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THE RADICAL ANION OF SODIUM 9,10-ANTHRAQUINONE-2-SULFONATE STABILIZED BY BINDING WITH MICELLES1)

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The radical anion of sodium 9,10-anthraquinone-2-sulfonate, which was produced by the photolysis of the quinone in aerobic aqueous solution (pH 8.0) containing appropriate amounts of anionic and/or non-ionic surfactants, was detected by means of ESR and UV spectroscopy. The formation of the radical anion was observed above pH 6.8. Relationship between the concentration of surfactant and that of the radical anion gave a profile which showed the typical micellar effects. It is suggested that the micelles protect the radical anion from quenchers, such as oxygen, water, and other reagents, because the radical anion is incorporated into the micellar interior.

The photo- and radiation chemistry of anthraquinones has been widely investigated in relation to the photofading and phototendering of anthraquinoid vat dyes.2) Complex reactions proceed in the photolysis of anthraquinone sulfonates in aqueous solutions. Broadbent and Newton have found that the major products of the photolysis of sodium 9,10-anthraquinone-2-sulfonate (AQS) in aqueous solution are 1- and 2-hydroxy-9,10-anthraquinone-6-sulfonates.3) Phillips et al. have carried out flash photolysis of AQS in aqueous solution and found that the radical cation (AQS$^{\dot{+}}$) and radical anion (AQS$^{\dot{-}}$) are formed in the primary process.4) In order to explain the formation of AQS$^{\dot{-}}$ in the photolysis of AQS in aqueous alkaline solution, Blyumenfel'd et al. suggested that AQS* abstracts an electron from hydroxyl anion.5)

Recently, we have reported that the photodecomposition of p-benzoquinone in aqueous solution is accelerated by the addition of anionic surfactants, such as sodium laurate (NaL) and sodium lauryl sulfate (NaLS).6) In this paper, we wish to report that AQS$^{\dot{-}}$ was surprisingly stabilized when it was produced by the photolysis of AQS in micellar system (pH 6.8-8.0).

Irradiation of the aerobic phosphate buffer solution (pH 8.0) of AQS gave colored stable products whose major components are 1- and 2-hydroxy-9,10-anthraquinone-6-sulfonates.3) At pH 8.0, the quantum yield for the disappearance of AQS excited with 313 nm light was 0.01. The absorption bands of AQS$^{\dot{-}}$ as reported by Phillips et al.4) could not be detected and no ESR signal was observed with this solution.

Aerobic solution (pH 8.0) of AQS containing NaL above the CMC7) in a sealed

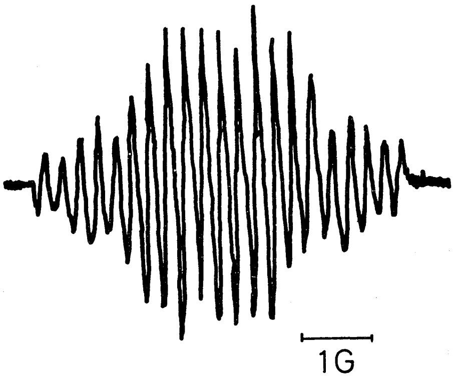

Fig. 1. ESR spectrum of AQS$^{\dot{-}}$ formed by the photolysis of AQS (0.003 M) in 0.033 M phosphate buffer (pH 8.0) containing NaL (0.02 M), (X-band).

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. 1). On the analysis of the hyperfine structure, the spectrum was assigned to the radical anion of AQS as reported by Baugh et al.$^{9)}$ The splitting constant (ΔH), number of lines, and the g-value were 0.25 gauss, 21, and 2.0042, respectively. Phillips et al. have measured the ESR spectrum of AQS$^{\dot{-}}$ during the photolysis of the anaerobic alkaline solution (pH>11) of AQS.$^{4)}$ They have reported that no ESR signal was obtained below pH 11. By the use of flash technique, they have also found that AQS$^{\dot{-}}$ have a relatively long life-time in an anaerobic solution (several msec), and rapidly decayed in the aqueous solution by the addition of oxygen. Surprisingly, AQS$^{\dot{-}}$ obtained in micellar system in the present experiment lived over two monthes in a sealed tube even in the case of aerobic solution. On mixing the solution with air, the signals of AQS$^{\dot{-}}$ gradually decayed away. These facts suggest that AQS$^{\dot{-}}$ is stabilized in the presence of NaL.

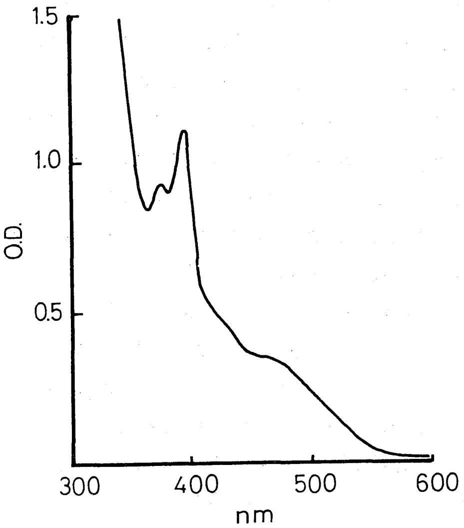

Fig. 2. UV spectrum of AQS$^{\dot{-}}$ formed by the photolysis of AQS (0.001 M) in the aerobic phosphate buffer (0.033 M, pH 8.0) containing NaL (0.02 M). The spectrum was measured after irradiation for 10 min with a 100-W high-pressure mercury lamp at room temperature.

AQS$^{\dot{-}}$ was also detected by means of UV spectroscopy (Fig. 2). When the aerobic solution of AQS (pH 8.0) containing appropriate amounts of NaL was irradiated, the absorption maxima were observed at 378 and 394 nm which coincide with those of AQS$^{\dot{-}}$ reported in the literatures.$^{4,10)}$ However, the absorption band at 505 nm, which has been attributed to AQS$^{\dot{-}}$,$^{4,10)}$ can not be detected in our experiments. The absorption band might be hidden under the broad band observed in the region between 400 and 600 nm. Two bands at 378 and 394 nm were gradually disappeared on mixing the solution with air. The compound with λ_{max} at 378 and 394 nm was rapidly converted to 9,10-dihydroxyanthraquinone-2-sulfonic acid (AQSH$_2$) on contact with 0.15 N H_2SO_4. The relevant reactions may be given by the following equations:

$$\mathrm{AQS}^{\dot{-}} \xrightarrow{O_2} \mathrm{AQS} \tag{1}$$

$$\mathrm{AQS}^{\dot{-}} + \mathrm{H}^+ \longrightarrow \mathrm{AQSH}\cdot \tag{2}$$

$$2\,\mathrm{AQSH}\cdot \longrightarrow \mathrm{AQSH_2} + \mathrm{AQS} \tag{3}$$

where AQSH· represents semiquinone radical of AQS. On the basis of these observations, the absorption bands at 378 and 394 nm are assigned to $AQS^{\dot{-}}$. When AQS was irradiated in the presence of NaLS and polysorbate 80 (P-80), the formation of $AQS^{\dot{-}}$ was also detected by means of UV spectroscopy. Then pH dependence of the formation of $AQS^{\dot{-}}$ in the presence of P-80 was examined by the use of phthalate and phosphate buffers (pH 4.0-8.0). The formation of $AQS^{\dot{-}}$ was detectable above pH 6.8, which coincide with the result obtained by the flash photolysis in the absence of surfactant.4) It is clear that $AQS^{\dot{-}}$ was also stabilized by non-ionic surfactant (P-80), and that $AQS^{\dot{-}}$ was not produced by the electron-transfer from the anion of NaL and/or NaLS to AQS^*.

$$\mathrm{AQS}^* + \sim\!\sim\!\sim\mathrm{COO^-}/\sim\!\sim\!\sim\mathrm{OSO_3^-} \nrightarrow \mathrm{AQS}^{\dot{-}} + \sim\!\sim\!\sim\mathrm{COO}\cdot/\sim\!\sim\!\sim\mathrm{OSO_3}\cdot \tag{4}$$

The influence of the surfactant concentration on the formation of $AQS^{\dot{-}}$ was studied with NaLS. In Fig. 3, the optical density at 378.5, 394 ($AQS^{\dot{-}}$ formation), and 256 nm (AQS disappearance) was plotted against the concentration of NaLS. For this purpose, the aerobic solution of AQS (5×10^{-4} M) in 0.033 M phosphate buffer (pH 8.0) containing appropriate amounts of NaLS were irradiated with a 100-W high-pressure mercury lamp for 5 min. The concentration of $AQS^{\dot{-}}$ markedly increased above the CMC11) and the plateau region was observed at higher concentrations. This profile suggests the presence of typical micellar effects. Therefore, it may be reasonable to suggest that $AQS^{\dot{-}}$ was stabilized by the binding with micelles. In agreement with this suggestion, the concentration of $AQS^{\dot{-}}$ was considerably reduced when sodium n-hexanoate was used in place of NaL. In the presence of micelles, $AQS^{\dot{-}}$ may be incorporated into the micellar interior so that $AQS^{\dot{-}}$ will be protected from quenchers such as oxygen, water etc.

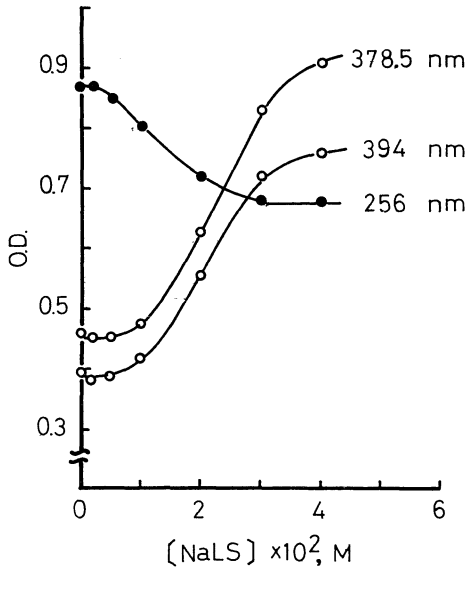

Fig. 3. Effect of NaLS concentration on the disappearance of AQS and the formation of $AQS^{\dot{-}}$.

The similar results have been obtained in the riboflavin photochemistry in aqueous media.12) Kowarski have found that NaLS and P-80 accelerate both the formation and the degradation of the semiquinone radical of flavin mononucleotide.12c) In our case, the rate of the photolysis of AQS was similarly accelerated in the presence of NaLS (Fig. 3). On the other hand, AQS$^{\dot{-}}$ obtained was greatly stabilized in the presence of micelles. Since considerable amounts of AQS$^{\dot{-}}$ can be trapped for long time in micellar system, the present method may be very useful to investigate the reactivity of AQS$^{\dot{-}}$ toward many reagents.

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