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Anomalous Electrochemical Behavior of 1,4-Benzoquinone upon the Addition of Silver Ion

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A cyclic voltammogram of 1,4-benzoquinone showed a couple of redox waves in aqueous solution. Upon adding a trace amount of silver ion, the cyclic voltammogram exhibited an anomalous behavior: a shift of the reduction peak toward a negative potential and the appearance of a new re-oxidation peak at a much more positive potential. This anomalous electrochemical behavior was investigated in terms of both interactions in bulk and on the electrode surface using some kinds of metal-ion additives and some working-electrode materials. It is suggested that the underpotential deposition of silver ion is primarily responsible for the anomalous electrochemical behavior of 1,4-benzoquinone. This was demonstrated by a measurement of cyclic voltammograms using a silver-deposited electrode at an underpotential.

Biological substances have been widely studied electroanalytically using solid electrodes. However, for many compounds, heterogeneous electron transfers between an electrode and a substrate are very slow, leading to ill-defined voltammograms. This is sometimes ascribed to a poisonous substance adsorbed on the electrode, an unfavorable adsorptive orientation of redox species for electron transfer from an electrode, and so on. Thus, several activation methods have been developed which may be used for a solid electrode surface.[1—7] These procedures have been investigated to obtain an electrocatalysis for biological substrates as well as to improve the irreversibility of electron transfer.

We investigated the oxidation of L-ascorbic acid, finding that well-defined voltammograms were obtained upon pretreating the working electrode. This pretreatment, which was accomplished by potential sweeps toward the positive direction only within a narrow potential range in a sample solution, activated the working electrode for the oxidation of L-ascorbic acid. This was ascribed to the self-catalysis of L-ascorbic acid adsorbed oxidatively on the electrode by the pretreatment.[8]

Quinones in biological systems serve as an active site for quinoenzymes or as a coupler of electron and proton transfers in energy-transducing membranes for respiration and photosynthesis.[9—12] The importance of electron-transfer processes of quinones has been recognized in biological redox systems and the catalysis of acids and metal ions on their processes has been investigated thermodynamically, kinetically, and electrochemically.[13—15] Gupta et al. have reported that the second redox process of quinones was affected more significantly than the first redox process in the presence of hydroxyl additives.[13] We found that the redox process of quinones was significantly affected in the presence of metal-ion additives: 1,4-benzoquinone would exhibit an anomalous electrochemical behavior upon the addition of a trace amount of silver ion. In this study, the origin of this behavior was examined with respect to the interaction of quinones with silver ion both in bulk solution and at a working electrode.

Experimental

Materials and Solution. 1,4-Benzoquinone, 2,5-dihydroxy-1,4-benzoquinone, and sodium 9,10-anthraquinone-2-sulfonate were purchased from Wako Pure Chemicals. 1,4-Benzoquinone was of guaranteed reagent grade; 2,5-dihydroxy-1,4-benzoquinone and sodium 9,10-anthraquinone-2-sulfonate were of reagent grade. Deuterated solvents for ^{1}H NMR measurements were purchased from Aldrich. All other reagents were of guaranteed grade and were used without further purification. The pH of a sample solution was adjusted to 2 with sulfuric acid. Sodium sulfate and tetrabutylammonium hexafluorophosphate were used as a supporting electrolyte for cyclic voltammetry at a concentration of 0.10 mol dm^{-3} in an aqueous solution and in an acetonitrile solution, respectively. All sample solutions were deaerated with nitrogen gas before each measurement.

Measurements. The absorption spectra were measured by means of a Hitachi 228 spectrophotometer. ^{1}H NMR measurements were carried out by a JOEL JNM GSX-400 NMR spectrometer and chemical shifts were obtained using sodium 3-(trimethylsilyl)-1-propanesulfonate and tetramethylsilane as an internal standard in deuterated water and in acetonitrile-d_3, respectively. Electrochemical measurements were performed by a BAS 100B/W electrochemical workstation using a three-electrode assembly. The working electrodes were a polycrystalline gold disk, a polycrystalline platinum disk, and a glassy carbon disk with a diameter of 6 mm embedded in Teflon®. The counter electrode was a platinum coil. Ag/AgCl and Ag/AgNO$_3$ electrodes were used as a reference electrode in aqueous and acetonitrile solution, respectively. A Ag/AgNO$_3$ electrode was customarily constructed with immersing a silver wire into a 0.01 mol dm^{-3} AgNO$_3$ acetonitrile solution and was used by connecting with a sample solution through a liquid junction of an acetonitrile solution of 0.10 mol dm^{-3} tetrabutylammonium hexafluorophosphate. The working electrode was polished to a bright mirror finish with slurries of 1.0, 0.3, and 0.05 μm alumina powder, and was washed by sonication for 5 min in 0.05 mol dm^{-3} sulfuric acid and subsequently was washed with a solvent. Sweeps were initiated at 50 mV s^{-1} in the cathodic direction.

Results and Discussion

A cyclic voltammogram of 1,4-benzoquinone exhibited a redox couple at about 0.4 V vs. (Ag/AgCl) in an aqueous solution of pH 2, which corresponds to a two-electron transfer reaction with a two-proton transfer.[16—18] As shown in Fig. 1, however, the addition of a trace amount of silver ion caused an anomalous change in the cyclic voltammograms: a new oxidation peak appeared at 0.66 V vs. (Ag/AgCl) instead of a disappearance of the oxidation peak at 0.43 V vs. (Ag/AgCl), while the reduction peak at 0.31 V vs. (Ag/AgCl) shifted toward the negative direction with increasing silver-ion concentrations. Both currents of the new oxidation peak and the reduction peak increased linearly with the concentration of 1,4-benzoquinone. This indicates that the new oxidation peak originates from 1,4-benzoquinone, itself, and the reduction peak of 1,4-benzoquinone is also affected in any way upon the addition of silver ion. As can be seen in Fig. 2, the oxidation peak disappeared abruptly with increasing the silver-ion concentration. Instead, a new oxidation peak appeared at a silver-ion concentration of 2.0×10^{-5} mol dm^{-3}, and the current increased abruptly with increasing the silver-ion concentration and became constant. Also, it is noted that the new oxidation peak would be accompanied by a small and broad peak at a more cathodic potential than that of the original oxidation peak. It is supposed that a part of hydroquinone is subjected to one-electron oxidation on the deposited silver surface at a more cathodic potential, and subsequently the oxidized product forms a less oxidizable adduct with the deposited silver on the electrode surface. This phenomenon is interesting from a catalysis point of view. Firstly, the interaction of 1,4-benzoquinone with silver ion in bulk solution was examined by UV-vis spectrophotometry and ^{1}H NMR spectrometry. Upon addition of silver ion, no change was detected in the UV-vis and ^{1}H NMR spectra of 1,4-benzoquinone in aqueous solution. Therefore, an experiment in an aprotic solvent was performed to investigate the possibility of an interaction of the one- or two-electron reduced product with silver ion and or deposited silver.

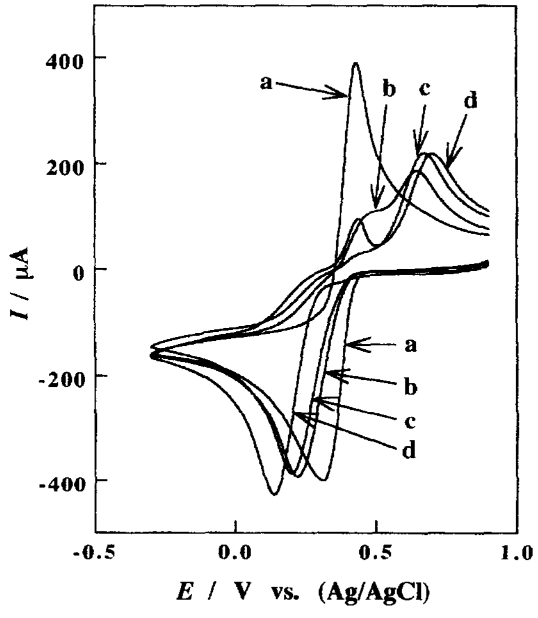

Fig. 1. Effect of silver ion on cyclic voltammograms of 1,4-benzoquinone at pH 2 in aqueous solution, using a polycrystalline gold disk as a working electrode. Concentration of 1,4-benzoquinone is 5.0×10^{-3} mol dm^{-3}. Concentrations of silver ion for curves a, b, c, and d are 0, 2.0×10^{-5}, 1.0×10^{-4}, and 5.0×10^{-4} mol dm^{-3}, respectively.

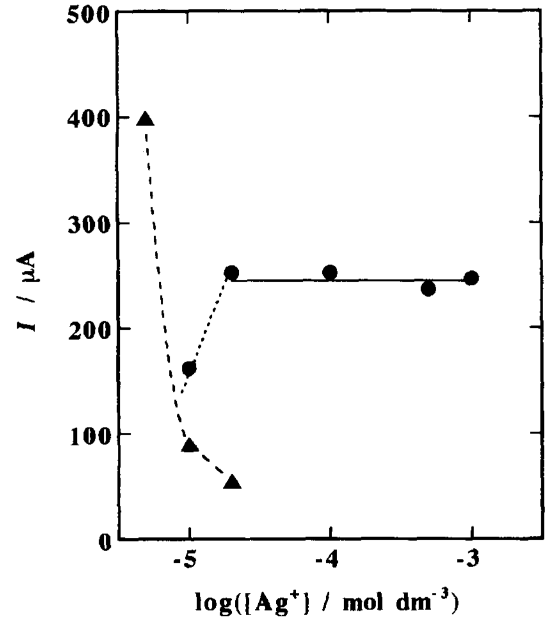

Fig. 2. Dependences of peak current for oxidation on silver-ion concentration. Currents for the original oxidation peak (▲) and the new oxidation peak (●). Concentration of 1,4-benzoquinone is 5.0×10^{-3} mol dm^{-3}.

A redox of 1,4-benzoquinone is observed as a two-electron transfer step in aqueous solution, although the redox involves two electron-transfer processes: quinone-monoanion radical and monoanion radical-dianion redox processes.[19,20] On the contrary, two redox processes have been separately observed in aprotic solvents.[13] Thus, cyclic voltammograms of 1,4-benzoquinone upon the addition of silver ion were also measured in an acetonitrile solution in order to examine which redox process may be affected by silver ion. As shown in Fig. 3, 1,4-benzoquinone exhibited two separate couples at −0.8 and −1.5 V vs. (Ag$^+$/Ag), corresponding to the quinone-monoanion radical and monoanion radical–dianion redox steps. Both waves had rather large peak-separations at the sweep rate in this experiment, 150 and 570 mV, due to the slow electron-transfer rate of 1,4-benzoquinone on the gold electrode. Accordingly, the peak separation of the first redox couple decreased along with a decrease in the sweep rate, and finally reached a quasi-reversible value. On the other hand, the peak separation of the second redox couple decreased with the sweep rates, but still had a large value

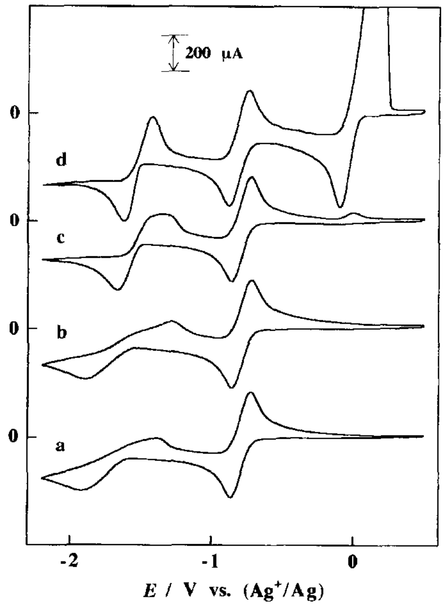

Fig. 3. Effect of silver ion on cyclic voltammograms of 1,4-benzoquinone in acetonitrile solution, using a polycrystalline gold disk as a working electrode. Concentration of 1,4-benzoquinone is 5.0×10^{-3} mol dm^{-3}. Concentrations of silver ion for curves a, b, c, and d are 0, 7.5×10^{-5}, 5.0×10^{-4}, and 7.5×10^{-3} mol dm^{-3}, respectively.

of ca. 300 mV at a sweep rate of 10 mV s^{-1}. Upon the addition of silver ion, however, the peak separation of the second couple was greatly reduced, and became ca. 200 mV, while that of the first couple remained unchanged. The reversibility of the second waves was significantly improved by the addition of silver ion. In an acetonitrile solution, a silver ion also showed no change in the UV-vis and ^{1}H NMR spectra of 1,4-benzoquinone. It is apparent that only the monoanion radical-dianion redox process was affected by the addition of silver ion. Accordingly, it is regarded that a silver ion may affect the same process in aqueous solution. This effect operates in the opposite direction to a different extent in an aqueous solution and in an acetonitrile solution: less reversible in an aqueous solution and more reversible in an acetonitrile solution. It may be responsible for adducts of reduced products of 1,4-benzoquinone with the deposited silver. It is speculated that the orientation and/or adsorption of the reduced product toward the deposited silver may be reflected in the difference between the behavior in an aqueous solution and in an acetonitrile solution; it sounds like charge-transfer adsorption in the aqueous solution and electrostatic adsorption in the acetonitrile solution. At present, this problem is in question.

Cyclic voltammograms of 1,4-benzoquinone were measured in an aqueous solution at pH 2 on addition of other metal ions with various redox potentials. No effect on the voltammograms was observed upon addition of Ni^{2+}, Fe^{2+}, or Cu^{2+}. Table 1 lists the redox peak potentials of those metal ions together with that of silver ion under the conditions of this experiment. From the redox peak potentials in Table 1, this result was explained as follows. The reduction potentials of Ni^{2+} and Cu^{2+} are more negative than that of 1,4-benzoquinone, though that of silver ion is more positive. Although Fe^{3+} shows a more positive reduction potential than that of 1,4-benzoquinone, a reduced product, Fe^{2+}, did not deposit onto the gold electrode, unlike silver ion. Thus, the addition of Fe^{2+} had no effect on the voltammogram of 1,4-benzoquinone. In other words, the electrochemical behavior of quinones may be perturbed only by the metal ions which are reduced and deposited onto the electrode at a more positive potential than the reduction potential of quinones. This consideration was demonstrated by the Cu^{2+} and 9,10-anthraquinone-2-sulfonate system; Cu^{2+} is reduced and is deposited at a more positive potential than the reduction potential of 9,10-anthraquinone-2-sulfonate.

Table 1. Electrochemical Data of Metal Ions at pH 2 in Aqueous Solution

Redpx system	E_{pc}/V vs. (Ag/AgCl)	E_{pa}/V vs. (Ag/AgCl)
Fe^{3+}/Fe^{2+}	0.411	0.516
Ag^{+}/Ag	0.350	0.454
Cu^{2+}/Cu	−0.054	0.064
Ni^{2+}/Ni	< -0.5	< -0.5

E_{pc} and E_{pa} represent peak potentials of reduction and oxidation, respectively.

Figure 4 shows cyclic voltammograms of 9,10-anthraquinone-2-sulfonate upon the addition of copper(II) ion at pH 2 in aqueous solution. 9,10-Anthraquinone-2-sulfonate exhibited a couple of redox waves at −0.14 V vs. (Ag/AgCl). Upon the addition of copper(II) ion, the oxidation peak dis-

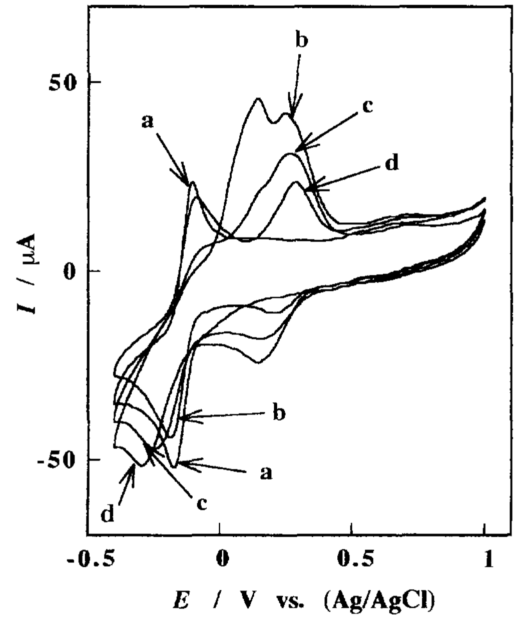

Fig. 4. Cyclic voltammograms of 9,10-anthraquinone-2-sulfonate on addition of copper(II) ion at pH 2 in aqueous solution, using a polycrystalline gold disk as a working electrode. Concentration of 9,10-anthraquinone-2-sulfonate is 5.0×10^{-4} mol dm^{-3}. Concentrations of copper ion for curves a, b, c, and d are 0, 1.0×10^{-4}, 2.0×10^{-4}, and 5.0×10^{-4} mol dm^{-3}, respectively.

appeared along with the appearance of a new oxidation peak at a very positive potential, while the reduction peak shifted toward the negative direction with increasing copper(II) ion concentration. The addition of copper(II) ion caused the same change in cyclic voltammograms of 9,10-anthraquinone-2-sulfonate as that of 1,4-benzoquinone upon adding silver ion, although the dissolution peak of the deposited bulk copper overlaps the new oxidation peak. Therefore, the effect of metal ions on the voltammograms of quinones should be ascribed to the deposition of metal ions onto the working electrode at a more positive potential than the reduction potential of quinones.

The deposition feature of silver ion onto the electrode may be dependent on the materials of the working electrode. Thus, the effect of the addition of silver ion on cyclic voltammograms of 1,4-benzoquinone was investigated at pH 2 in aqueous solution using various metal working electrodes. No effect of silver ion on the voltammograms could be estimated by using a nickel, copper, or silver electrode, because of their narrow potential windows. By using platinum and glassy carbon as a working electrode, however, the voltammograms of 1,4-benzoquinone upon the addition of silver ion varied in the same manner as in the case of the gold electrode, but to a different extent, depending on the material of the working electrode: the degree of the effect of silver ion is in the order of glassy carbon < platinum < gold as the material of the working electrode. Considering that the deposited bulk silver already dissoluted at the potential of the new reoxidation peak of reduced 1,4-benzoquinone, this dependence on the electrode materials suggests that the deposited silver at an underpotential causes a change in the voltammograms of 1,4-benzoquinone.

The underpotential deposition of silver ion onto a polycrystalline gold electrode was examined in order to prepare a silver underpotential deposited gold electrode (Ag–UPD gold electrode).[21—24] The dissolution voltammograms of deposited silver were measured by differential pulse voltammetry, and are shown in Fig. 5. The voltammograms show a dissolution peak of deposited bulk silver at 0.43 V, two dissolution peaks of underpotential deposited silver at 0.7 and 0.95 V, and a peak of the oxidation of gold surface at 1.08 V vs. (Ag/AgCl).[23] The deposition of silver is dependent on the deposition potential: the deposition of bulk silver decreased with increasing the deposition potential, and no bulk silver can deposit at 0.7 V vs. (Ag/AgCl). The amount of deposition at 0.7 V vs. (Ag/AgCl) was independent of the deposition time in the range of 250 to 1000 s within the error limits, owing to small currents. It is difficult to examine the effect of the coverage. Accordingly, a Ag–UPD gold electrode was prepared by holding a gold electrode in an aqueous solution of 1.0×10^{-4} mol dm^{-3} $AgNO_3$ at 0.7 V vs (Ag/AgCl) for 500 s. Figure 6 shows a cyclic voltammogram of 1,4-benzoquinone at pH 2 in aqueous solution using this Ag–UPD gold as a working electrode, together with voltammograms of 1,4-benzoquinone on a gold electrode in the absence and presence of silver ion. On the Ag–UPD gold electrode, the voltammogram exhibited an oxidation peak at a much positive potential and a reduction peak at a more negative potential than that on the gold electrode. As can be seen in Fig. 6, this voltammogram agreed with that in the presence of a trace amount of silver ion on the gold electrode. This fact implies that the deposited silver at an underpotential causes a change in the voltammograms of 1,4-benzoquinone upon the addition of a trace amount of silver ion. This phenomenon was also observed for other quinones

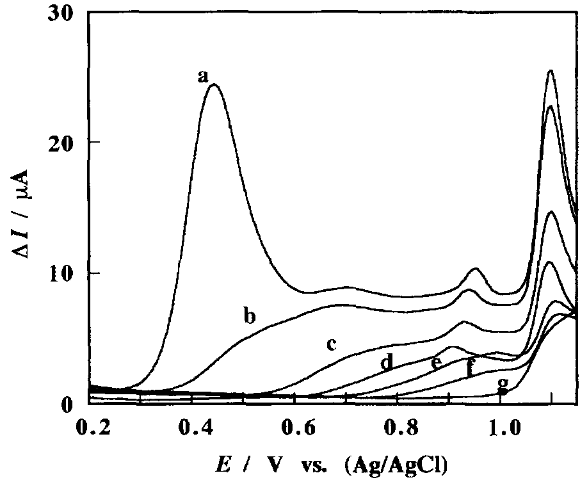

Fig. 5. Differential pulse voltammograms of dissolution of silver deposited on gold electrode in aqueous solution of supporting electrolyte. Silver was deposited for 500 s in aqueous solution of 1.0×10^{-4} mol dm^{-3} silver ion at (a) 0.35 V, (b) 0.4 V, (c) 0.6 V, (d) 0.7 V, (e) 0.8 V, and (f) 0.9 V vs. (Ag/AgCl). Curve (g) is a voltammogram of gold electrode (blank).

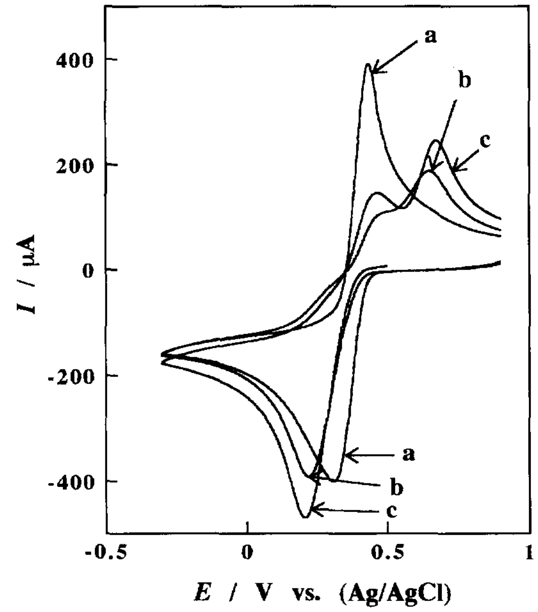

Fig. 6. Cyclic voltammograms of 1,4-benzoquinone at pH 2 in aqueous solution. A concentration of 1,4-benzoquinone is 5.0×10^{-3} mol dm^{-3}. (a) A working electrode is a polycrystalline gold. (b) A working electrode is a polycrystalline gold electrode in the presence of 2.0×10^{-5} mol dm^{-3} silver ion. (c) A working electrode is the Ag–UPD gold electrode.

on the Ag–UPD gold electrode. A similar behavior to that in Fig. 6 was observed to a less extent in a system of 2,5-dihydroxy-1,4-benzoquinone, showing a redox potential of 0.137 V vs (Ag/AgCl).

Conclusion

The electrochemical behavior of 1,4-benzoquinone was significantly influenced by the addition of silver ion. In aqueous solution, its addition made the cyclic voltammogram to be more irreversible. Only the second waves, on the other hand, were influenced, and their reversibility was extremely improved in an acetonitrile solution by the addition of silver ion; that is, the redox process between monoanion and dianion became more reversible by the addition of silver ion. Only the metal ion, which is reduced and deposited onto the electrode at a more positive potential than the reduction potential of quinones, is effective for modifying the voltammograms of quinones. The anomaly in the voltammograms of quinones in the presence of metal ion is ascribed to the deposition of metal as a monolayer, as demonstrated by the Ag–UPD electrode; the adduct formation of reduced products of 1,4-benzoquinone with the deposited silver may play an important role. Studies on the role of deposited silver both in aqueous and acetonitrile solution are under way in our laboratory.

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