorophyll through electron transfer from other electron donors. The key steps in the photosynthetic conversion of light energy to chemical potential energy include not only photodriven charge separation but also prevention of the back-electron-transfer. The reduction of quinones sensitized by porphyrin derivatives has been tried extensively in inter- and intramolecular electron-transfer systems;[1-5] however, it has been difficult to inhibit the back electron transfer.

It is described in this chapter that Eosin Y (EY^{2-}) sensitizes efficiently the reduction of quinones like duroquinone (DQ) and sodium anthraquinone-2-sulfonate (AQS) into their almost persistent radical anions in the presence of triethanolamine (TEOA) as an electron donor. It was found that the resulting radical anions of quinones were persistently alive without back electron transfer under the optimum conditions.

The mechanism of this electron transfer is discussed, especially on the primary reaction process of triplet-state EY^{2-}. It has already been reported that EY^{2-} can be reduced[6-8] and oxidized[9,10] photochemically in the presence of electron donors and electron acceptors, respectively.[11] The photoreduction of EY^{2-} in deaerated solutions leads to the bleaching of EY^{2-} and the original dye is not recovered by introduction of air to the bleached solution. On the other hand, the photooxidation of EY^{2-} with p-benzoquinone[9] leads to the formation of $EY^{-\cdot}$ and benzosemiquinone radical anion.

When a solution of EY^{2-} contains both electron donor (TEOA) and electron acceptor (DQ or AQS) in such a reaction system as presented here, reactions of excited-state EY^{2-} can proceed through a reduction or an oxidation course. In order to investigate which mechanism is suitable for the excited-state EY^{2-} to afford efficiently the quinone radical anions, the effect of duroquinone concentration on the quantum yield for DQ radical anion ($DQ^{-\cdot}$) formation sensitized by EY^{2-} and the rate constants of the reductive and oxidative quenching of triplet-state EY^{2-} were measured. From these experimental results the best conditions for the quinone radical anion formation sensitized by EY^{2-} will be presented.

Experimental Section

Materials. Eosin Y (Chroma) was recrystallized three times from a 9:1 ethanol-water mixture. Sodium anthraquinone-2-sulfonate (Nakarai Chemicals) was salted out from an aqueous sodium chloride solution and then was recrystallized twice from distilled water. 2-Propanol (Nakarai Chemicals) was used after distillation. Duroquinone (Nakarai Chemicals) and water (non-fluorescent, Wako Chemicals) were used as received.

Quantum Yield Measurements. Samples were irradiated with 480 ±10-nm light through a monochromator (Shimadzu, 1200 grooves/mm) from a 500-W xenon lamp (Ushio U1-501C). The irradiating light intensity was measured by means of a potassium tris(oxalato)ferrate(III) (0.15 M) chemical actinometer to be 1.67×10^{-7} einstein/min. The concentration of $DQ^{-\cdot}$ produced by irradiation was determined from an absorbance at 440 nm ($\varepsilon = 7600\ M^{-1}cm^{-1}$).[12]

Apparatus. The electronic absorption spectra were measured on a spectrophotometer (Hitachi, 200-20). ESR spectra were measured on an ESR spectrometer (JEOL, JES-ME). Continuous irradiation was carried out using a 500 W xenon lamp (Ushio, U1-501C) through a cut-off filter (Toshiba, Y50). Nanosecond laser flash photolyses were performed using a Lambda Physik Laser (EMG 101) with nitrogen emission (337 nm, 5 mJ/pulse, 6-ns fwhm) and a xenon discharge lamp (Wacom

R.&D., KXL-151) as a probe beam. The transient signals were recorded on a storage scope (Iwatsu TS-8123). The system of laser flash photolysis was schematically depicted in Figure 1.

Results and discussion

1. EY^{2-} sensitized reduction of DQ and AQS

In the presence of DQ (1.0×10^{-4} M), TEOA (1.9×10^{-3} M) and sodium hydroxide (0.1 M) in an equivolume mixture of water and 2-propanol, EY^{2-} (1.5×10^{-5} M) was irradiated with light of wavelengths longer than 500 nm through a Toshiba Y50 filter from a 500-W xenon lamp under argon atmosphere. In this condition, the irradiation led to the formation of duroquinone radical anion ($DQ^{-\cdot}$).[19] The production of $DQ^{-\cdot}$ was clearly detected by the growth of its characteristic absorption bands with the maxima around 416 and 440 nm[13] as shown in Figure 2. Formation of $DQ^{-\cdot}$ was also detected by its characteristic ESR spectrum composed of thirteen lines with a hyperfine splitting constant of about 0.16 mT[14] as depicted in Figure 3. The resulting radical anions were alive on standing overnight.[15,16] On the contrary, in the absence of EY^{2-} under otherwise the same conditions DQ was not reduced.

The reduction of anthraquinone-2-sulfonate (AQS) was also tried under similar conditions.[19] In the presence of AQS (2.0×10^{-3} M), TEOA (5.6×10^{-3} M) and sodium hydroxide (1.0×10^{-3} M), EY^{2-} (1.5×10^{-5} M) was irradiated in an equivolume mixture of water and 2-propanol under similar conditions. The production of AQS radical anion ($AQS^{-\cdot}$) was clearly detected by the growth of its characteristic absorption bands[17] around 400, 500, 780, and 870 nm as shown in Figure 4. The ESR spectrum observed after irradiation [Figure 5-(a)] was in agreement with that of $AQS^{-\cdot}$ produced by electrochemical reduction [Figure 5-(b)]. On the contrary, in the absence of EY^{2-} under otherwise the same conditions, AQS was not reduced.

In both cases of DQ and AQS, on introduction of air to the irradiated solutions, the absorption of quinone radical anions disappeared completely through their oxidation and the original absorption of EY^{2-} was recovered without any decrease in intensity. This shows that EY^{2-} is quite durable for visible light irradiation under the conditions examined.

In contrast, in the absence of quinones under otherwise the same conditions, irradiation of EY^{2-} led to its photobleaching by formation of $EY^{3-\cdot}$.[18] In the absence of TEOA under otherwise the same conditions, irradiation of EY^{2-} led to formation of neither $DQ^{-\cdot}$ nor $AQS^{-\cdot}$.

It should be noted that the present system comprised of EY^{2-}, TEOA and quinones could be used as a potential electron transferring system through almost persistent radical anions of quinones. The mechanism is discussed below.

2. Quantum Yield for $DQ^{-\cdot}$ Formation

When the quantum yield for $DQ^{-\cdot}$ formation sensitized by EY^{2-} was measured in various DQ concentrations, an interesting DQ concentration effect was observed, giving useful information about the mechanism.

In the presence of DQ, TEOA (1.9×10^{-3} M) and sodium hydroxide (0.1 M), EY^{2-} (1.2×10^{-4} M) was excited with 480 nm light in an equivolume mixtures of water and 2-propanol under argon atmosphere. The concentration of DQ was changed from 1.0×10^{-5} to 1.0×10^{-3} M. Under these conditions the quantum yield for $DQ^{-\cdot}$ formation ($\Phi_{DQ^{-\cdot}}$) was dependent on the DQ concentration; the obtained values of $\Phi_{DQ^{-\cdot}}$ are listed in Table 1. When the concentration of DQ was 1.0×10^{-5} M, EY^{2-} was rapidly photobleached on irradiation, and $\Phi_{DQ^{-\cdot}}$ was zero. When the concentration of DQ was 5.0×10^{-5} M, the photobleaching of EY^{2-} was not observed, and $\Phi_{DQ^{-\cdot}}$ attained to 0.47. On the contrary, when the concentration of DQ was increased to 5.0×10^{-4} M, $\Phi_{DQ^{-\cdot}}$ decreased to 0.23.

3. Laser Flash Photolysis

If the rate constant for the oxidative electron-transfer quenching of triplet-state EY^{2-} by quinones (k_{ox}) and that for the reductive electron-transfer quenching of triplet-state EY^{2-} by TEOA (k_{red}) are measured, quantitative discussion about the DQ concentration effect on $\Phi_{DQ^{-}\cdot}$ will be possible.

Since it has already been known that the triplet-state EY^{2-} shows a broad $T_n \leftarrow T_1$ absorption band around 600 nm,[20] quenching of this absorption by DQ and TEOA was tried to estimate k_{ox} and k_{red} as described below in (a)-(c).

(a) Triplet-State Lifetime of EY^{2-}

On irradiation of EY^{2-} (4.0×10^{-4} M) in an equivolume mixture of water (pH 10) and 2-propanol under argon atmosphere with nitrogen laser (337 nm, 5 mJ/pulse, 6 ns-fwhm), the transient absorption of triplet-state EY^{2-} ($T_n \leftarrow T_1$ absorption) was observed around 600 nm. From its decay curve at 600 nm the lifetime of triplet-state EY^{2-} was obtained to be longer than 100 μs (beyond the long time resolution of our apparatus).

(b) Oxidative Quenching of Triplet-State EY^{2-}

In the presence of DQ (1.0×10^{-4} M) under otherwise the same conditions as those in part (a) triplet-state EY^{2-} was quenched efficintly by DQ, and its lifetime was decreased to 5 μs. Furthermore, $DQ^{-}\cdot$ absorption at 400 nm[13] grew with the same rate as the decay rate of triplet-state EY^{2-}, which shows that the quenching of triplet-state EY^{2-} occurs through electron transfer from triplet-state EY^{2-} to DQ. As the concentration of DQ is much larger than that of triplet-state EY^{2-}, k_{ox} can be estimated from the pseudo-first-order kinetic analysis of $T_n \leftarrow T_1$ absorption to be 2 x 10^9 $M^{-1}s^{-1}$.

(c) Reductive Quenching of Triplet-State EY^{2-}

In the presence of TEOA (1.0 x 10^{-3} M) under otherwise the same conditions as those in part (a), triplet-state EY^{2-} was quenched by electron transfer from TEOA and its lifetime was determined to be 50 μs. By the same analysis as that employed in part (b), k_{red} can be estimated to be 2 x 10^7 $M^{-1}s^{-1}$.

It was found that k_{ox} was about a hundred times larger than k_{red}.

4. Reaction Mechanism

The DQ concentration effect on $\Phi_{DQ^{-}\cdot}$ indicates that two kinds of reactions occur in triplet-state EY^{2-} as shown below,

<Oxidation Cycle>

$$EY^{2-}(T)^{*} + Q \xrightarrow{k_{ox}} EY^{-}\cdot + Q^{-}\cdot \qquad (1)$$

$$EY^{-}\cdot + TEOA \longrightarrow EY^{2-} + TEOA^{+}\cdot \qquad (2)$$

$$EY^{-}\cdot + Q^{-}\cdot \longrightarrow EY^{2-} + Q \qquad (3)$$

<Reduction Cycle>

$$EY^{2-}(T)^{*} + TEOA \xrightarrow{k_{red}} EY^{3-}\cdot + TEOA^{+}\cdot \qquad (4)$$

$$EY^{3-}\cdot \longrightarrow \text{decomposition} \qquad (5)$$

$$EY^{3-}\cdot + Q \longrightarrow EY^{2-} + Q^{-}\cdot \qquad (6)$$

where $EY^{2-}(T)^{*}$ and Q represent triplet-state EY^{2-} and a quinone, respectively. The former is so-called oxidation cycle. In this mechanism triplet-state EY^{2-} formed on irradiation of EY^{2-} reacts with a quinone (Q) to give $EY^{-}\cdot$ and $Q^{-}\cdot$. The resulting $EY^{-}\cdot$ accepts an electron from TEOA or $Q^{-}\cdot$. The latter is so-called reduction cycle in which the triplet-state EY^{2-} is reduced by TEOA, and $EY^{3-}\cdot$ and $TEOA^{+}\cdot$ are formed primarily. The resulting $EY^{3-}\cdot$ is mainly decomposed unimolecularly since the intermolecular electron transfer process (reaction 6) may be slower.

By using the values of k_{ox} and k_{red} obtained by laser flash photolysis, an attempt was made to compare between the apparent quenching rate constants of triplet-state EY^{2-} by DQ (k_{ox}[DQ]) and by TEOA (k_{red}[TEOA]) under the conditions where the quantum yield measurements were made as described above. k_{ox}[DQ] and k_{red}[TEOA] are listed in Table 1 with $\Phi_{DQ^{-}\cdot}$. k_{red}[TEOA] is larger than k_{ox}[DQ] at [DQ] = 1.0 x

10^{-5} M where $\Phi_{DQ^{-}\cdot}$ is 0, and k_{ox}[DQ] is larger than k_{red}[TEOA] at [DQ] = 5.0 x 10^{-5} M where $\Phi_{DQ^{-}\cdot}$ is 0.47. When the reductive quenching of triplet-state EY^{2-} by TEOA prefers to the oxidative quenching, $\Phi_{DQ^{-}\cdot}$ is negligible; on the contrary, when the oxidative quenching of triplet-state EY^{2-} by DQ prefers to the reductive quenching, $\Phi_{DQ^{-}\cdot}$ attains the considerable value. However, when the concentration of DQ is higher than 5.0 x 10^{-4} M, $DQ^{-}\cdot$ can supply an electron for $EY^{-}\cdot$ before TEOA supplies it as k_{ox}[DQ] becomes much faster than k_{red}[TEOA] , and such condition makes $\Phi_{DQ^{-}\cdot}$ reduced.

Furthermore, the Gibbs free energy change (ΔG°) for the oxidative electron transfer from triplet state EY^{2-} to quinones indicates that the electron transfer processes (reaction 1) is energetically possible. Using the values of EY^{2-} triplet energy (45 kcal/mol)[21] and the redox potentials, $E(EY^{-}\cdot/EY^{2-})=1.11$,[22] $E(AQS/AQS^{-}\cdot)=-0.66$, and $E(DQ/DQ^{-}\cdot)=-0.56$ V vs. NHE, ΔG°'s for AQS and DQ were calculated through Weller's equation[23] to be -4.1 and -6.4 kcal/mol, respectively (the Coulombic energy term was neglected because of much polar solvent). These values are preferable for the reaction to occur.

From the results of laser flash photolysis experiments, quantum yield measurements and Gibbs free energy changes, it was clarified that $Q^{-}\cdot$ formation sensitized by EY^{2-} is efficient when triplet-state EY^{2-} reacts through the oxidation cycle but not through the reduction cycle.

Conclusion

1) EY^{2-} sensitized electron transfer from TEOA to quinones with visible light irradiation. Under optimum condition, the resulting quinone radical anions were persistently alive after irradiation, and EY^{2-} was quite durable for irradiation.

2) A remarkable DQ concentration effect was observed on the quantum yields for EY^{2-} sensitized reduction of DQ. When the reaction of triplet-state EY^{2-} was changed from the reduction cycle to the oxidation cycle with increasing DQ concentration, the quantum yield for $DQ^{-\cdot}$ formation was increased.

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Table 1. The quantum yields for $DQ^{-\cdot}$ formation sensitized by EY^{2-}, and the apparent quenching rate constants of triplet-state EY^{2-} through oxidation by DQ and reduction by TEOA.

[DQ]/M	$\Phi_{DQ^{-\cdot}}$	$k_{ox}[DQ]/s^{-1}$	$k_{red}[TEOA]/s^{-1}$
1.0×10^{-5}	0.00	2×10^{4}	4×10^{4}
5.0×10^{-5}	0.47	1×10^{5}	4×10^{4}
1.0×10^{-4}	0.47	2×10^{5}	4×10^{4}
5.0×10^{-4}	0.23	1×10^{6}	4×10^{4}
1.0×10^{-3}	0.23	2×10^{6}	4×10^{4}

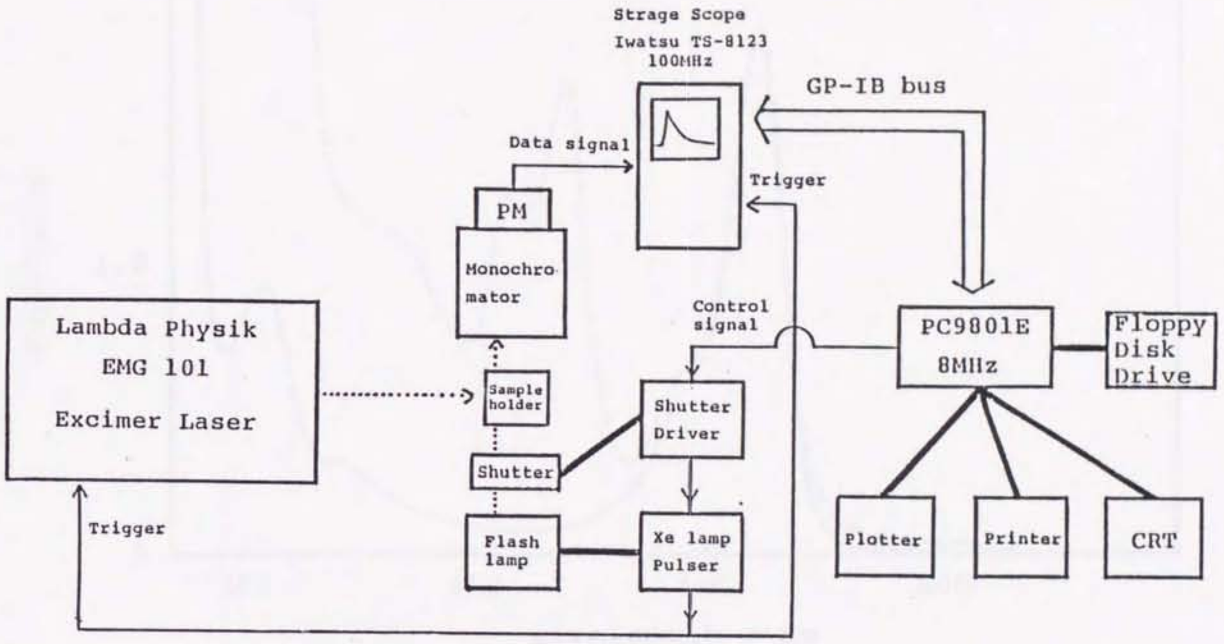

Figure 1. The block diagram of nanosecond laser flash photolysis system.

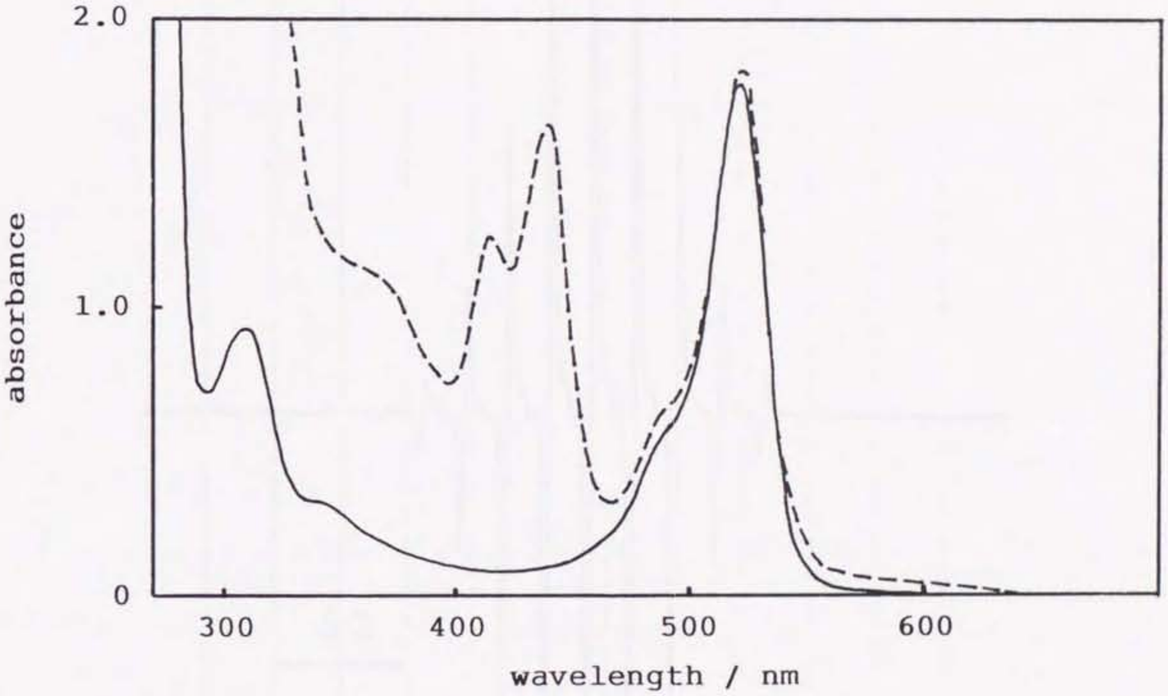

Figure 2. The absorption spectra before (——) and after (---) visible light (≥ 500 nm) irradiation of the EY^{2-}/DQ system under argon atmosphere. The solution contains EY^{2-} (1.5×10^{-5} M), DQ (1.0×10^{-4} M), TEOA (1.9×10^{-3} M), and NaOH (0.1 M) in an equivolume mixture of water and 2-propanol.

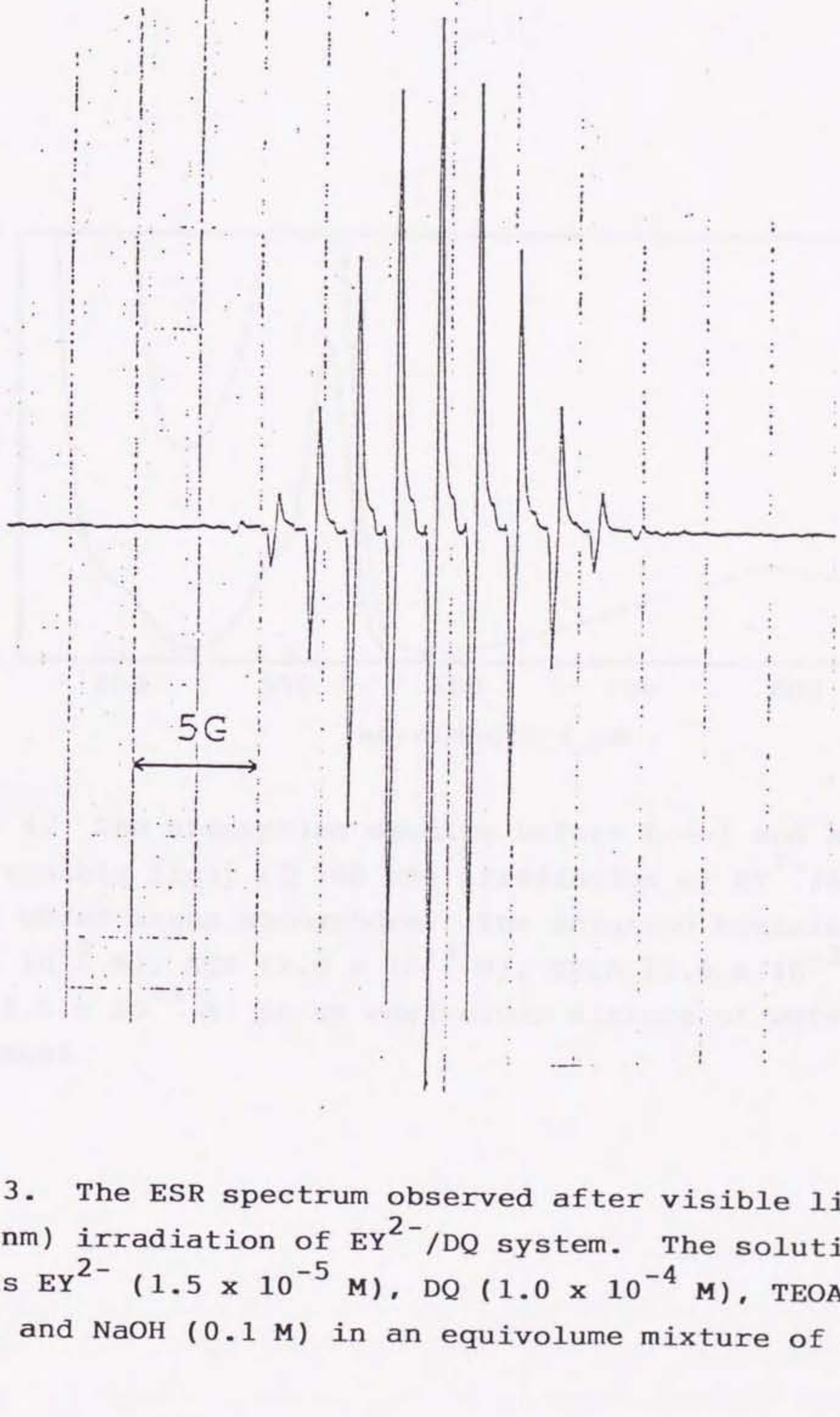

Figure 3. The ESR spectrum observed after visible light (≥ 500 nm) irradiation of EY^{2-}/DQ system. The solution contains EY^{2-} (1.5×10^{-5} M), DQ (1.0×10^{-4} M), TEOA (1.9×10^{-3} M) and NaOH (0.1 M) in an equivolume mixture of water.

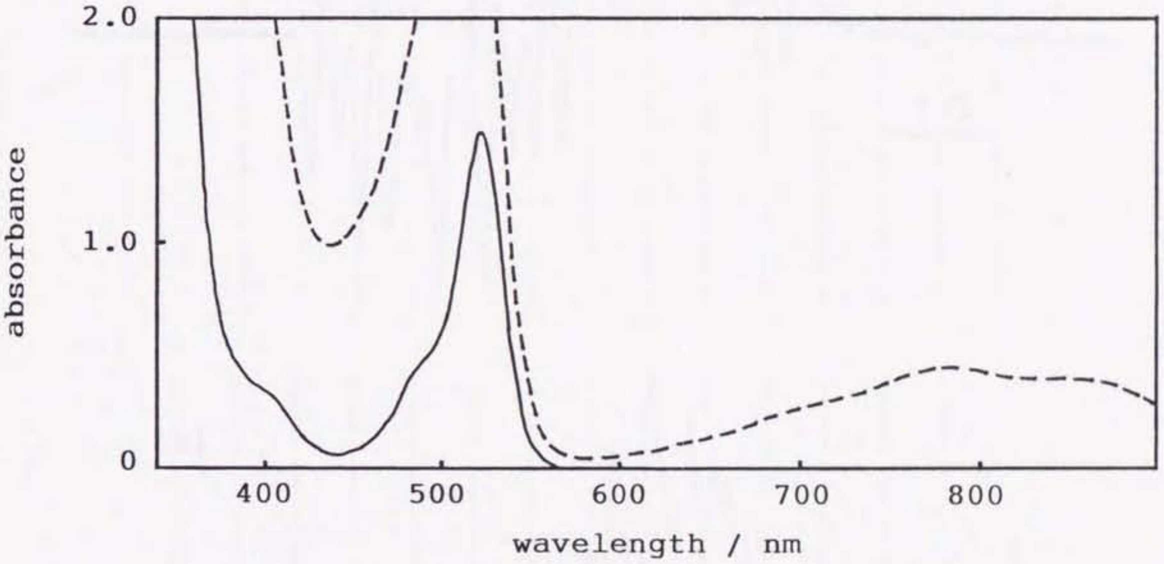

Figure 4. The absorption spectra before (——) and after (---) visible light (≥ 500 nm) irradiation of EY^{2-}/AQS system under argon atmosphere. The solution contains EY^{2-} (1.5×10^{-5} M), AQS (2.0×10^{-3} M), TEOA (5.6×10^{-3} M) and NaOH (1.0×10^{-3} M) in an equivolume mixture of water and 2-propanol.

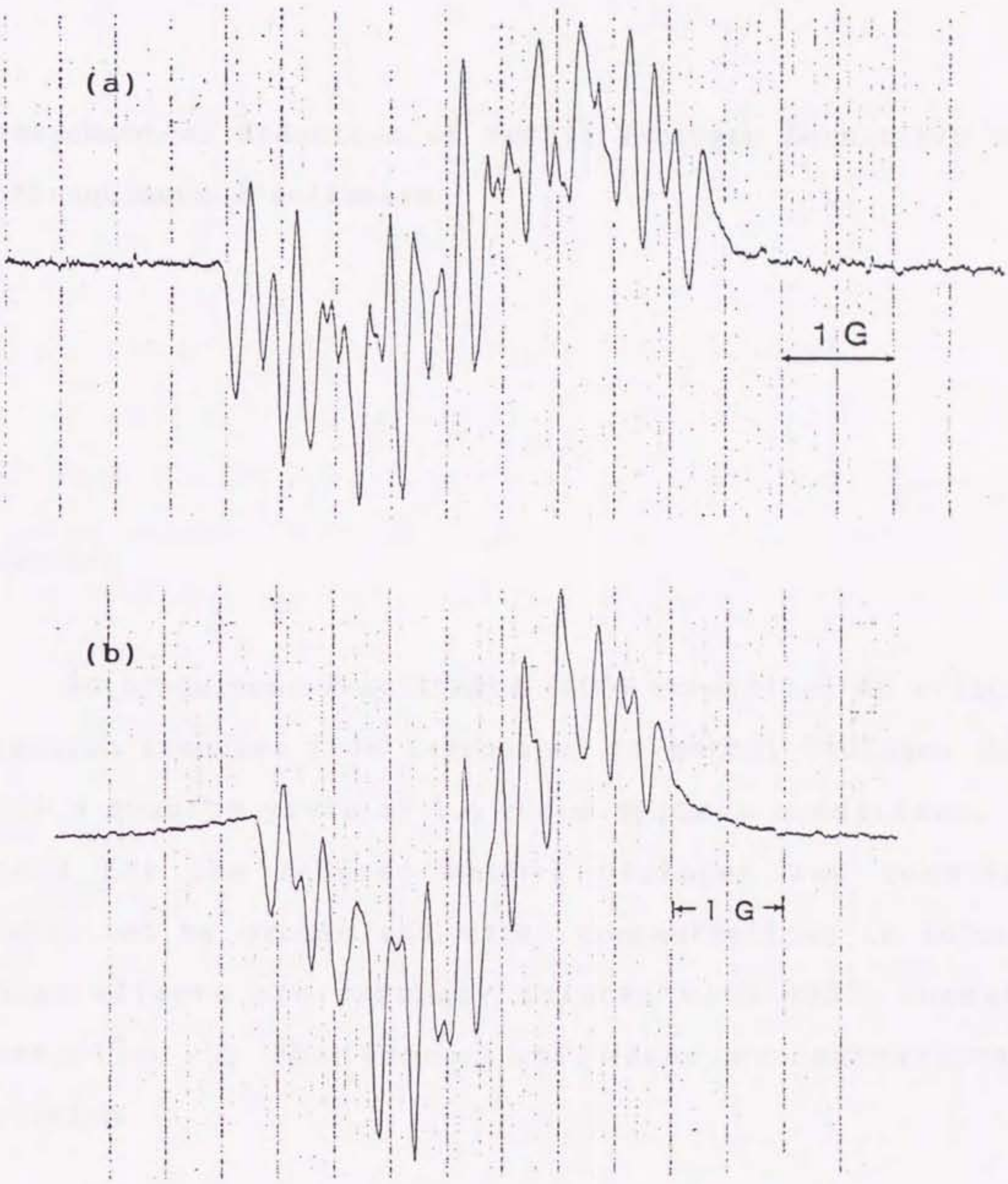

Figure 5. (a) The ESR spactrum observed after visible light (≥ 500 nm) irradiation of EY^{2-}/AQS system. (b) The ESR spectrum of AQS$^{-\cdot}$ pruduced by the electrochemical reduction of AQS in an equivolume mixture of water and 2-propanol.

Chapter 2

Photochemical Reduction of Methyl Viologen Sensitized by Anthraquinone-2-sulfonate

Abstract

Anthraquinone-2-sulfonate (AQS) sensitized an efficient electron transfer from 2-propanol to methyl viologen (MV^{2+}) with a quantum yield of 1.4 under optimum conditions. The yield for the reduced methyl viologen was remarkably controlled by proton and water concentrations in solution. These effects are strongly related with $AQS^{-\cdot}$ formation controlled by the proton and water concentrations in solution.

Introduction

There have been various attempts to achive hydrogen evolution from water by means of photosensitized reduction of methyl viologen (MV^{2+})[1] because MV^{2+} has a redox potential enough to reduce water and its reduced form is persistently alive without electron acceptors. In most cases the photosensitized reduction of MV^{2+} needed sacrificial electron donors such as amines. If a more general material like alcohol is used as an electron donor, it will make an advance in the above MV^{2+} reduction systems.[2-5]

When anthraquinone-2-sulfonate (AQS) was used as a sensitizer,[6-15] alcohols worked as an "electron donor" for MV^{2+} reduction. On excitation of AQS in the presence of 2-propanol in deaerated solution the reduced AQS radicals whose redox potentials are cathodic enough to reduce MV^{2+} are formed through the hydrogen abstraction mechanism[14] as follows:

$$\mathrm{AQS} \xrightarrow{h\nu} \mathrm{AQS(S)}^{*} \xrightarrow{\mathrm{isc}} \mathrm{AQS(T)}^{*} \qquad (1)$$

$$\mathrm{AQS(T)}^{*} + (\mathrm{CH_3})_2\mathrm{CHOH} \longrightarrow \mathrm{AQSH}\cdot + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \qquad (2)$$

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + \mathrm{AQS} \longrightarrow \mathrm{AQSH}\cdot + (\mathrm{CH_3})_2\mathrm{CO} \qquad (3)$$

$$\mathrm{AQSH}\cdot \rightleftharpoons \mathrm{AQS}^{-}\cdot + \mathrm{H}^{+} \qquad (4)$$

$$2AQSH\cdot \longrightarrow AQSH_2 + AQS \qquad (5)$$

where $AQS(S)^*$, $AQS(T)^*$ and AQSH· stand for the excited siglet-state AQS, triplet-state AQS and anthrasemiquinone-2-sulfonate radical, respectively.

The yield of reduced MV^{2+} ($MV^{+\cdot}$) was found to be remarkably dependent on proton and water concentration in solution. Similar effects were also observed on the photochemical reduction of AQS with 2-propanol.

On the basis of the results continuous irradiation, laser flash photolyses, electrochemical experiments and quantum yield measurement, the mechanism of $MV^{+\cdot}$ formation and the effects of proton and water concentration on $MV^{+\cdot}$ formation will be discussed in this chapter.

Experimental Section

Materials. Sodium anthraquinone-2-sulfonate (Nakarai Chemicals) was salted out from an aqueous sodium chloride solution and then recrystallized twice from distilled water. Methyl Viologen, acetonitrile, and tert-butyl alcohol were purchased from Nakarai Chemicals and used as received. 2-Propanol (Nakarai Chemicals) was used after distillation. Water(non-fluorescent, Wako Chemicals) was used as received.

pH-Controlled Water. pH of water was controlled by the following buffers: phthalate (pH 3-5), phosphate (pH 6-7), and borate (pH 8-10). The buffer concentration was 0.05 M.

Quantum Yield Measurements. Samples were irradiated with 350 nm light through a monochromator (Shimadzu, 1200 grooves/mm) from a 500-W xenon lamp (Ushio U1-501C). Light intensity was measured by means of a potassium tris(oxalato)ferrate(III) (0.15 M) actinometer and determined to be 1.91 x 10^{-8} einstein/min. The concentrations of $MV^{+\cdot}$ and $AQS^{-\cdot}$ produced on irradiation were determined from the absorbance at 606 (ε=11900 $M^{-1} cm^{-1}$)[16] and 507 (ε=7000 $M^{-1}cm^{-1}$)[15] nm, respectiely.

Apparatus. The absorption spectra were measured on a spectrophotometer (Hitachi, 200-20).

The electrochemical reduction was carried out in a cell equipped with three electrodes which are working (Pt), counter(Pt) and reference (SCE) electrodes. The potential of the working electrode was kept constant during electrolysis with a potentiostat (Hokuto, HA201). After the electrolysis the solution containing reduced species was transferred to a spectrum measurement cell under argon atmosphere. The system of the electrolysis is schematically depicted in Figure 1.

Nanosecond laser flash photolyses were carried out using a Lambda Physik Laser (EMG-101) with nitrogen emission at 337 nm (5 mJ/pulse, 6-ns fwhm) and a xenon discharge lamp (Wacom R.&D., KXL-151) as a probe beam source. The transient signals were recorded on a storage scope (Iwatsu TS-8123). The system of laser flash photolysis was schematically depicted in Figure 1 in chapter 1.

Results and Discussion

1. pH Effects on the Yield of $MV^{+\cdot}$ Formation

i) pH Dependence of $MV^{+\cdot}$ Yield

In the presence of MV^{2+} (1.0×10^{-3} M) a solution of AQS (1.0×10^{-4} M) in an equivolume mixture of 2-propanol and pH-adjusted water was irradiated with 360 ±30-nm light (Toshiba UV-D36B filter) from a 500-W xenon lamp under argon atmosphere and the reaction was followed by spectrophotometry.

When water of low pH (pH<5) was used, the irradiation did not lead to reduction of MV^{2+} but resulted in reduction of AQS to 9,10-dihydroxyanthracene-2-sulfonate ($AQSH_2$) as revealed by appearance of its absorption band around 384 nm.[6] A typical absorption spectrum change at the low pH region was depicted in Figure 2. When pH of water was higher than 6, however, AQS sensitized efficiently the reduction of MV^{2+} to $MV^{+\cdot}$ as revealed by appearance of its 605 nm[17] absorption band. A typical absorption spectrum change at the high pH region was depicted in Figure 3.

Furthermore, irradiation of AQS in water (pH 10) in the absence of 2-propanol scarcely reduced MV^{2+}, which indicates that the alcohol is essential to efficient reduction of MV^{2+}.

On introduction of air to the irradiated solution the absorption of $MV^{+\cdot}$ disappeared and the original absorption of AQS was found to remain without decrease. This fact shows that AQS is durable on irradiation under these conditions.

Figure 4 depicts the effect of pH of water in aqueous solution on the efficiency of MV^{2+} reduction. The efficiencies were determined by irradiating AQS for a given period (3 min) in a 1:1 mixture of 2-propanol and water of various pHs. This figure indicates that the efficiency of MV^{2+} reduction depends remarkably on pH of water used and attains higher values at pHs higher than 8.[19]

In the absence of MV^{2+}, irradiation of AQS under the same conditions led to production of $AQSH_2$ and AQS radical anions ($AQS^{-\cdot}$) when low pH water (pH 5) and high pH water (pH 10) was used, respectively. The production of $AQS^{-\cdot}$ was revealed by its absorption[7,8,15] and ESR spectra[9,10] as depicted in chapter 1. In these cases the original absorption of AQS was completely recovered on exposure of the irradiated mixtures to air.

From these experimental results, it is supposed that $AQS^{-\cdot}$ can reduce MV^{2+} but $AQSH_2$ cannot. In order to see whether $AQS^{-\cdot}$ can reduce MV^{2+} or not, the electrochemical experiments were carried out.

ii) Electrochemical Experiments on Electron Transfer from $AQS^{-\cdot}$ to MV^{2+}

As a control experiment, MV^{2+} was treated with $AQS^{-\cdot}$ produced by electrochemical reduction of AQS. A solution of AQS (1.0×10^{-3} M) in an equivolume mixture of water (pH 10) and 2-propanol was electrochemically reduced at -0.70 V (vs. SCE) for 162 minutes under argon atmosphere. The resulting $AQS^{-\cdot}$ was transferred from the electrolysis cell to an optical cuvet cell by using argon gas pressure and then its absorption spectrum was measured. The absorption spectrum depicted in Figure 5 clearly shows that $AQS^{-\cdot}$ was formed through the electrochemical reduction. When MV^{2+} (1.0×10^{-3} M) was added to this $AQS^{-\cdot}$ solution under argon atmosphere, $AQS^{-\cdot}$ disappeared and $MV^{+\cdot}$ was formed efficiently as shown in absorption spectrum change (Figure 5). This result indicates that an electron was transferred from $AQS^{-\cdot}$ to MV^{2+}. It is also supported from comparison of redox potentials:[18] $E(AQS/AQS^{-\cdot}) = -0.92$ and $E(MV^{2+}/MV^{+\cdot}) = -0.68$ V vs. SCE in acetonitrile.

iii) Quantum Yields for $MV^{+\cdot}$ and $AQS^{-\cdot}$ Formation

In the presence of MV^{2+} (1.0×10^{-3} M), AQS (1.0×10^{-3} M) was excited with 350 nm light in an equivolume mixture of water (containing 1.0×10^{-3} M of NaOH) and 2-propanol under argon atmosphere. Under these conditions the quantum yield for $MV^{+\cdot}$ formation was 1.4. In the absence of MV^{2+} under otherwise the same conditions, $AQS^{-\cdot}$ was formed with a quantum yield of 1.6.

The facts that the quantum yield for MV^{2+} reduction exceeds unity and that the quantum yield for $AQS^{-\cdot}$ production in the absence of MV^{2+} is close to two indicate that both $AQS^{-\cdot}$ and $(CH_3)_2\dot{C}OH$ act as electron donors as depicted below.[9,12]

$$AQS(T)^{*} + (CH_3)_2CHOH \longrightarrow AQSH\cdot + (CH_3)_2\dot{C}OH$$

$$(CH_3)_2\dot{C}OH + AQS \longrightarrow (CH_3)_2CO + AQSH\cdot$$

$$AQSH\cdot \rightleftharpoons AQS^{-\cdot} + H^{+}$$

$$2AQSH\cdot \longrightarrow AQSH_2 + AQS \qquad \text{(in acidic solution)}$$

$$AQS^{-\cdot} + MV^{2+} \longrightarrow AQS + MV^{+\cdot} \qquad \text{(in alkaline solution)}$$

$$(CH_3)_2\dot{C}OH + MV^{2+} + OH^{-} \longrightarrow (CH_3)_2CO + MV^{+\cdot} + H_2O \qquad \text{(in alkaline solution)}$$

iv) Laser Flash Photolysis Experiments

To see electron transfer from photochemically formed $AQS^{-\cdot}$ to MV^{2+} laser flash photolysis experiments were carried out. In the presence of MV^{2+} (3.3×10^{-5} M or 8.0 x

10^{-4} M), AQS (4.0×10^{-4} M) was excited with nitrogen laser (337 nm, 5 mJ/pulse, 6-ns fwhm) in an equivolume mixture of water (pH 10) and 2-propanol under argon atmosphere. The formation of $AQS^{-\cdot}$ and $MV^{+\cdot}$ was monitored at 500 and 602 nm, respectively.

Typical oscilloscope traces are depicted in Figure 6. Figure 6-(a) and (b) shows the formation of $AQS^{-\cdot}$ and $MV^{+\cdot}$, respectively. When the concentration of MV^{2+} was 3.3×10^{-5} M, the growth of $AQS^{-\cdot}$ was observed at 500 nm; however, when the concentration of MV^{2+} was increased to 8.0×10^{-4} M, the decay of $AQS^{-\cdot}$ was observed after its rapid growth. The yields of $MV^{+\cdot}$ and $AQS^{-\cdot}$ are larger and smaller in the higher MV^{2+} concentration, respectively.

From the analysis of $MV^{+\cdot}$ formation curve, the rate constant for the electron transfer from $AQS^{-\cdot}$ to MV^{2+} was estimated to be about 1.0×10^{10} $M^{-1}s^{-1}$. As will be shown in chapter 3, the rate constant for the deprotonation of $AQSH^{\cdot}$ is about 1.0×10^{6} s^{-1} in 50 vol% water content. Since at 8.0×10^{-4} M of MV^{2+} concentration the electron transfer rate becomes faster than the deprotonation rate of $AQSH^{\cdot}$, the resulting $AQS^{-\cdot}$ would not be kept in sufficiently high concentration to be observed. This is also supported by the following comparison, that is, the time profile of $AQS^{-\cdot}$ formation at $[MV^{2+}] = 3.3 \times 10^{-5}$ M where the electron-transfer rate will be slower than the deprotonation rate is in close agreement with the time profile of $MV^{+\cdot}$ formation at $[MV^{2+}] = 8.0 \times 10^{-4}$ M where the electron-transfer rate will be faster than the deprotonation rate. Futhermore, as mentioned in the experiment of pH effect, the reduction of MV^{2+} by AQSH· is not efficient. Therefore, the results of laser flash photolysis are well explained by the electron transfer from $AQS^{-\cdot}$ to MV^{2+}.

2. Water Concentration Effects on the Yields for $MV^{+\cdot}$ and $AQSH_2$

From experiments of (i) 2-propanol concentration effects and (ii) water concentration effects on the yields for $MV^{+\cdot}$ and $AQSH_2$ formation, the reaction between triplet-state AQS and 2-propanol was found to be influenced by the water content in the solution.

(i) 2-Propanol Concentration Effects

$MV^{+\cdot}$ Formation. In the presence of MV^{2+} (8.0×10^{-3} M) AQS (8.0×10^{-5} M) was irradiated with 360 ±30-nm light (Toshiba UV-D36B filter) from a tungsten-halogen lamp (Sylvania, 24 V, 150 W) under argon atmosphere. In three kinds of solvents employed, water, an equivolume mixture of water-acetonitrile and an equivolume mixture of water - tert butyl alcohol, 2-propanol was added in various concentrations, and the relative yields of the resulting $MV^{+\cdot}$ were determined from the absorbance at 605 nm after 10-min irradiation and normalized at the value in the water-acetonitrile mixture with 2-propanol (3.27 M). pH of water in all solvents was adjusted to 7 by using 0.01 M phosphate buffer.

The relative $MV^{+\cdot}$ yield was plotted in Figure 7 as a function of 2-propanol concentration in three kinds of solvents. It is shown that in each solvent the $MV^{+\cdot}$ yield tends to increase with 2-propanol concentration as a sigmoid curve. In water, the relative $MV^{+\cdot}$ yields were always smaller than those in the mixed solvents, and attained the highest value when 2-propanol concentration was higher than 6.54 M where water content is smaller than 50 vol%. When water-acetonitrile and water-tert-butyl alcohol mixed solvents were used as solvents, 2-propanol concentration dependence of the relative $MV^{+\cdot}$ yields was almost the same, and at a 2-propanol concentration of ca. 3 M the relative $MV^{+\cdot}$ yield attained almost the same value as the highest yield in water. It can be said that $MV^{+\cdot}$ formation is efficient in the solvents which contains 50-vol% or smaller than 50 vol% water.

The fact that the relative $MV^{+\cdot}$ yields in the mixed solvents are higher than those in water at the same 2-propanol concentration (at the region from 0 to 3.27 M) indicates that the water concentration also influences the $MV^{+\cdot}$ yield.

$AQSH_2$ Formation. If water concentration affects the interaction between triplet-state AQS and 2-propanol, it is expected that similar 2-propanol concentration effects will be observed for the $AQSH_2$ yield.

In the absence of MV^{2+}, 2-propanol concentration effect on the $AQSH_2$ yield was examined in the three kinds of solvents used above. The experimental conditions were the same as those of the above experiments except for MV^{2+} concentration. The relative $AQSH_2$ yields were determined from the absorbance at 420 nm after 10-min irradiation and normalized at the value in water with 2-propanol (3.27 M). Under these experimental conditions the absorbance at 420 nm is almost due to $AQSH_2$.[6]

The relative $AQSH_2$ yield was plotted in Figure 8 as a function of 2-propanol concentration in the three kinds of solvents. It shows that the ralative $AQSH_2$ yields in the mixed solvents are higher than those in water at the 2-propanol concentration smaller than 0.82 M.

The fact that 2-propanol concentration affects both yields of $MV^{+\cdot}$ and $AQSH_2$ differently in water and the mixed solvents indicates that the reaction efficiency between triplet-state AQS and 2-propanol is dependent on the water content. In the next part the water concentration effects will be described on the yields of $MV^{+\cdot}$ and $AQSH_2$.

(ii) Water Concentration Effects

$MV^{+\cdot}$ Formation. In the presence of MV^{2+} (8.0×10^{-3} M) and 2-propanol (0.82 M), AQS (8.0×10^{-5} M) was irradiated with 360 ±30-nm light (same as above experiments) under argon atmosphere. The used solvents were water-acetonitrile and water-tert-butyl alcohol mixed solvents, and the water contents in the mixed solvents were changed from 0.64 to 1.0 in water mole fraction. pH of water was adjusted to 7 by using 0.01 M phosphate buffer. The relative $MV^{+\cdot}$ yields were determined from the absorbance at 605 nm after 10-min irradiation and normalized at the values in water mole fractions of 0.76 and 0.64 for water-tert-butyl alcohol and water-acetonitrile mixtures, respectively.

The relative $MV^{+\cdot}$ yields in both mixed solvents were depicted in Figure 9 as a function of water mole fraction in the mixed solvents. In both mixed solvents the relative $MV^{+\cdot}$ yield showed a maximum at a water mole fraction about 0.7 and rapidly decreased with increasing water mole fraction to higher than 0.75. Since it was shown, in the preceding part of 2-propanol concentration effects, that the relative $MV^{+\cdot}$ yields in the absence of 2-propanol were negligible in the mixed solvents, the decrease of $MV^{+\cdot}$ yields with increasing water content is not due to the decrease of the reaction of excited-state AQS with solvent molecules. This result indicates that the $MV^{+\cdot}$ yield is controlled by the water content in the mixed solvents.

$AQSH_2$ Formation. In the presence of 2-propanol (0.082 M) AQS (8.0×10^{-5} M) was irradiated with 360 ±30-nm light under argon atmosphere. The used solvents were water-acetonitrile and water-tert-butyl alcohol mixed solvents, and the water content in the mixed solvents were changed from 0.75 to 1.0 (water mole fraction). pH of water was adjusted to 7 by using the same buffer. The relative $AQSH_2$ yields were determined from the absorbance at 420 nm after 10-min irradiation and normalized at the values in water mole fractions of 0.84 and 0.74 for water-tert-butyl alcohol and water-acetonitrile mixtures, respectively.

The relative $AQSH_2$ yields in both mixed solvents were shown in Figure 10 as a function of water mole fraction in the mixed solvents. In both mixed solvents the relative $AQSH_2$ yields decreased with increasing water content. Since in the absence of 2-propanol the $AQSH_2$ yield was negligible in both mixed solvents as shown in Figure 8, $AQSH_2$ is formed mainly through the reaction of triplet-state AQS with 2-propanol. This water concentration effect indicates that the $AQSH_2$ yield was controlled by the water content in the mixed solvent.

The fact that the similar water concentration effects were observed on $MV^{+\cdot}$ and $AQSH_2$ yields suggests that the water concentration influences the reactivity of triplet-state AQS with 2-propanol.[20] Details of this water concentration effect on the reaction of triplet- state AQS with 2-propanol were investigated by means of laser flash photolysis, and they will be described in the next chapter.

Conclusion

1) AQS worked as a very durable and efficient sensitizer for reduction of MV^{2+}. The distinguished points of this system for the energy conversion are as follows:

- i) 2-propanol works as an "electron donor",
- ii) the quantum yield for $MV^{+\cdot}$ formation exceeds unity.

2) The remarkable pH effect on the yield of $MV^{+\cdot}$ formation was observed. This pH effect is caused by the equilibrium between $AQSH^{\cdot}$ and $AQS^{-\cdot}$. Since an electron was transferred from $AQS^{-\cdot}$ to MV^{2+} as indicated by electrochemical and laser flash photolysis experiments, the yield of $MV^{+\cdot}$ formation was higher in higher pH region.

3) The yields of $MV^{+\cdot}$ and $AQSH_2$ showed similar water concentration dependence. The yields decreased with increasing water mole fraction to higher than 0.7. This suggested that the reaction of triplet-state AQS with 2-propanol would be suppressed by the interaction of triplet-state AQS with water molecules.

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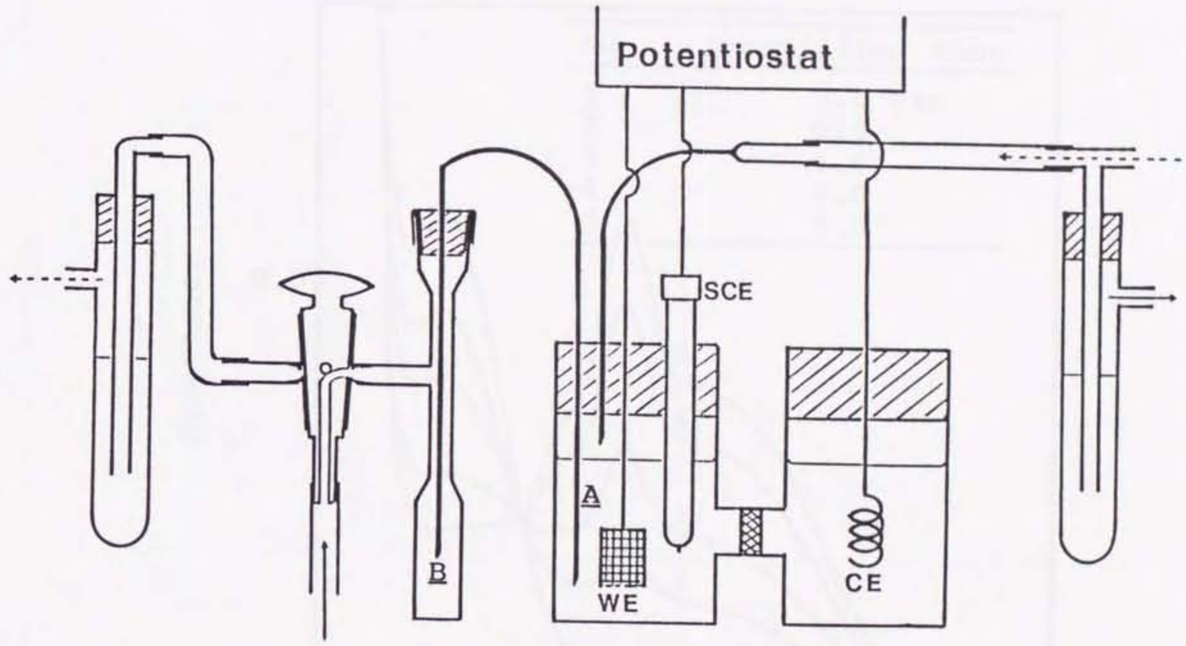


Figure 1. Schematic electrochemical reduction system. ⟶ indicates the flow of argon gas during the electrolysis. ····▸ indicates the flow of argon gas as transferring a solution from A to B. WE, CE and SCE stand for working, counter and saturated calomel electrode

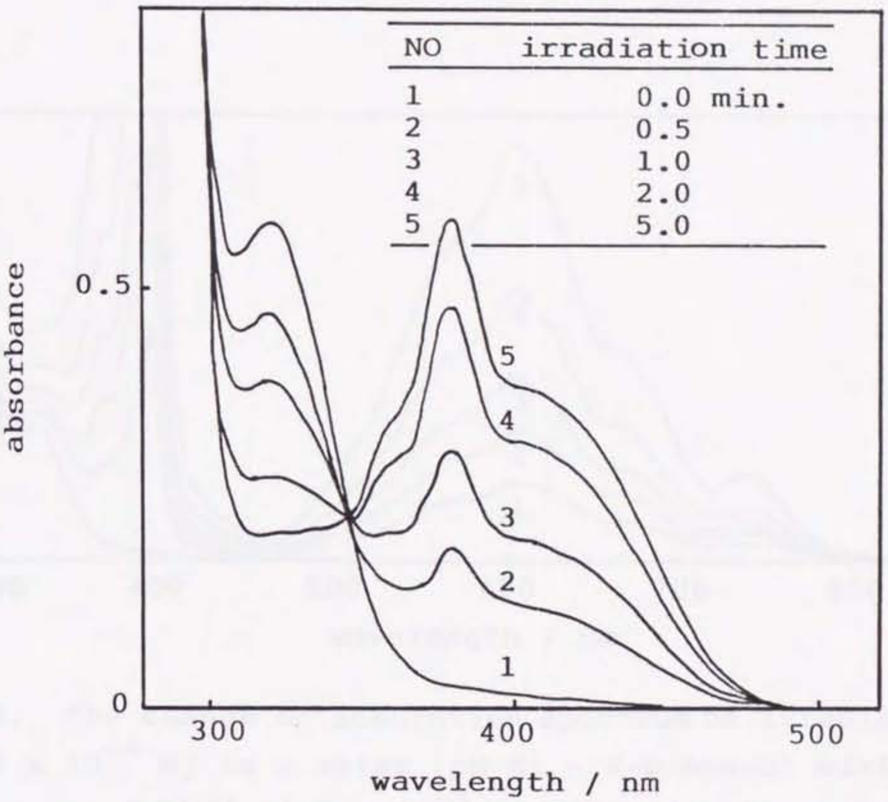


Figure 2. The change of absorption spectrum on irradiation of AQS (1.0×10^{-4} M) in a water (pH 3)-2-propanol mixture in the presence of MV^{2+} (1.0×10^{-3} M).

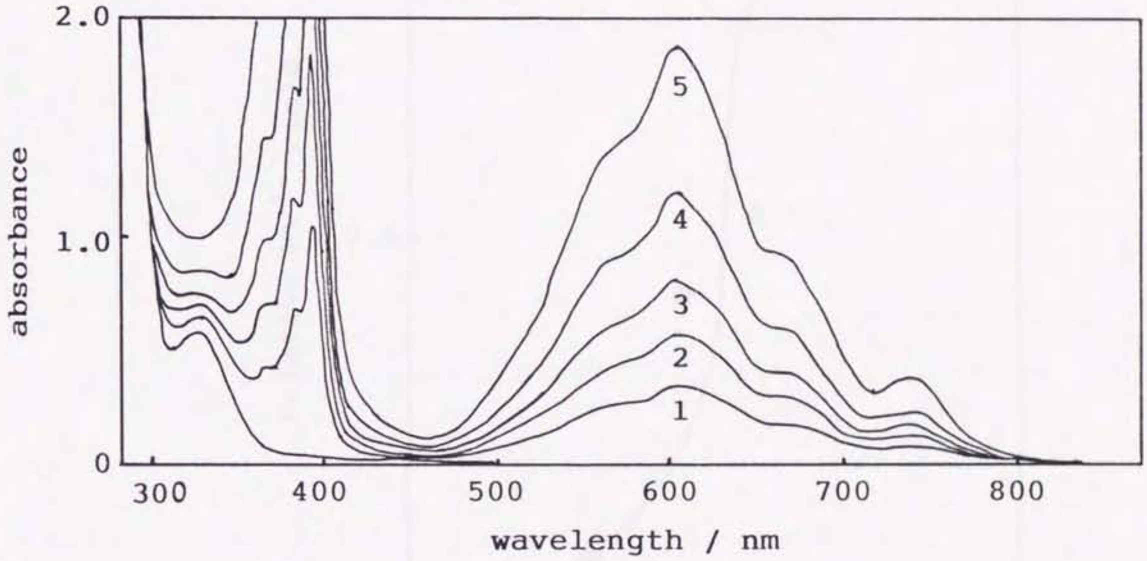


Figure 3. The change of absorption spectrum on irradiation of AQS (1.0×10^{-4} M) in a water (pH 8) - 2-propanol mixture in the presence of MV^{2+} (1.0×10^{-3} M). Irradiation time; 1: 0, 2: 20, 3: 40, 4: 60, 5: 100, 6; 180 sec.

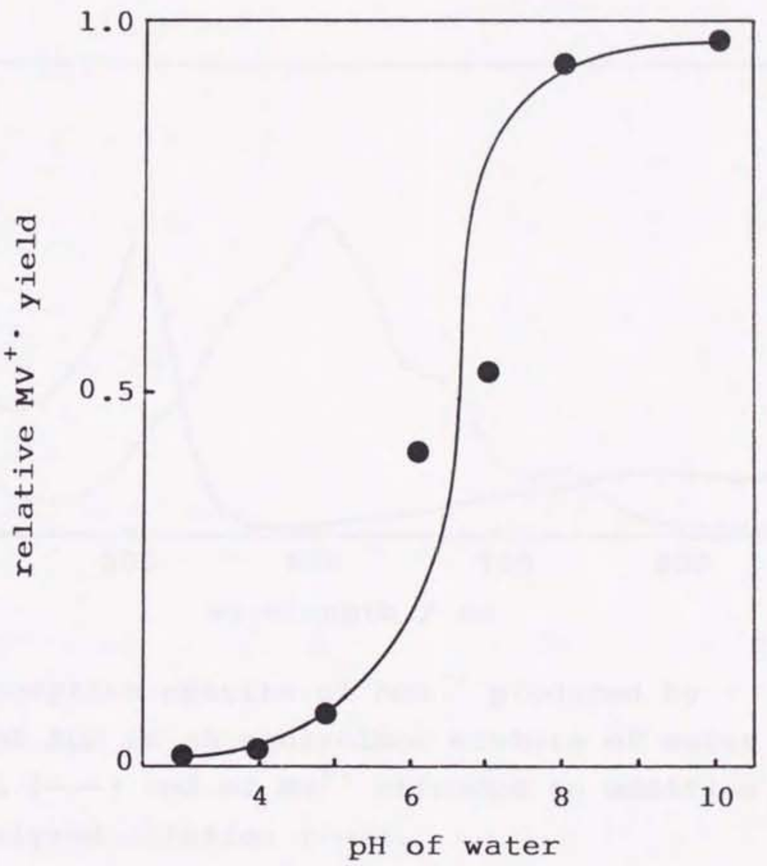


Figure 4. The effect of pH on MV$^{+\cdot}$ formation sensitized by AQS in an equivolume mixture of water and 2-propanol.

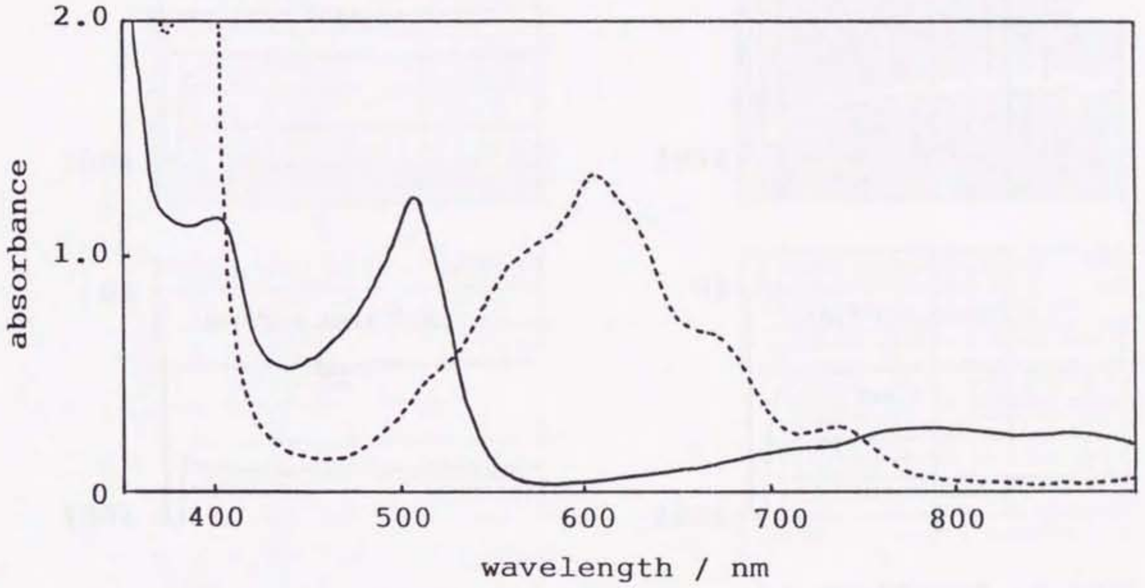
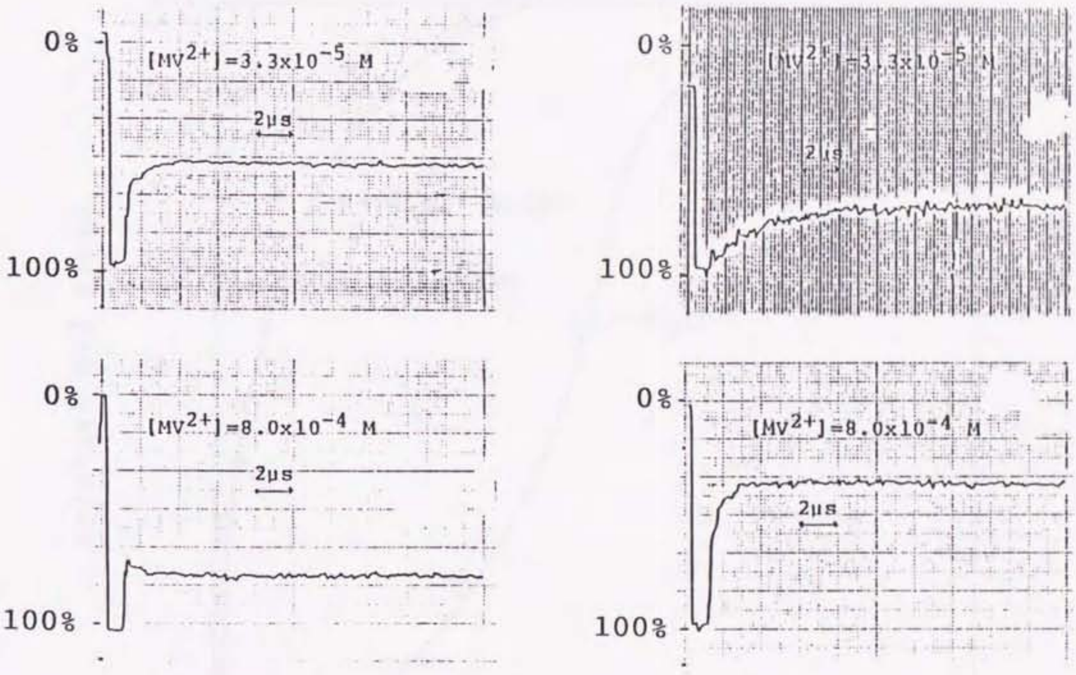


Figure 5. Absorption spectra of $AQS^{-\cdot}$ produced by electrolysis of AQS in an equivolume mixture of water (pH 10) and 2-propanol (——) and of $MV^{+\cdot}$ afforded on addition of MV^{2+} to the electrolyzed solution (------).



(a) monitored at 500 nm (b) monitored at 602 nm

Figure 6. The oscilloscope traces of the transient signals monitored at 500 nm (a) and 602 nm (b) on irradiation of AQS with nitrogen laser. [AQS] = 4.0×10^{-4} M, [MV^{2+}] = 3.3×10^{-5} M, or 8.0×10^{-4} M, in an equivolume mixture of water (pH 10) and 2-propanol, under argon atmosphere.

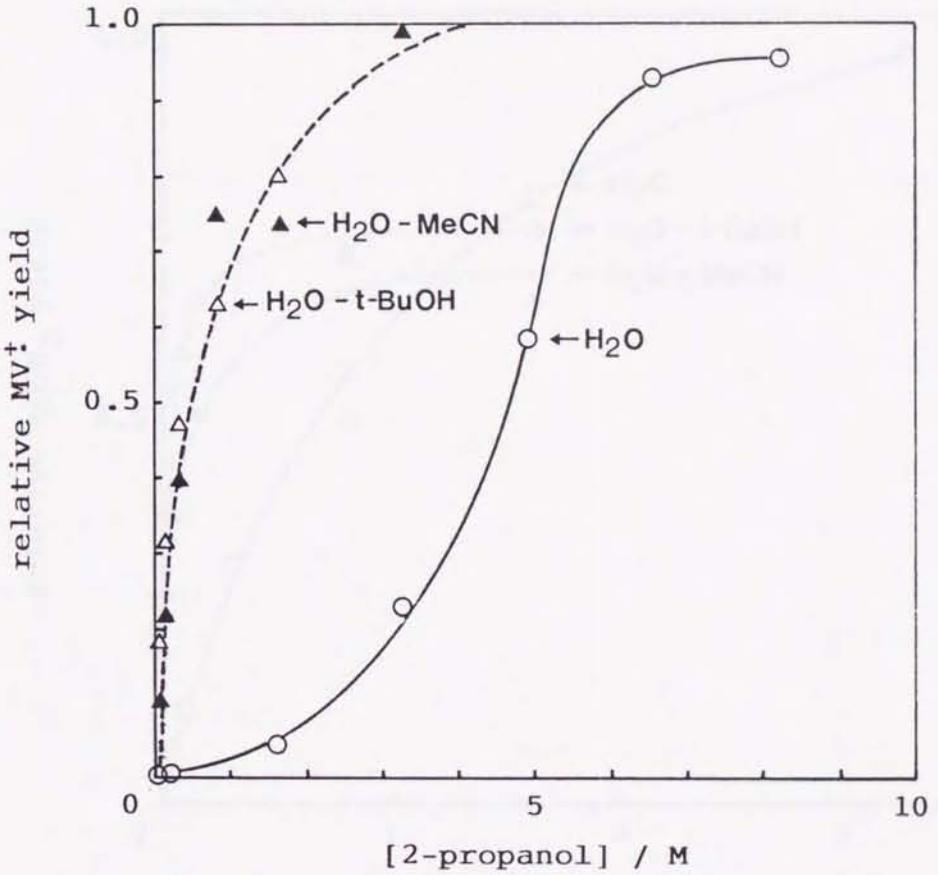


Figure 7. 2-Propanol concentration effects on relative $MV^{+\cdot}$ yield in water (○), water-tert-butyl alcohol (△), and water-acetonitrile (▲). The relative $MV^{+\cdot}$ yield was determined from the absorbance at 605 nm after 10-min irradiation and normalized at the value in the water-acetonitrile mixture with 2-propanol (3.27 M). [AQS] = 8.0×10^{-5} M, $[MV^{2+}] = 8.0 \times 10^{-3}$ M, under argon atmosphere.

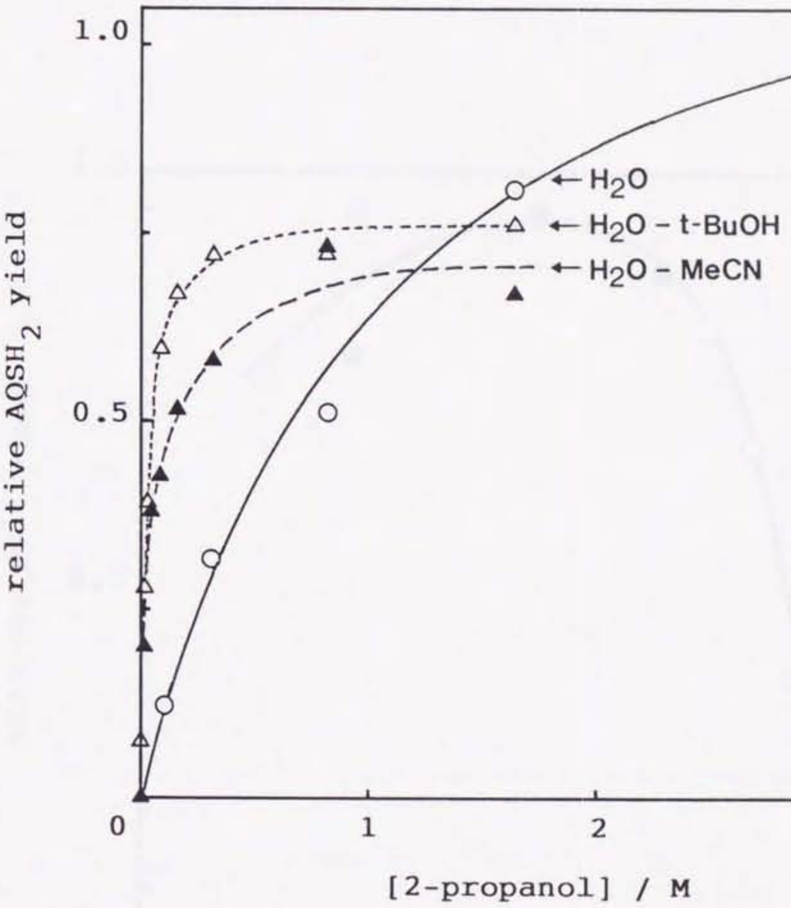


Figure 8. 2-Propanol concentration effects on relative $AQSH_2$ yield in water (○), water-tert-butyl alcohol (△), and water-acetonitrile (▲). The relative $AQSH_2$ yields were determined from the absorbance at 420 nm after 10-min irradiation and normalized at the value in water with 2-propanol (3.27 M).
[AQS] = 8.0×10^{-5} M, under argon atmosphere.

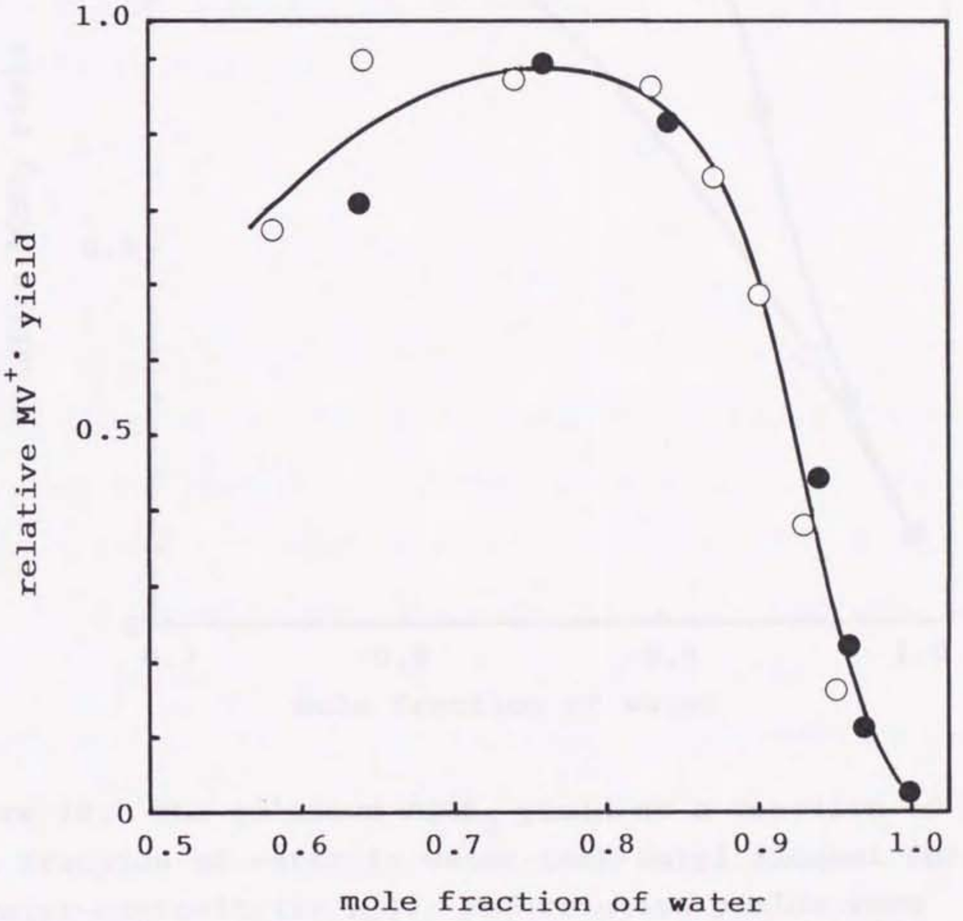


Figure 9. The relative $MV^{+\cdot}$ yield as a function of the mole fraction of water in water-tert-butyl alcohol (●), and in water-acetonitrile (○). The relative $MV^{+\cdot}$ yields were determined from the absorbance at 605 nm after 10-min irradiation and normalized at the values in water mole fractions of 0.76 and 0.64 for water-tert-butyl alcohol and water-acetonitrile mixtures, respectively. $[AQS] = 8.0 \times 10^{-5}$ M, $[MV^{2+}] = 8.0 \times 10^{-3}$ M, [2-propanol] = 0.82 M, under argon atmosphere.

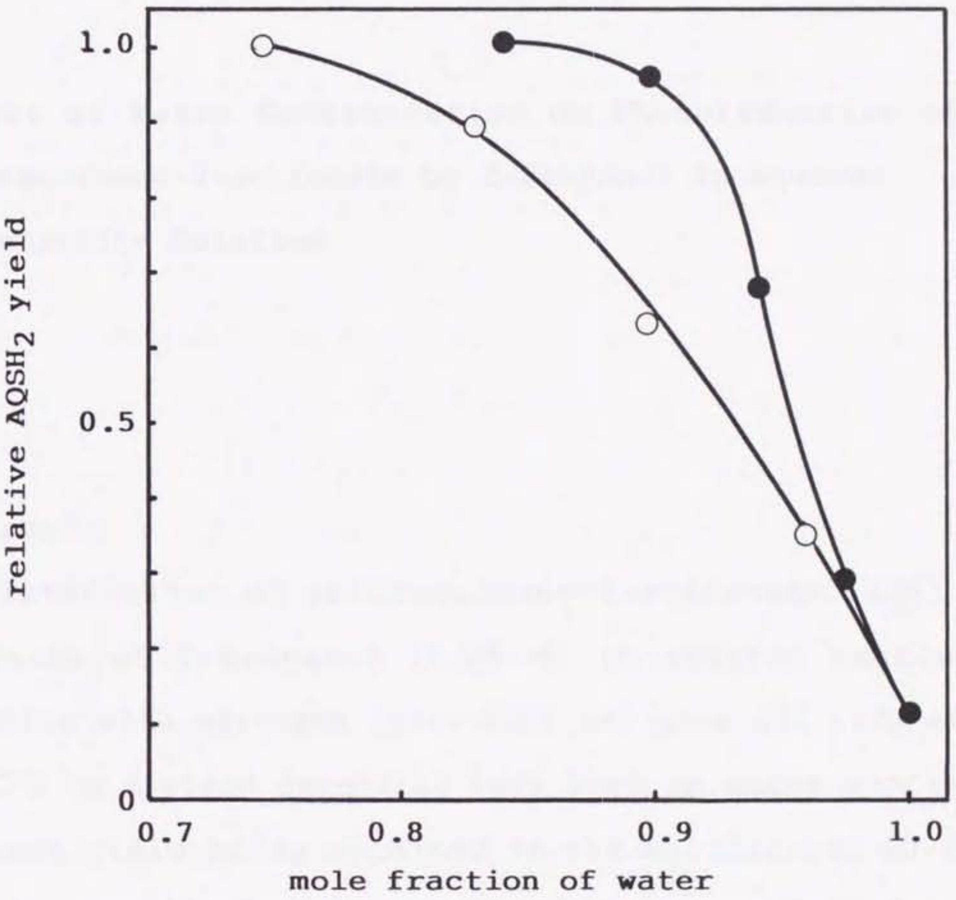


Figure 10. The relative AQSH$_2$ yield as a function of the mole fraction of water in water-tert-butyl alcohol (●), and in water-acetonitrile (○). The relative yields were determined from the absorbance at 420 nm after 10-min irradiation and normalized at the values in water mole frctions of 0.84 and 0.74 for water-tert-butyl alcohol and water-acetonitrile mixtures, respectively. [AQS] = 8.0 x 10^{-5} M, [2-propanol] = 0.082 M, under argon atmosphere.

Chapter 3

Effect of Water Concentration on Photoreduction of Anthraquinone-2-sulfonate by 2-Propanol in Aqueous Acetonitrile Solution

Abstract

Irradiation of anthraquinone-2-sulfonate (AQS) in the presence of 2-propanol (0.08 M) in aqueous acetonitrile solution with nitrogen laser (337 nm) gave AQS radical anion ($AQS^{-}\cdot$) in a yield depending very much on water content, the highest yield being obtained in the solution of 40-60 vol% water content. This is attributable to exponential increase with water concentration of the decay rate of triplet AQS and of the deprotonation rate of AQSH· resulting from hydrogen abstraction of triplet AQS from 2-propanol. The dependence of these rates on water concentration was treated satisfactorily with Perrin's equation to give an average value of 3.3 Å for the radius of the solvation sphere surrounding triplet AQS and AQSH· in which a water molecule must exist to quench triplet AQS and to accept a proton from AQSH·, respectively. Laser excitation and continuous irradiation gave apparently different pK_a values of AQSH·. The meaning of this observation was also discussed.

Introduction

The photophysics and photochemistry of anthraquinones have been extensively studied over the past three decades[1-19] not only because of their relevance to photodegradation of dyed fiber materials and photosensitizing activity but also perhaps because of the complexity of the experimental results. Recently, the behavior of anthraquinone-2-sulfonate in aqueous acetonitrile mixtures has been precisely investigated by Loeff et al.[6] and Moore et al.[7] to elucidate the nature of the transient species and the mechanism of quenching of the triplet state by water and hydroxide anion.

On the mechanism of the photoreduction of anthraquinone sulfonates (AQS) in the presence of alcohols in aqueous solution, as early as 1961, Wells[8] deduced from the relative reactivity of various alcohols that the primary chemical step, after excitation (1), was hydrogen abstraction from the alcohol (4):

$$\mathrm{AQS} \xrightarrow{h\nu} \mathrm{AQS}^{*} \qquad \Phi_T \qquad (1)$$

$$\mathrm{AQS}^{*} \longrightarrow \mathrm{AQS} \qquad k_T \qquad (2)$$

$$\mathrm{AQS}^{*} \xrightarrow[H_2O]{} \mathrm{AQS\ or\ products} \qquad k_W \qquad (3)$$

$$\mathrm{AQS}^{*} + \mathrm{RCH_2OH} \longrightarrow \mathrm{AQSH}\cdot + \mathrm{R\dot{C}HOH} \qquad k_r \qquad (4)$$

Reaction 2 is the intrinsic deactivation of the triplet-state AQS (AQS*), and reaction 3 is quenching of AQS* by water followed by either chemical reactions or deactivation.[6,7]

AQSH· dissociates to a radical anion AQS^{-}· and a proton. Hulme et al.,[9] using pulse radiolysis, determined the pK$_a$ value of AQSH· radical to be 3.2, which is in good

$$\mathrm{AQSH}\cdot \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \mathrm{AQS}^{-}\cdot + \mathrm{H}^{+} \qquad K_a = k_a/k_{-a} \qquad (5)$$

agreement with that reported by Hayon et al., 3.9.[10] Hulme et al.[9] also showed, directly for the first time, that in benzene the unsubstituted anthraquinone triplet state reacted with 2-propanol according to reaction 4.

Recently, however, Roy and Aditya,[11] based on their flash photolysis study of AQS in the presence of formate in aqueous solution, stated that the photoreduction of AQS proceeded through electron transfer rather than hydrogen atom transfer to the excited quinone and estimated pK$_a$ for equilibrium 5 as 8.2. Earlier, Gill and Stonehill[12] reported a similar value (9.2) using a polarographic technique.

In chapter 2 it was shown that the mixing ratio of water and organic solvents (tert-butyl alcohol or acetonitrile) exhibits a remarkable effect on the efficiency of the reaction between triplet AQS and the alcohol affording 9,10-dihydroxyanthracene-2-sulfonate (AQSH$_2$) and that the concentration of proton influences the yield of AQS^{-}· which reduces methyl viologen. These experimental results showed that proton and water concentrations are important factors controlling photoreduction processes of

AQS.

It is described here that the effect of water concentration on the photochemistry of AQS in the presence of 2-propanol in aqueous acetonitrile as studied by both laser flash photolysis and continuous irradiation, propose particularly a new approach to understand the observed interesting effects of water concentration on the AQS triplet lifetime and the acid dissociation of the resulting AQSH·, and furthermore discuss the meaning of the difference between the pK_a values of AQSH· observed on pulsed laser excitation and on continuous irradiation.

Experimental Section

Sodium anthraquinone-2-sulfonate (AQS), acetonitrile, and 2-propanol were all purchased from Nakarai Chemicals and used as received. The following buffers were used in the pH dependent experiments: phthalate (pH 3-5), phosphate (pH 6-7), and borate (pH >8). The buffer concentration was always 0.01 M.

The apparatus for laser flash photolysis is shown in Figure 1 in chapter 1. Nanosecond laser flash photolyses were carried out using a Lambda Physik laser (EM-101) with nitrogen emission at 337 nm (5 mJ/pulse, 6-ns fwhm) and a xenon discharge lamp (Wacom R. & D., KXL-151) as a probe beam source. The transient signals were recorded on a storage scope (Iwatsu TS-8123) and then fed into a microcomputer for averaging and analysis. A sample cell was attached to a flow system with a sample reservoir through which argon gas was bubbled during the measurements.

Continuous irradiation experiments were performed using a projector with a tungsten-halogen lamp (Sylvania, 24 V, 150 W). Sample solutions in quartz tubes were irradiated with 360±30 nm light through a Toshiba UV-D36B filter under argon atmosphere.

Results and Discussion

1. Photochemistry of AQS in the Presence of 2-Propanol in Water-Acetonitrile Mixed Solvents

To examine the effect of water concentration on the photoreduction of AQS by alcohol, AQS [$(2.2\text{-}3.0)\times10^{-4}$ M] was excited under argon atmosphere with a nitrogen laser (337 nm) in various mixtures of water and acetonitrile in the presence of a constant concentration (0.08 M) of 2-propanol.

Typical time-resolved transient absorption spectra are depicted for runs in the mixtures of 0, 25, 50, and 90 vol% of water and acetonitrile in Figures 1, a, b, c, and d, respectively. The results in Figure 1 indicate clearly that the formation of $AQS^{-\cdot}$ with λ_{max} at 500 nm was not observed at all in 100% acetonitrile (0% water), but increased with increasing water content to 25 and 50 vol% and largely decreased again in higher concentrations of water like 90%. The relative yields of $AQS^{-\cdot}$ were determined from the maximum optical density of the transient spectrum and normalized at the value in 50% water content. The results are illustrated in Figure 2. Thus, the relative yield of $AQS^{-\cdot}$ attained the highest value in the solution of 40-60% water content and decreased with decreasing and increasing water content from these compositions.

To reveal the origin of the above finding, the effect of water content was investigated on the triplet lifetime of

AQS, the dissociation of AQSH· into $AQS^{-}\cdot$, and the rate constant for the reaction of triplet-state AQS with 2-propanol.

2. Lifetime of Triplet State AQS

Upon excitation of AQS (2.2×10^{-4} M) with nitrogen laser, the transient spectrum of triplet-state AQS^{*} was immediately detected in 360-430-nm region. In Figure 1, the initial spectra are those of the AQS triplet state, as assigned previously.[6,7]

In the absence of 2-propanol, the decay rate constant k_{obs} of the AQS triplet state was determined by the first order kinetic analysis of its decay curve measured at 380 nm, close to its maximum absorbance.[6] Figure 3a depicts a typical decay curve. As Figure 4 shows, k_{obs} was varied with the mixing ratio of acetonitrile and water. In 100% acetonitrile the decay rate constant was 5×10^{4} s^{-1} and no product was observed at all in the spectrum. In a 1:1 water-acetonitrile mixture (by volume) the lifetime of the AQS triplet was reduced by one order of magnitude and in 100% water by two orders of magnitude, due to quenching by water (reaction 3). These results are very similar to those reported by Loeff et al.[6] They explained the dependence of triplet decay rate (k_d) on the water content by the preferential solvation by acetonitrile around AQS.[6] Using a preferential solvation parameter obtained from the solvation of hexathiocyano chromate(III) in aqueous acetonitrile,[23] they showed that the triplet decay rate can be correlated with the number of water molecules in the solvation layer of AQS.[6] This implies that for the quenching of AQS^* by water to occur the water molecule must be in the solvation shell and that water molecules located outside of the solvation shell do not effectively undergo diffusional encounter with AQS^*.

It is now pointed out that the above mechanism is very similar to quenching in solid matrices where diffusion is negligible. Then, the competition between reactions 2 and 3 can be treated with Perrin's equation:[24,25]

$$(I/I_0)^{-1} = \exp(VN'[H_2O]) \qquad (6)$$

where I/I_0 is the fraction of the excited molecules not quenched by water, i.e., $k_T/(k_T + k_W)$. $N' = 6.02 \times 10^{20}$ molecules/cm^3, and V is the volume of the quenching sphere in cm^3. In the present case the quenching sphere is the volume surrounding an AQS molecule. A water molecule must be in this sphere for reaction 3 to occur. Assuming that k_T is independent of the acetonitrile-water mixing ratio and given by the decay rate in 100 % acetonitrile and that $k_T + k_W = k_{obs}$, $\ln(k_{obs}/k_T)$ was plotted against $[H_2O]$ (insert in Figure 4).

The insert in Figure 4 shows that a good fit is obtained despite the above approximations. From the slope (VN') the quenching sphere volume V and thus its radius R $[R = (3V/4\pi)^{1/3}]$, which represents the average AQS-water distance, were calculated; R was found to be 3.3 Å. This value is very reasonable in view of the molecular dimensions of AQS. Therefore, the present results, that is, the good fit to Perrin's equation 6 and the estimated quenching radius, support the mechanism proposed previously considering the preferential solvation.[6]

It is noticeable that Perrin's equation which treats very simply the surrounding medium of an excited molecule can give reasonable R values. Thus, an AQS triplet molecule is reasonably supposed to be preferentially solvated by more hydrophobic acetonitrile molecules around its carbon nuclear skeleton, whereas its sulfonate group may be solvated by water molecules. The interaction of the AQS triplet and water has to take place near the carbon atom moiety since it results in nuclear hydroxylation products, though in a low quantum yield.[6,7] Therefore, for the quenching by water to occur, water molecules must be in the solvation shell of acetonitrile surrounding the AQS carbon skeleton. It is probable that, in the solvent with low content of water, the carbon skeleton of the AQS molecule is mostly surrounded by acetonitrile molecules, and water molecules may exist in the bulk solution; however, high water content increases the probability of water molecules in the solvation shell, and this probability may increase exponentially with water content.

3. Deprotonation and Disproportionation of AQSH·

As Figure 1 indicates, the initially resulting triplet AQS (λ_{max} = 370 nm) reacts with 2-propanol to give AQSH· through hydrogen atom transfer. AQSH· exhibits an absorption band in nearly the same region as triplet AQS; however, they can be distinguished, since AQSH· shows an absorption maximum slightly shifted to longer wavelengths and a characteristic shoulder at 420 nm.

Depending on the solvent composition, AQSH· was observed to either deprotonate or disproportionate immediately after its formation. For example, Figure 1c shows that in a 1:1 mixture of water and acetonitrile containing 2-propanol (0.08 M), following the formation of AQSH·, it deprotonates to give $AQS^{-\cdot}$ radical exhibiting a characteristic spectrum with maxima at 390 and 500 nm. By contrast, Figure 1a shows that in 100% acetonitrile containing 2-propanol (0.08 M), AQSH· disproportionates into $AQSH_2$ and AQS. The $AQSH_2$ spectrum resembles that of AQSH·; however, the former is broader with a characteristic shoulder at 410-430 nm. Moreover, as will be mentioned later, the decay of the transient absorption around 370 nm observed at 3-17 μs after laser excitation in 100% acetonitrile obeys exactly second order kinetics, indicating that the disproportionation of AQSH· takes place.

For AQSH· to deprotonate according to equilibrium 5 the presence of a suitable solvent molecule is required as a proton acceptor. Water is clearly much more suitable than acetonitrile for this purpose. The deprotonation rate constant k_a of AQSH·, as estimated by the first order kinetic analysis of the growth of AQS^{-}· measured at 500 nm (e.g., Figure 3b), was strongly dependent on the water content of the solvent. The variation of k_a with solvent composition is shown in Figure 5; the higher the water content, the faster the deprotonation rate.

As mentioned above, triplet AQS is preferentially solvated by acetonitrile, and for the water molecule to work as a quencher it must be in the solvation shell. Then, the question arises on whether or not this is also the case for the deprotonation of AQSH·. In other words, must a water molecule be in the solvation shell of AQSH· for the deprotonation to occur? To examine this point, Perrin's equation (6) was made use of again. In this case ln k_a was plotted against $[H_2O]$. The insert in Figure 5 shows a very good fit to Perrin's equation. From the slope the radius of reaction sphere was calculated as 3.2 Å. This is in excellent agreement with the value of R determined from the triplet state quenching by water (3.3 Å). Therefore, it is clear that not only triplet AQS but also AQSH· is preferentially solvated by acetonitrile.

It is very remarkable that the present treatment gave nearly the same values of the radius of the reaction sphere (R) for the two processes concerning triplet AQS and AQSH·. The above findings might be related to the effects of cluster or local structure of water molecules in the solution.[26-33] Robinson et al. reported[29-32] that the rate of electron ejection of excited indole and anilinonaphthalenes and the rate of proton dissociation of excited naphthol exhibit a highly nonlinear dependence on water concentration in water/alcohol mixtures. These rate constants increase sharply in water concentrations higher than 50 vol%. They revealed that the clusters containing 4 ± 1 water molecules play an important role as electron and proton acceptor; an increase in alcohol concentration decreases the rates of the electron ejection and proton dissociation by prohibiting the formation of water clusters. It is noticeable that in the present investigation the rate constants for AQS triplet decay, k_{obs}, and AQSH· deprotonation, k_a, behave very similarly to the above cases, increasing remarkably in water concentrations higher than 50 vol%.

The intercept in Figure 5 gives the deprotonation rate constant k_a of AQSH· in 100% acetonitrile containing 2-propanol, namely $5 \times 10^4\ s^{-1}$. This could not be measured directly because the deprotonation rate was too slow to be observed due to an unfavorable competition with the disproportionation according to the following equilibrium:

$$AQSH\cdot + AQSH\cdot \underset{k_{-dis}}{\overset{k_{dis}}{\rightleftharpoons}} AQSH_2 + AQS \qquad K_{dis} = k_{dis}/k_{-dis} \qquad (7)$$

As mentioned earlier, the formation of $AQSH_2$ can be seen in Figure 1a. The decay rate of AQSH· follows exactly second order kinetics as expected from equations 8 and 9 (Figure 3c). From the slope of the insert in Figure 3c k_{dis}/ε was found to be 5.0 x 10^4 cm s^{-1} where ε and OD are the molar extinction coefficient and the optical density of AQSH· at 370 nm, respectively. Assuming that ε is the same in 100 % acetonitrile as in water,[9] then k_{dis} is ca. 5.5 x 10^8 $M^{-1}s^{-1}$.

$$-d[AQSH\cdot]/dt = 2k_{dis}[AQSH\cdot]^2 \qquad (8)$$

$$1/OD - 1/OD_0 = 2(k_{dis}/\varepsilon)t \qquad (9)$$

Finally, from equilibrium 5 it is evident that if $[H^+]$ in solution is sufficiently high so that $k_{-a}[H^+] >> k_a$, then no net deprotonation will be observed irrespective of the solvent composition as presented below.

4. Rate Constant for the Reaction of Triplet-State AQS with 2-Propanol

Water concentration effects on the rate constant (k_r) for the reaction between triplet-state AQS and 2-propanol were examined. Since the absorption of AQSH· is difficult to be observed separately, k_r was derived from 2-propanol concentration effects on the yield of $AQS^{-}\cdot$. The 2-propanol concentration effects were examined in acetonitrile-water mixtures with different mixing ratios to see water concentration effects on k_r.

In water-acetonitrile mixtures (water content: 25, 50, and 75 vol%) containing varying concentrations of 2-propanol under argon atmosphere AQS (2.2×10^{-4} M) was excited with nitrogen laser. The relative yields of $AQS^{-\cdot}$ were determined from the maximum optical density of the transient spectrum and normalized at the value in 50 vol% water content with 2-propanol (0.08 M).

Assuming that $AQS^{-\cdot}$ is formed through the following mechanism (reactions 10 - 15):

$$AQS^{*}(T) \xrightarrow{k_r[2\text{-PrOH}]} AQSH\cdot + (CH_3)_2\dot{C}OH \qquad (10)$$

$$AQS^{*}(T) \xrightarrow{k_d} AQS \qquad (11)$$

$$(CH_3)_2\dot{C}OH \xrightarrow{k_r'[AQS]} AQSH\cdot + (CH_3)_2CO \qquad (12)$$

$$(CH_3)_2\dot{C}OH \xrightarrow{k_d'} \text{non-radical products} \qquad (13)$$

$$AQSH\cdot \xrightarrow{k_a} AQS^{-}\cdot + H^{+} \qquad (14)$$

$$AQSH\cdot \xrightarrow{k_{dis}} (1/2)(AQSH_2 + AQS) \qquad (15)$$

the quantum yields for formation of $AQSH\cdot$ and $AQS^{-}\cdot$ are derived as follows:

$$\Phi_{AQSH\cdot} = \Phi_T \frac{k_r[2\text{-PrOH}]}{k_d + k_r[2\text{-PrOH}]}\left(1 + \frac{k_r'[AQS]}{k_d' + k_r'[AQS]}\right) \qquad (16)$$

$$\Phi_{AQS^{-}\cdot} = \Phi_{AQSH\cdot} \frac{k_a}{k_a + k_{dis}[AQSH^{\cdot}]} \qquad (17)$$

where Φ_T, $\Phi_{AQSH\cdot}$ and $\Phi_{AQS^{-}\cdot}$ represent the quantum yields for the formation of triplet-state AQS, AQSH· and AQS^{-}·, respectively. Under these experimental conditions, as the value of k_a is larger than 2.2×10^5 s^{-1}, and [AQSH·] is smaller than 2.2×10^{-4} M, the relation $k_a >> k_{dis}$[AQSH·] is roughly assumed to be satisfied. Then $\Phi_{AQS^{-}\cdot}$ can be assumed to be equal to $\Phi_{AQSH\cdot}$ and is represented by a function of [2-PrOH],

$$\frac{1}{\Phi_{AQS^{-}\cdot}} = \frac{1}{A\Phi_T}\left(1 + \frac{k_d}{k_r}\frac{1}{[2\text{-PrOH}]}\right) \qquad (18)$$

where $A = 1+(k_r'[AQS]/(k_d'+k_r'[AQS]))$, and is a constant for a fixed [AQS]. Figure 6 plots the reciprocal of the resulting relative AQS^{-}· yield against the reciprocal of 2-propanol concentration.

From the ratio of the slope to the intercept in Figure 6, k_d/k_r is obtained in each solvent and listed in Table 1. Since reaction 11 includes the deactivation processes through the interaction with water, the value of k_{obs} in each solvent can be used as k_d, and then k_r is derived. The obtained values of k_r are also listed in Table 1. The result indicates that the rate constant for the reaction between triplet-state AQS and 2-propanol does not show any strong dependence on the water content. This will be correlated with the fact that 2-propanol molecules will be able to exist in the solvation shell of AQS in each solvent.

5. Effect of Proton Concentration

An attempt was made to determine pK_a of equilibrium 5 by monitoring the concentration of $AQS^{-\cdot}$ resulting from irradiation of AQS (2.2×10^{-4} M for laser flash photolysis and 8.0×10^{-5} M for continuous irradiation) in 1:1 mixtures of acetonitrile and water of various pHs in the presence of 2-propanol (0.16 M). The relative $AQS^{-\cdot}$ yields were measured from the maximum optical density of the transient absorption and the optical density after 20-min continuous irradiation. Figure 7 illustrates the results obtained on laser flash photolysis and continuous irradiation as curves a and b, respectively, in different profiles. On continuous irradiation, as curve b shows, $AQS^{-\cdot}$ formation was observed at pH values higher than 7 with an apparent pK_a of ca. 8.5. However, on laser flash photolysis (curve a), the pK_a was found to be 3.5. The difference of the observed pK_a values is reasonably explained below.

Curve a represents the equilibrium between $AQSH^{\cdot}$ and $AQS^{-\cdot}$ and thereby the observed pK_a value of ca. 3.5 corresponds to the equilibrium 5 in a 1:1 water-acetonitrile mixture. The observed value is nearly the same as the reported values in 100 % water (3.2 or 3.9)[9,10] although pK_a must vary somewhat with solvent composition.

On the other hand, curve b represents the equilibrium between $AQSH_2$ and $AQS^{-\cdot}$. In other words, it is the sum of equilibria 5 and 7. On nanosecond laser flash photolysis,

$$AQSH_2 + AQS \rightleftharpoons 2AQS^{-\cdot} + 2H^+ \qquad K_o = K_a^2/K_{dis} \qquad (19)$$

$AQSH_2$ formation from $AQS^{-\cdot}$ was not observed in the range of pH between 3.5 and 8 until 10 μs after laser excitation, because the transient [AQSH·] was very low and therefore the rate of its disproportionation was very slow beyond the long time resolution of our apparatus. However, in a long time (millisecond) resolution of a conventional flash photolysis apparatus, such as used by Roy and Aditya,[11] the equilibration between $AQS^{-\cdot}$ and $AQSH_2$ can be detected. Furthermore, the spectra of AQSH· and $AQSH_2$ are similar, which may cause the confusion in the pK_a values mentioned in the Introduction.

There is another simple argument that the pK_a value of equilibrium 5 cannot be 8.2 or 9.2 as reported.[11,12] The deprotonation rate constant k_a of AQSH· is about 7×10^6 s^{-1} in 100% water (extrapolated from the plot in the insert in Figure 5). If the pK_a value is 8.2 then k_{-a} (= k_a/K_a) is 10^{15} $M^{-1}s^{-1}$. Such a value is impossible for a reaction in water, the upper limit being on the order of 10^{11} $M^{-1}s^{-1}$. However, pK_a of 3.5 gives k_{-a} as 2.2×10^{10} $M^{-1}s^{-1}$, a very reasonable value.

From the apparent pH dependence of the equilibrium between $AQS^{-\cdot}$ and $AQSH_2$ (equilibrium 19), K_o can be calculated. Since curve b was shifted to the higher pH regions for continuous irradiation as expected from equilibrium 19, K_o was evaluated from a series of concentrations of $AQS^{-\cdot}$ and AQS. The average value for K_o was found to be 5×10^{-19} M^2. From the values of K_o and K_a, K_{dis} was calculated to be 2×10^{11}.

Conclusion

1. The yield of AQS$^{-\cdot}$, on irradiation of AQS in the presence of 2-propanol in water-acetonitrile mixtures, is highly dependent on the water content in the solvent, the highest being at the medium ratios of water. The decrease of AQS$^{-\cdot}$ yield at higher and lower water content is due to the decrease in the AQS triplet lifetime, $(k_{obs})^{-1}$, and in the deprotonation rate constant of AQSH$\cdot$, k_a, respectively.

2. To quench the AQS triplet state or to deprotonate AQSH$\cdot$, water molecules must be in the solvation shell of the respective species. This solvation shell has an average radius of ca. 3.3 Å, as determined from Perrin's equation.

3. The pK_a value of AQSH$\cdot$ is 3.5 in a 1:1 water-acetonitrile mixture, in good agreement with the reported value in 100 % water.[9,10] Reported pK_a values between 8 and 9[11,12] are impossible on kinetic grounds and probably due to the confusion with the equilibrium between $AQSH_2$ and AQS$^{-\cdot}$ which gives 8.5 as an apparent pK_a value in a 1:1 water-acetonitrile mixture.

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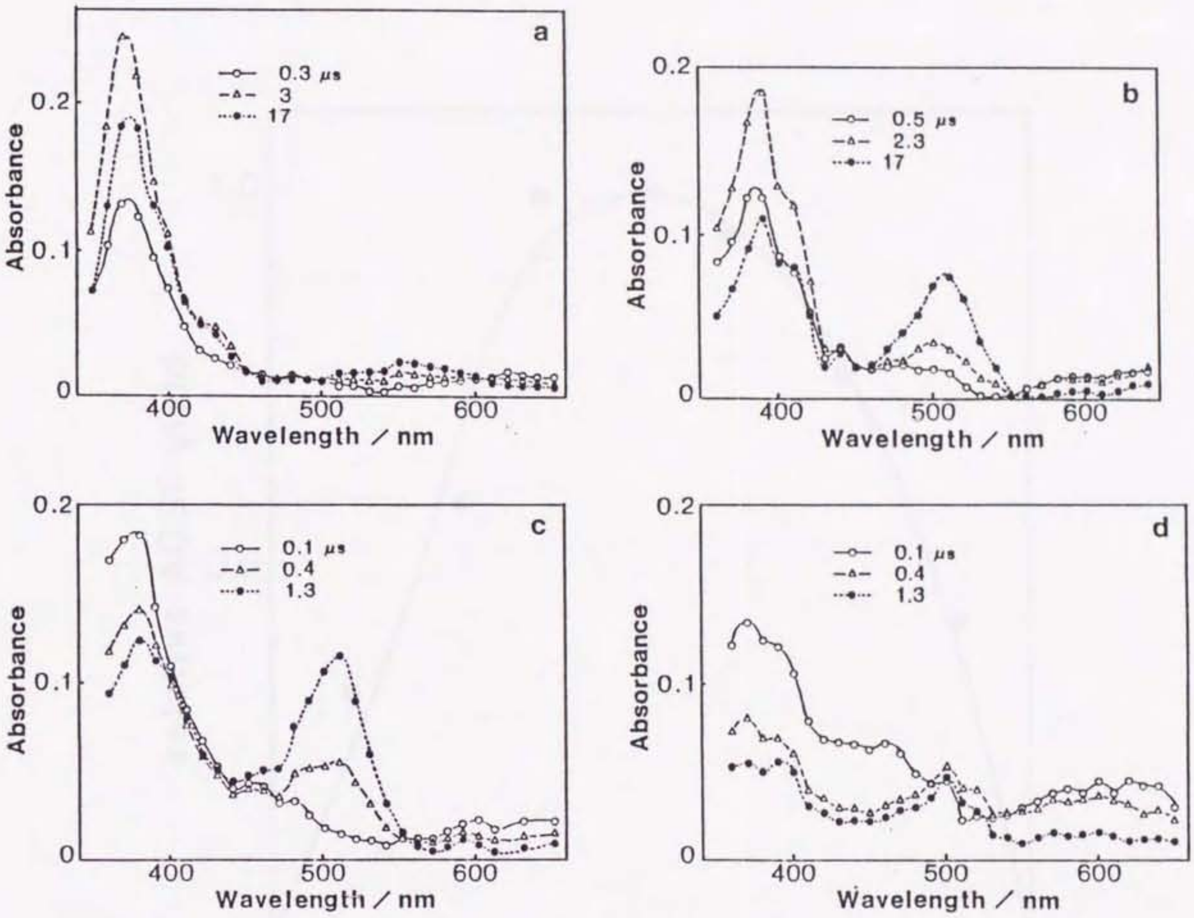

Figure 1. Transient absorption spectra on nitrogen pulsed laser excitation of AQS in various mixtures of water and acetonitrile in the presence of 2-propanol (0.08 M) at various time delays. Water contents (vol%) in solvent and AQS concentrations are as follows: (a) 0%, 2.4×10^{-4} M; (b) 25%, 2.2×10^{-4} M; (c) 50%, 3.0×10^{-4} M; (d) 90%, 3.0×10^{-4} M.

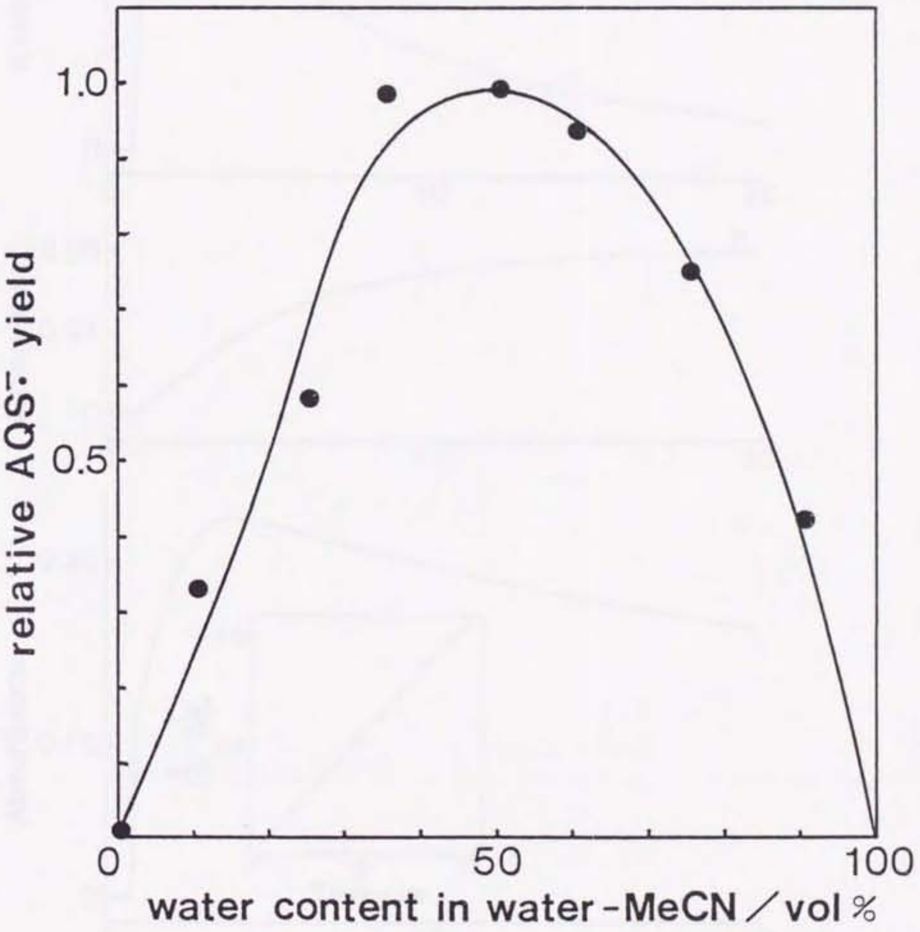

Figure 2. Relative AQS$^{-\cdot}$ yields observed transiently after nitrogen pulsed laser excitation as a function of water content (vol%) in water-acetonitrile mixtures in the presence of 2-propanol. [AQS] = 2.2 x 10^{-4} M, [2-propanol] = 0.08 M.

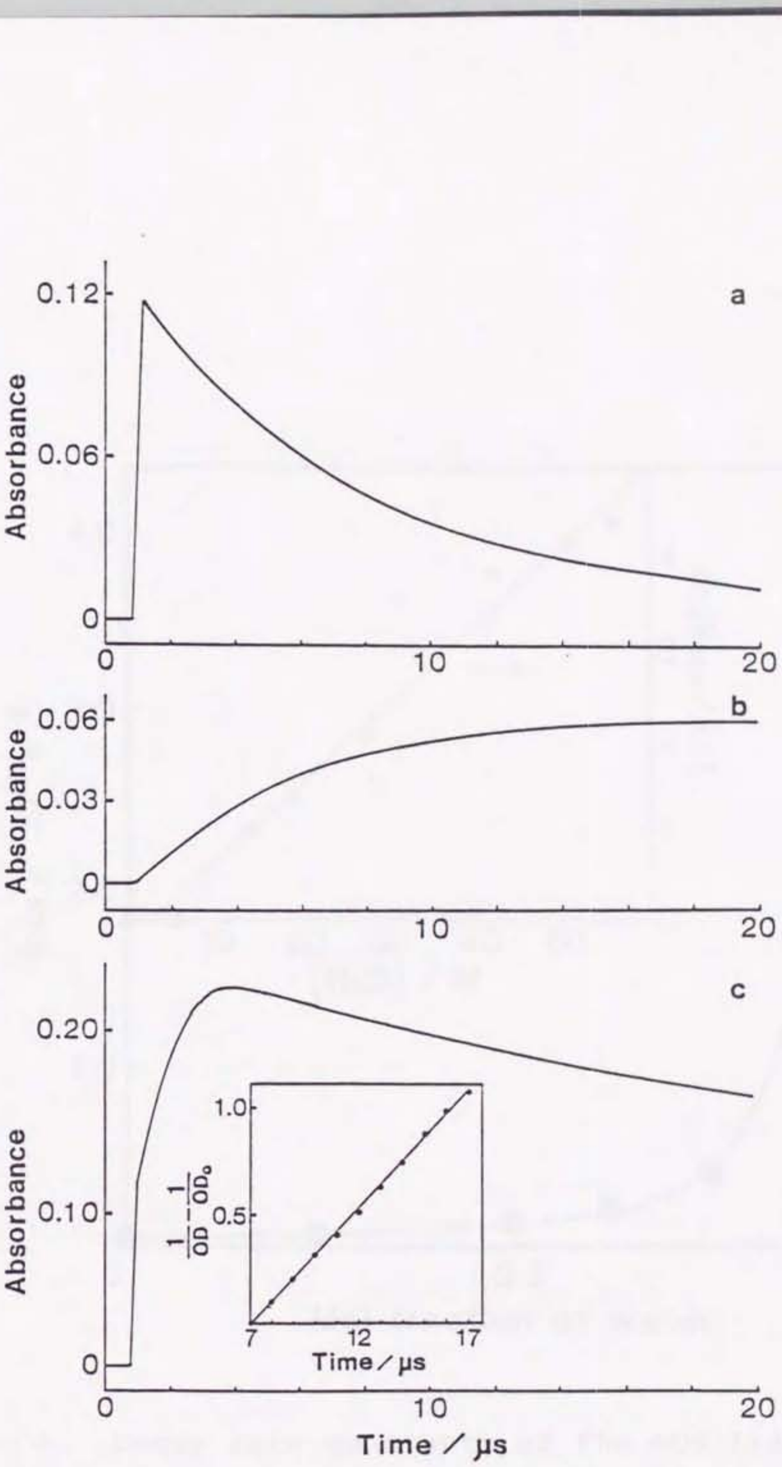

Figure 3. Time profiles of transient absorption. (a) Kinetic trace for AQS triplet decay measured at 380 nm in a 1:3 mixture of water and acetonitrile in the absence of 2-propanol, [AQS] = 2.2 x 10^{-4} M. (b) Kinetic trace showing the growth of $AQS^{-\bullet}$ measured at 500 nm in a 1:3 mixture of water and acetonitrile in the presence of 2-propanol (0.08 M), [AQS] = 2.2 x 10^{-4} M. (c) Kinetic trace showing the growth and decay of $AQSH^{\bullet}$ measured at 370 nm in pure acetonitrile in the presence of 2-propanol (0.08 M), [AQS] = 2.4 x 10^{-4} M. Insert: the second-order kinetic analysis according to eq 9.

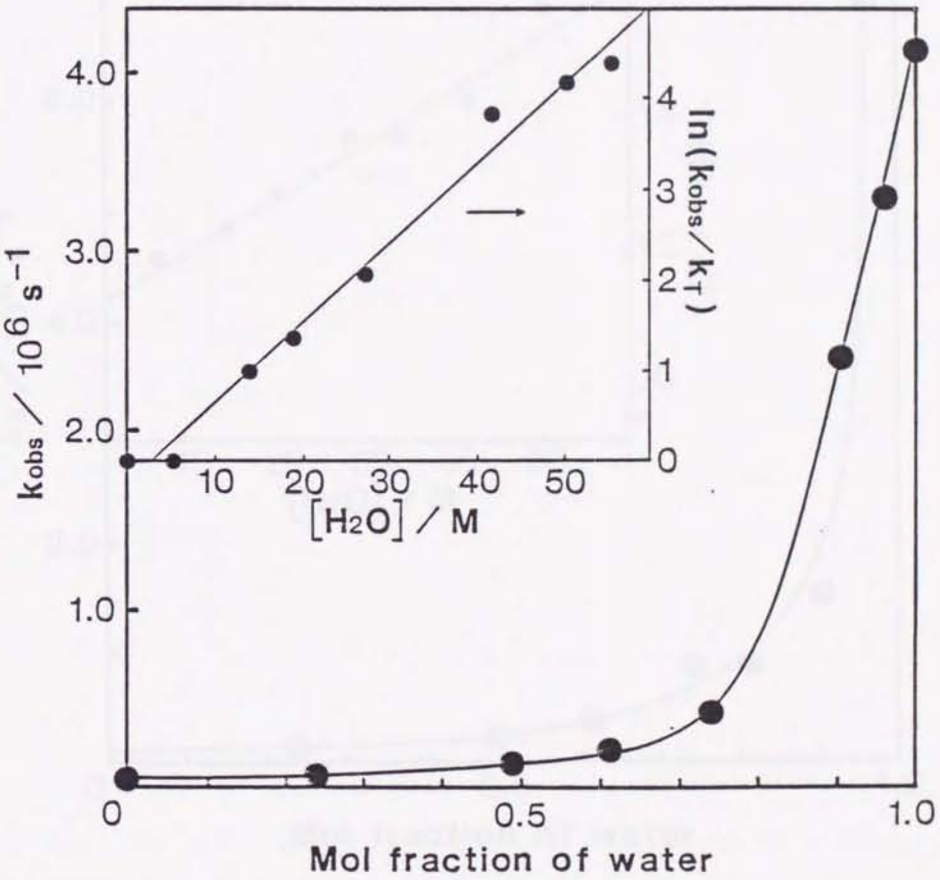

Figure 4. Decay rate constants of the AQS triplet as a function of water content (mole fraction) in water-acetonitrile mixtures in the absence of 2-propanol. Insert: logarithmic plot of k_{obs}/k_T versus water concentration in the solvent. [AQS] = 2.2×10^{-4} M.

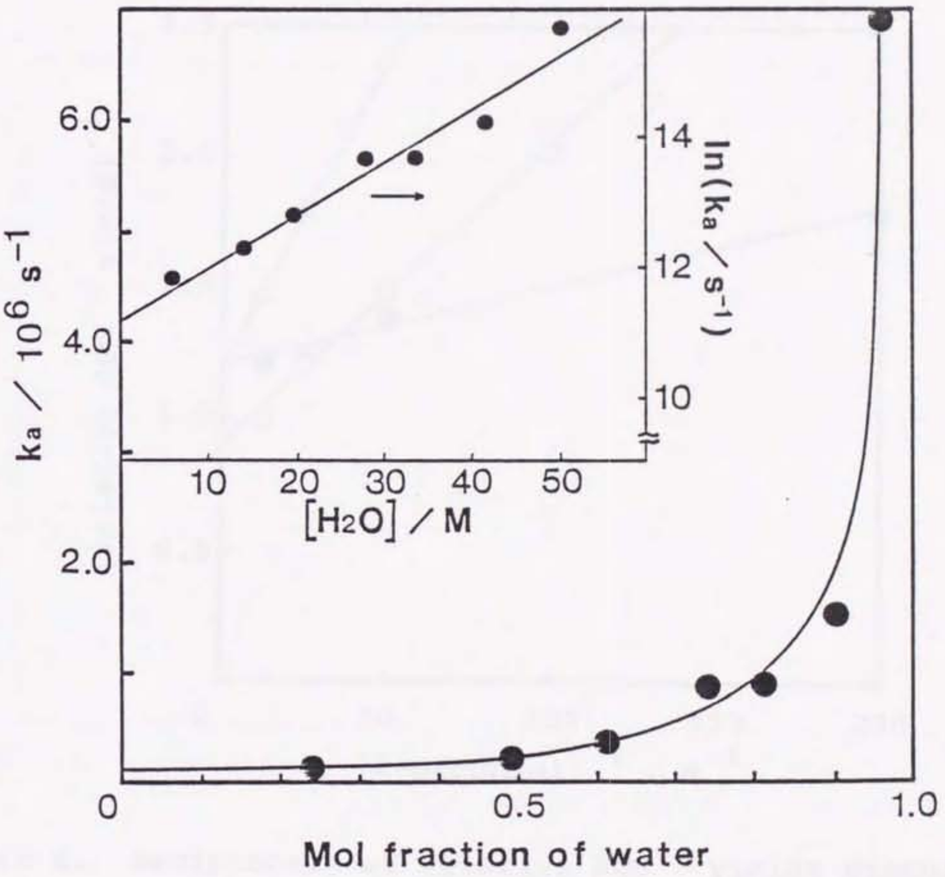

Figure 5. Deprotonation rate constanta (k_a) of AQSH$^{\bullet}$ as a function of water content (mole fraction) in water-acetonitrile mixtures in the presence of 2-propanol. Insert: logarithmic plot of k_a versus water concentration in the solvent. [AQS] = 2.2×10^{-4} M, [2-propanol] = 0.08 M.

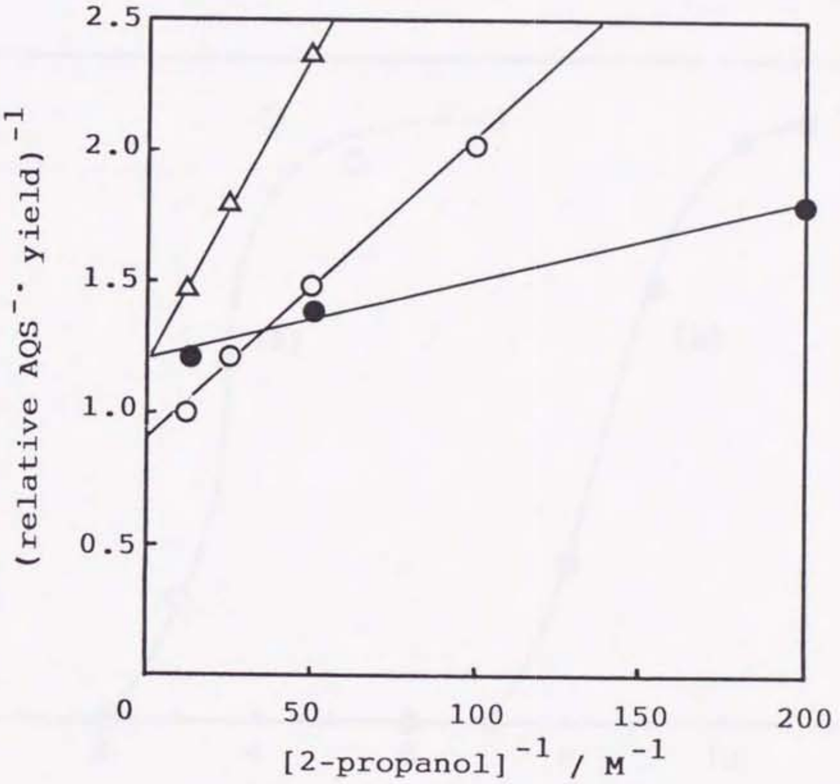

Figure 6. Reciprocals of relative AQS$^{-\cdot}$ yields produced by irradiation of AQS with nitrogen laser as a function of the reciprocal of 2-propanol concentration. [AQS] = 2.2×10^{-4} M, in water-acetonitrile mixtures (water content: 25 (●), 50 (○) and 75 vol% (△), under argon atmosphere.

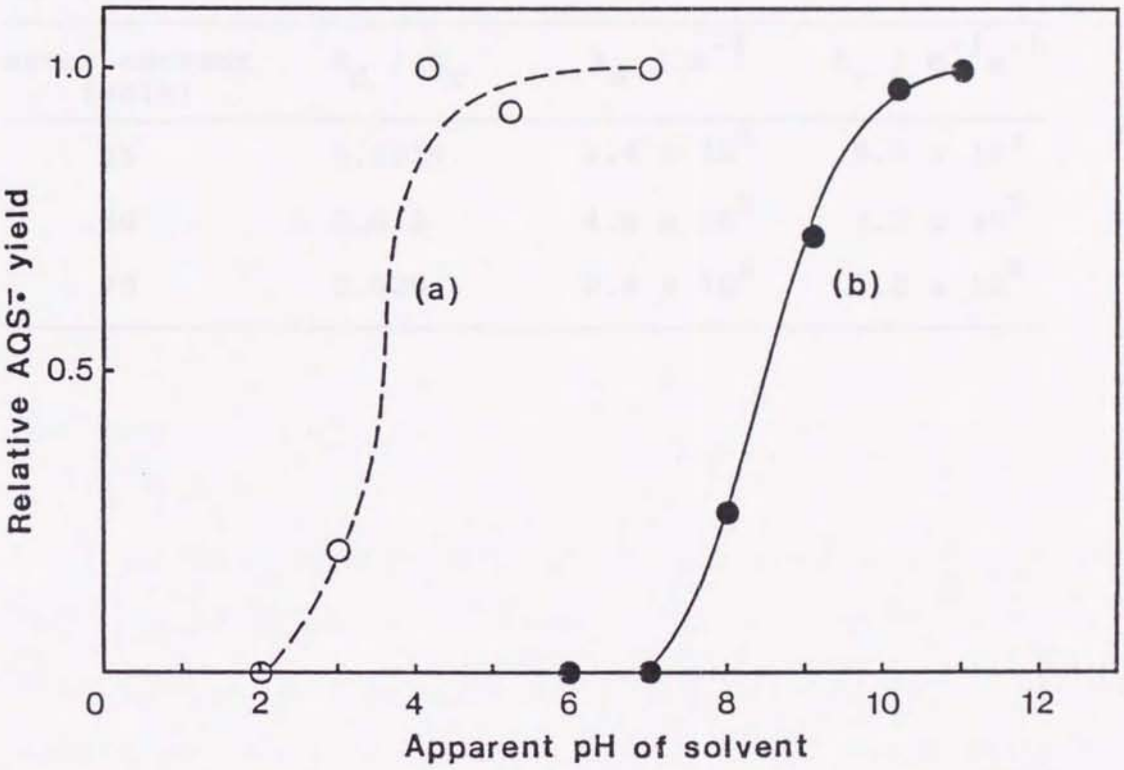

Figure 7. Dependence of $\mathrm{AQS}^{-\bullet}$ yield on pH of water in equivolume mixtures of water and acetonitrile in the presence of 2-propanol (0.16 M): curve a, $\mathrm{AQS}^{-\bullet}$ yield on laser flash photolysis, [AQS] = 2.2×10^{-4} M; curve b, $\mathrm{AQS}^{-\bullet}$ yield on continuous irradiation, [AQS] = 8.0×10^{-5} M.

Table 1. Rate constants for the reaction of triplet-state AQS with 2-propanol

water content (vol%)	k_d / k_r	k_d / s^{-1}	k_r / $M^{-1}s^{-1}$
25	0.0025	1.4×10^5	5.6×10^7
50	0.013	4.0×10^5	3.2×10^7
75	0.020	2.4×10^6	1.2×10^8

Chapter 4

Water Content Dependence of Decay Rate Constants of Triplet-State Anthraquinone Derivatives

Abstract

The decay rate constants of triplet-state anthraquinone (AQ), anthraquinone-2-sulfonate (AQS) and anthraquinone-2,6-disulfonate (AQDS) increased exponentially with increasing water concentration in water-acetonitrile mixed solvent. It was shown that the decay rate constants of triplet-state anthraquinone derivatives were controlled by the number of water molecules in their solvation shell by the following three kinds of correlations: i) application of Perrin's equation, ii) application of an adsorption model, and iii) correlation of the relative partial vapor pressure of acetonitrile in water-acetonitrile mixtures. The observed water concentration effects were strongly related with preferential solvation of anthraquinone derivatives by acetonitrile in water-acetonitrile mixtures. On the other hand, when benzene was used as a quencher, the apparent decay rate constant of triplet-state AQ linearly increased

with increasing benzene concentration. It means that the interaction of benzene molecules with triplet-state AQ is not controlled by the solvation of AQ with acetonitrile since AQ is well soluble in benzene. Thermodynamic functions, which $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$, for the deactivation processes of triplet-state AQS and AQ were remarkably dependent on the water content and the decay rate constants of triplet-state AQ were smaller in D_2O-acetonitrile than in H_2O-acetonitrile. These results indicate that it is not the environmental effect such as solvent polarlity that reduces the triplet lifetime, but the direct interaction between water molecules and triplet molecules.

Introduction

It was shown in chapter 3 that the photochemical reaction of sodium anthraquinone-2-sulfonate (AQS) with 2-propanol in aqueous acetonitrile was controlled by water concentration in solution. Both of the observed decay rate constant of triplet-state AQS (k_{obs}) and the deprotonation rate constant of anthrasemiquinone-2-sulfonate radical (k_a) were almost constant at water mole fractions lower than 0.7; however, they rapidly increased with increasing water mole fractions higher than 0.7. The fact that the rate constants of the different processes, k_{obs} and k_a, show similar characteristic water concentration dependence indicates that the rate constants are correlated with the solvation of AQS and that the number of water molecules in the solvation shell increases rapidly at water mole fractions higher than 0.7.

It is described in this chapter that the decay rate constants of some triplet-state anthraquinone derivatives are dependent on the water concentration in water-acetonitrile mixtures similarly to the case of AQS. To analyze the water concentration effect, application of Perrin's equation and an adsorption model, and correlation with the partial vapor pressure of acetonitrile in water-acetonitrile mixtures were examined.

Perrin's equation[1.2] can be applied to generally in quenching in rigid matrices. The excited state molecule has a "quenching sphere", and if a quencher molecule is within this sphere, the quenching occurs with unit efficiency. In a liquid phase, if an excited state molecule is preferentially solvated by inert solvent, the quencher molecules outside of this solvation shell will not be able to interact with the excited-state molecule. In such situation the quenching sphere will exist in the liquid phase and Perrin's equation will be applied.

An adsorption model was presented by Kokubun[3] on quenching of fluorescence of acridine. The fluorescence lifetime of acridine in water-ethanol and water-glycerol mixtures decreased with increasing amount of the organic component. Since neither static nor dynamic quenching mechanism was applicable to such a kind of solvent quenching, he presented the following adsorption model, that is, using a Langmuir-type adsorption formula the fraction of organic solvent component adsorbed on the acridine surface was estimated and the radiationless decay rate constant was assumed to linearly increase with the fraction of organic solvent. In the present work, to analyze the water concentration effect on the decay rate constants for triplet-state anthraquinone derivatives in aqueous acetonitrile solution application of this Langmuir-type adsorption model[4,5] and another Temkin-type adsorption model[6] were examined.

The preferential solvation by acetonitrile in water-acetonitrile mixtures will be controlled by the activity of acetonitrile. The partial vapor pressure of acetonitrile in water-acetonitrile mixtures seems to be one of the parameters showing the activity of acetonitrile in the mixed solvent.[7] The preferential solvation of hexakis(isothiocyanato)chromate(III) by acetonitrile in water-acetonitrile mixtures is correlated with the partial vapor pressure of acetonitrile in aqueous solution[8] as will be shown in Appendix 1. Accordingly, variation of the decay rate constant of triplet state anthraquinone derivatives in aqueous acetonitrile is correlated with the partial vapor pressure of acetonitrile in the solution.

The water concentration dependence of thermodynamic functions for deactivation of triplet-state anthraquinone derivatives and difference of the observed decay rate constant between water-acetonitrile and heavy water-acetonitrile was also examined. It will be discussed from these results what a kind of interaction reduces the triplet lifetime of anthraquinone derivatives.

As for other solvent systems, in water-acetone mixtures the water concentration effect on the triplet lifetime was examined. It should be noted that the partial vapor pressure of acetone in water-acetone mixtures shows similar water concentration dependence to the case of acetonitrile in water-acetonitrile.

In comparison with water as a quencher, when benzene was used as a quencher in acetonitrile, a remarkably different effect of quencher concentration on the decay rate constant of triplet-state AQ was observed. The difference between water and benzene will be discussed in terms of difference in solvation.

Experimental Section

Materials. Anthraquinone (AQ) (Nakarai Chemicals) was recrystallized twice from ethanol. Disodium anthraquinone-2,6-disulfonate (AQDS) (Tokyo Chemical Industry) was purified by salting-out from an aqueous sodium chloride solution. Sodium anthraquinone-2-sulfonate (AQS) (Nakarai Chemicals) was used as received. Perfluoroanthraquinone (AQF) was kindly gifted by Dr. Kikuchi (Central Glass Co., Ltd.) Acetonitrile(SP grade, Nakarai Chemicals), water (Dotite luminasol) and benzene (Dotite luminasol) were used as received. Acetone (Nakarai Chemicals) was used after distillation.

Laser Flash Photolysis. The apparatus for laser flash photolysis was depected in Figure 1 in chapter 1 except for wavelength of pulsed laser.

Temperature Control. Temperature was controlled by using a flow-cell in which constant-temperature water was circulated with a cryostat (HAAKE F3-K digital).

Results and Discussion

1. Decay Rate Constants of Triplet-State Anthraquinone Derivatives in Water-Acetonitrile Mixtures

The measurements of water concentration effects on the triplet-state decay rate constant of each anthraquinone derivative were carried out under argon atmosphere as follows;

AQ; Upon excitation of AQ(5.0×10^{-5} M) with XeCl excimer laser (308 nm, 120 mJ, 10-ns fwhm) in acetonitrile-water mixtures, the transient absorption spectrum of triplet-state AQ was immediately detected in 360-430-nm region, which was in good agreement with the published spectrum. The decay rate constants of the AQ triplet state, k_{obs}, were determined by first order kinetic analysis of the decay curves of the $T_n \leftarrow T_1$ absorption measured at its λ_{max} (370 nm).[9] Typical decay curves are depicted in Figure 1. Water contents (vol%) in the mixed solvents were 0, 20, 30, 40, 50, 60, and 70%.

AQS; AQS(2.2×10^{-4} M) was excited with N_2 laser (337 nm, 5 mJ/pulse, 6-ns fwhm). k_{obs} of AQS triplet state was determined from its $T_n \leftarrow T_1$ absorption decay curve monitored at 380 nm.[10] Water contents (vol%) in the mixed solvent were 0, 10, 25, 35, 50, 75, 90, and 100%.

AQDS; AQDS(6.0×10^{-5} M) was excited with XeF excimer laser (351 nm, 30 mJ/pulse, 14-ns fwhm). k_{obs} of AQDS triplet state was determined from its $T_n \leftarrow T_1$ absorption decay curve monitored at 390 nm.[11,12] Water contents (vol%) in the mixed solvents were 10, 20, 40, 60, 70, 80, 90, and 100%.

AQF; AQF(5.0×10^{-5} M) was excited with XeF excimer laser. k_{obs} of AQF triplet state was determined from its $T_n \leftarrow T_1$ absorption decay curve monitored at 380 nm. Water contents (vol%) in the mixed solvents were 0, 10, 30, and 50%.

Observed transient absorption spectra for AQ, AQS, AQDS, and AQF are shown in Figures 2, 3, 4, and 5, respectively.

The decay rate constants (k_{obs}) of the triplet-state anthraquinone derivatives obtained from first order kinetic analysis of $T_n \leftarrow T_1$ absorption decay curves were plotted in Figure 6 as a function of water mole fraction.

For all derivatives k_{obs}'s increased with increasing water content. In cases of AQ, AQS and AQDS, the change of k_{obs} was small at the water mole fractions lower than 0.6; however, k_{obs} increased rapidly at those higher than 0.7.

If the deactivation of triplet-state anthraquinone derivatives in aqueous solutions are through two processes expressed by the following equations, some analyses presented here will be possible to explain above characteristic water concentration effect on k_{obs}.

$$AQ^{*} \xrightarrow{k_T} AQ \tag{1}$$

$$AQ^{*} \xrightarrow[H_2O]{k_W} AQ \text{ or products} \tag{2}$$

Reaction 1 is the intrinsic deactivation of the triplet-state anthraquinone derivatives, and reaction 2 is quenching of triplet-state anthraquinone derivatives by water followed by either chemical reactions which results in nuclear hydroxylation products[10-14] or deactivation through the vibrational interaction between triplet-state anthrquinone derivatives and water molecules.

2. The Application of Perrin's Equation

Perrin's equation[1,2] was applied to the analysis of the water concentration effect on the decay rate constants for triplet-state anthraquinone derivatives. Perrin's equation assumes to be satisfied with the following assumption;

i) There exists a "quenching sphere" (radius R) around an excited-state molecule, and if a quencher molecule is within this quenching sphere, the excited-state molecule is deactivated with unit efficiency.

ii) If a quencher molecule is outside of the quenching sphere, it does not quench the excited-state molecule at all.

Perrin's model for quenching of emission predicts the following relationship:

$$(\Phi/\Phi_0)^{-1} = \exp(VN'[H_2O]) \qquad (3)$$

where Φ and Φ_0 are quantum yields for emission in the presence and absence of quencher, respectively, V is the active sphere of quenching (in cm^3), $N' = 6.02 \times 10^{20}$ molecules/cm^3, and [Q] is the concentration of quencher in M.

When anthraquinone derivatives are solvated preferentially with acetonitrile in water-acetonitrile mixtures, water molecules outside of these solvation shell will not be able to interact with triplet-state anthraquinone derivatives. In such situation the solvation shell is assumed to be the "quenching sphere" and Perrin's equation will be applied to the analysis of water concentration effect on the decay rate constants of triplet-state anthraquinone derivatives. Since Φ/Φ_0 corresponds to the fraction of the excited molecules not quenched by water, k_T/k_{obs}, the triplet-state decay rate constant in aqueous acetonitrile (k_{obs}) is treated with equation 4 or 5:

$$(k_T/k_{obs})^{-1} = \exp(VN'[H_2O]) \qquad (4)$$

$$\ln k_{obs} = \ln k_T + VN'[H_2O] \qquad (5)$$

where $k_{obs} = k_T + k_W$ (reactions 1 and 2) and V is the quenching sphere volume in cm^3 around a molecule of triplet-state anthraquinone derivatives. The value of k_W is dependent on the water content in the mixed solvent. A water molecule must be in this sphere for reaction 2 to occur, and if a water molecule is outside of the quenching sphere, it does not interact with a triplet-state molecule. It is assumed that a water molecule cannot diffuse from bulk solution to the solvation layer (quenching sphere) during triplet lifetime.

According to equation 5, ln k_{obs} was plotted as a function of water concentration in Figure 7. All of the anthraquinone derivatives investigated show linear relationship in Figure 7. From the slope (VN') the quenching sphere volume V and thus its radius R [$R = (3V/4\pi)^{1/3}$] were calculated. The obtained values of V and R are listed in Table 1. The obtained values of R are all about 3 Å for anthraquinone derivatives except AQF, whose R is a little smaller (2.78 Å) probably because of its strongly hydrophobic property. The similarity in R values indicates that the interaction of water with triplet-state anthraquinone derivatives examined are of nearly the same magnitude. Since a quinone moiety is supposed to be preferentially solvated by acetonitrile, for a water molecule to have an strong interaction with triplet-state anthraquinone derivatives, a water molecule must be in their solvation shells. It is probable that the solvation shell of anthraquinones preferentially occupied by acetonitrile corresponds to the "quenching sphere" in Perrin's equation.

3. The Analysis by an Adsorption Model

As predicted from the analysis by Perrin's equation, the quenching of the triplet-state anthraquinones through the interaction with water occurs when water molecules exist inside the quenching sphere (solvation shell), and the rate constant for the decay of triplet-state anthraquinones are dependent on the number of water molecule in the quenching sphere. In other words, it will be possible to suppose that this quenching rate is dependent on the fraction of water molecules contained in the quenching sphere. If the fractional coverage by water molecules in the limited sphere (quenching sphere) about the substrate is affected by an equilibrium of adsorption of water molecules into the quenching sphere, it is obtained as a function of water volume fraction (v) in the mixed solvent by the following analyses.

Assuming that θ is the fractional coverage by water in the adsorption site (the quenching sphere) as depicted in

Figure 8, the adsorption rate of water molecule is described as $f(v)(1-\theta)$, where $f(v)$ is a function of v and $1-\theta$ corresponds to a fraction uncovered with water, and the desorption rate is in proportion to θ, $k_{out}\theta$.

Two kinds of adsorption models are presented here depending on the type of $f(v)$. One is the case in which $f(v)$ is in proportion to v, $f(v) = k_{in}v$, where k_{in} is a constant, and the other is the case in which $f(v)$ is an exponential function of v, $f(v) = C\exp(\alpha v)$, where C and α are constants.

i) $f(v) = k_{in}v$

In this case θ is represented by the same type of formula as Langmuir's adsorption isotherm[4,5] in which the adsorption rate is in proportion to the pressure in gas phase.

In the equilibrium between adsorption and desorption of water molecules, their rates equal each other, leading to equation 6, and then θ is obtained from equation 6 (equation 7).

$$k_{in}v(1-\theta) = k_{out}\theta \qquad (6)$$

$$\theta = v/(K + v) \qquad (K = k_{out}/k_{in}) \qquad (7)$$

If the apparent decay rate constants (k_{obs}) of triplet-state anthraquinone derivatives obtained from first-order kinetic analysis is composed of the two kinds of deactivation processes, that is, a unimolecular deactivation process (k_u) and a deactivation process induced by an intermolecular interaction with water molecules (k_b), k_{obs} is represented by equation 8. From equations 7 and 8, the relation between k_{obs} and v is derived as indicated in equation 9.

$$k_{obs} = (1-\theta)k_u + k_b\theta \qquad (8)$$

$$k_u/(k_{obs}-k_u) = (k_u/(k_b-k_u))(1+(K/v)) \qquad (9)$$

The observed decay rate constant in pure acetonitrile corresponds to k_u. Figure 9 plots $k_u/(k_{obs}-k_u)$ against v^{-1} for AQ, AQS and AQDS. These plots do not fit a linear relation for the whole range of v^{-1}, but are composed of two linear parts with different slopes at higher and lower than about 0.6 water mole fractions.

In this model the adsorption rate is assumed to be proportional to the water volume fraction in bulk solution. However, as the above results indicate, this type of adsorption model does not fit for the whole water fractions, and cannot express the large change of quenching rate constants observed at higher water fractions.

ii) $f(v) = C\exp(\alpha v)$

At low water contents the quenching sphere of anthraquinones will be preferentially occupied by acetonitrile molecules, and water molecules will be very difficult to be present in the quenching sphere. This means that there is a large activation barrier for water molecules to be adsorbed in the vicinity of anthraquinone moiety from the bulk solution. However, with increasing water content, it will become easy for water molecules to enter the quenching sphere, that is, the activation energy for the adsorption of water will be reduced.

If the activation energy (ΔE_s) for adsorption of water molecules decreases linearly with increasing water content, f(v) is described by equation 10:

$$
\begin{aligned}
f(v) &= A\exp(-\Delta E_s/RT) \\
&= A\exp(-(\Delta E_0 - \alpha v)/RT) \qquad (10)
\end{aligned}
$$

where ΔE_0 is the activation energy in pure acetonitrile and A and α are constants. This formula is very similar to Temkin's isotherm^6 for the adsorption of a gas on a solid catalysts in which the enthalpy for adsorption is dependent on the pressure in gas phase. At a constant temperature, f(v) is to be increased exponentially with v (equation 11):

$$f(v) = C\exp(\alpha v) \qquad (11)$$

where C is a constant.

In the equilibrium between the adsorption and the desorption of water molecules, equation 12 is derived and then θ is described by equation 13.

$$(C\mathrm{exp}(\alpha v))(1 - \theta) = k_{out}\theta \qquad (12)$$

$$\theta = (1 + K\mathrm{exp}(- V))^{-1} \qquad (K = k_{out}/C,\ 0< \theta <1) \qquad (13)$$

By using equation 8, k_{obs} is represented by equation 14.

$$\ln[((k_b - k_u)/(k_{obs} - k_u)) - 1] = \ln K - \alpha v \qquad (14)$$

In Figure 10, plots of $\ln[((k_b - k_u)/(k_{obs} - k_u)) - 1]$ against v give fairly good linear relationships for AQ, AQS and AQDS in which k_u and k_b are the decay rate constants in 100 % acetonitrile and 100 % water, respectively. The slopes and intercepts of Figure 10 afford the values for α and lnK. The ratio of the rate constants for adsorption and desorption (K') at v = 0.9 (equation 15) was calculated from α and K (= k_{out}/C).

$$K' = (C\mathrm{exp}(\alpha v))/k_{out} \qquad (15)$$

The α and K' values estimated at v=0.9 values are listed in Table 1. The maximum values for α and K' are offered for AQS and the minimum for AQF. These results mean that the quinone molecule which is easily adsorbed by water molecules is efficiently quenched by them at its triplet state.

The above adsorption model considering the activation energy for the transfer of water molecules from bulk to the adsorption layer, in which the adsorption rate constant increases exponentially with water volume fraction, can clearly explain the experimental observation much better than the Langmuir-type model.

The adsorption model has some common properties to Perrin's model. There is the limited sphere for the quenching by water molecules and k_{obs} is represented by the exponential function of the water content. The α and R values are correlated with each other. The molecule with a large quenching sphere radius has a large α value, which means efficient adsorption.

4. The Correlation with Partial Vapor Pressure of Acetonitrile in the mixed Solvent

In Perrin's model and the adsorption model, it was shown that k_{obs} is dependent on the fraction occupied by water molecules in the "quenching sphere", which is not linearly but exponentially increased with total water content in the mixture.

This exponential dependence is undoubtedly based on the variation of the interaction between water and acetonitrile molecules with their mixing ratio. It is supposed that anthraquinones are preferentially solvated by acetonitrile in water-acetonitrile mixtures where the activity of acetonitrile is the same as that in pure acetonitrile.

The partial vapor pressure of acetonitrile in a mixed solvent[15] is presented as one of the parameters which show the interaction between water and acetonitrile molecules. The activity of acetonitrile in water-acetonitrile mixtures is defined by the ratio of the partial vapor pressure of acetonitrile in the mixture (P) to that in pure acetonitrile (P_0), P/P_0.[7] Figure 11 shows P/P_0 as a function of mole fraction of water in the mixture. The P/P_0 values rapidly decreases with increasing water content at water mole fractions higher than 0.7, but nearly constant at water mole fractions lower than 0.7. It shows that the activity of acetonitrile at water mole fractions lower than 0.7 is nearly equal to that in pure acetonitrile, meaning that water does not interact with acetonitrile. If a substrate which prefers the solvation with acetonitrile is in water-acetonitrile mixtures where water mole fractions are lower than 0.7, its solvation layer will be exclusively occupied by acetonitrile molecules; however, with increasing water mole fraction to higher than 0.7, the number of water molecules in the solvation layer will rapidly increase because the activity of acetonitrile rapidly decreases.

The water content dependence of k_{obs}'s for anthraquinone derivatives is very similar to that of P/P_0. As shown in Figure 6, k_{obs}'s rapidly increase at water mole fractions higher than 0.7, but nearly constant at water mole fraction lower than 0.7. From the good correlation of the water content dependence of k_{obs} with that of the activity of acetonitrile (P/P_0), it can be said that the preferential solvation of anthraquinone derivatives by acetonitrile in water-acetonitrile mixtures controls the interaction of water molecules with triplet-state anthraquinone derivatives, that is; i) anthraquinones are preferentially solvated by acetonitrile at water mole fraction lower than 0.7, ii) it becomes easy at water mole fraction higher than 0.7 for water molecules to enter the solvation shells of anthraquinone derivatives.

Assuming that the fraction occupied by acetonitrile molecules in the solvation shells of anthraquinone derivatives is proportional to P/P_0, $1-(P/P_0)$ corresponds to the fraction occupied by water molecules.

According to the same assumption as made in the adsorption model that the increase of k_{obs} is linearly dependent on the fractional coverage with water molecules, it is expected that k_{obs} will be also linearly dependent on $1-(P/P_0)$. Actually, when k_{obs} was plotted against $1-(P/P_0)$, the linear relation was obtained as depicted in Figure 12.

It should be noted that the fraction of water molecules in the quenching sphere is controlled by the interaction between solvent molecules.

5. The Contribution of Water-Clusters

It is well-known that water molecules are aggregated to form cluster structure.[16-19] The number of water-clusters in water-acetonitrile mixtures will increase with increasing water content as shown in the case of water-alcohol mixtures by Robinson et al.[16] It is probable that triplet-state anthraquinone derivatives are deactivated through the interaction with the water-clusters.

Assuming that the water-clusters are formed through the following equilibria,

$$2H_2O \xrightleftharpoons{K_2} (H_2O)_2 \qquad K_2 = \frac{[(H_2O)_2]}{[H_2O]^2} \qquad (16)$$

$$(H_2O)_2 + H_2O \xrightleftharpoons{K_3} (H_2O)_3 \qquad K_3 = \frac{[(H_2O)_3]}{[(H_2O)_2][H_2O]} \qquad (17)$$

$$(H_2O)_{n-1} + H_2O \xrightleftharpoons{K_n} (H_2O)_n \qquad K_n = \frac{[(H_2O)_n]}{[(H_2O)_{n-1}][H_2O]} \qquad (18)$$

where K_2, K_3 and K_n are equilibrium constants, the concentration of the water cluster containing n molecules will be described by equation 19.

$$[(H_2O)_n] = K_n K_{n-1} \cdots K_2 [H_2O]^n \qquad (19)$$

When the triplet-state anthraquinone derivatives are deactivated with a specific rate constant by the interaction with the water cluster comprising of a specific numbers, n molecules, of water, k_{obs}'s are represented by equation 20.

$$k_{obs} = k'(\prod_{x=2}^{n} K_x)[H_2O]^n \qquad (20)$$

$$\ln k_{obs} = \ln(k' \prod_{x=2}^{n} K_x) + n\ln[H_2O] \qquad (21)$$

where k' is a constant.

Figure 13 depicts the plots of $\ln k_{obs}$ against $\ln[H_2O]$ for AQ, AQS and AQDS, and indicates that the slope "n" was different between higher and lower water concentrations. For AQ, AQS and AQDS the slopes are about 3 at the water mole fractions higher than 0.7 and are about 1 at the water mole fractions lower than 0.7.

Since the slopes in Figure 13 are taken to indicate the numbers of water molecules composing the water-cluster to interact with the triplet-state anthraquinones, in the region of lower water concentration the monomeric water molecules will interact with triplet-state anthraquinones. On the other hand, in the region of higher water concentration the water cluster containing three molecules will interact with triplet-state anthraquinone derivatives more efficiently.

The value of 0.7 of water mole fraction corresponds to the water content where the partial vapor pressure of acetonitrile in water-acetonitrile mixed solvent starts decreasing rapidly (Figure 11). Therefore, the molecular arrangement of acetonitrile-water mixed solvent is remarkably changed when the water mole fraction exceed around 0.7.

The change in the solvent structure will bring about the change in interaction between water and anthraquinones, and , accordingly, the change in solvation around anthraquinones.

6. The Quenching of Triplet-State AQS in Water-Acetone

Likewise in water-acetonitrile the decay rate constant of triplet-state AQS, k_{obs}, was measured in water-acetone mixed solvents. AQS (1.0×10^{-4} M) was excited with XeF laser (351 nm, 30 mJ/pulse, 14-ns fwhm) under argon atmosphere. The water content was varied from 50 to 100%. k_{obs} of AQS was determined through first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curve monitored at 380 nm.

Figure 14-(a) plots the obtained k_{obs} against water mole fraction, and shows that k_{obs} rapidly increases with water mole fractions when it is higher than 0.7.

In Figure 14-(b) plot of $\ln k_{obs}$ against water concentration affords linear relationship. The slope of the plot gives the quenching sphere radius as 3.08 Å according to the treatment by Perrin's equation.

This result is very similar to that in acetonitrile-water mixed solvent, and attributed to the preferential solvation by acetone.

This is also supported by correlation with the partial vapor pressure of acetone. The partial vapor pressure of acetone in acetone-water mixed solvents[20] shows similar dependence on water concentration to that of acetonitrile (Figure 15). As shown in Figure 15, since acetone molecules also repulse water molecules and the activity in the mixed solvents is nearly constant up to 0.7 of the water mole fraction, acetone can solvate AQ preferentially in aqueous mixed solvents.

7. The Quenching of Triplet-State AQ by Benzene

It has been known that benzene quenches the (n, π^*) triplet state of carbonyl compounds through addition-elimination.[21,22] Since AQ is well soluble in benzene but scarcely soluble in water, the effect of solvation on the quenching of triplet-state AQ can be examined by the comparison between water and benzene concentration dependence of AQ triplet lifetime in acetonitrile.

Quenching of $T_n \leftarrow T_1$ absorption of AQ by benzene was studied in acetonitrile under nitrogen atmosphere. The concentration of benzene was changed from 0.006 to 0.35 M. Other experimental conditions are the same as those for the quenching of triplet-state AQ by water.

The decay rate constants (k_B) of the AQ triplet state in the presence of benzene were determined by pseudo-first order kinetic analysis of the decay curves of T_n-T_1 absorption measured at 370 nm.

k_B is plotted against the concentration of benzene according to equation 22,

$$k_B = k_0 + k_r[\text{benzene}] \qquad (22)$$

where k_0 is a decay rate constant in the absence of benzene and k_r is a bimolecular reaction rate constant between the triplet-state AQ and benzene. The plot gives linear relationship as depicted in Figure 16. The slope gives k_r as $2.5 \times 10^6\ M^{-1}s^{-1}$.

This concentration effect of benzene is quite different from the water concentration effect in acetonitrile. The difference of the concentration effect between water and benzene will be due to difference in the affinity to anthraquinone. It is indicated that the water molecule has some activation energy to enter the solvation shell of acetonitrile because of hydrophobic interaction, but that benzene molecules have no activation energy to contact with triplet-state AQ since AQ is more soluble in benzene than in acetonitrile.

In the case of quenching by benzene the observed concentration effect is explained by diffusional encounter; however, the quenching by water is not explained by this process. In other words, the probability that benzene molecule contacts with triplet-state AQ is proportional to the benzene concentratrion; however, the probability for water molecule to contact with triplet-state AQ is not linearly dependent on water concentration. Comparison between the quenching by water and benzene suggests that the quenching of the triplet-state AQ is strongly related with its solvation.

8. The Temperature Effects on Quenching of Triplet-State Anthraquinones by Water

It is expected that thermodynamic functions offer important informations about solute-solvent interactions. The thermodynamic functions for the quenching of triplet-state AQS and AQ by water were obtained from Arrhenius plots of their decay rate constants.

The decay rate constants of triplet-state AQS (k_{obs}) were measured at 11, 27, 42 and 57 °C in acetonitrile-water mixtures. The water contents were 25, 50, 75, 90 and 100 vol%. AQS(1.0×10^{-4} M) was excited with XeCl laser (308 nm, 120 mJ, 10-ns fwhm) under argon atmosphere, and k_{obs} of AQS was determined through first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curve monitored at 380 nm.

Arrhenius plots are shown in Figure 17. From the slope and intercept the values of E_a and A were obtained and are listed in Table 2 as well as $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$. Figure 18 depicts these thermodynamic functions against mole fraction of water. As Figure 18 shows, $\Delta G^{\neq}$ monotonously decreases with increasing water fraction, which means that the quenching of the triplet state is favorable in higher water fractions. On the other hand, at a water mole fraction about 0.9 $\Delta H^{\neq}$ and $-T\Delta S^{\neq}$ shows a maximum and a minimum, respectively. Therefore, at water contents lower than 0.9 the decrease in $\Delta G^{\neq}$ with increasing water content is mainly due to increase of $\Delta S^{\neq}$, and at water contents higher than 0.9 the decrease in $\Delta G^{\neq}$ is mostly attributed to decrease of $\Delta H^{\neq}$. The changes in $\Delta S^{\neq}$ and $\Delta H^{\neq}$ will be considered below;

i) The change of $\Delta S^{\neq}$

The $\Delta S^{\neq}$ value involved in process 23, in which a contact pair is formed between triplet-state AQS and water molecules, is negative. The value of $|\Delta S^{\neq}|$ decreases with

$$AQS^{*} + H_2O \xrightarrow{\Delta S^{\neq},\ \Delta H^{\neq}} AQS^{*}\text{---}H_2O \qquad (23)$$

increasing water content, because the static interaction between AQS and water increases in the ground state;

however, at water molefractions higher than 0.9 $|\Delta S^{\neq}|$ increases with increasing water content, because highly organized water structure is formed. If the water structure is more ordered, $\Delta S^{\neq}$ for process 23 will become more negative.

ii) The change in $\Delta H^{\neq}$

The value of $\Delta H^{\neq}$ at the water mole fraction 0.9 is very close to the activation energy for diffusion of water (4.59 kcal/mol). $\Delta H^{\neq}$ would correspond to the activation energy for diffusion of water in the solvation shell as shown in Figure 19 schematically. Since in very high and very low water content an AQS molecule is exclusively covered with water and acetonitrile, respectively, the observed temperature effect becomes small in those regions. If the observed $\Delta H^{\neq}$ corresponds to the activation energy for a reaction of triplet-state AQS with water, it will not decrease with increasing water content.

The thermodynamic functions for the deactivation processes of triplet-state AQ were also determined in the mixtures of acetonitrile and 0, 30 and 60-vol% water. AQ(1.0×10^{-4} M) was excited with XeCl laser under nitrogen atmosphere at 0.5, 16, 30, 42 and 56.5 °C. k_{obs} of AQ was determined through first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curve measured at 370 nm. E_a and A were obtained from Arrhenius plots (Figure 20), and $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were calculated. The resulting thermodynamic functions are listed in Table 3.

The water content dependence of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for AQ is similar to that for AQS. Especially, the value of E_a in a water mole fraction of about 0.8 is 4.5 kcal/mol or so for both AQS and AQ. The temperature dependence of k_{obs} can be attributed to the activation energy for the diffusion of water molecules in the solvation shell.

The temperature effects support that the efficiency for quenching of the triplet-state anthraquinone derivatives by water is related to their solvation and controlled by the number of water molecules in their solvation shell.

The thermodynamic functions in a mixture of 60:40 heavy water-acetonitrile were measured for AQ and the obtained values are compared with those in water-acetonitrile in Table 3. The experimental conditions were the same as those for AQ in water-acetonitrile.

As will be shown in the following section, k_{obs} in water-acetonitrile was about 1.4 times larger than that in heavy water-acetonitrile. Generally, the solvent deuterium effect is explained by difference in the zero-point energy in the solute-solvent interaction, which causes increase of E_a in deuterated solvents.[23] However, E_a obtained in heavy water-acetonitrile is smaller than E_a in water-acetonitrile. The smaller value of k_{obs} in heavy water-acetonitrile seems to be attributed to the smaller frequency factor (A) (or entropy of activation). It is supposed that the structure of the activated state is more ordered in heavy water-acetonitrile than in water-acetonitrile probably because heavy water has stronger hydrogen-bonding ability. If the triplet-state anthraquinone is deactivated through the vibrational interaction with water molecule, the difference in the A value will reflect the difference of the frequency in normal vibration between water and heavy water.

9. Heavy Water Effect on Deactivation of Triplet-State Anthraquinone

It has already been shown in this chapter that the triplet-state anthraquinones were quenched by water. But it has not been clear what kind of interaction is involved between the triplet-state anthraquinone and water.

If the triplet-state AQ interacts with water directly, it is expected that k_{obs} in heavy water will be different from k_{obs} in water. So k_{obs} in heavy water-acetonitrile was compared with that in water-acetonitrile.

AQ (5.0×10^{-5} M) was excited with XeCl laser (308 nm, 120 mJ, 10-ns fwhm) under argon atmosphere. The solvents used were heavy water (CEA, deuterium oxide, >99.85%)-acetonitrile mixtures and water-acetonitrile mixtures. D_2O and H_2O contents in the mixed solvents were 40, 50, 60 and 70 vol%. k_{obs} of AQ were obtained by the first order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curves monitored at 370 nm.

The obtained values of k_{obs} in H_2O-MeCN and D_2O-MeCN are listed in Table 4 and depicted in Figure 21 as a function of H_2O and D_2O content (vol%). The results indicate that k_{obs} in H_2O-MeCN is larger than that in D_2O-MeCN at all mixing ratio, and that the ratio of k_{obs} in H_2O - MeCN to that in D_2O - MeCN is about 1.4 at water content higher than 50 vol%.

This heavy water effect indicates that the decrease of AQ triplet lifetime with increasing water content in the solvent is not attributable to the environmental effect such as solvent polarity, but to the direct interaction of water with triplet-state AQ. As described in the preceding part, it was not the increase of activation energy that makes k_{obs} in heavy water-acetonitrile mixtures smaller, but the decrease of the frequency factor. Since the transient absorption spectra of triplet-state AQ in D_2O-MeCN was almost the same as that in H_2O-MeCN as depicted in Figure 22, the electronic configurations of the triplet-state AQ does not change in both solvents.

As a result, it is supposed that the vibrational interaction of triplet-state AQ with water molecules will be suitable for the direct interaction. The fact that the deactivation is more efficient in H_2O-MeCN than in D_2O-MeCN is explained by assuming that the triplet energy of AQ is relaxed through the vibrational modes of water molecules.

Since the normal vibrational frequency of H_2O is 1.4 times higher than that of D_2O (Table 5), the deactivation through the H_2O vibrational mode will become more efficient.

Conclusion

1) k_{obs}'s of AQ, AQS, and AQDS in water-acetonitrile mixtures increased exponentially with increasing water concentration. This effect can be explained in terms of both Perrin's equation and the adsorption model, indicating that k_{obs} is controlled by the number of water molecules in the solvation shells of anthraquinone derivatives.

2) The water concentration dependence of k_{obs} was in good agreement with that of the relative partial vapor pressure of acetonitrile in water-acetonitrile mixtures. At the water mole fractions 0 to 0.7 in the mixtures the relative partial vapor pressure of acetonitrile is close to the value in pure acetonitrile. In this region, the change of k_{obs} is very small. On the other hand, at the water mole fractions higher than 0.7, the relative partial vapor pressure of acetonitrile and k_{obs} rapidly decrease and increase, respectively. Since the partial vapor pressure corresponds to the activity in the mixed solvent, the water concentration dependence of k_{obs} is attributed to the preferential solvation of anthraquinone derivatives by acetonitrile.

3) The same kind of water concentration effect on k_{obs} for AQS as observed in water-acetonitrile mixtures was also observed in water-acetone mixtures. Since the relative partial vapor pressure of acetone in water-acetone mixtures

shows similar water concentration dependence to that of acetonitrile in water-acetonitrile mixtures, the preferential solvation of AQS by acetone causes the similar water concentration effect to the case for acetonitrile. On the other hand, when benzene in which AQ is well soluble was used as a quencher of triplet-state AQ in acetonitrile, the apparent first-order quenching rate constant k_B was linearly increased with benzene concentration. These results indicate that the decay rates of triplet-state anthraquinone derivatives are correlated with the number of quencher molecules in the solvation shell.

4) The thermodynamic functions for the deactivation process of triplet-state AQS and AQ were remarkably dependent on the water content in water-acetonitrile mixtures. The observed activation energy can be attributed to that of the diffusion of water molecule.

5) k_{obs} for AQ in H_2O-acetonitrile was about 1.4 times larger than that in D_2O-acetonitrile. From Arrhenius plots, it is found that the difference of k_{obs} between H_2O-acetonitrile and D_2O-acetonitrile originates from the difference in the frequency factor (A), but not from the activation energy term (E_a). These results indicate that the deactivation of triplet-state anthraquinones through the vibrational interaction with water molecule is the most probable in aqueous solutions with high water contents.

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Table 1. Values of VN' and quenching sphere radii in Perrin's equation, and K' and α values in adsorption model.

compound	Perrin's equation		adsorption model	
	VN'	quenching sphere radius (Å)	K'	α
AQ	0.0705	3.03	1.66	7.11
AQS	0.0880	3.27	3.97	8.33
AQDS	0.0645	2.95	2.22	6.08
AQF_8	0.0540	2.78	0.53	(3)

Table 2. Thermodynamic functions for the deactivation of AQS triplet

water (vol%)	Ea (kcal/mol)	A (s^{-1})	at 298K $\Delta H^{\neq}$ (kcal/mol)	 $\Delta S^{\neq}$ (cal mol^{-1} K^{-1})	 $\Delta G^{\neq}$ (kcal/mol)
25	1.85	3.72×10^{6}	1.26	-31	10.3
50	3.86	3.25×10^{8}	3.27	-22	9.71
75	4.91	6.53×10^{9}	4.32	-16	8.97
90	3.40	1.09×10^{9}	2.81	-19	8.53
100	1.94	9.89×10^{7}	1.35	-24	8.50

Table 3. Thermodynamic functions for the deactivation of AQ triplet

water (vol%)	Ea (kcal/mol)	A (s^{-1})	at 298 K $\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
0 (H_2O)	1.31	9.46×10^5	0.72	-33	10.62
30 (H_2O)	4.10	1.12×10^8	3.51	-24	10.58
60 (H_2O)	4.61	9.67×10^8	4.02	-19	9.81
60 (D_2O)	3.93	2.30×10^8	3.34	-22	9.99

Table 4. Observed decay rate constants of AQ triplet in water-acetonitrile and heavy water-acetonitrile.

H_2O, D_2O content(vol%)	$k_{obs}/10^5\ s^{-1}$ H_2O/MeCN	$k_{obs}/10^5\ s^{-1}$ D_2O/MeCN	$k(H_2O)/k(D_2O)$
40	1.5	1.3	1.15
50	2.6	1.8	1.44
60	3.8	2.8	1.36
70	6.2	4.6	1.35

Table 5. Vibrational absorption band of H_2O and D_2O. (Eisenberg-Kauzmann, 1969)

vibrational quantum number			central wavenumber of vibrational absorption band (cm^{-1})	
ν_1	ν_2	ν_3	H_2O	D_2O
0	1	0	1594.59	1178.33
1	0	0	3656.65	2671.46
0	0	1	3755.79	2788.05
0	2	0	3151.4	
0	1	1	5332.0	3956.21
0	2	1	6874	5105.44
1	0	1	7251.6	5373.98
1	1	1	8807.05	6533.37
2	0	1	10613.12	7899.80
0	0	3	11032.36	

ν_1: symmetric stretching, ν_2: deformation,
ν_3: antisymmetric stretching vibration.

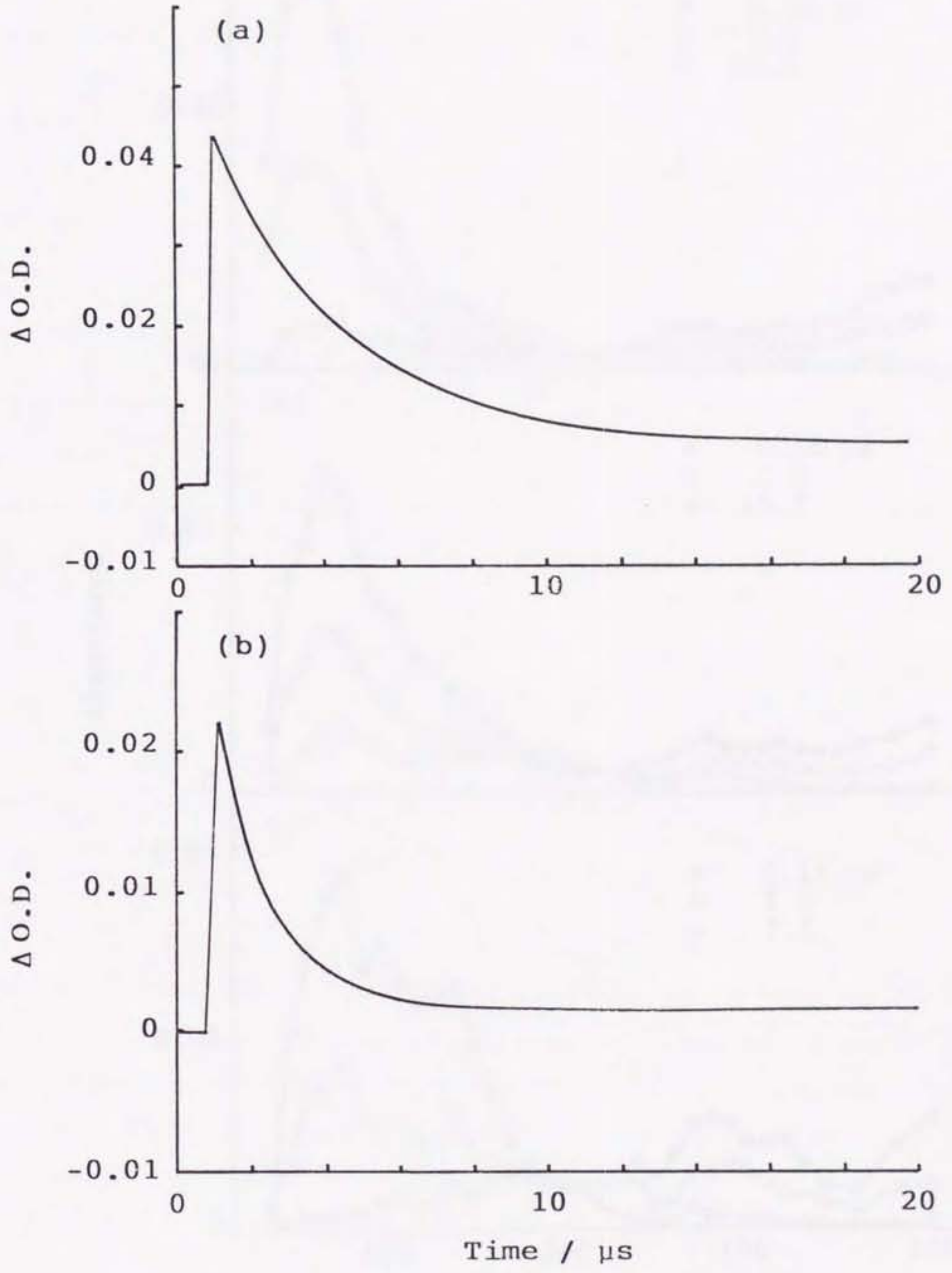


Figure 1. The decay curves of $T_n \leftarrow T_1$ absorption of AQ on excitation with XeCl laser (308 nm) under argon atmosphere in water 50 - acetonitrile 50 vol% (a) and water 70 - acetonitrile 30 vol% (b). [AQ] = 5.0 x 10^{-5} M

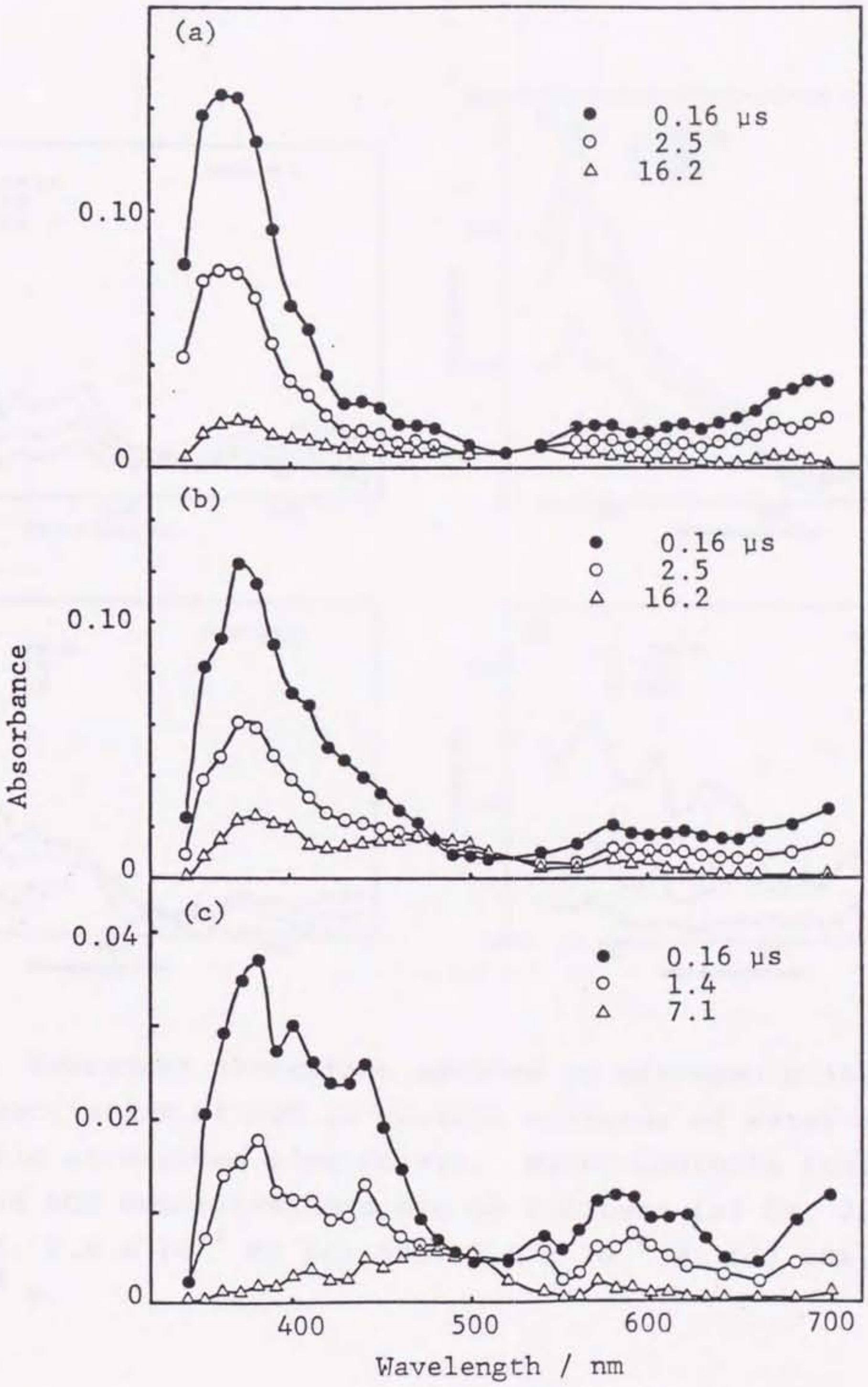


Figure 2. Transient absorption spectra on XeCl pulsed laser (308 nm) excitation of AQ (1.0 x 10^{-4} M) in various mixtures of water and acetonitrile under argon atmosphere at various time delays. Water contents (vol%) in solvent are as follows; (a) 0 %, (b) 50 %, and (c) 70 %.

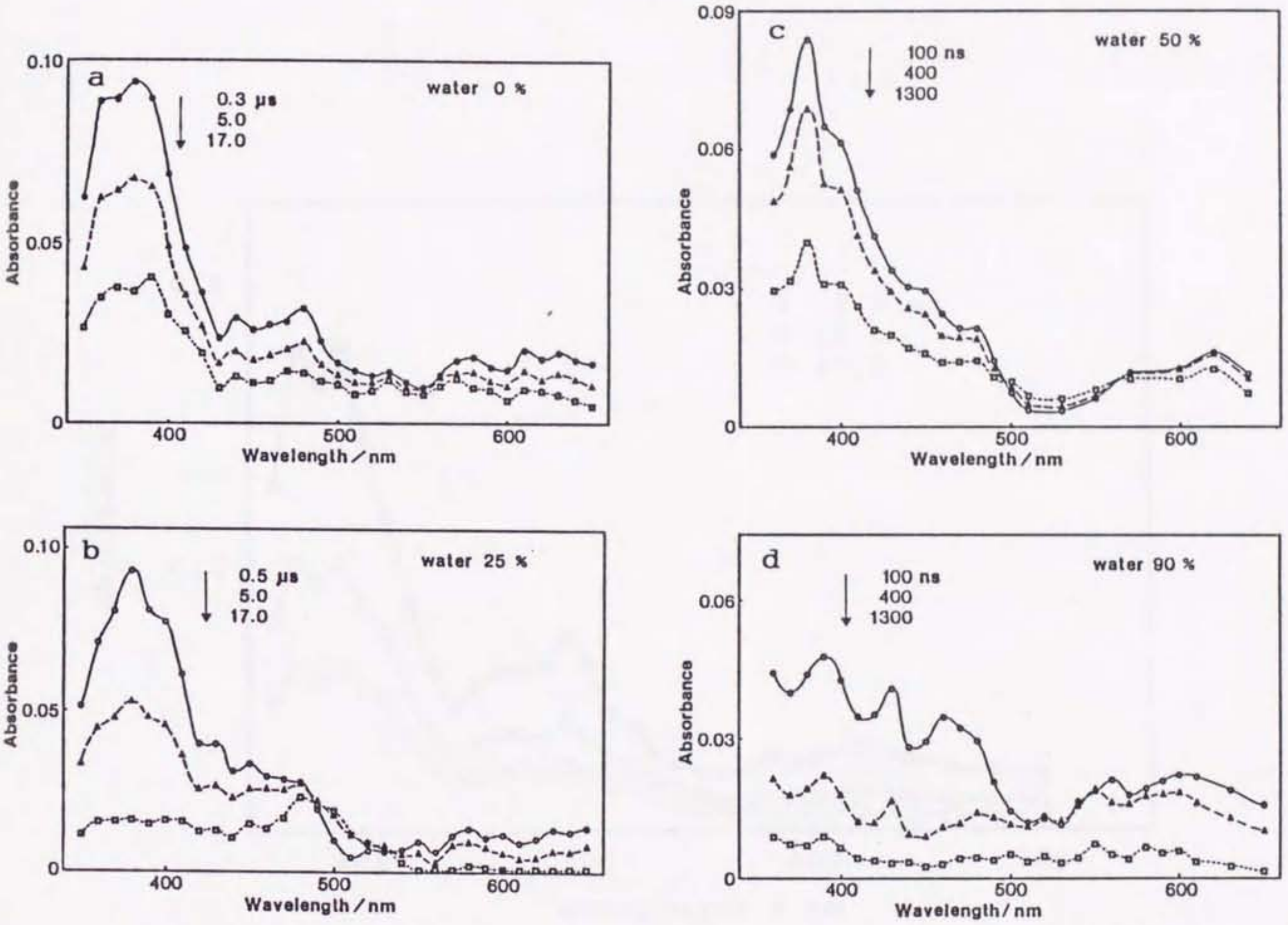


Figure 3. Transient absorption spectra on nitrogen pulsed laser (337 nm) excitation of AQS in various mixtures of water and acetonitrile at various time delays. Water contents (vol%) in solvent and AQS concentrations are as follows: (a) 0%, 2.4×10^{-4} M; (b) 25%, 2.4×10^{-4} M; (c) 50%, 3.1×10^{-4} M; (d) 90%, 3.1×10^{-4} M.

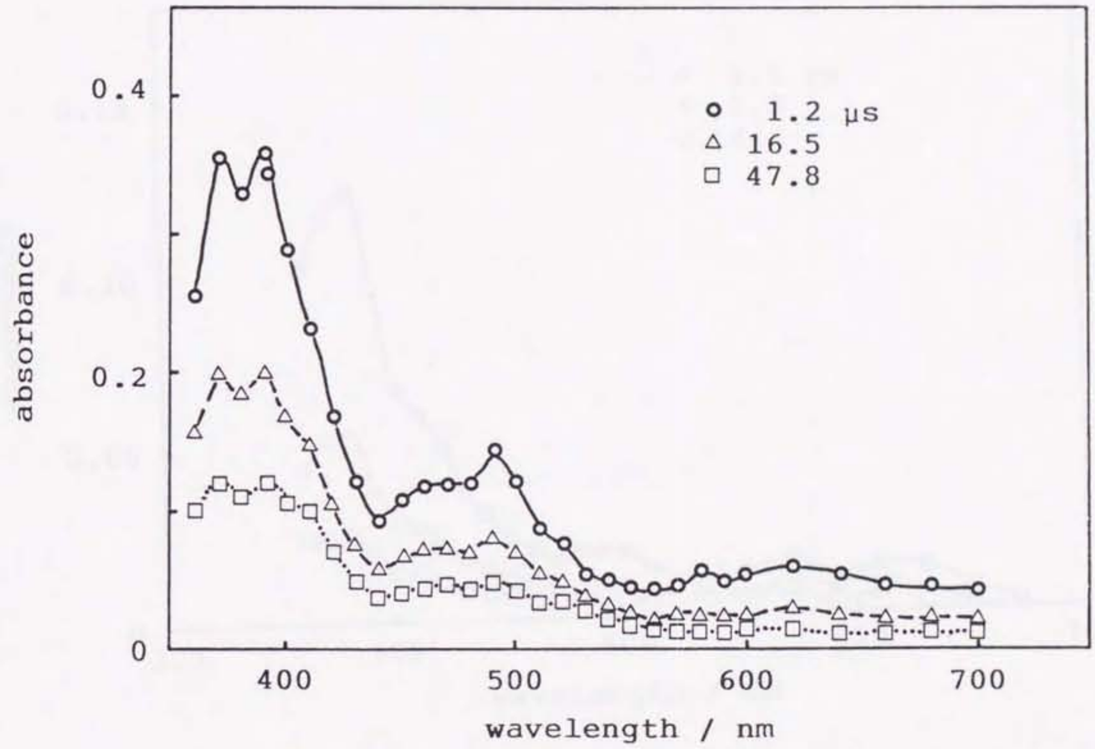


Figure 4. Transient absorption spectra on XeF pulsed laser (351 nm) excitation of AQDS (2.0×10^{-4} M) in 10:90 water-acetonitrile at various time delays under nitrogen atmosphere.

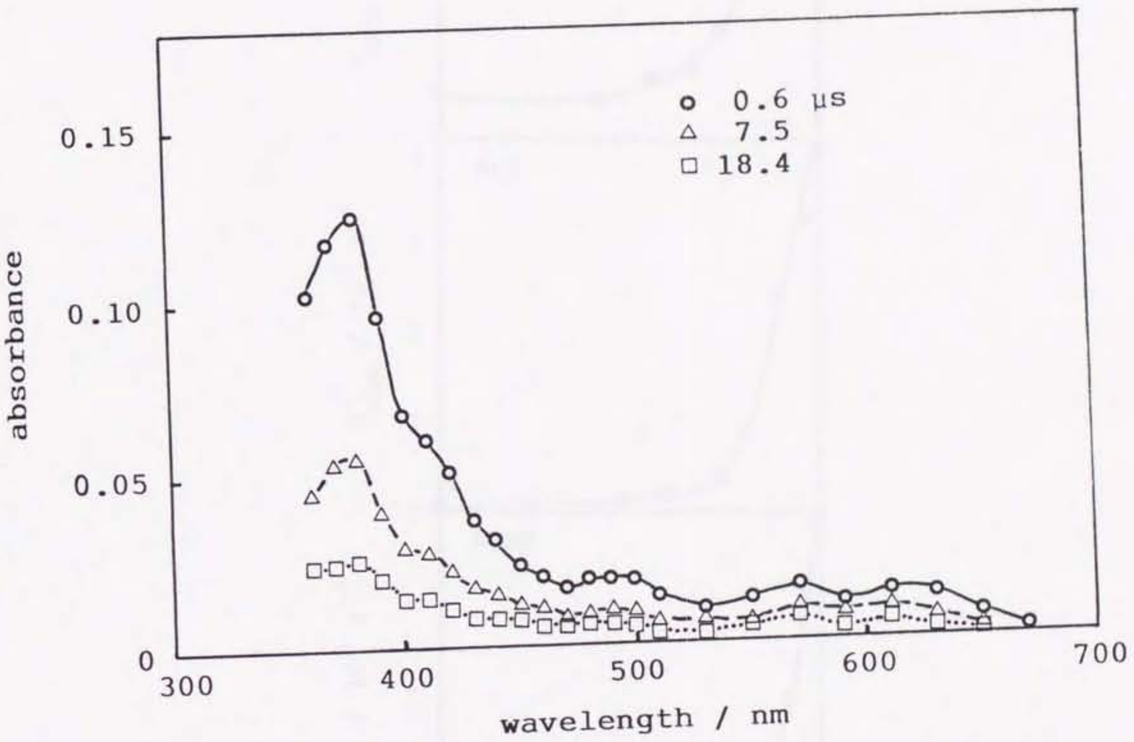


Figure 5. Transient absorption spectra on XeF pulsed laser (351 nm) excitation of AQF (5.0 x 10 M) in 100% acetonitrile under nitrogen atmosphere at various time delays.

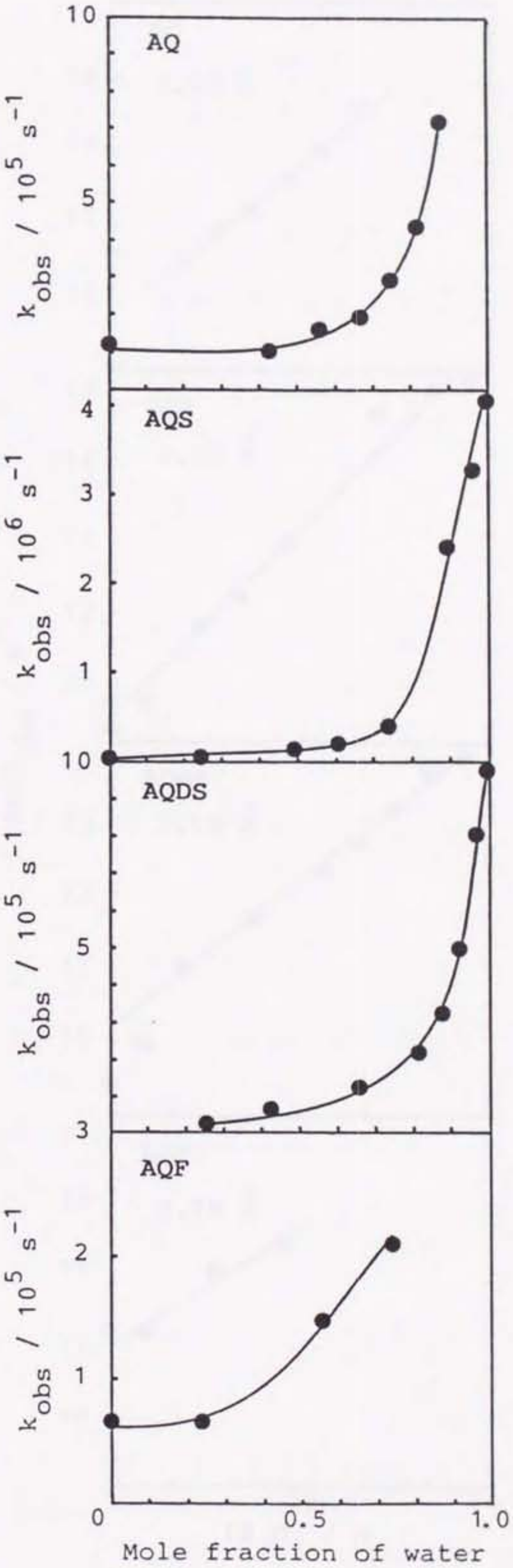


Figure 6. Decay rate constants of triplet-state anthraquinone derivatives determined by first-order kinetic analysis as a function of water mole fraction.

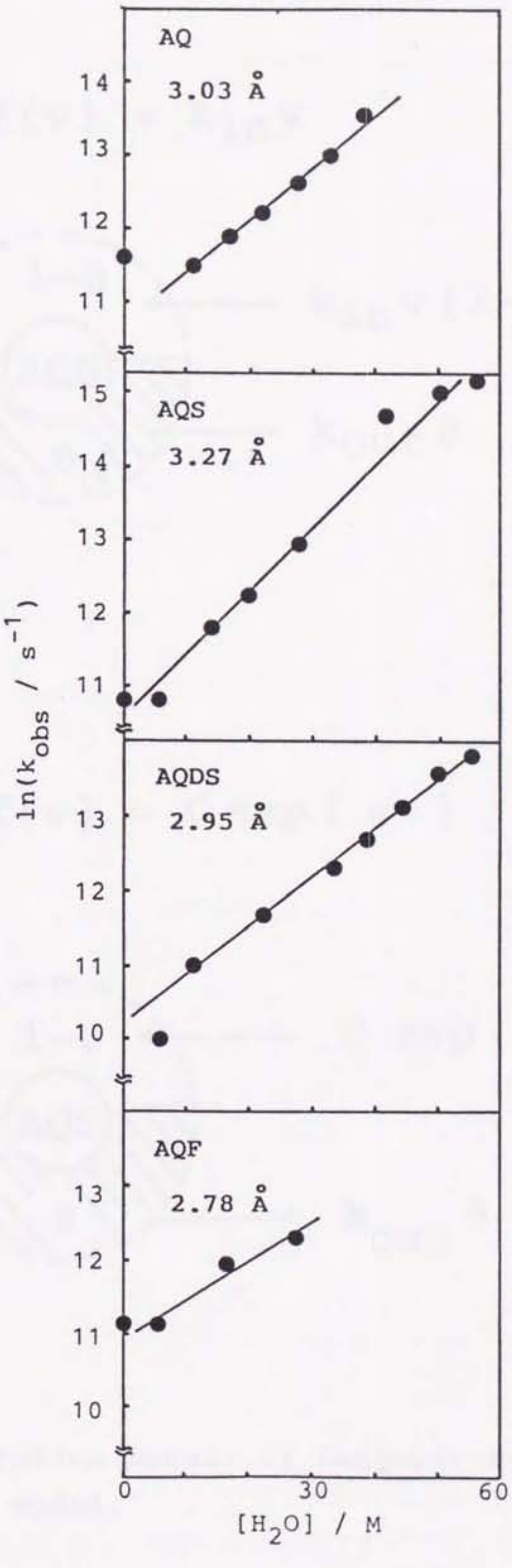
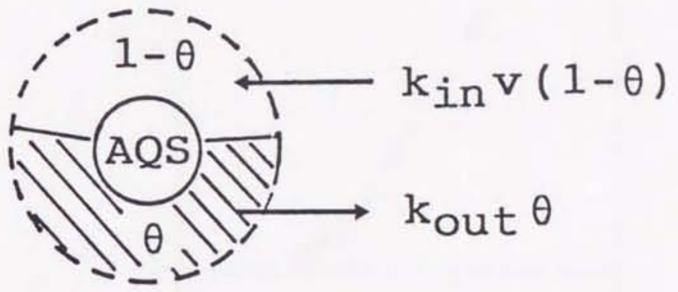


Figure 7. Logarithmic plots of decay rate constants of triplet-state anthraquinone derivatives as a function of water concentration.

i) $f(v) = k_{in} v$



ii) $f(v) = C \exp(\alpha v)$

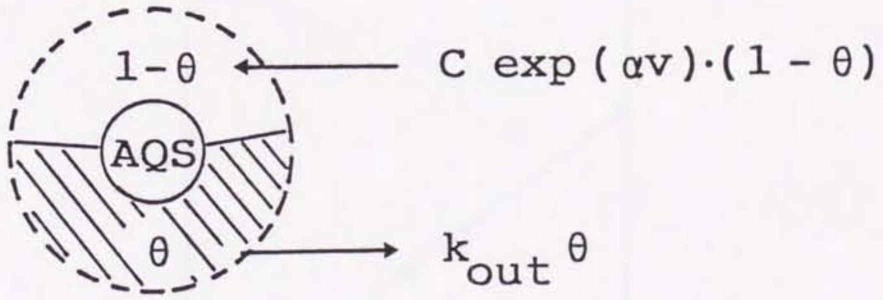


Figure 8. Adsorption model: i) Langmuir-type model, ii) Temkin-type model.

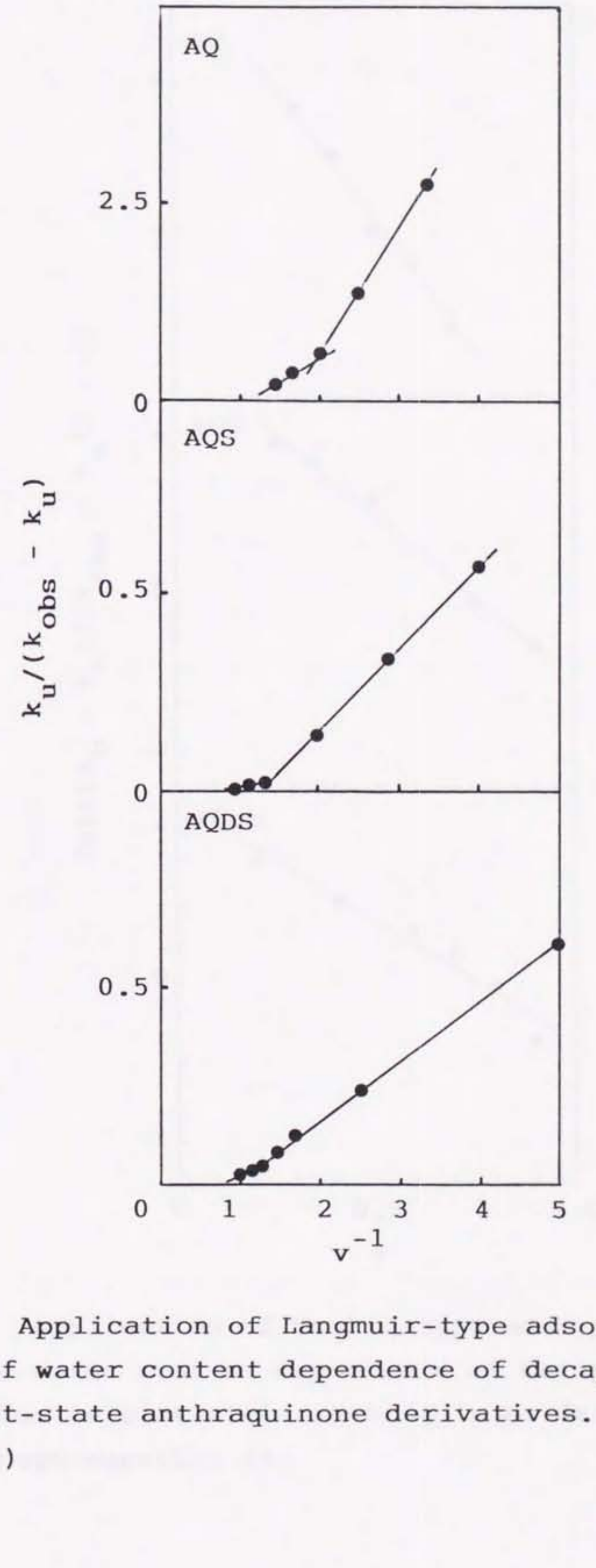


Figure 9. Application of Langmuir-type adsorption model to analysis of water content dependence of decay rate constants for triplet-state anthraquinone derivatives. (Plots through equation 9)

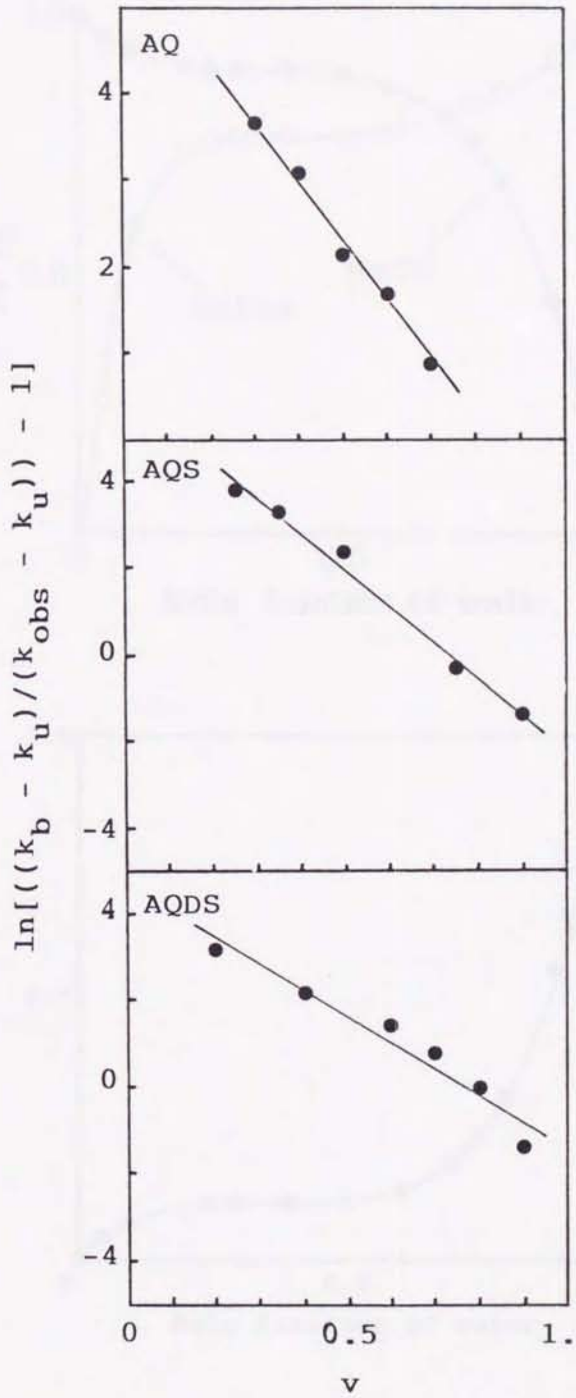


Figure 10. Application of Temkin-type adsorption model to analysis of water content dependence of decay rate constants for triplet-state anthraquinone derivatives. (Plots through equation 14)

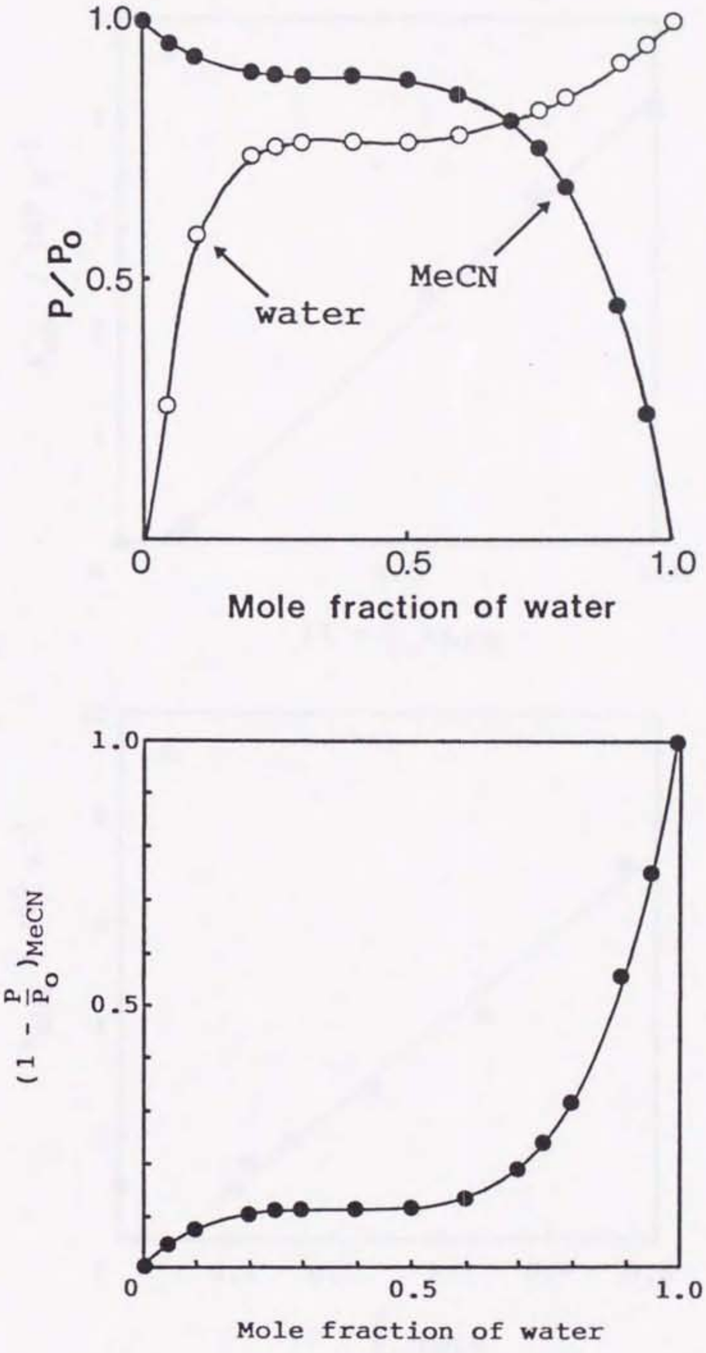


Figure 11. Partial vapor pressures of acetonitrile and water in water-acetonitrile mixtures relative to the vapor pressure over the pure solvent as a function of mole fraction of water (above). $[1 - (P/P_0)]$ for acetonitrile as a function of mole fraction of water (below).

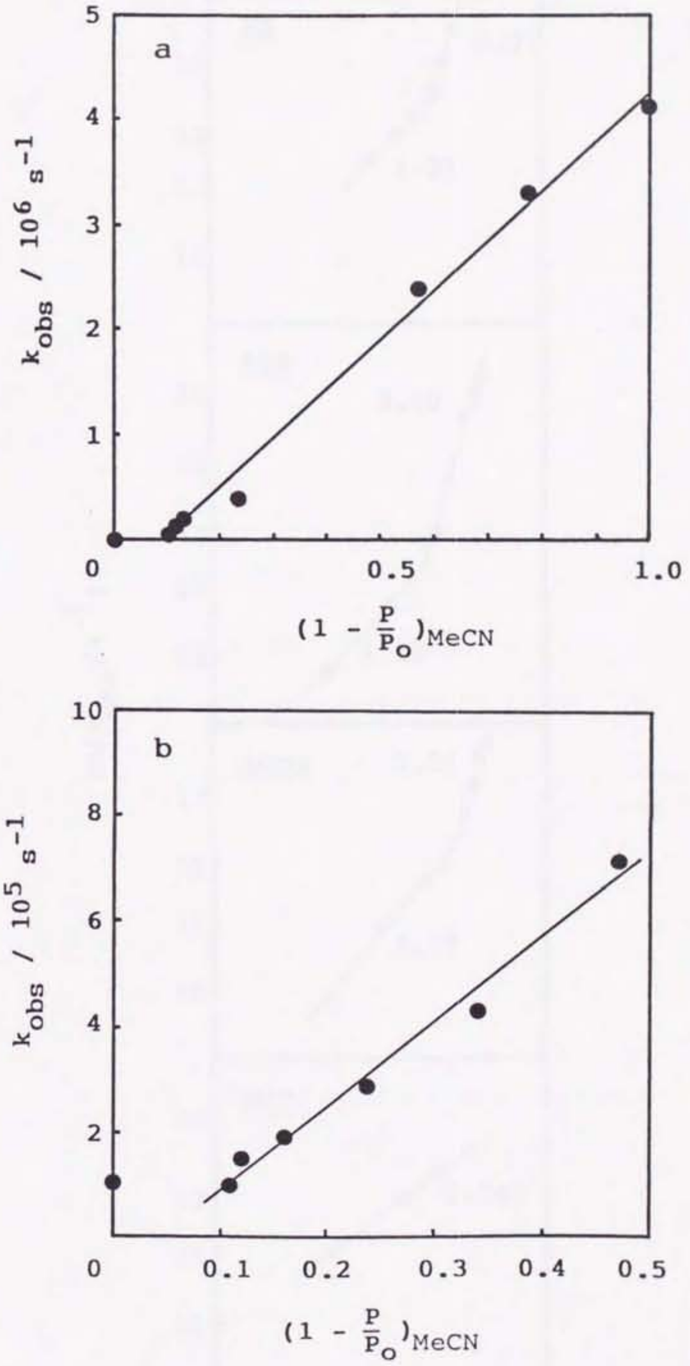


Figure 12. Plots of k_{obs}'s for AQS (a) and AQ (b) against $[1 - (P/P_0)]_{MeCN}$.

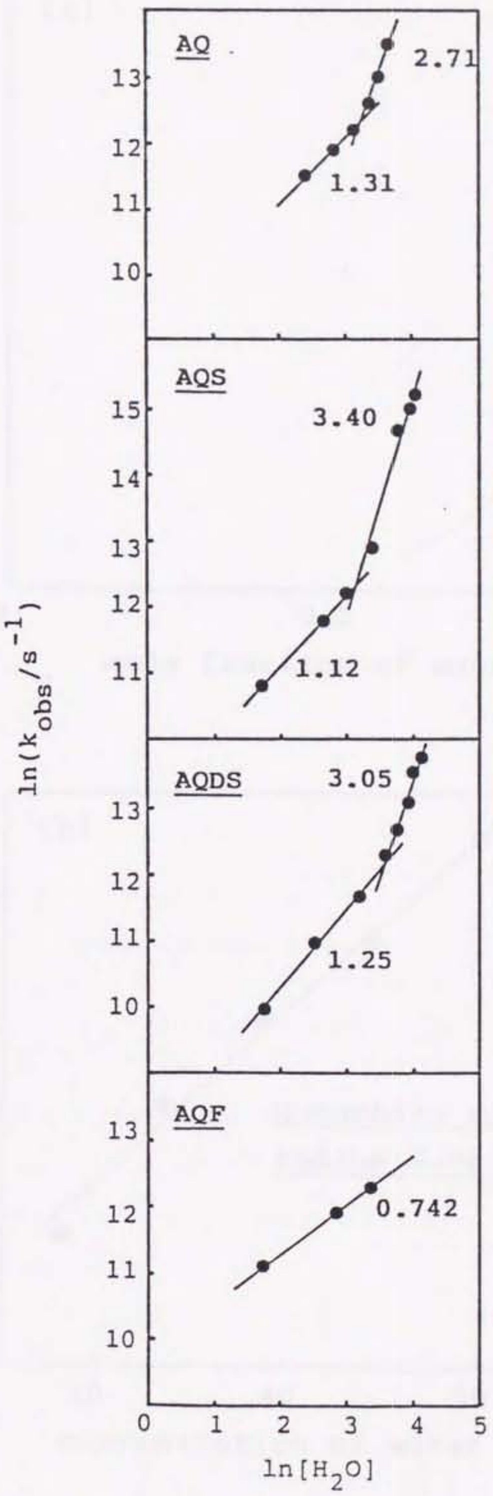


Figure 13. Logarithmic plots of decay rate constants for triplet-state anthraquinone derivatives against ln[H_2O]. Values of slopes are described in figure.

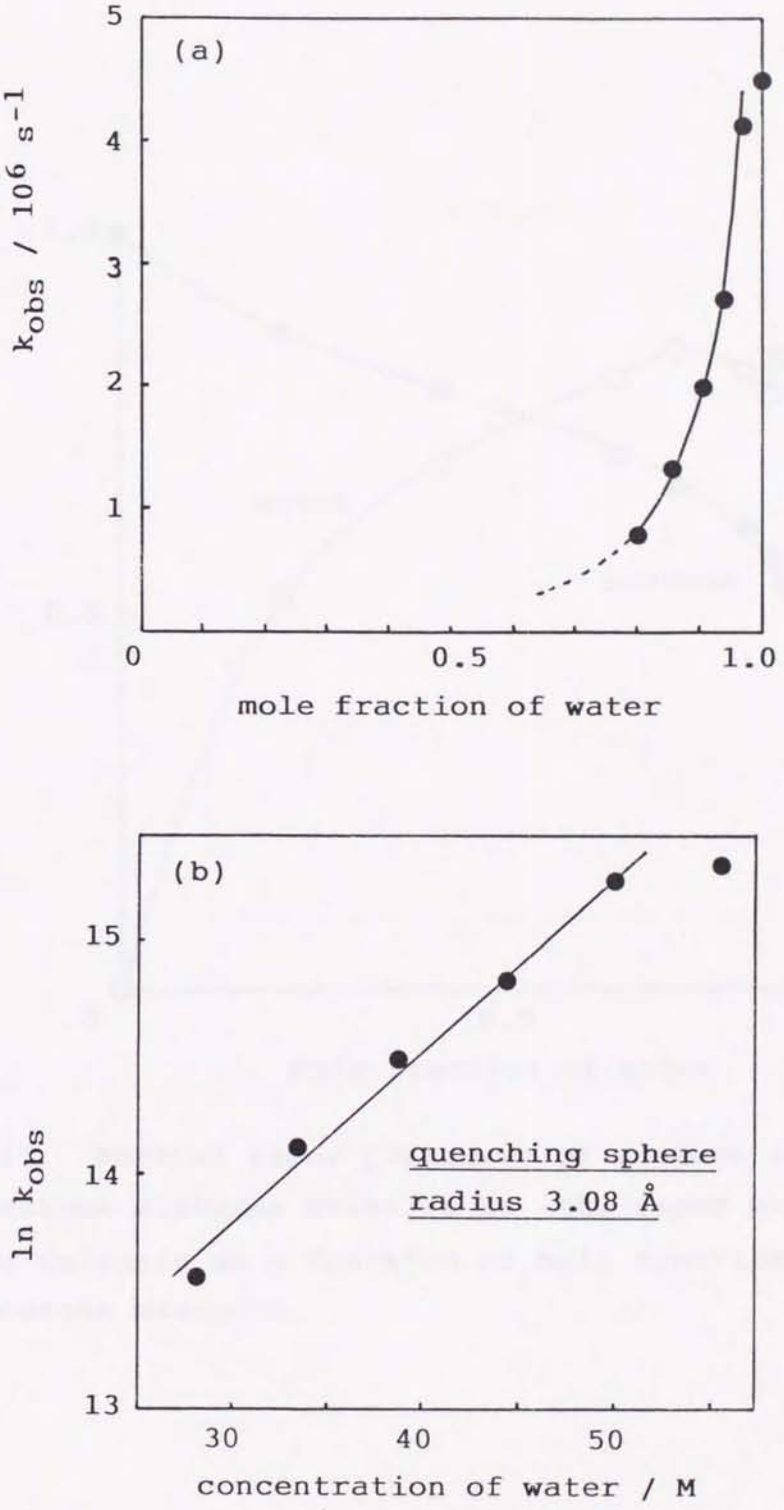


Figure 14. (a) Decay rate constants of AQS triplet as a function of water mole fraction in water-acetone mixtures. (b) Logarithmic plot of k_{obs} for AQS against water concentration in water-acetone mixtures.

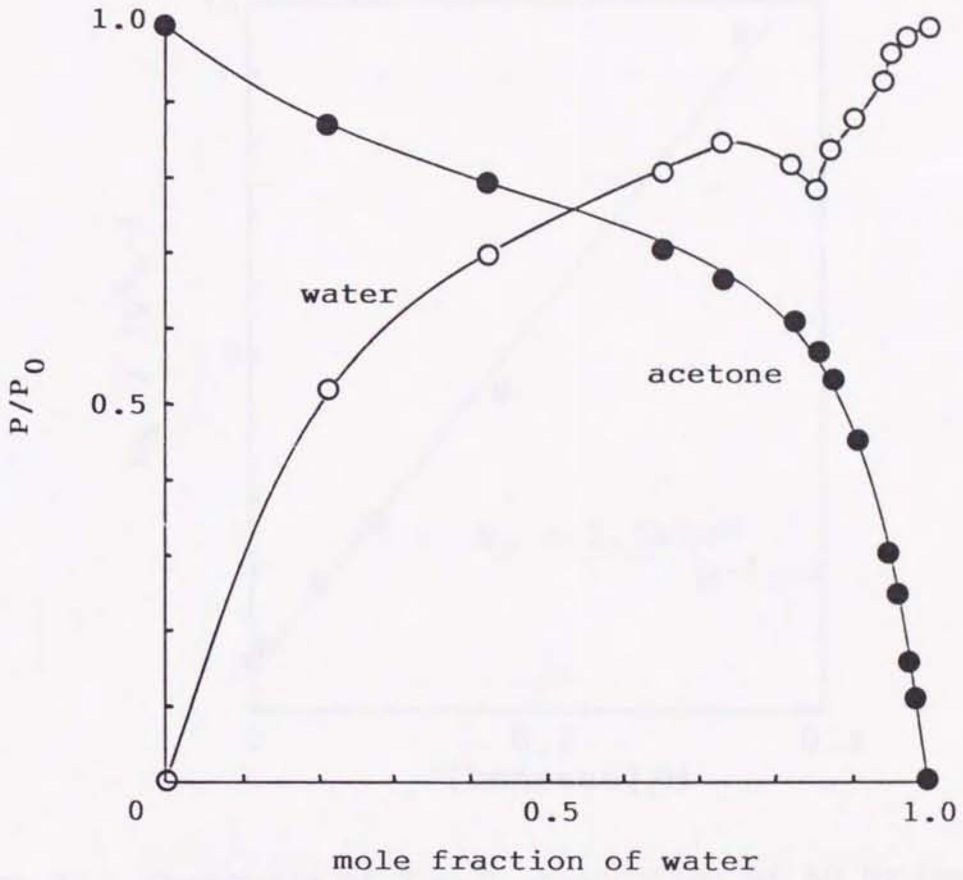
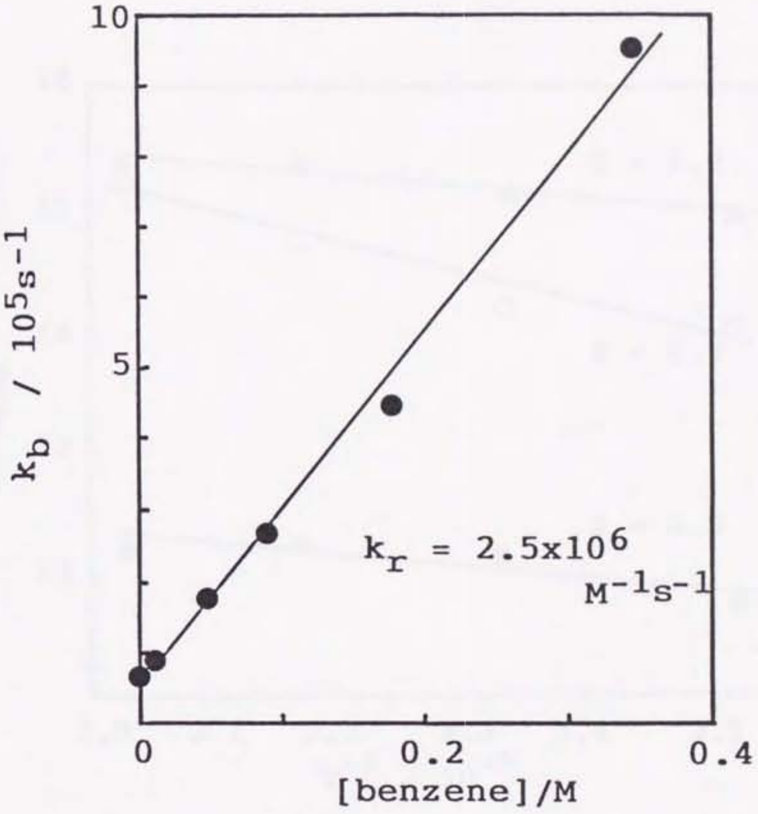


Figure 15. Partial vapor pressures of acetone and water in water-acetone mixtures relative to the vapor pressures over the pure solvents as a function of mole fraction of water in water-acetone mixtures.



Firure 16. Quenching of $T_n \leftarrow T_1$ absorption of AQ by benzene. Decay rate constants of AQ triplet were determined by pseudo-first-order kinetic analtsis as a function of benzene concentration.

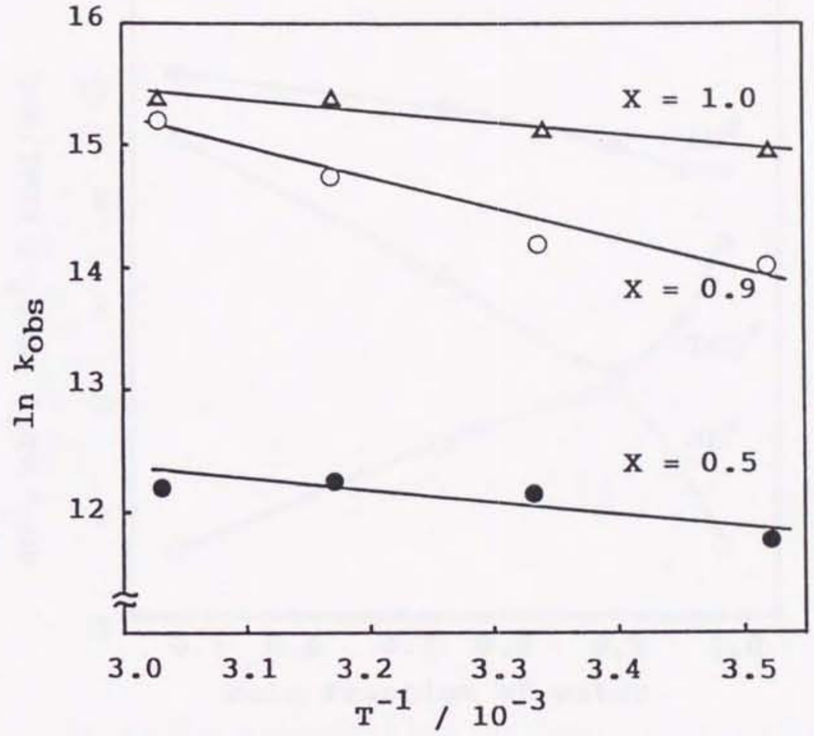


Figure 17. Arrhenius plots for the decay rate constants of AQS triplet in water-acetonitrile mixtures. k_{obs}'s were determined from first-order kinetic analysis of the $T_n \leftarrow T_1$ absorption. X represents mole fraction of water in the solvent.

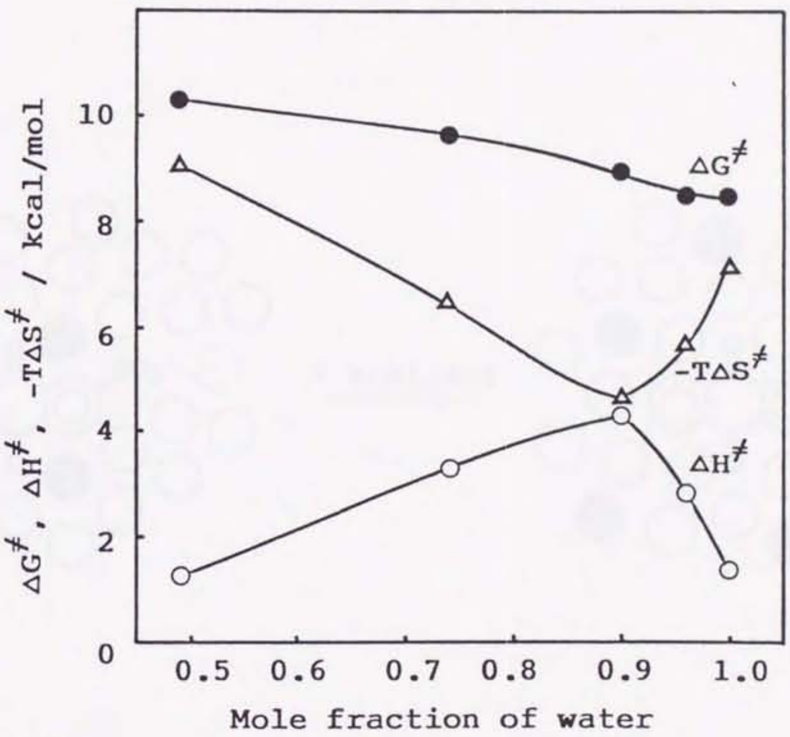


Figure 18. Thermodynamic functions for the deactivation processes of AQS triplet in water-acetonitrile mixtures at 298 K.

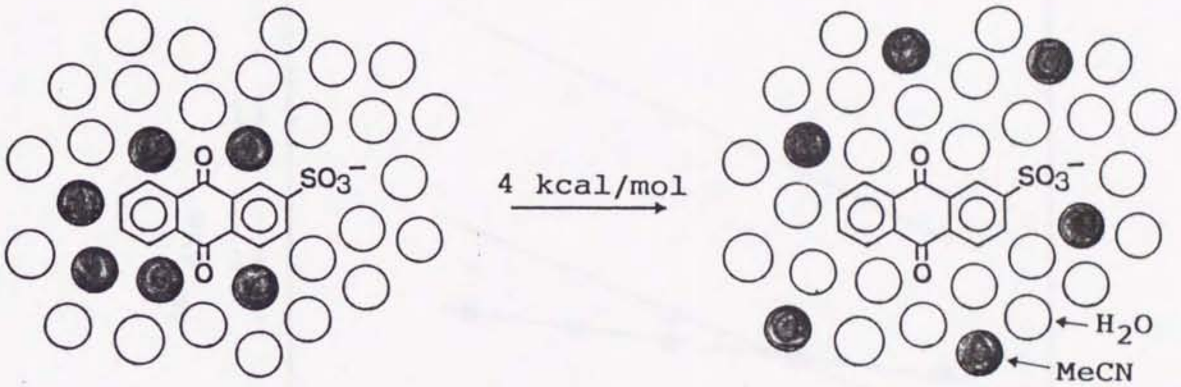


Figure 19. An activation process for deactivation of triplet-state AQS in a water-acetonitrile mixture.

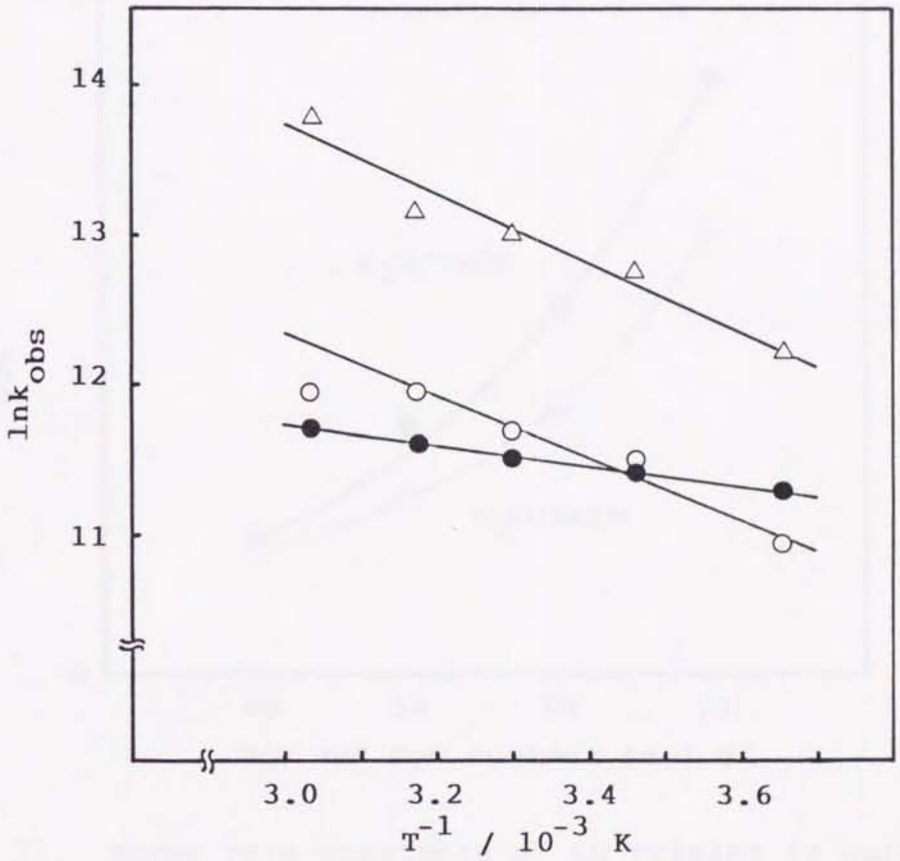


Figure 20. Arrhenius plots for the decay rate constants of AQ triplet in water-acetonitrile mixtures. Water contents (vol%) in the mixed solvents are 0% (●), 30% (○), and 60% (△). k_{obs}'s were determined by first-order kinetic analysis of the $T_n \leftarrow T_1$ absorption.

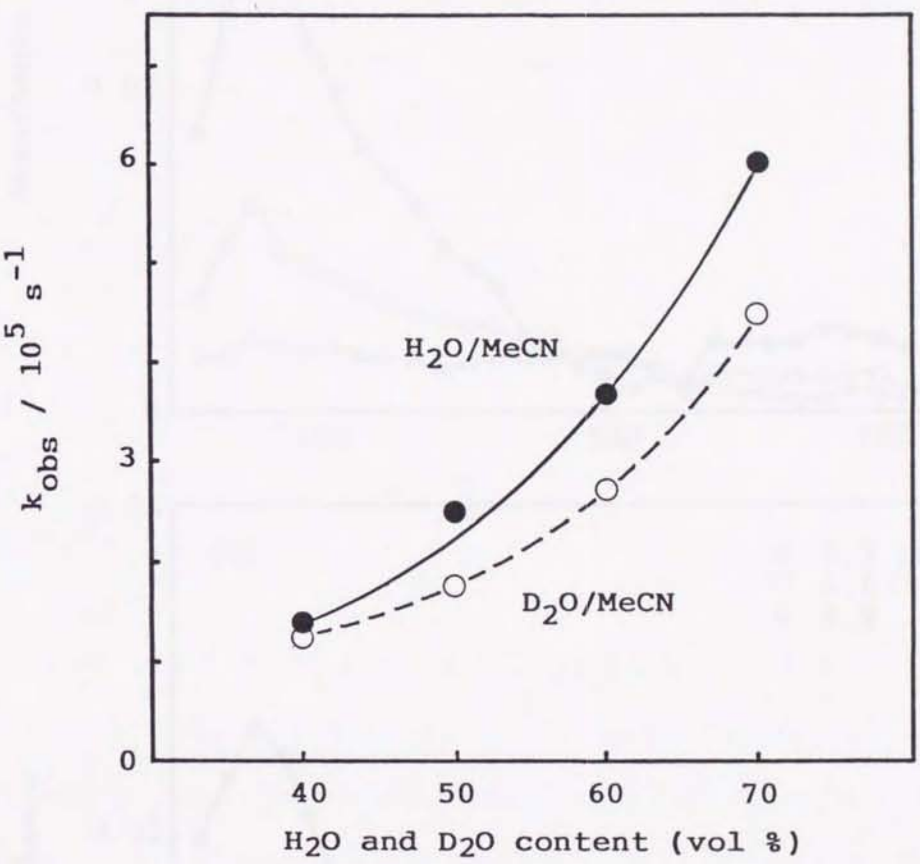


Figure 21. Decay rate constants of AQ triplet in water-acetonitrile (●) and heavy water-acetonitrile (○).

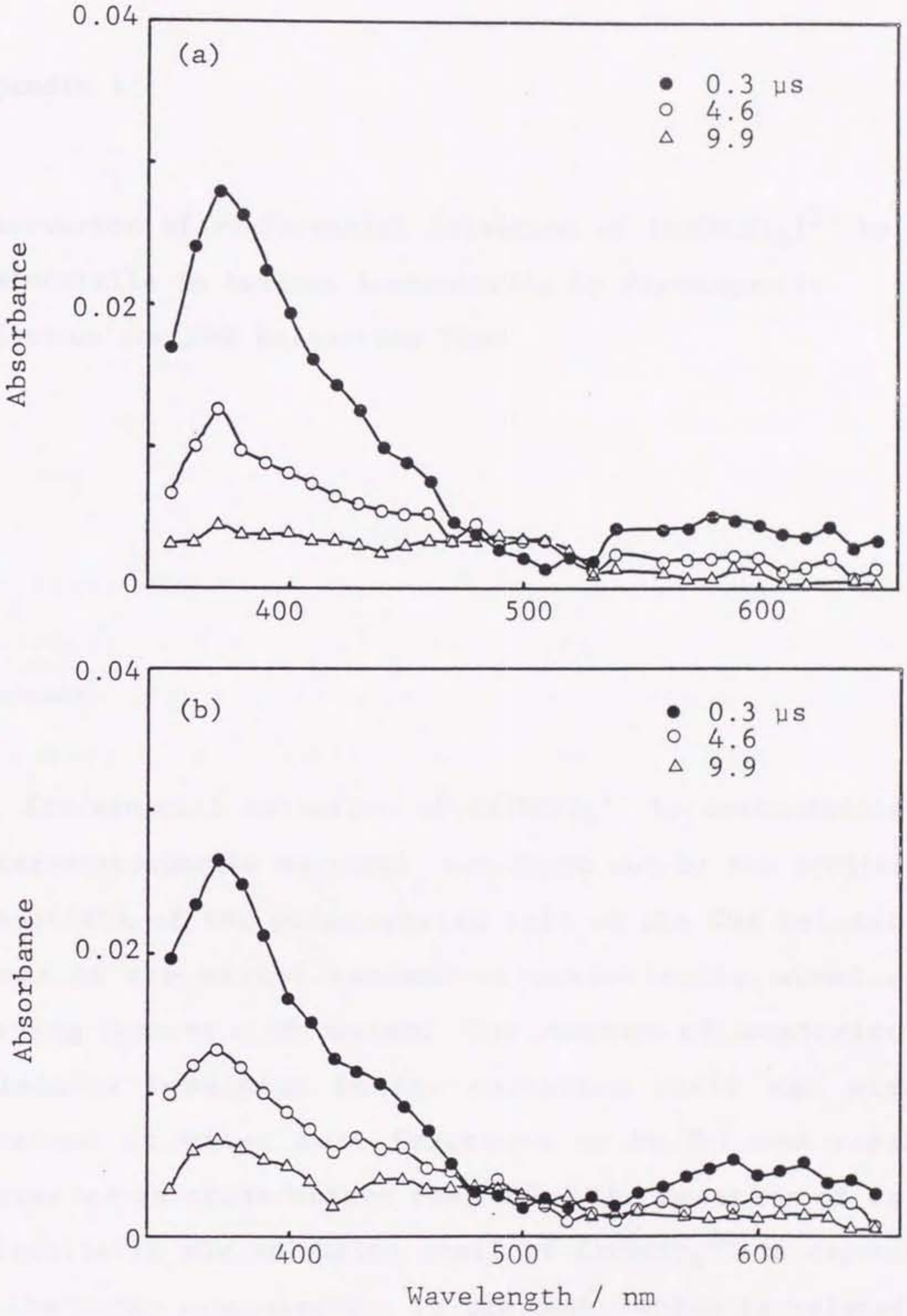


Figure 22. Transient absorption spectra on XeCl pulsed laser excitation of AQ (5.0 x 10^{-5} M) in water-acetonitrile equivolume mixture (a) and in heavy water-acetonitrile equivolume mixture (b) under argon atmosphere at various time delays.

Appendix 1

Observation of Preferential Solvation of $[Cr(NCS)_6]^{3-}$ by Acetonitrile in Aqueous Acetonitrile by Paramagnetic Effect on the NMR Relaxation Time

Abstract

Preferential solvation of $Cr(NCS)_6{}^{3-}$ by acetonitrile in water-acetonitrile mixtures was borne out by the studies of the effect of the paramagnetic salt on the NMR relaxation times of the methyl protons of acetonitrile mixed with varying amounts of water. The number of acetonitrile molecules remaining in the solvation shell was almost constant at water mole fractions up to 0.7 and rapidly decreased at those higher than 0.7. The fraction of water molecules in the solvation shell of $Cr(NCS)_6{}^{3-}$ is dependent on the water concentration in the bulk, which is related to the activity of acetonitrile in water-acetonitrile mixtures.

Introduction

As shown in the preceding chapter, the decay rate constants for triplet-state anthraquinone derivatives (k_{obs}) in water-acetonitrile mixtures are dependent on water concentration, which is very similar to change of the partial vapor pressure of acetonitrile in water-acetonitrile mixtures. It has been shown that k_{obs}'s are strongly correlated with the number of water molecules in their solvation shells of anthraquinone derivatives which are preferentially solvated by acetonitrile. In other words, when the activity of acetonitrile in the mixed solvent decreases, water molecules can easily enter into the solvation shells. As a result, the number of water molecules in the solvation shells is controlled by the composition of the mixed solvent.

It is expected that the number of water molecules in the solvation shells of other compounds which are preferentially solvated by acetonitrile in water-acetonitrile mixtures will also show similar water concentration dependence. This is the case for a solution of potassium hexakis(isothiocyanato)chromate(III) in water-acetonitrile mixtures.[2] Measurements of NMR relaxation times of the solvent molecules afford information about the solvation through the paramagnetic interaction with solvent molecules.[1-3]

The transverse relaxation time, T_2, of the protons of a solvent molecule is generally greatly reduced by a paramagnetic solute. The solution is assumed to be partitioned into a paramagnetic environment (the solvation layer) and a diamagnetic environment (the bulk solution). When exchange between these two environments is rapid, McConnell's equation is applied:[3]

$$1/T_2 = P_D/T_{2D} + P_M/T_{2M} \qquad (1)$$

where T_2 is the observed relaxation time, P_D and P_M are the probabilities that a solvent molecule is in the diamagnetic environment (bulk) and in the paramagnetic environment (solvation shell), respectively. and T_{2D} and T_{2M} are relaxation times characteristic of the diamagnetic and magnetic environments, respectively. P_M/T_{2M} is simply related to the excess width at half-height in the NMR absorption signal:

$$\pi\Delta\nu = P_M/T_{2M} \qquad (2)$$

where $\Delta\nu$ is the excess width at half height of the signal produced by the paramagnetic solute. Assuming that T_{2M} = T_{2M0} where T_{2M} is the relaxation time for the methyl protons of acetonitrile in a water-acetonitrile mixture and T_{2M0} is that in pure acetonitrile, the following relation is derived,

$$\Delta\nu/\Delta\nu_0 = P_M/P_{M0} \qquad (3)$$

$$P_M/P_{M0} = (n/N)/(n_0/N_0) = (n/n_0)(N_0/N) \qquad (4)$$

where N_0 and N are the numbers of acetonitrile molecules/ml in pure acetonitrile and in the mixed solvent, respectively, n_0 and n the numbers of acetonitrile molecules in the solvation shell in pure acetonitrile and in the mixed solvent, respectively, and P_{M0} the probability that a solvent molecule is in the paramagnetic environment in pure acetonitrile.

Since both $\Delta\nu$ and $\Delta\nu_0$ are obtained experimentally and both N and N_0 are calculated from the solvent mixing ratio, the fraction of acetonitrile, n/n_0, remaining in the solvation shell in the mixed solvent can be estimated. This value represents a preferential solvation parameter for acetonitrile.

In the mixtures of water-acetonitrile with various mixing ratios, $\Delta\nu$ was measured and the value of n/n_0 was determined. The water concentration dependence of n/n_0 is compared with that of acetonitrile partial vapor pressure.

Experimental Section

Materials. $K_3[Cr(NCS)_6]$ was prepared according to the literature[4] from chromium(III) potassium sulfate and potassium thiocyanate, and purified by recrystallization from ethanol. Acetonitrile (Nakarai Chemicals) was used after successive distillation over CaH_2, P_2O_5 and K_2CO_3. Water (non fluorescent, Kanto Chemicals) was used as received.

NMR spectra. NMR spectra were recorded on a 100-MHz NMR spectrometer (JEOL, JNM-MH-100) with 40 r.p.s.

Results and Discussion

The typical NMR spectra of the methyl protons of acetonitrile in water-acetonitrile mixtures containing $Cr(NCS)_6^{3-}$ (0.05 M) are depicted in Figure 1. Figure 1-(a) shows the spectra in pure acetonitrile in the presence and absence of $Cr(NCS)_6^{3-}$ and Figure 1-(b) the spectra in a water-acetonitrile (90:10 by volume %) mixture. As predicted from equation 2, $\Delta\nu$ is larger in higher water contents. $\Delta\nu$ for the methyl protons of acetonitrile in the mixtures of water-acetonitrile containing $Cr(NCS)_6^{3-}$ (0.05 M) and the values of n/n_0 are listed in Table 1. The values of n/n_0 are depicted in Figure 2 as a function of the water mole fraction in the mixed solvent. The result shows that the number of acetonitrile molecules remaining in the solvation shell in the mixed solvent is almost constant at the water mole fractions from 0 to 0.8 and is rapidly reduced at the water mole fractions higher than 0.8. These results show that $Cr(NCS)_6^{3-}$ is preferentially solvated by acetonitrile. The water concentration dependence observed here is very similar to that of the decay rate constants of triplet-state anthraquinone derivatives as described in chapter 4.

This strong preference of solvation of both $Cr(NCS)_6^{3-}$ and anthraquinone derivatives by acetonitrile is related to the activity of acetonitrile in the mixed solvent. Figure 3 shows the relative partial vapor pressures of acetonitrile and water as a function of mole fraction of water in the water-acetonitrile mixtures.[5] It does not follow Raoult's law except mixtures containing a very small amount of a component. Based on the data of partial vapor pressure, at low mole fractions of either component (about 0.3), the activity of that component will approach that of the pure solvent. When a molecule has a preference of one solvent component in the water-acetonitrile mixture, its preferential solvation by that component will be attained even at low mole fractions of that solvent component.

$Cr(NCS)_6^{3-}$ and anthraquinone derivatives are preferentially solvated by acetonitrile in the water-acetonitrile mixture, and the same water concentration dependence is observed for the partial vapor pressure of acetonitrile in water-acetonitrile mixed solvents. Such kind of solvent content dependence will be general for the solvation of compounds to prefer a solvent component in the mixed solvents.

Conclusion

The water concentration dependence of the fractions of water (or acetonitrile) molecules remaining in the solvation shells of anthraquinone derivatives and $Cr(NCS)_6^{-3}$ are similar to each other. They are related with the activity of acetonitrile in the mixed solvent as shown by partial vapor pressure of acetonitrile.

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Table 1. Excess line broadening of ^{1}H NMR signal of acetonitrile in water-acetonitrile mixtures and values of preferential solvation parameter (n/n_0).

mole fraction of water	$\Delta\nu$ / Hz	n/n_0
0	3.81	1
0.421	4.05	0.848
0.555	4.61	0.847
0.660	5.64	0.888
0.744	6.27	0.825
0.813	7.98	0.836
0.872	8.94	0.705
0.921	10.20	0.536
0.963	10.59	0.278
0.982	9.83	0.129

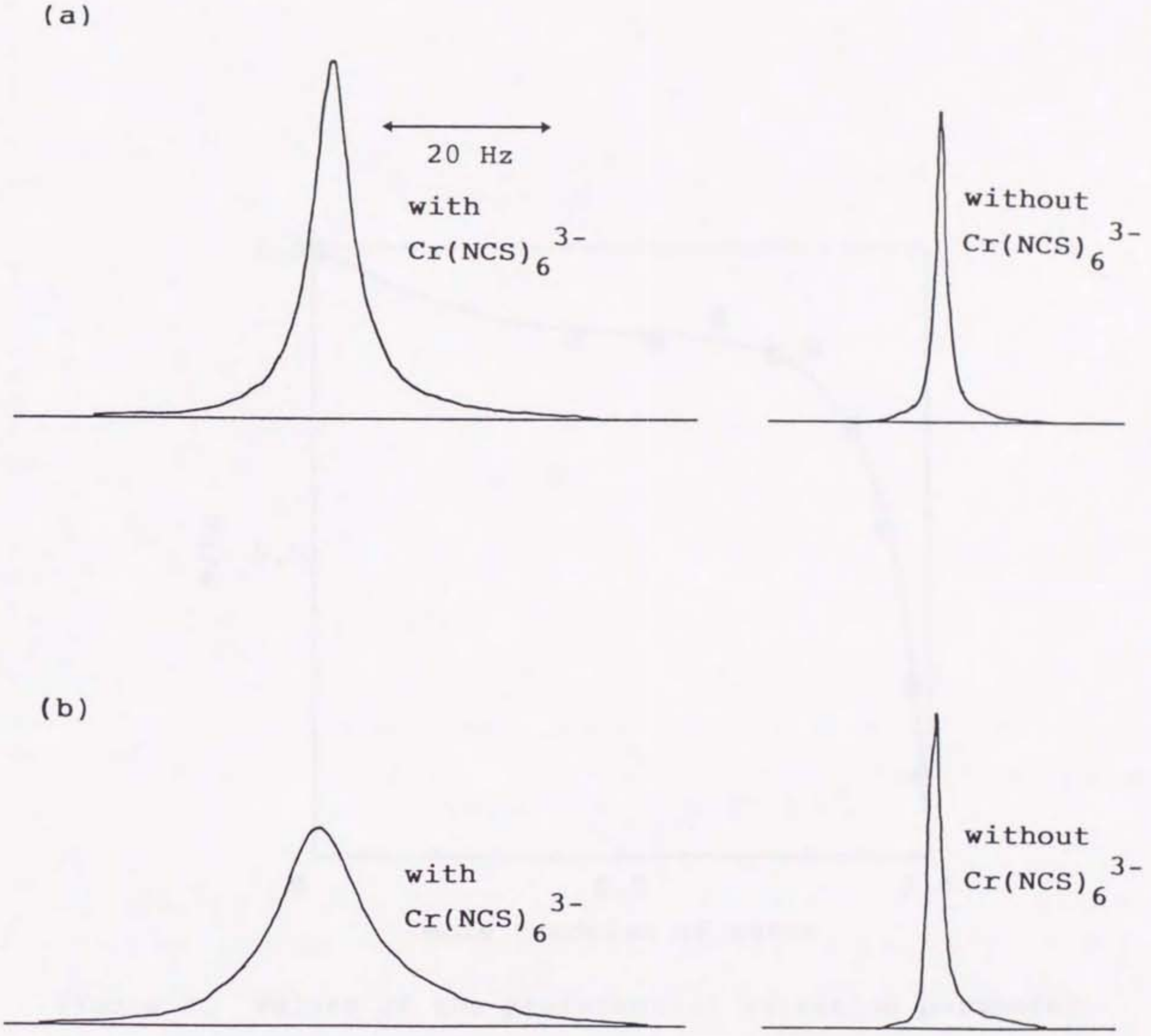

Figure 1. NMR spectra of methyl protons of acetonitrile with (0.05 M) and without $Cr(NCS)_6^{3-}$ in acetonitrile 100% (a) and in 90:10 water-acetonitrile.

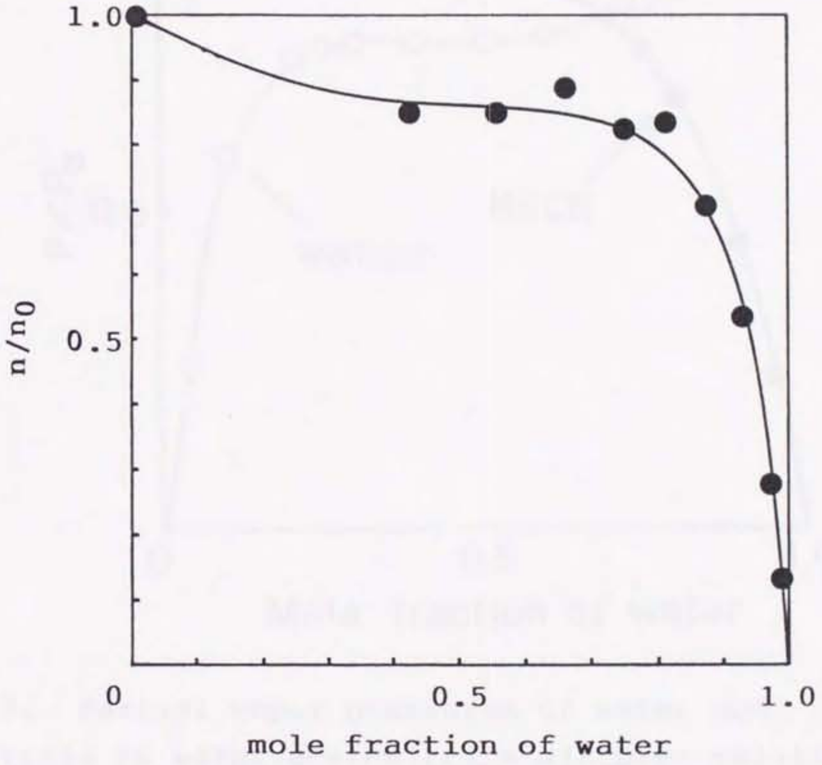

Figure 2. Values of the preferential solvation parameter for MeCN in water-acetonitrile mixtures as a function of the mole fraction of water.

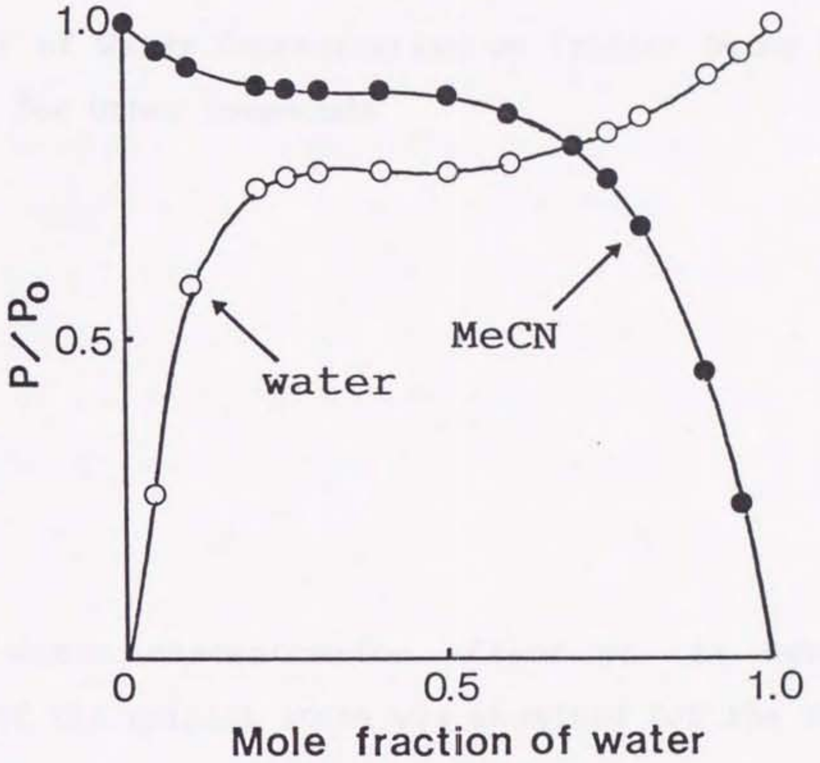

Figure 3. Partial vapor pressures of water and acetonitrile in water-acetonitrile mixtures relative to the vapor pressures over the pure solvents as a function of mole fraction of water. The data were obtained at 20 °C. (J. Am. Chem. Soc., 91, 2236 (1969))

Appendix 2

The Effect of Water Concentration on Triplet Decay Rate Constants for Other Compounds

Abstract

The water concentration effect on the decay rate constant of the triplet state was examined for the following compounds: 1-chloroanthraquinone, 2-chloroanthraquinone, 2-methylanthraquinone, naphthoquinone, 2-methylnaphthoquinone, duroquinone, benzophenone, 9-fluorenone and anthracene. A remarkable water concentration effect was observed only for 2-chloroanthraquinone and naphthoquinone.

Introduction

It was described in chapter 4 that the decay rate constants of the triplet-state anthraquinone derivatives (AQ, AQS and AQDS) exponentially increase with increasing water content. In this chapter the water concentration effect is examined on the decay rate constants of the triplet state of other compounds. The results will be discussed in relation to the electronic configuration in the lowest excited triplet state and structure of the compounds investigated.

Experimental Section

Materials. 1-Chloroanthraquinone, 2-methylanthraquinone, naphthoquinone, duroquinone, benzophenone, and 9-fluorenone were all purchased from Nakarai Chemicals and used after recrystallization from ethanol. 2-Chloroanthraquinone was purchased from Wako Chemicals and used after recrystallization from ethanol. Anthracene was recrystallized from toluene.

Laser Flash Photolysis. The apparatus for laser flash photolysis has been described in chapter 3. Laser flash photolyses were carried out with XeCl laser (308 nm, 120 mJ, 10-ns fwhm) as excitation light.

Results and discussion

1. Several Anthraquinone Derivatives

i) 1-Chloroanthraquinone

1-Chloroanthraquinone (1-CAQ, 5.0×10^{-5} M) in water-acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content in the mixed solvent was changed from 0 to 80 vol%.

The transient absorption spectra observed in pure acetonitrile and in 80:20 water-acetonitrile are depicted in Figure 1-(a) and (b), respectively. The absorption band around 390 nm has already been assigned to the $T_n \leftarrow T_1$ absorption.[1] The decay rate constant of triplet-state 1-CAQ, k_{obs}, was obtained by first-order kinetic analysis of the $T_n \leftarrow T_1$ absorption decay curves monitored at 380 and 390 nm.

The obtained values of k_{obs} for 1-CAQ were plotted in Figure 2-(a) as a function of the water mole fraction in the mixed solvent. k_{obs} observed in 80 vol% water (2.6×10^5 s^{-1}) is about 2.5 times larger than that in pure acetonitrile (1.1×10^5 s^{-1}). Logarithmic plot of k_{obs} as a function of water concentration is depicted in Figure 2-(b). From the slope, the quenching sphere radius was obtained to be 2.03 Å according to Perrin's equation.[2,3]

ii) 2-Chloroanthraquinone

2-Chloroanthraquinone (2-CAQ, 5.0 x 10^{-5} M) in water-acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content in the mixed solvent was changed from 0 to 70 vol%. The transient absorption sperctra observed in pure asetonitrile and 60:40 water-acetonitrile are depicted in Figure 3-(a) and (b), respectively. The spectrum in pure acetonitrile with an absorption maximum around 370 nm and a broad absorption band at wavelengths longer than 600 nm has already been assigned to its $T_n \leftarrow T_1$ absorption.[1] On the other hand, the spectrum shape in 60:40 water-acetonitrile is very different from that in pure acetonitrile. This means that the electronic configuration of the triplet state will be changed by interaction with water. The decay rate constant of triplet-state 2-CAQ, k_{obs}, was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curves monitored at 370 and 470 nm.

The obtained k_{obs}'s of 2-CAQ were plotted in Figure 4-(a) as a function of water mole fraction in the mixed solvent. k_{obs} in 70:30 water-acetonitrile (4.9 x 10^5 s^{-1}) is more than five times larger than that in pure acetonitrile (9.0 x 10^4 s^{-1}). Logarithmic plot of k_{obs} of 2-CAQ is depicted in Figure 4-(b) as a function of water concentration. From the slope the quenching sphere radius was obtained to be 2.89 Å according to Perrin's equation.

iii) 2-Methylanthraquinone

2-Methylanthraquinone (AQM, 5.0×10^{-5} M) in water-acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content in the mixed solvent was changed from 0 to 80 vol%. The transient absorption spactra observed in pure acetonitrile and 80:20 water-acetonitrile are depicted in Figure 5-(a) and (b), respectively. The absorption maximum around 380 nm observed in pure acetonitrile becomes small in 80:20 water-acetonitrile. The decay rate constant of triplet-state AQM, k_{obs}, was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curves monitored at 450 nm. The obtained values of k_{obs} of AQM are plotted in Figure 6-(a) as a function of water mole fraction. The value in 80:20 water-acetonitrile (3.7×10^5 s^{-1}) is about four times larger than that in pure acetonitrile (8.2×10^4 s^{-1}). Logarithmic plot of k_{obs} of AQM is depicted in Figure 6-(b) as a function of water concentration. From the slope the quenching sphere radius was obtained to be 2.44 Å according to Perrin's equation.

2. Other Quinones

i) Naphthoquinone

Naphthoquinone (NQ, 2.0×10^{-4} M) in water-acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content in the mixed solvent was changed from 0 to 90 vol%. The transient absorption spactra observed in pure acetonitrile and in 80:20 water- acetonitrile are depicted in Figure 7-(a) and (b), respectively. The decay rate constant of triplet-state NQ, k_{obs}, was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curves monitored at 360 and 370 nm. The obtained values of k_{obs} of NQ are plotted in Figure 8-(a) as a function of water mole fraction. The value in 90:10 water-acetonitrile (3.8×10^6 s^{-1}) is about thirteen times larger than that in pure acetonitrile (3.0×10^5 s^{-1}). Logarithmic plot of k_{obs} of NQ is depicted in Figure 8-(b) as a function of water concentration. From the slope the quenching sphere radius was obtained to be 2.75 Å according to Perrin's equation.

ii) 2-Methylnaphthoquinone

2-Methylnaphthoquinone (NQM, 2.0×10^{-4} M) in water acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content in the mixed solvent was changed from 0 to 90 vol%. The transient absorption spectra observed in 50:50 water-acetonitrile are depicted in Figure 9. The decay rate constant of triplet-state NQM, k_{obs}, was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curves monitored at 380 and 390 nm. The obtained values of k_{obs} of NQM are depicted in Figure 10 as a function of water mole fraction. This result shows that k_{obs} of NQM is not influenced by water.

iii) Duroquinone

Duroquinone (DQ, 1.5×10^{-3} M) in water-acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content in the mixed solvent was 0, 40 and 70 vol%. The transient absorption spectra observed in pure acetonitrile and 40:60 water-acetonitrile are depicted in Figure 11-(a) and (b), respectively, which are in good agreement with the published absorption spectra of triplet-state DQ.[4-7] The decay rate constant of triplet-state DQ was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curves monitored at 450, 470, 480, 490, and 500 nm. The obtained values of k_{obs} are 1.0×10^5 s^{-1} in pure acetonitrile, 1.1×10^5 s^{-1} in 40-vol% water, 1.4×10^5 s^{-1} in 70-vol% water. Therefore, DQ triplet does not suffer the effect of water concentration on k_{obs}.

3. Several Aromatic Compounds

i) Benzophenone

Benzophenone (BP, 1.0 x 10^{-3} M in pure acetonitrile and 2.1 x 10^{-3} M in 70:30 water-acetonitrile) was excited with XeCl laser under argon atmosphere. The transient absorption spectra observed in above solvents are depicted in Figure 12 - (a) and (b), and in good agreement with the reported transient absorption spectrum of triplet-state BP.[8] The decay rate constant of triplet-state BP was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curve monitored at 525 nm. The obtained decay rate constants were 1.1 x 10^5 s^{-1} in pure acetonitrile and 9.7 x 10^4 s^{-1} in 70:30 water-acetonitrile. From this result it is concluded that the decay rate constant of triplet-state BP is not influenced by addition of water to acetonitrile.

ii) 9-Fluorenone

9-Fluorenone (FL, 1.0 x 10^{-4} M) was excited in pure acetonitrile and in 60:40 water-acetonitrile with XeCl laser under argon atmosphere. The transient absorption spectra observed in the above solvents are depicted in Figure 13-(a) and (b). The spectrum observed in pure acetonitrile is in good agreement with the reported transient absorption spectrum of triplet state FL in benzene,[9] and shows absorption maxima around 290, 320, 440, and 640 nm. The decay rate constant of triplet-state FL was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curve monitored at 430 nm. The obtained decay rate constants were 1.4×10^5 s^{-1} in pure acetonitrile and 8.9×10^4 s^{-1} in 60:40 water-acetonitrile. Therefore, the decay rate constant of triplet-state FL was not influenced by increasing water contents.

iii) Anthracene

Anthracene (AN, 9.0×10^{-5} M) in water-acetonitrile mixtures was excited with XeCl laser under argon atmosphere. The water content was changed from 0 to 70 vol%. The transient absorption spectra observed in pure acetonitrile and 50:50 water-acetonitrile are depicted in Figure 14 - (a) and (b), respectively. They are in good agreement with the reported transient absorption spectrum of triplet-state anthracene with absorption maxima around 400 and 420 nm.[10,11] The decay rate constant of triplet-state AN was obtained by first-order kinetic analysis of its $T_n \leftarrow T_1$ absorption decay curve monitored at 420 nm. The obtained decay rate constants were 7.0×10^4, 4.0×10^4, 4.3×10^4, and 2.7 x 10^4 s^{-1} in 0, 30, 50, and 70 vol% water content, respectively. The decay rate constant of triplet-state AN was reduced with increasing water content.

4. Properties of Molecules to Cause Quenching of their Triplet State by Interaction with Water

The remarkable water concentration effect on the decay rate constant of the triplet state was observed only for 2-CAQ and NQ among the compounds used here. Methyl substitution on quinone increases the character of (π,π^*) in the lowest excited triplet state,[12] and the lowest excited state of 1-CAQ has (π,π^*) property. It seems that strong (n,π^*) property in the lowest excited triplet state induces the quenching of triplet-state quinones by water molecule. Since the decay rate constants of triplet-state BP, FL and AN showed no water concentration effect, the present water concentration effect seems to be characteristic of quinone derivatives.

Conclusion

The quenching of the triplet state with water molecules was observed for quinone derivatives which have strong (n, π^*) character in the lowest excited triplet state.

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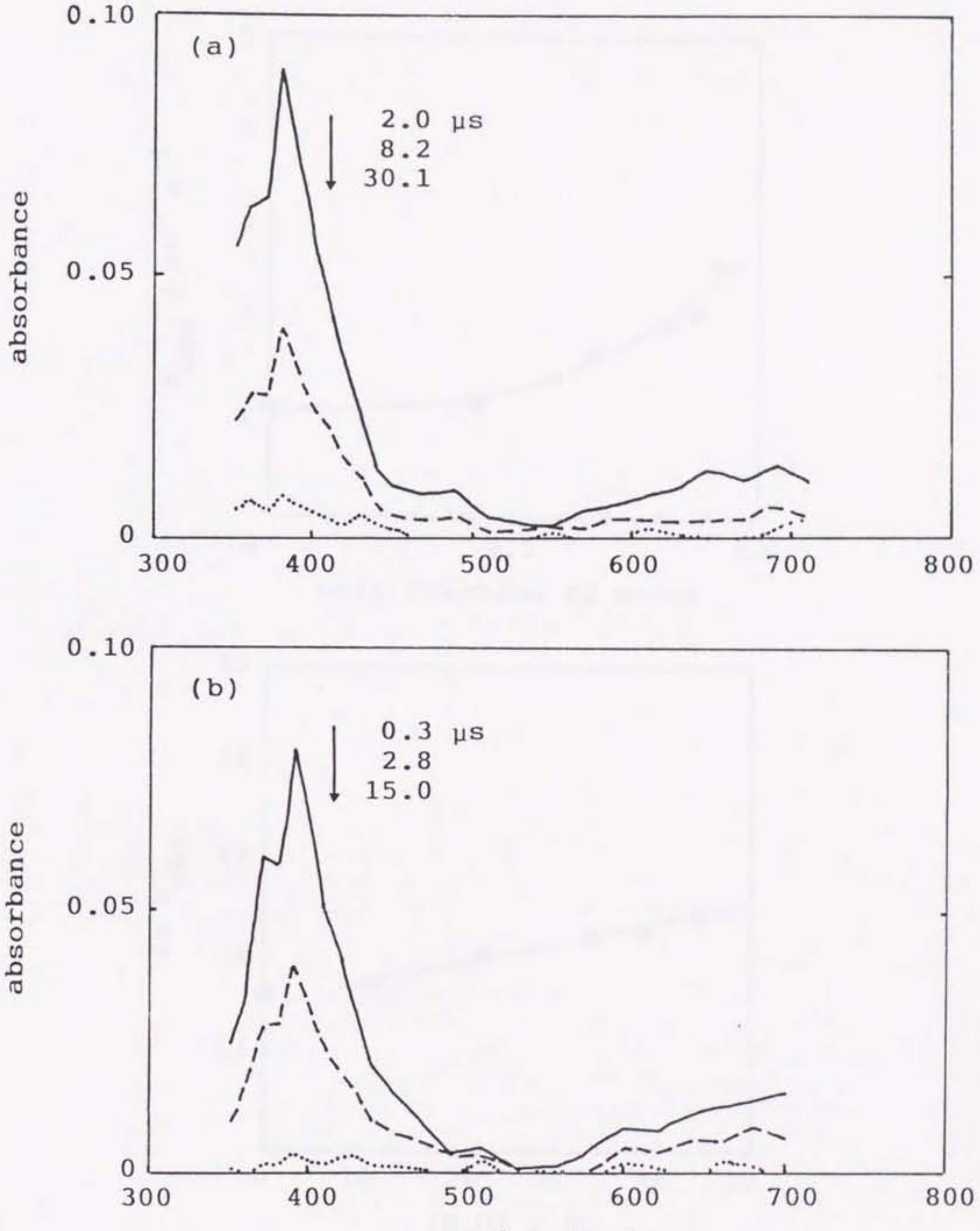


Figure 1. Transient absorption spectra on XeCl pulsed laser (308 nm) excitation of 1-CAQ (5.0×10^{-5} M) in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents (vol%) in solvent are 0% (a) and 80% (b).

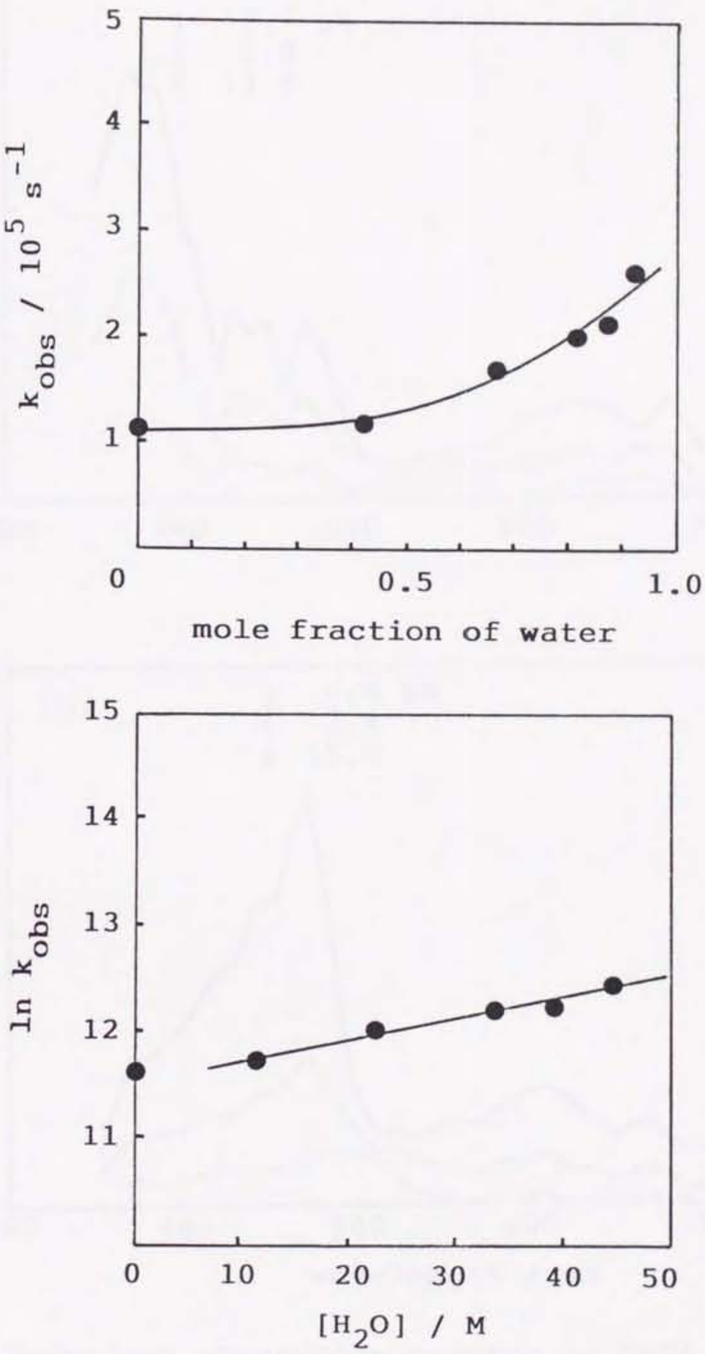


Figure 2. (a) Decay rate constants of 1-CAQ triplet as a function of water mole fraction in water-acetonitrile mixtures. (b) Logarithmic plot of k_{obs} versus water concentration in the solvent.

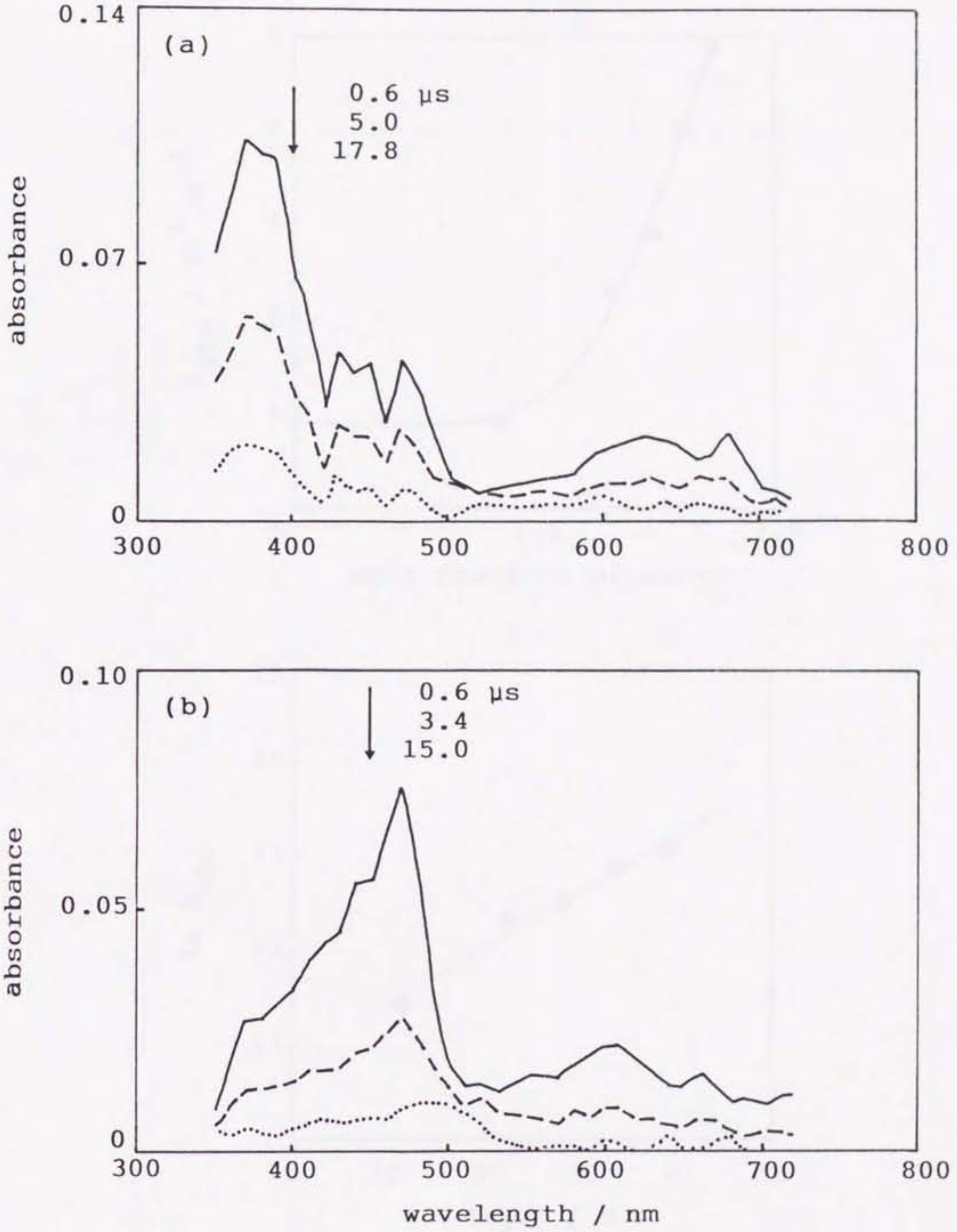


Figure 3. Transient absorption spectra on XeCl pulsed laser (308 nm) excitation of 2-CAQ (5.0×10^{-5} M) in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents (vol%) in solvent are 0% (a) and 60% (b).

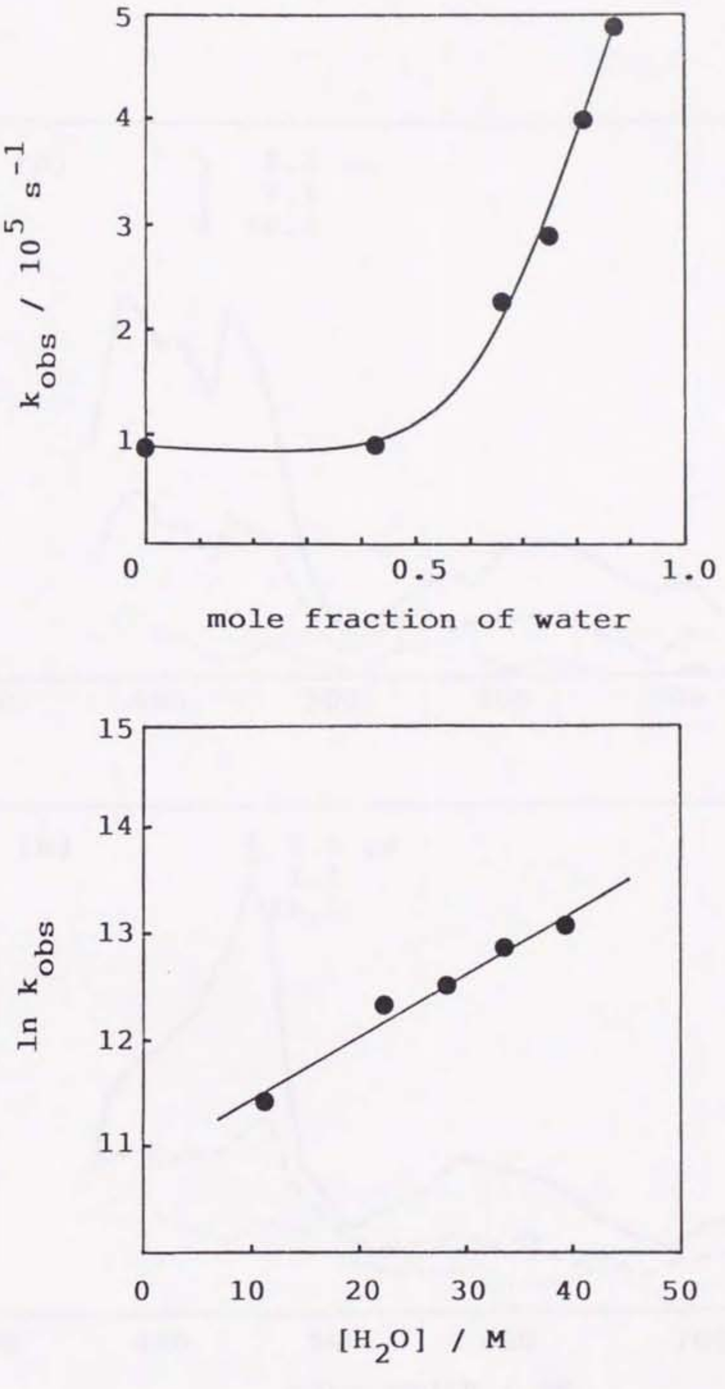


Figure 4. (a) Decay rate constants of 2-CAQ triplet as a function of water mole fraction in water-acetonitrile mixtures. (b) Logarithmic plot of k_{obs} versus water concentration in the solvent.

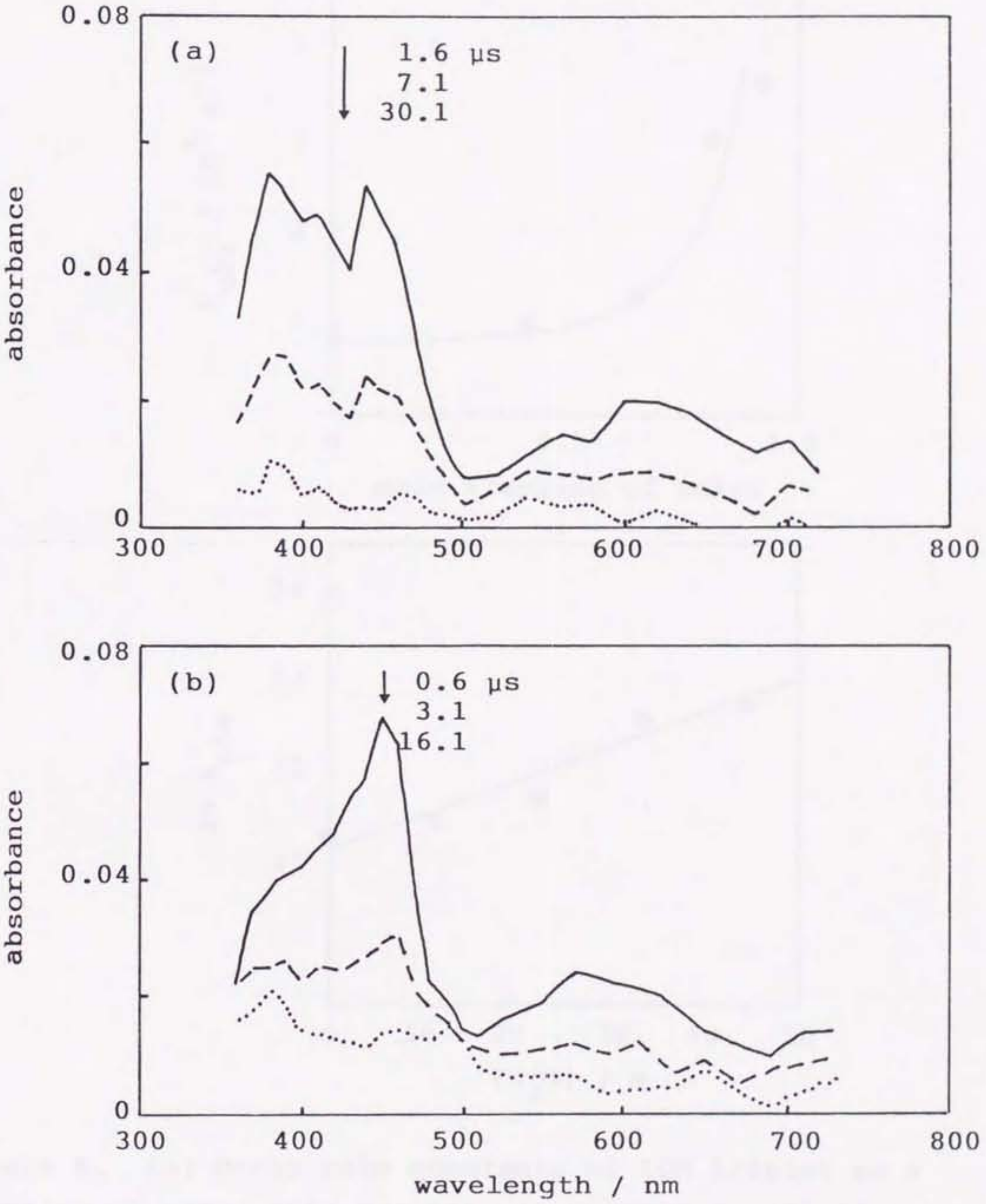


Figure 5. Transient absorption spectra on XeCl pulsed laser (308 nm) excitation of AQM (5.0×10^{-5} M) in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents (vol%) in solvent are 0% (a) and 80% (b).

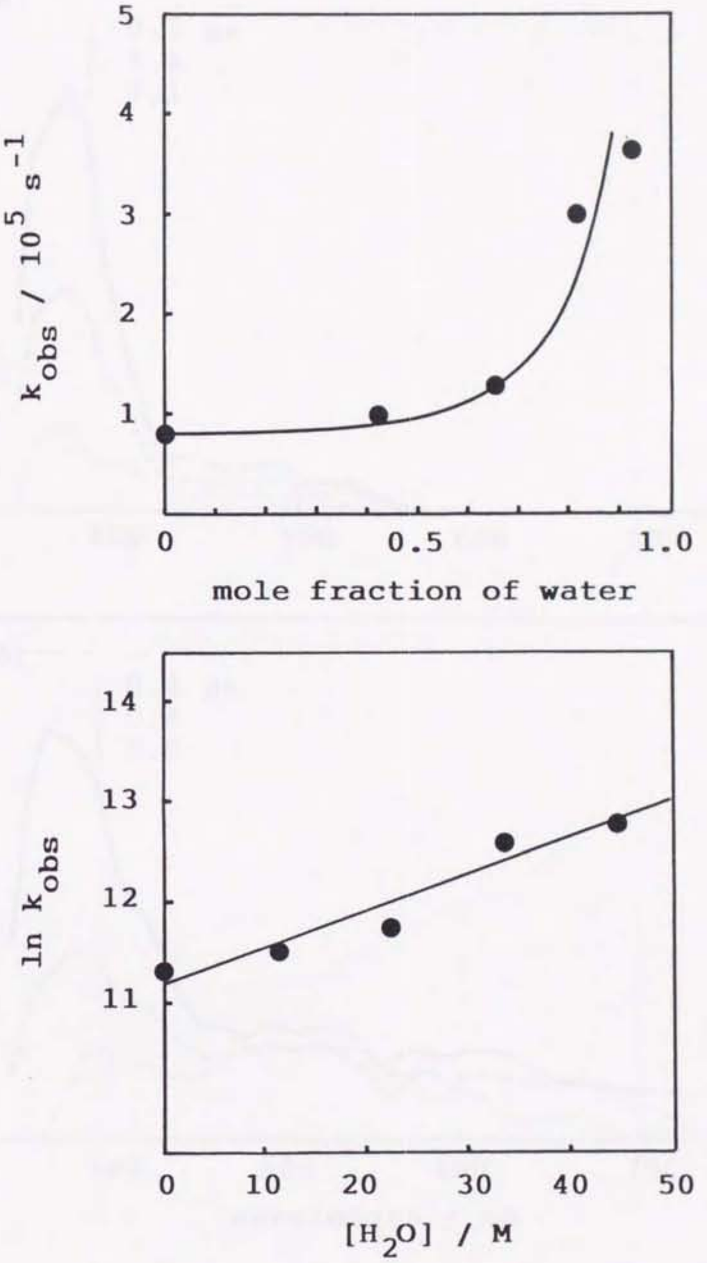


Figure 6. (a) Decay rate constants of AQM triplet as a function of water mole fraction in water-acetonitrile mixtures. (b) Logarithmic plot of k_{obs} versus water concentration in the solvent.

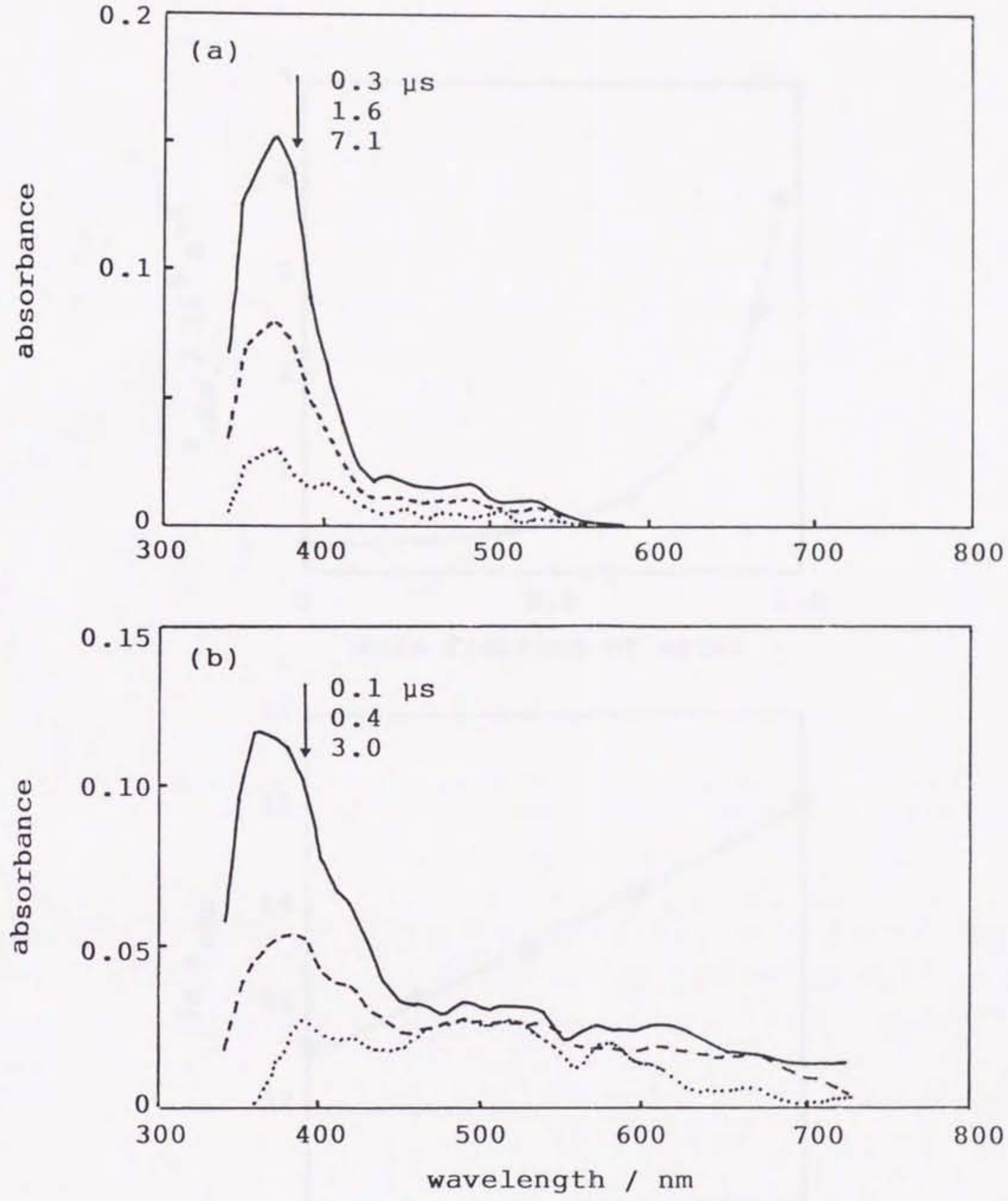


Figure 7. Transient absorption spectra on XeCl pulsed laser (308 nm) excitation of NQ (2.0×10^{-4} M) in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents (vol%) in solvent are 0% (a) and 80% (b).

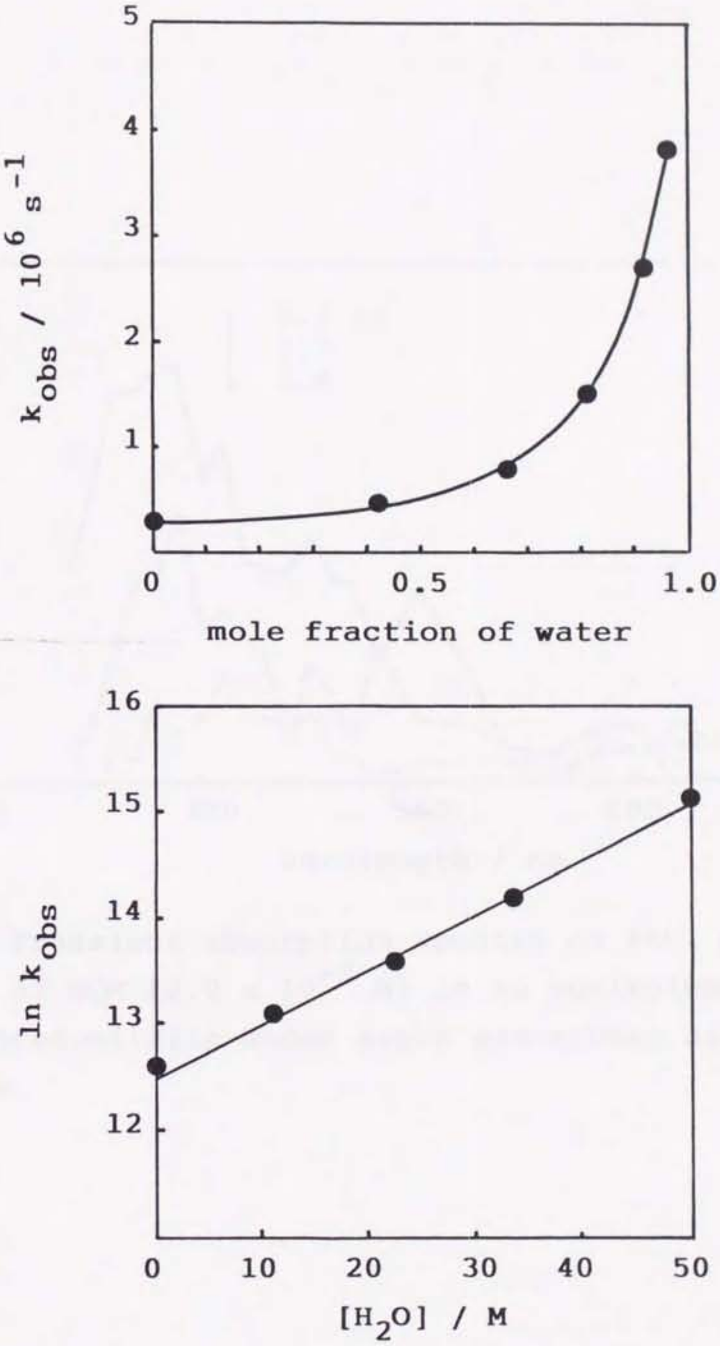


Figure 8. (a) Decay rate constants of NQ triplet as a function of water mole fraction in water-acetonitrile mixtures. (b) Logarithmic plot of k_{obs} versus water concentration in the solvent.

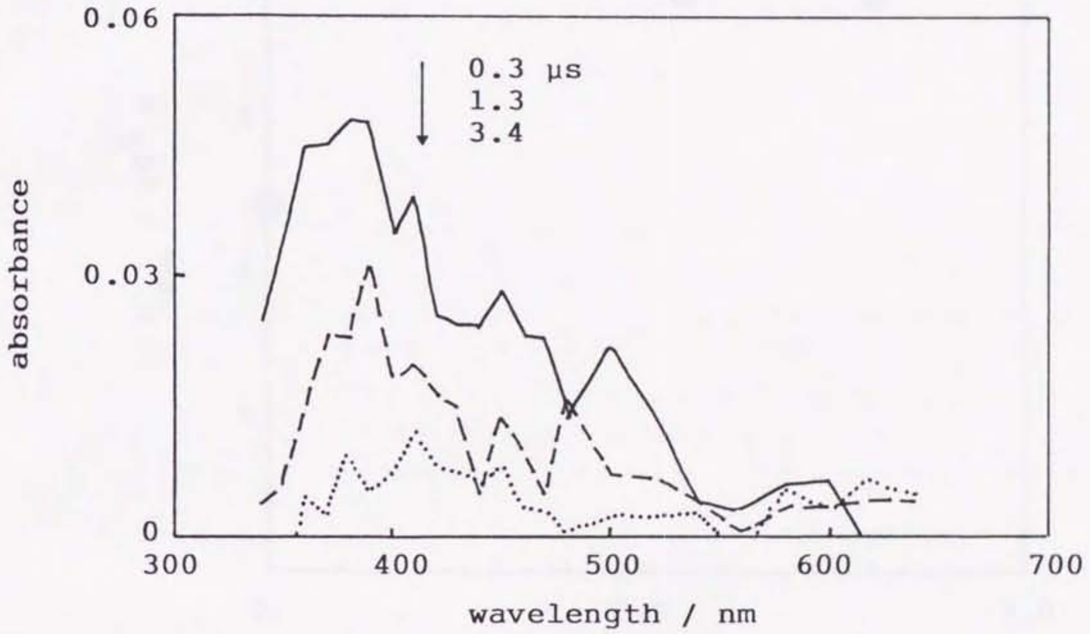


Figure 9. Transient absorption spectra on XeCl pulsed laser excitation of NQM (2.0×10^{-4} M) in an equivolume mixture of water and acetonitrile under argon atmosphere at various time delays.

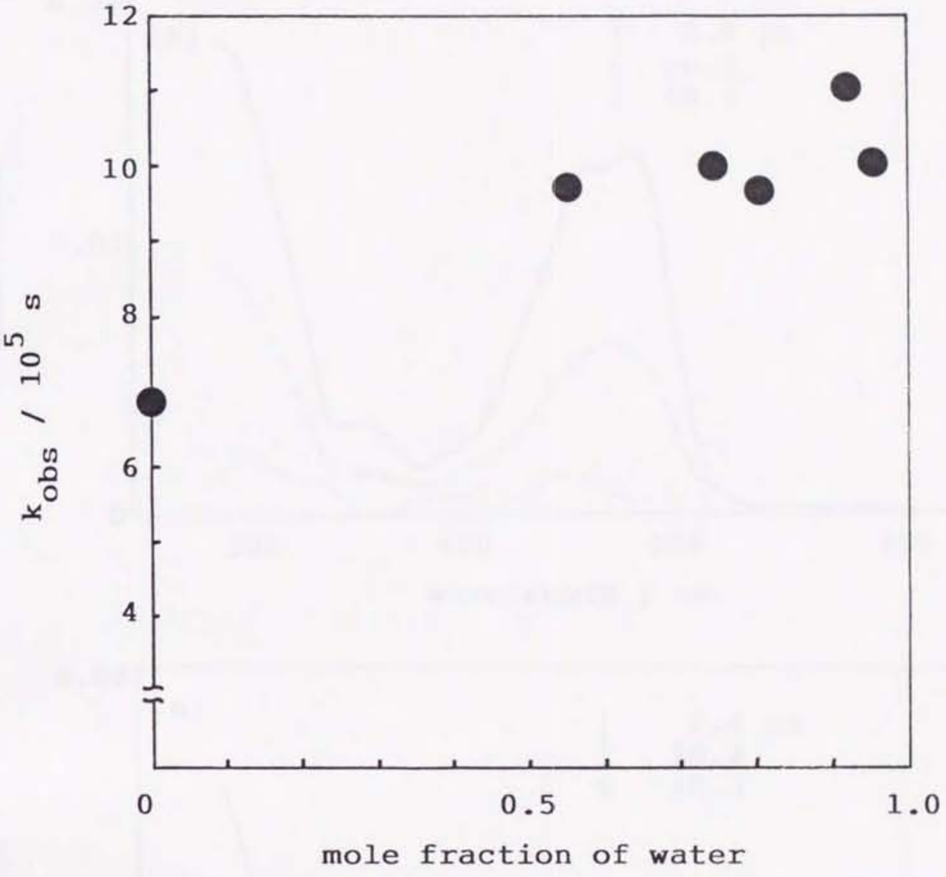


Figure 10. Decay rate constants of NQM triplet as a function of water mole fraction in water-acetonitrile mixtures.

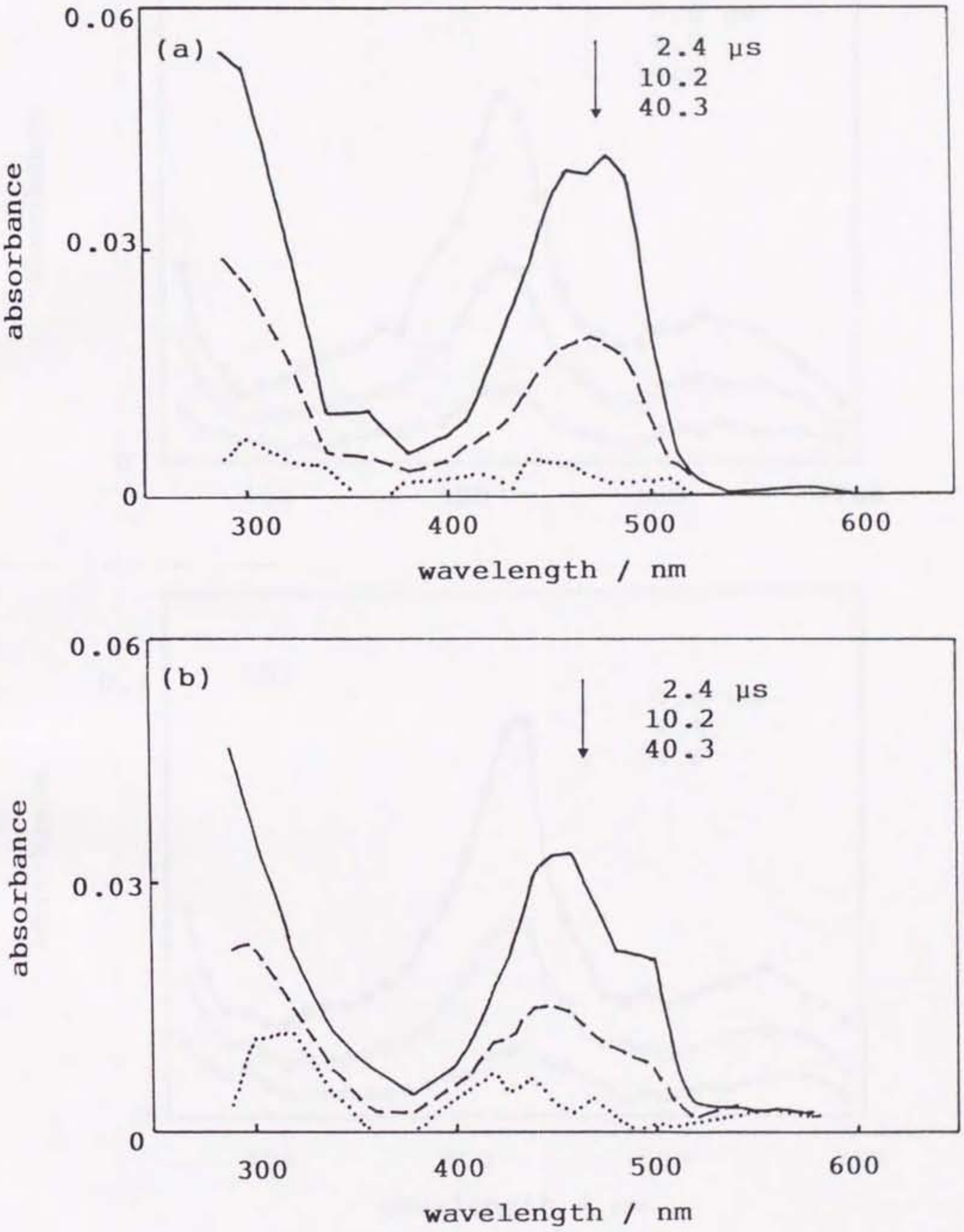


Figure 11. Transient absorption spectra on XeCl pulsed laser excitation of DQ (1.5×10^{-3} M) in water-acetonitrile mixtures under argon atmosphere. Water contents (vol%) in solvent are 0% (a) and 60% (b).

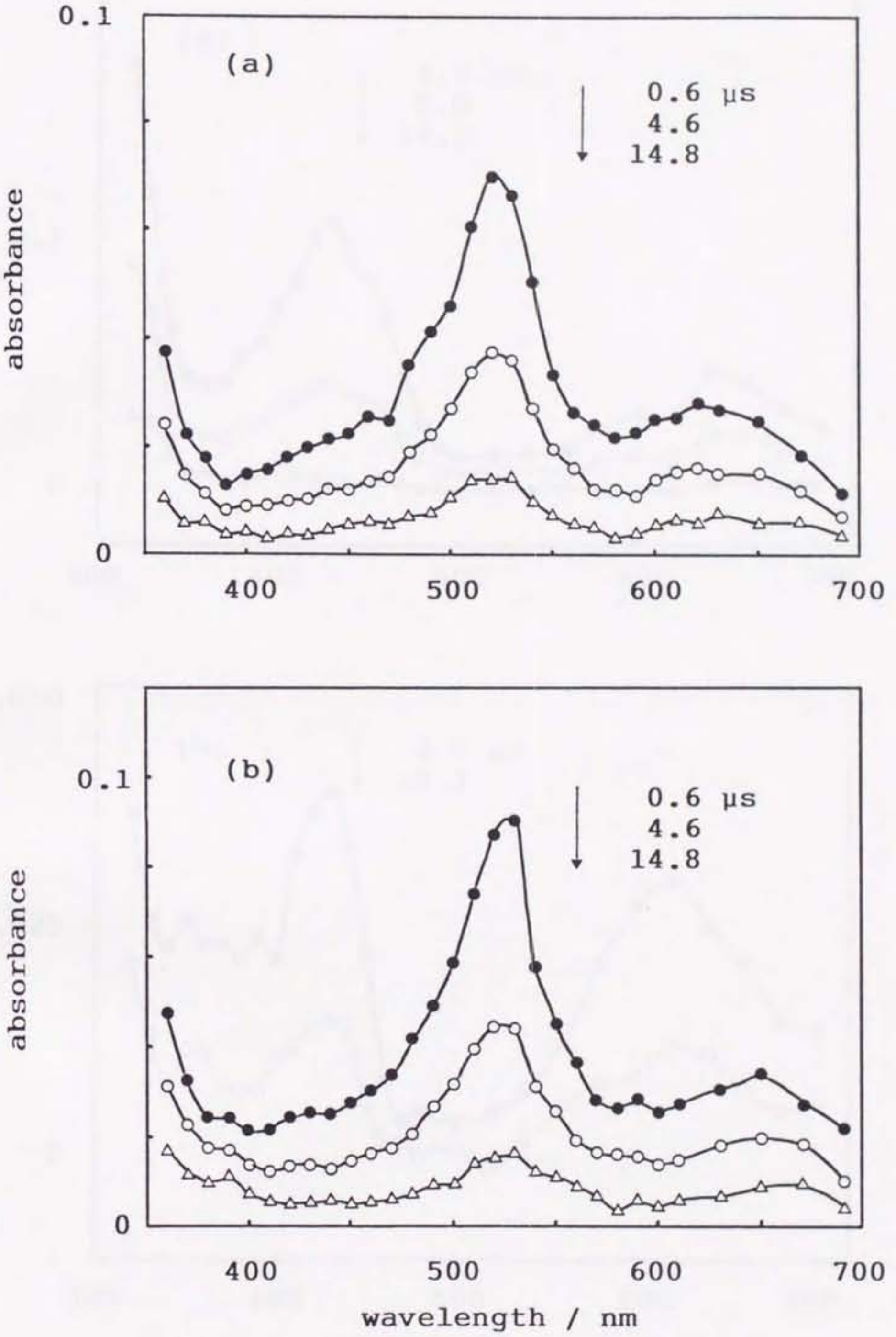


Figure 12. Transient absorption spectra on XeCl pulsed laser excitation of BP in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents (vol%) in solvent and BP concentrations are as follows: (a) 0%, 1.0×10^{-3} M; (b) 70%, 2.1×10^{-3} M.

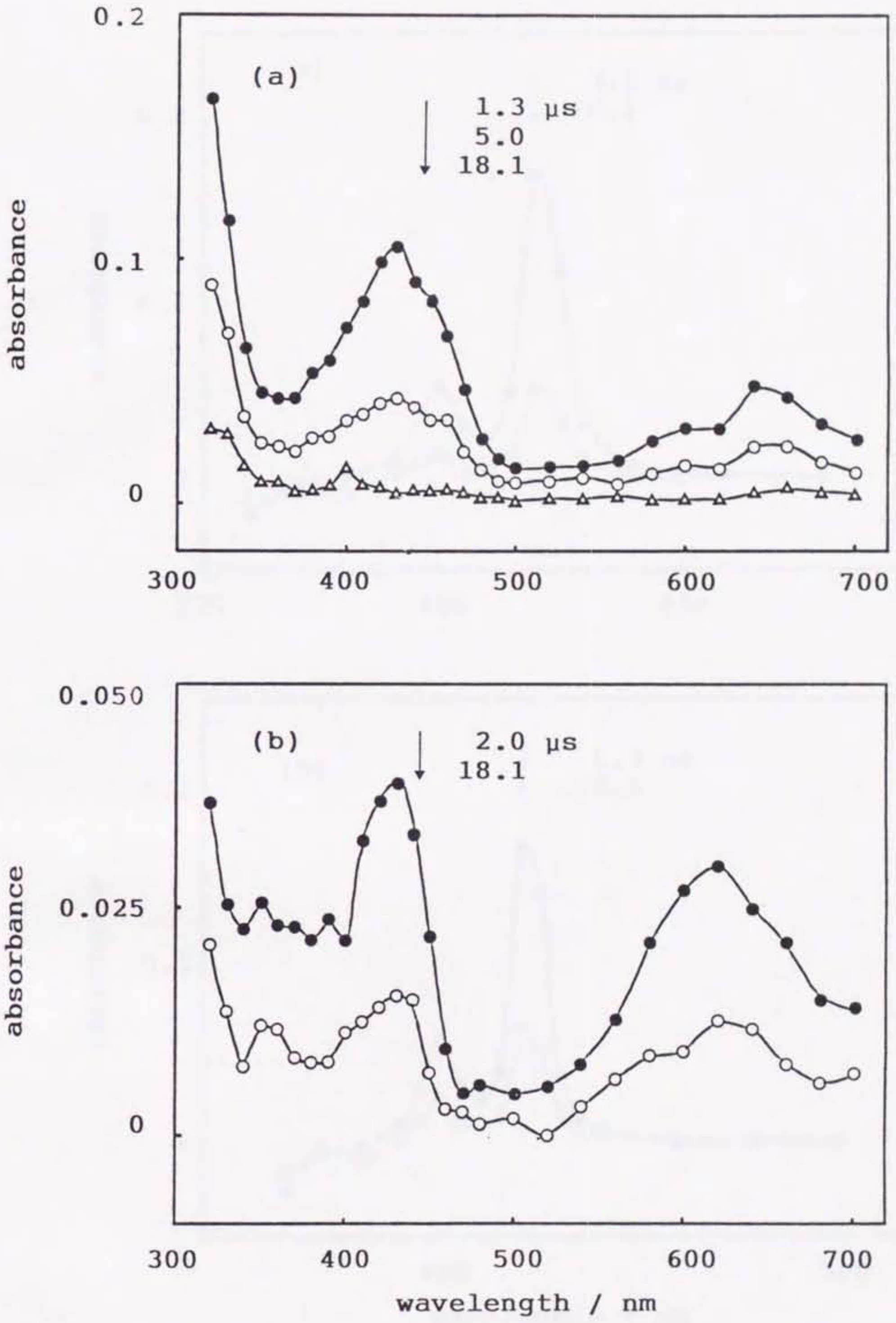


Figure 13. Transient absorption spectra on XeCl pulsed laser excitation of FL (1.0 x 10^{-4} M) in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents in solvent (vol%) are 0% (a) and 60% (b).

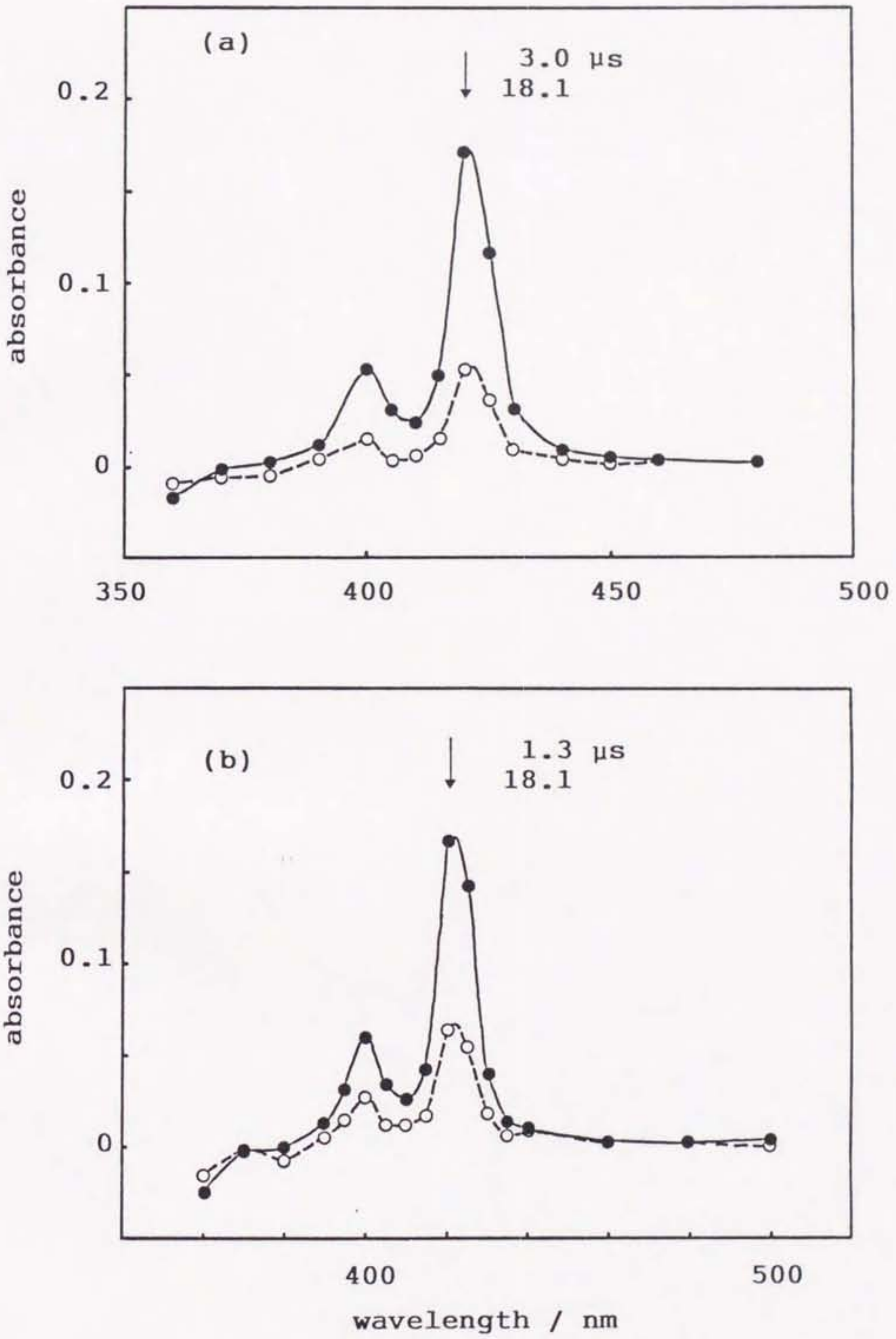
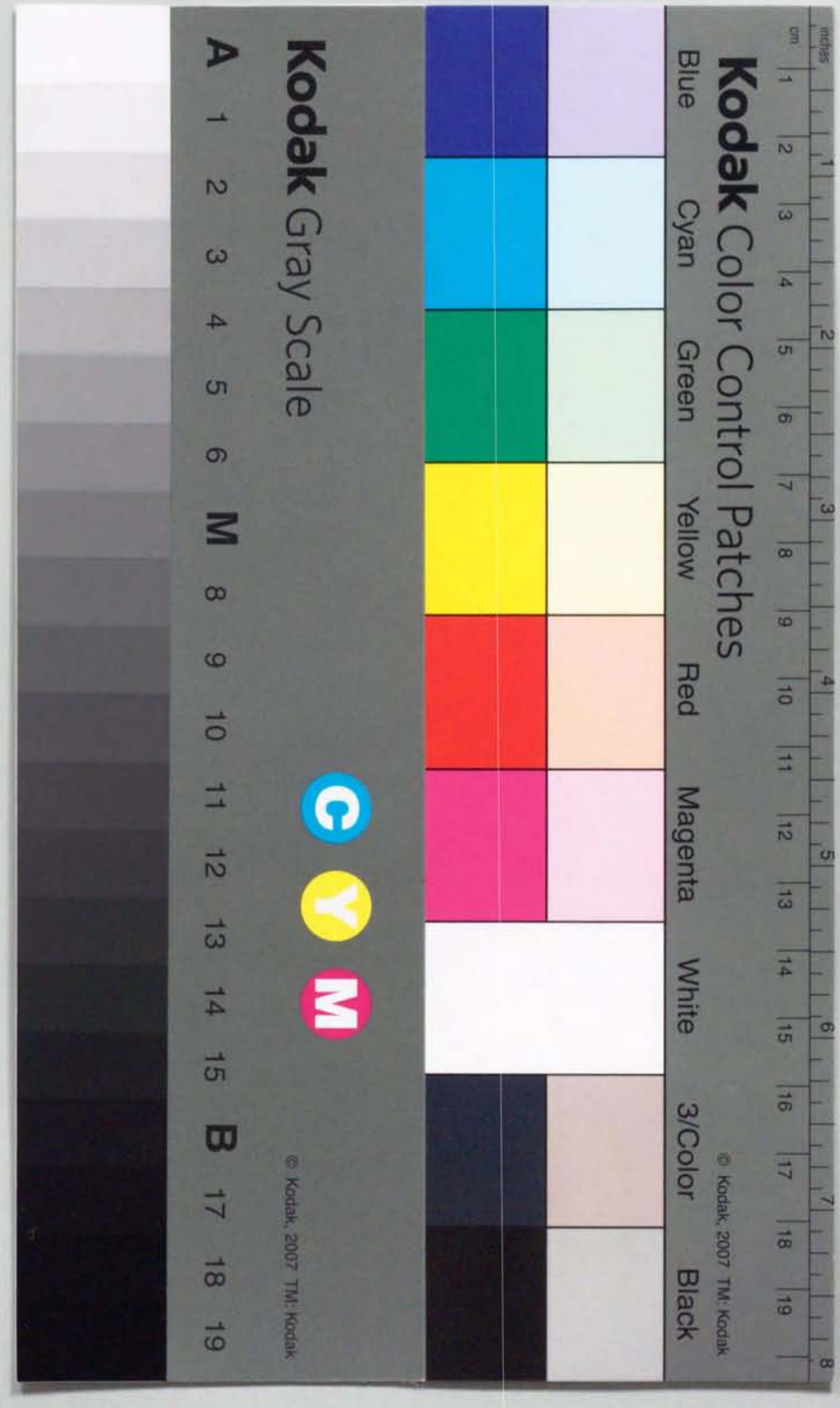


Figure 14. Transient absorption spectra on XeCl pulsed laser excitation of AN (9.0 x 10^{-5} M) in water-acetonitrile mixtures under argon atmosphere at various time delays. Water contents (vol%) in solvent are 0% (a) and 50% (b).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