Photochemistry in Micellar System. I. Stabilization of the Radical Anions of Anthraquinonesulfonates[1]

Koji KANO and Taku MATSUO*

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

(Received March 15, 1974)

Micellar effects on the photochemical reactions of sodium 9,10-anthraquinone-2-sulfonate and disodium 9,10-anthraquinone-2,6-disulfonate were studied by means of ESR and electronic spectroscopy. In the presence of anionic and non-ionic surfactants, irradiation of the quinones in aerobic phosphate buffer (pH 8.0) gave the corresponding radical anions, which were incredibly long-living (over several weeks) as compared with irradiation without surfactant. Plausible mechanisms of the micellar effects on the stabilization of the radical anions are discussed.

Micellar effects have been observed for many thermal reactions which indicate a close resemblance between micelle- and enzyme-catalyzed reactions.[2-4] In the case of photochemical reactions, however, only a few investigations have been carried out. Photoinduced substitution of some nitroaromatics was found to be affected by the addition of surfactants in a manner indicative of typical micellar effects.[5] Both anionic and nonionic surfactants have been reported to accelerate the photoreduction of riboflavin and flavin mononucleotide.[6-9] The photodecomposition of *p*-benzoquinone was also found to be accelerated in the presence of anionic surfactants.[10]

In the present paper, micellar effects on the photochemistry of anthraquinone sulfonates are described. In addition to the extensively investigated photofading and phototendering of anthraquinoid vat dyes,[11,12] anthraquinones have been known to be good sensitizers in photooxidation of organic substrates, where a cyclic process involving the semiquinone radical was suggested to play an important role.[13] Reduction-oxidation cycle of quinones is also very important for electron transport in biological membranes. We have studied the photochemistry of sodium 9,10-anthraquinone-2-sulfonate (AQS) in micellar systems, and found that the radical anion ($AQS^{\cdot-}$) is extremely stabilized in the presence of surfactants.[14] The behavior of the stabilized radical anions in micellar systems is discussed in detail.

Experimental

Materials. Sodium 9,10-anthraquinone sulfonates and sodium laurate, NaL (Tokyo Kasei Kogyo Co. Ltd.) were recrystallized from water and 50% aqueous methanol, respectively. Sodium lauryl sulfate (NaLS) of three different grades was used; extra pure grade (Tokyo Kasei), that used for biochemistry (Wako Pure Chem.), and NaLS (Tokyo Kasei) recrystallized from 50% aqueous methanol. The results were all the same. Polysorbate-80 (P-80) (Ishizu Pharm. Co.) was used without further purification. Water was distilled and deionized with a column of ion-exchange resin.

The critical micelle concentrations (CMC) of NaLS and NaL were determined by the fluorescent probe method at room temperature. Magnesium 1-anilinonaphthalene-8-sulfonate (ANS) was chosen as a model probe suitable for examining the binding of sodium 9,10-anthraquinone sulfonates. An abrupt increase in fluorescence yields of ANS (1.0×10^{-4} M) in water was observed on the addition of NaLS above 8.5×10^{-3} M and also of NaL above 2.8×10^{-2} M. The values are in good agreement with the CMC of NaLS and NaL in the literature.[2] It is well-known that the CMC of anionic and cationic surfactants are lowered by addition of inorganic salts.[3] Most experiments were carried out in phosphate buffer solutions; the CMC of the anionic surfactants in our systems is expected to be lower than those in pure water.

Irradiation. *Method A*: The solution in a Pyrex tube (ϕ 15 mm) was irradiated with a Riko 100 W high-pressure mercury lamp using a Riko rotary photolysis apparatus RH 400—10 W at room temperature.

Method B: The solution in a quartz cell (10 mm width) placed 5 cm from the center of the lamp, was irradiated with a Riko 100 W high-pressure mercury lamp at room temperature.

ESR Measurement. The ESR spectra of the photolyzed solution in a Pyrex capillary tube (ϕ *ca.* 1 mm) were measured with a JEOL Model JES-ME-3X spectrometer (X-band), using 100 kHz field modulation. Peroxylamine sulfonate was used as standard material for determining the *g*-value.

Results

Spectral Change during Photolysis. Irradiation of AQS and/or disodium 9,10-anthraquinone-2,6-disulfonate (AQDS) in aqueous media without surfactants gives colored stable products, whose major components are hydroxylated anthraquinones.[15,16] Progressive spectral changes during the photolysis (method B) of AQS and AQDS in the aerobic phosphate buffer (pH 8.0) are shown in Fig. 1.

In the presence of NaLS above the CMC,[17] the spectral changes under irradiation (method B) of the aerobic solutions (pH 8.0) of both anthraquinone sulfonates (AQS and AQDS) differ drastically from those shown in Fig. 1. The absorption maxima of the photoproducts from AQS were observed at 378.5, 394.5, ~420, and ~470 nm (Fig. 2). In the case of AQDS, the absorption maxima were found at 382, 401, and 473 nm. These absorption bands gradually disappeared on mixing the solution with air. The bands at 378.5 (AQS) and 382 nm (AQDS) were assigned to the corresponding diol derivatives ($AQSH_2$ and $AQDSH_2$) by comparing the spectra with those of

* To whom inquiries should be addressed.

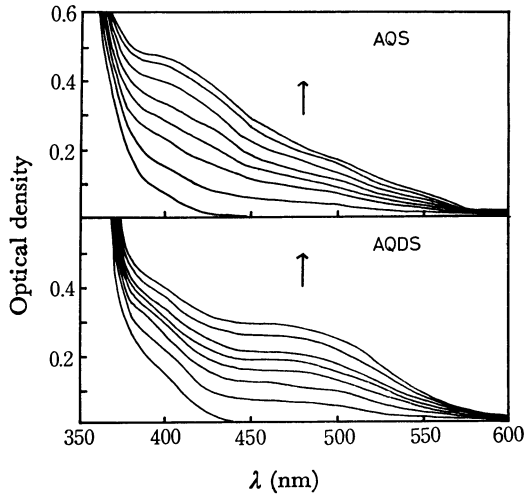

Fig. 1. Progressive spectral changes during photolysis of AQS and AQDS in non-micellar systems: $[AQS]_0 = 5.0 \times 10^{-4}$ M, $[AQDS]_0 = 1.0 \times 10^{-3}$ M, in 0.033 M phosphate buffer (pH 8.0). The spectra were measured at intervals of 20 s.

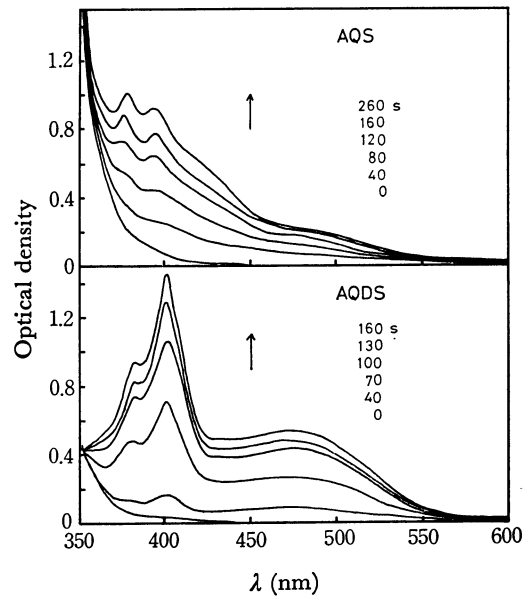

Fig. 2. Progressive spectral changes during photolysis of AQS and AQDS in micellar system: $[AQS]_0 = 5.0 \times 10^{-4}$ M, $[AQDS]_0 = 2.0 \times 10^{-4}$ M, $[NaLS] = 2.0 \times 10^{-2}$ M, in 0.033 M phosphate buffer (pH 8.0).

authentic samples. Essentially, the same absorption bands were observed when NaL and P-80 were used in place of NaLS except for the fact that the absorption at ~470 nm in AQS–NaLS system shifted towards 460 nm in the case of NaL and P-80. The absorption maxima at 394.5 (AQS) and 401 nm (AQDS) coincide with those of the radical anions of AQS ($AQS^{\cdot-}$) and AQDS ($AQDS^{\cdot-}$) obtained by flash technique.[18,19] The absorption bands at 505 nm of $AQS^{\cdot-}$ [18] and at 520 nm of $AQDS^{\cdot-}$,[19] however, could not be detected in the presence of surfactants. These bands were presumably shifted towards shorter wavelengths (~470 and 473 nm) by the influence of surfactants.

ESR Spectra Measurement. An aerobic solution (pH 8.0) of AQS containing NaL near the CMC[20] in a pyrex tube (ϕ 1 mm) was irradiated with a 100 W high-pressure mercury lamp for 20 min, and the yellow solution obtained was examined by means of ESR spectroscopy at room temperature (Fig. 3). The splitting constant (ΔH), number of lines, and g-value were 0.25 gauss, 21, and 2.0042, respectively. No ESR signal was obtained when the aerobic solution (pH 8.0) was irradiated in the absence of surfactants. In the case of AQDS, long-living ESR signals were obtained upon irradiation of the aerobic aqueous solution (pH 8.0) in the presence of NaLS (Fig. 4). The same ESR signals were also observed even in the absence of surfactants, but the spectra disappeared in a few hours after irradiation. The splitting constant, number of lines, and g-value were 0.45 gauss, 11, and 2.0044, re-spectively.

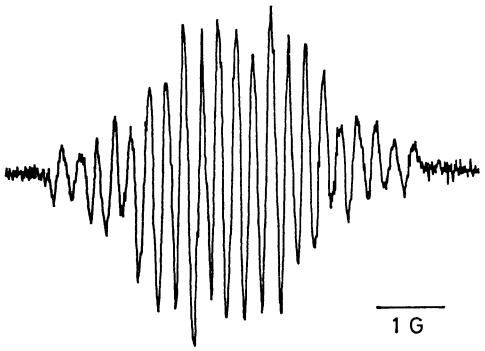

Fig. 3. ESR spectrum of $AQS^{\cdot-}$ generated by the photolysis of aerobic aqueous buffered solution (pH 8.0) of AQS (3.0×10^{-3} M) containing NaL (2.0×10^{-2} M).

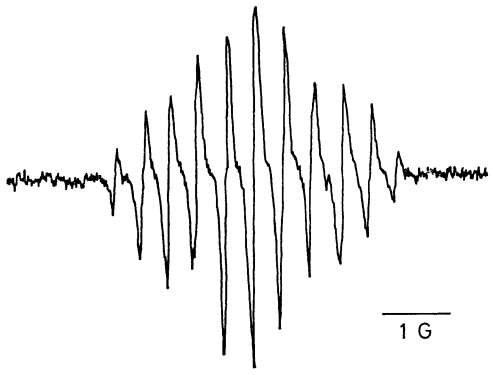

Fig. 4. ESR spectrum of $AQDS^{\cdot-}$ generated during the photolysis of aerobic aqueous buffered solution (pH 8.0) of AQDS (5.0×10^{-3} M) containing NaLS (4.0×10^{-2} M).

As regards the analysis of the hyperfine structure, the above ESR spectra were identified with those of the radical anions of AQS and AQDS.[21]

Phillips *et al.* obtained the ESR spectra of $AQS^{\cdot-}$ during the photolysis of anaerobic alkaline solutions (>pH 11) of AQS.[18,21] They reported that no ESR signal was obtained below pH 11.[18] By the use of flash technique, they also found that $AQS^{\cdot-}$ has a relatively long lifetime in an anaerobic solution (several ms), and rapidly decays in the aqueous solution by

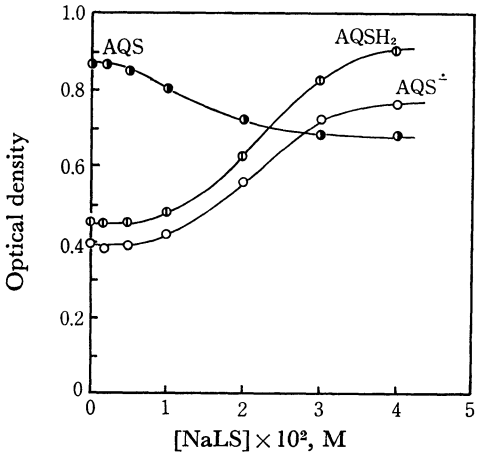

Fig. 5. Effect of NaLS concentration on $AQS^{\cdot-}$ and $AQSH_2$ formation: $[AQS]_0=5.0\times10^{-4}$ M, in 0.033 M phosphate buffer (pH 8.0). The solutions were irradiated for 5 min at room temperature, and the optical density at 256 nm was measured after the photolyzed solutions were diluted by 25-fold with water.

the addition of oxygen.[18] $AQS^{\cdot-}$ we obtained in the presence of NaL lived over two months in a sealed tube even in the case of aerobic solution. Although, $AQDS^{\cdot-}$ has a considerably long lifetime (a few hours) even in the absence of surfactant, it lived over several weeks in the aerobic solution in the presence of NaLS. These observations suggest that both $AQS^{\cdot-}$ and $AQDS^{\cdot-}$ are markedly stabilized in the presence of surfactants.

Effect of Surfactant Concentration on $AQS^{\cdot-}$ Formation. An aerobic aqueous solution (pH 8.0) of AQS containing appropriate amounts of NaLS was irradiated for 5 min (method A). The optical density at the absorption maxima of $AQS^{\cdot-}$ (394 nm), diol derivative ($AQSH_2$, 378.5 nm), and AQS (256 nm) is plotted against the concentration of NaLS in Fig. 5. The

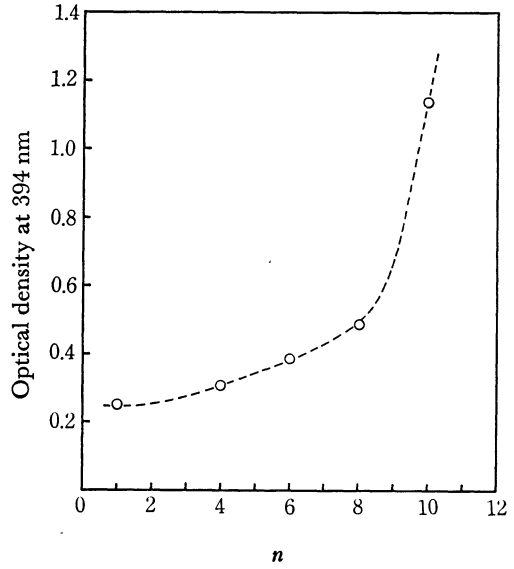

Fig. 6. Effect of alkyl chain length of sodium carboxylate on $AQS^{\cdot-}$ formation: $[AQS]_0=1.0\times10^{-3}$ M, $[CH_3(CH_2)_nCOONa]=2.0\times10^{-2}$ M, in 0.033 M phosphate buffer (pH 8.0). The solutions were irradiated for 20 s at room temperature.

formation of $AQS^{\cdot-}$ and $AQSH_2$ and the disappearance of AQS markedly increased at NaLS concentrations above *ca.* 1.0×10^{-3} M, plateau regions being observed at higher NaLS concentrations. This surfactant concentration profile suggests that the micelles formed by aggregation of the surfactant in aqueous solution contribute to the stabilization of $AQS^{\cdot-}$.

Effect of Alkyl Chain Length of Surfactant on Stabilization of $AQS^{\cdot-}$. An aerobic aqueous solution (pH 8.0) of AQS containing sodium carboxylates ($CH_3(CH_2)_n$-COONa) was irradiated for 20 s (method B). The optical density at 394 nm ($AQS^{\cdot-}$ formation) is plotted against the number of methylene groups (n) in the alkyl chain in Fig. 6. Since the formation of $AQS^{\cdot-}$ becomes significant for $n>8$, it is evident that $AQS^{\cdot-}$ is greatly stabilized by binding with an aggregate of carboxylates capable of forming micelles.

Table 1. Effect of acetone content on stabilization of $AQDS^{\cdot-}$ [a]

Aceton, % (v/v)	Φ/Φ_0 [b]
0	1
5	0.87
10	0.82
15	0.64
20	0.55

a) Aerobic phosphate buffer solutions (0.033 M, pH 8.0) of AQDS (2.0×10^{-4} M) containing NaLS (2.0×10^{-2} M) and acetone were irradiated at room temperature for 1 min. b) Relative quantum yields were determined by measurement of optical density at 475 nm, absorption maximum of $AQDS^{\cdot-}$.

Effect of Acetone on Stabilization of $AQDS^{\cdot-}$. The effects of acetone were studied in the AQDS–NaLS system. The relative quantum yields for the formation of $AQDS^{\cdot-}$ in solutions containing various amounts of acetone are given in Table 1. The generation of $AQDS^{\cdot-}$ was suppressed with increasing acetone content, as was also the formation of $AQDSH_2$. Not only acetone but *tert*-butanol also greatly reduced the formation of $AQDS^{\cdot-}$ and $AQDSH_2$. The relative quantum yield for the formation of $AQDS^{\cdot-}$ was 0.58 when the aerobic 10% (v/v) aqueous *tert*-butanol solution (pH 8.0) of AQDS (2.0×10^{-4} M) containing NaLS (2.0×10^{-2} M) was irradiated.

Salt Effect on $AQDS^{\cdot-}$ Formation. It is known that ionic-micellar catalysis tends to be significantly affected by addition of electrolyte.[22] We have studied the salt effects on the radical anion formation in the AQDS–NaLS system.

Aqueous solutions (pH 8.1) of AQDS containing

Table 2. Salt effect on $AQDS^{\cdot-}$ formation [a]

Electrolyte	Φ/Φ_0
—	1
$MgSO_4(2.0\times10^{-2}M)$	0.48
$Na_2SO_4(2.0\times10^{-2}M)$	0.84

a) $[AQDS]_0=2.0^{-4}\times10^{-2}$M, $[NaLS]=2.0\times10^{-2}$ M in 0.033 M phosphate buffer (pH 8.1).

NaLS and appropriate amounts of salts were irradiated with filtered light (>350 nm). The optical density at 470 nm ($AQDS^{\cdot-}$ formation) was monitored and the relative quantum yields for $AQDS^{\cdot-}$ formation were determined. The results obtained are summarized in Table 2. The formation of $AQDS^{\cdot-}$ was significantly supressed by the addition of Mg^{2+}.

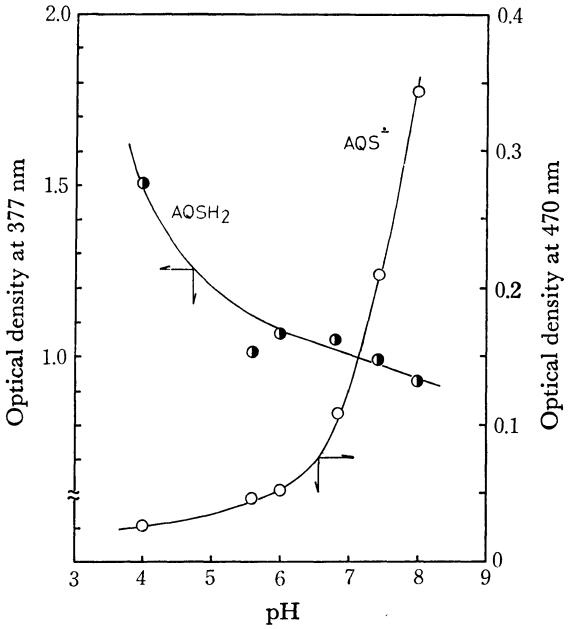

Fig. 7. pH dependence on $AQS^{\cdot-}$ and $AQSH_2$ formation: $[AQS]_0=5.0\times10^{-4}$ M, [P-80]=0.2116 g/dl. The phthalate (pH 4.0, 0.1 M) and phosphate buffers (pH 5.6—8.0, 0.033 M) were used. The solutions were irradiated for 10 min under a nitrogen atmosphere at room temperature.

pH Dependence on $AQS^{\cdot-}$ and $AQSH_2$ Formation. The pH dependence on the formation of $AQS^{\cdot-}$ and $AQSH_2$ in the presence of P-80 was examined by the use of phthalate and phosphate buffers (pH 4.0—8.0). Anaerobic solutions of AQS containing P-80 (0.2116 g/dl)[23] were irradiated for 10 min (method A). The formation of $AQSH_2$ and $AQS^{\cdot-}$ was monitored by optical density at 377 and 470 nm, respectively. The pH profile is shown in Fig. 7. The yield of $AQSH_2$ decreased with increasing pH, the formation of $AQS^{\cdot-}$ being apparently enhanced above pH 6.8. Exactly the same pH dependence of the $AQS^{\cdot-}$ formation was reported in the flash photolysis of AQS in the absence of surfactant.[18]

Reaction of Radical Anions with H^+. Since the radical anions of AQS and AQDS are greatly stabilized in micellar systems, the reactivity of $AQS^{\cdot-}$ and/or $AQDS^{\cdot-}$ can be easily investigated. We first studied the reaction of radical anions with H^+.

An aerobic solution of AQDS (2.0×10^{-4} M) in 0.033 M phosphate buffer (pH 8.0) containing 2.0×10^{-2} M of NaLS was irradiated for 3 min (method B). After the photolyzed solution was carefully diluted 20-fold either with water or with 0.75 N sulfuric acid, the UV spectra were measured (Fig. 8). The absorption maxima in water were observed at 262, 273, and 284 nm. The spectra were compared with those of

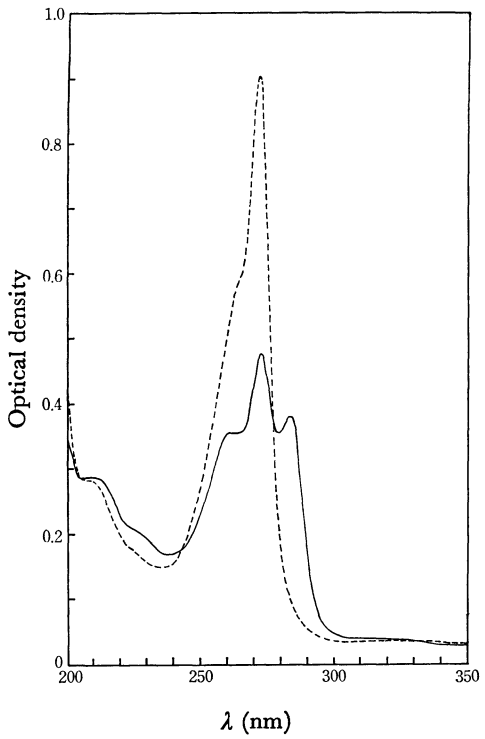

Fig. 8. UV spectra of photolyzed solution of AQDS which were diluted with water (solid line) and with 0.75 N sulfuric acid (dotted line).

authentic samples, and the absorption bands at 262 and 273 nm were assigned to AQDS and $AQDSH_2$, respectively. In the sulfuric acid solution, the absorption band at 284 nm completely disappeared and the intensity of the absorption band at 273 nm ($AQDSH_2$) increased. These spectral data suggest that the absorption band at 284 nm is attributed to $AQDS^{\cdot-}$ and that

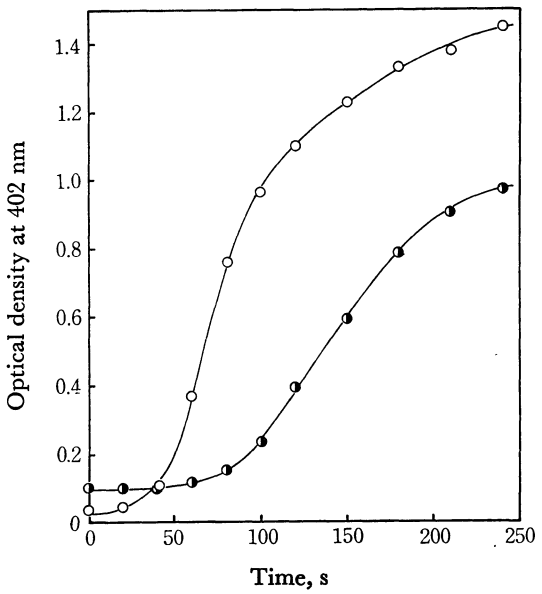

Fig. 9. Effect of Fe^{3+} on $AQDS^{\cdot-}$ formation: the aerobic phosphate buffer solutions (0.033 M, pH 8.0) of AQDS (2.0×10^{-4} M) containing NaLS (2.0×10^{-2} M) were irradiated in the absence (—○—) and in the presence of Fe^{3+} (—◑—, $[FeCl_3]=5.2\times10^{-4}$ M) at room temperature.

$AQDS^{\cdot-}$ reacts with H^+ to produce the anthrahydroquinone.

The same results were obtained in the reaction of $AQS^{\cdot-}$. The absorption maxima of AQS, $AQSH_2$, and $AQS^{\cdot-}$ were observed at 259, 269, and 277 nm, respectively.

Reaction of $AQDS^{\cdot-}$ with Fe^{3+}. We next examined the electron transfer reaction from $AQDS^{\cdot-}$ to ferric ion.

An aerobic aqueous solution (pH 8.0) of AQDS containing NaLS was irradiated in the presence of Fe^{3+} (method B). The formation of $AQDS^{\cdot-}$ monitored at 402 nm is plotted against irradiation time in Fig. 9.

In the absence of Fe^{3+}, the formation of $AQDS^{\cdot-}$ was observed after a short induction period (*ca.* 20 s). In the presence of Fe^{3+}, however, the induction period for the formation of the radical anion was considerably prolonged (*ca.* 60 s), the yield of $AQDS^{\cdot-}$ being reduced. After irradiation, *o*-phenanthroline, 0.1 N sulfuric acid, and sodium acetate–sulfuric acid buffer (pH 4.4) were added to the photolyzed solution. A red solution was obtained and the spectra clearly indicated the formation of *o*-phenanthroline–Fe^{2+} complex (λ_{max} 500 nm). Thus it could be concluded that $AQDS^{\cdot-}$, the primary photoproduct, transfers an electron to Fe^{3+} which affords AQDS and Fe^{2+} as the final products.

Discussion

Phillips *et al.* found that flash photolysis of AQS in air-saturated aqueous solution (pH 3.07) gives two transient species with absorption maxima at 455 and 505 nm.[18] They assigned the transient bands at 455 and 505 nm to the cation and anion radicals of AQS, respectively. From the results the formation of $AQS^{\cdot-}$ was explained by the following reaction:

$$AQS^* + AQS \longrightarrow AQS^{\cdot+} + AQS^{\cdot-} \quad (1)$$

This scheme involving triplet excimer, however, was not supported by the kinetic data obtained by means of ns laser photolysis.[12]

Kuzmin and Chibisov studied the flash photolysis of aqueous AQDS solutions in the presence of inorganic anions (0.1 M) and found that an electron is transferred from inorganic anions (CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, SO_3^{2-}, SeO_3^{2-}, and SCN^-) to AQDS in the triplet state yielding $AQDS^{\cdot-}$ (two strong bands at 400 and 520 nm) and one-electron oxidized inorganic anions:[19]

$$AQDS^* + X^{n-} \longrightarrow AQDS^{\cdot-} + X^{(n-1)\cdot-} \quad (2)$$

In our system also anions such as CO_2^-, OSO_3^-, HPO_4^{2-}, and $H_2PO_4^-$ coexisted with AQS or AQDS. The radical anions, however, could not be detected by means of ESR and electronic spectroscopy in the case of AQS with no surfactants, the quantum yield for the formation of $AQDS^{\cdot-}$ in the presence of micelles not increasing with addition of SO_4^{2-} (Table 2). $AQS^{\cdot-}$ and $AQDS^{\cdot-}$ were also stabilized in the presence of P-80, non-ionic surfactant, as in the case of NaL and/or NaLS system. The results suggest that the electron-transfer reactions from the above anions to photoexcited quinones are not significant to account for the formation of stabilized anion radicals in our systems.

By the use of pulse radiolysis and flash photolysis techniques, the pK values for the semiquinone radical-anions of AQS and AQDS have been determined to be 3.25[24] and 2.30[19] respectively. However, the pH effects on the $AQS^{\cdot-}$ formation in micellar system

$$A^{\cdot-} + H^+ \overset{K}{\rightleftharpoons} AH\cdot \quad (3)$$

we observed cannot be simply explained by the pK value. Below pH 6.0, only anthrahydroquinone ($AQSH_2$) was formed and the formation of $AQS^{\cdot-}$ became significant above pH 6.8 (Fig. 7). This is similar to the pH effects on the $AQS^{\cdot-}$ transient absorption 800 μs after flash photolysis in non-micellar system.[18] At low pH region, both radical anion and semiquinone radical seem to decay rapidly by the disproportionation:[25,26]

$$2A^{\cdot-} \longrightarrow A + A^{2-} \quad (4)$$

$$A^{2-} + 2H^+ \longrightarrow AH_2 \quad (5)$$

$$2AH\cdot \longrightarrow AH_2 + A \quad (6)$$

At higher pH (6.8—8.0), the photolyzed micellar solutions of AQS and/or AQDS contained A, $A^{\cdot-}$, and AH_2. In addition to $A^{\cdot-}$ (λ_{max} 396 and 472 nm) and AH_2 (λ_{max} *ca.* 380 nm), dianion of A (A^{2-}) was detected by means of electronic spectroscopy (λ_{max} 436 nm)[27] when AQS in 0.1 M NaOH was irradiated in the presence of NaLS. The following two equilibria involving A^{2-} should also be taken into consideration to account for the data obtained at higher pH region:

$$AH_2 + 2OH^- \rightleftharpoons A^{2-} + 2H_2O \quad (7)$$

$$A^{2-} + A \rightleftharpoons 2A^{\cdot-} \quad (8)$$

The anthrahydroquinones ($AQSH_2$ and $AQDSH_2$) are stable only in acidic media. They are very easily oxidized to original quinones in aerobic neutral and alkaline solutions without surfactants. In the presence of the anionic and non-ionic surfactants, however, these diol derivatives were scarcely oxidized even in 0.1 M NaOH. It is evident that the surfactants play an important role to stabilize the diol derivatives.

The surfactant concentration profile indicates that both $AQS^{\cdot-}$ and $AQSH_2$ are stabilized by binding with micelles (Fig. 5). Existence of typical micellar effects is also manifested by the fact that only micelle-forming carboxylates can stabilize $AQS^{\cdot-}$ (Fig. 6). It seems rather odd, however, that the anionic species such as $A^{\cdot-}$ bind with anionic micelles. In general, negatively charged substrates, such as 1-anilinonaphthalene-8-sulfonate (ANS) and *N,N*-dimethyl-1-anilinonaphthalene-5-sulfonate, are adsorbed by cationic and non-ionic micelles, but not anionic ones.[28] The binding constant for anthraquinone sulfonate ion-anion micelle system is thus expected to be quite small.[29] No matter how small the binding constant is, some of the anthraquinone sulfonate will be bound to the micelles. These bound species may give the radical anion on photoexcitation. The long lifetimes of the radical anions suggest that the rate of exchange between the micelles and bulk water is extremely small.

The absorption maxima of $AQS^{\cdot-}$ and $AQDS^{\cdot-}$ in non-micellar systems have been found at 395 and

505 nm[18] and 400 and 520 nm[19] respectively. In the presence of micelles, the longer wavelength absorption bands of the anion radicals exhibit a remarkable blue shift (~35 and 47 nm, respectively). When the charged substrates such as $AQS^{\cdot}$ and $AQDS^{\cdot}$ bind with anionic micelles, the substrates are incorporated to the Stern layer surrounded by highly concentrated counter cations. The radical anions within the Stern layer, therefore, might form a contact ion pair with cations in the charged double layer. The pair is expected to absorb at shorter wavelengths than the solvent separated ion pair in non-micellar system. In the case of non-ionic micelles, the contact ion pair may be stabilized at the micelle-water interface.

Organic solvents, such as dioxane and alcohols, influence the reactions in micellar systems.[2,3] Since dioxane and alcohols are not adequate because of their hydrogen donative properties, we examined the effects of organic additives with the use of acetone and *tert*-butanol, both of which markedly inhibit the formation of $AQDS^{\cdot}$ and $AQDSH_2$ in micellar systems. A possible explanation may be that the CMC of the surfactant increases on the addition of organic additives. An alternative may be that $AQDS^{\cdot}$ and $AQDSH_2$ are displaced from the micellar phase by the additives.[3] No matter which the case is, it is clear that the binding of $AQDS^{\cdot}$ and $AQDSH_2$ with micelles is essential for the stabilization of these substrates.

It has been reported that the microviscosity of the NaLS micelle interior increases about 3- to 6-fold with the addition of Mg^{2+}.[30] We have also studied the effects of Mg^{2+} on the photochemistry of AQDS–NaLS system. Addition of Mg^{2+} reduced the formation of both $AQDS^{\cdot}$ ($\Phi/\Phi_0=0.48$) and $AQDSH_2$ (Table 2). Contribution of the coexisting sulfate ion (SO_4^{2-}) is considered to be small as verified by the addition of Na_2SO_4 ($\Phi/\Phi_0=0.84$). The permeation of $AQDS^{\cdot}$ and/or $AQDSH_2$ into the micelles might change due to the contraction of charged heads and the increased rigidity of micelle interior as caused by the addition of Mg^{2+}.

All the results indicate that the anthraquinone radical anions and anthrahydroquinones are extremely stabilized by binding with micelles.

It is surprising that neither $A^{\cdot}$ nor AH_2 is oxidized in the micellar systems in spite of its aerobic alkaline conditions. One reason might be that the hydroxide ion concentration in the microenvironment of anionic micelles is lower than that in the bulk since the electrostatic repulsion keeps hydroxide anions away from the negatively charged micelle surface. Thus the micelle interior would afford a favorable environment for AH_2, which exists as a stable species only at low pH region. In contrast, rapid and complex reactions were observed for AQS and/or AQDS when they were irradiated in the presence of hexadecyltrimethylammonium bromide (cationic surfactant) whose micelle surface is covered with locally concentrated hydroxide ions.

In non-micellar system, $AQS^{\cdot}$ has been reported to react with oxygen very easily:[31]

$$AQS^{\cdot} + O_2 \xrightarrow{k} A + O_2^{\cdot} \quad k\ ca.\ 5\times10^8 M^{-1}\cdot s^{-1} \qquad (9)$$

Recently, the oxygen concentration and/or oxygen mobility in micelle interior were found to decrease appreciably with aging of the micellar system.[30,32,33] We found, however, that $A^{\cdot}$ and AH_2 were easily stabilized in fresh micellar solutions as well as in old ones. Since many problems remain unsolved as regards the oxygen concentration within micelles,[30,32-34] no detailed discussion could be given. However, it is clear at least that the scavenging of $A^{\cdot}$ by oxygen is markedly reduced in the presence of anionic and non-ionic micelles.

If the above micellar effects are simply ascribed to the protection of $A^{\cdot}$ and AH_2 from the attack of oxygen, $A^{\cdot}$ should also be stabilized in a well-degassed non-micellar system. In the absence of micelles, however, the photolysis of AQS in anaerobic aqueous media afforded only hydroxylated anthraquinones.[15,16] Studies of radiolysis in the micellar system revealed that the reaction of benzene with a hydroxyl radical is considerably inhibited in the presence of anionic, cationic, and non-ionic micelles,[34] and that the hydroxyl radical is rapidly scavenged by the surfactant to produce relatively inert radicals ($k\simeq10^9\ M^{-1}\cdot s^{-1}$).[35] The same type of protection against the hydroxyl radical would operate in the case of anthraquinones in a micellar system, since the hydroxylated anthraquinones have been reported to be formed by the attack of hydroxyl radicals.[12,15,16,24,27]

The radical anions of anthraquinone sulfonates are so stable in the presence of micelles that the reactivity of these radical anions was easily investigated.

The reactions of $AQS^{\cdot}$ and $AQDS^{\cdot}$ with H^+ yielded the corresponding anthrahydroquinones. Since pK of AQSH· and AQDSH· are 3.25[24] and 2.90[19] respectively, $AQS^{\cdot}$ and $AQDS^{\cdot}$ are protonated in 0.75 N H_2SO_4 to give semiquinone radicals, followed by disproportionation to produce anthrahydroquinones and original quinones:[26]

$$A^{\cdot} + H^+ \longrightarrow AH\cdot \qquad (10)$$

$$2AH\cdot \longrightarrow AH_2 + A \qquad (11)$$

It is well-known that some quinones and ferric ion play an important role as electron carriers in biological systems. Since micelles are known to be good models of biological membrane, we used a micellar solution to construct a model system of the electron transport across membrane: $AQDS^{\cdot}$ in NaLS micelles *vs.* ferric chloride in the aqueous phase. An electron was successfully transferred from $AQDS^{\cdot}$ to Fe^{3+} in this system:

$$AQDS^{\cdot} + Fe^{3+} \longrightarrow AQDS + Fe^{2+} \qquad (12)$$

Further improvement of the model system is expected to clarify the role of biological membranes in electron transport phenomena.

Conclusion

Remarkably long-living radical anions of 9,10-anthraquinone sulfonates are formed in the presence of micelles of anionic and non-ionic surfactants. All of the experimental data suggest that the stabilization of these radical anions is attributed to micellar effects, which are somewhat novel because the anionic species are

considered to be bound with anionic micelles. The relevant micellar effects can be summarized as follows:

a. Since hydroxyl radicals are efficiently scavenged by the surfactants, hydroxylation of the quinones does not take place in micellar systems.

b. The pH in a micellar system might favor the formation of the radical ions, which are involved in the following equilibria:

$$A^{\cdot-} + H_2O \rightleftarrows AH\cdot + OH^-$$
$$2AH\cdot \rightleftarrows AH_2 + A$$
$$AH_2 + 2OH^- \rightleftarrows A^{2-} + 2H_2O$$
$$A^{2-} + A \rightleftarrows 2A^{\cdot-}$$

c. The decay of the radical ion is extremely retarded because of low reactivities of quenchers such as oxygen in micellar interior.

The fact that the radical anions are stabilized by binding with micelles is interesting in relation to the electron transport in biological membranes.

References

1) Contribution No. 332 from the Department of Organic Synthesis, Faculty of Engineering, KyushuUniversity.

2) E. J. Fendler and J. H. Fendler, "Advances in Physical Organic Chemistry," Vol. 8, ed. by V. Gold, Academic Press, New York, N. Y., (1970), p. 271.

3) E. H. Cordes and C. Gitler, "Progress in Bioorganic Chemistry," Vol. 2, ed. by E. T. Kaiser and F. J. Kézdy, John Wiley and Sons, New York, N. Y., (1973), p. 1.

4) Ed. by E. H. Cordes, "Reaction Kinetics in Micelles," Plenum Publishing Co., New York, N. Y., (1973).

5) R. R. Hautala and R. L. Letsinger, *J. Org. Chem.*, **36**, 3762 (1971).

6) H. B. Kostenbauder and P. P. DeLuca, *J. Phys. Chem.*, **67**, 1395 (1963).

7) H. B. Kostenbauder and P. P. DeLuca, *Nature*, **199**, 999 (1963).

8) H. B. Kostenbauder, P. P. DeLuca, and C. R. Kowarski, *J. Pharm. Sci.*, **54**, 1243 (1965).

9) C. R. Kowarski, *ibid.*, **58**, 360 (1969).

10) K. Kano and T. Matsuo, *Chem. Lett.*, **1973**, 1127.

11) N. K. Bridge, *J. Soc. Dyers Colourist*, **76**, 484 (1960).

12) K. P. Clark and H. I. Stonehill, *J. Chem. Soc. Faraday I*, **68**, 577 (1972).

13) J. L. Bolland and H. R. Cooper, *Proc. Roy. Soc. Ser. A*, **225**, 405 (1954).

14) K. Kano and T. Matsuo, *Chem. Lett.*, **1974**, 11.

15) B. Mooney and H. I. Stonehill, *Chem. Ind.*, **1961**, 1309.

16) A. D. Broadbent, *Chem. Commun.*, **1967**, 382; A. D. Broadbent and R. P. Newton, *Can. J. Chem.*, **50**, 381 (1972).

17) The CMC of NaLS is 8.1×10^{-3} M (25 °C).[2)]

18) G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. R. Sharpe, *J. Chem. Soc. A*, **1969**, 767.

19) V. A. Kuzmin and A. K. Chibisov, *Chem. Commun.*, **1971**, 1559.

20) The CMC of NaL is 2.4×10^{-2} M (25 °C).[2)]

21) P. J. Baugh, G. O. Phillips, and J. C. Arthur, Jr., *J. Phys. Chem.*, **70**, 3061 (1966).

22) C. A. Bunton, "Reaction Kinetics in Micelles," ed. by E. H. Cordes, Plenum Publishing Co., New York, N. Y., (1973), p. 73.

23) The CMC of P-80 is 1.3×10^{-3} g/dl (25 °C).[2)]

24) B. E. Hulme, E. J. Land, and G. O. Phillips, *J. Chem. Soc. Faraday I*, **68**, 1992 (1972).

25) N. K. Bridge and G. Porter, *Proc. Roy. Soc. Ser. A*, **244**, 259 (1958).

26) N. K. Bridge and G. Porter, *ibid.*, **244**, 276 (1958).

27) K. P. Clark and H. I. Stonehill, *J. Chem. Soc. Faraday I*, **68**, 1676 (1972).

28) M. T. Flanagan and S. Ainsworth, *Biochim. Biopys. Acta*, **168**, 16 (1968).

29) Although Flanagan and Ainsworth[28)] have reported that ANS does not bound with anionic micelles, we have observed that the fluorescence intensity of ANS is markedly increased above the CMC of NaLS and NaL (see experimental section).

30) M. Gratzel and J. K. Thomas, *J. Amer. Chem. Soc.*, **95**, 6885 (1973).

31) R. L. Willson, *Trans. Faraday Soc.*, **67**, 3020 (1971).

32) R. C. Dorrance and T. F. Hunter, *J. Chem. Soc. Faraday I*, **68**, 1312 (1972).

33) S. C. Wallace and J. K. Thomas, *Radiat. Res.*, **54**, 49 (1973).

34) J. H. Fendler, G. W. Bogan, E. J. Fendler, G. A. Infante, and P. Jirathana, "Reaction Kinetics in Micelles," ed. by E. H. Cordes, Plenum Publishing Co., New York, N. Y., (1973), p. 53.

35) K. N. Bansal, L. K. Patterson, E. J. Fendler, and J. H. Fendler, *Int. J. Radiat. Phys. Chem.*, **3**, 321 (1971).