Redox Properties of 2,3-Diaminophenazine and Its Electropolymerized Product in Aqueous and Acetonitrile Solutions

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ABSTRACT

Redox properties of 2,3-diaminophenazine were investigated in acidic aqueous and acetonitrile solutions. In each case, continuous potential cycling generated deposited products, poly(2,3-diaminophenazine) (PDAP) on electrode surfaces. PDAP deposited from aqueous solution showed rather complicated redox response with reduction pre-peak that depended on the initial potential, while PDAP deposited from acetonitrile indicated well-defined adsorption properties in acidic aqueous solution.

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1. Introduction

Aromatic diamines are subjected to electropolymerization in acidic aqueous solution in a similar manner as aniline and deposited on an electrode as electroactive films.1 o-Phenylenediamine (oPD) is a representative compound and electrochemically polymerizes to poly(o-phenylenediamine) (PPD). From IR spectroscopic identification of PPD deposited on electrodes, it was reported that the polymeric backbone of the main part has a ladder like structure with phenazine rings (Scheme 1).2 The PPD films are stable even in strong acidic solution and their redox properties in the solution indicates almost chemically reversible response, which is quite different from those of polyamines. It seems reasonable to consider the structure of PPD backbone as the ladder polymer partially ring-opened with quinonen-imine type since the formal redox potential of PPD in acidic aqueous solution is close to that of phenazine due to $2e^-$ and $2H^+$ transfer reaction in addition of the spectroscopic investigation.2 Many applications of electropolymerized PPD films have been reported, e.g., electrocatalysts for oxygen reduction, electrode materials for polymer battery, fuel cells, and biosensors and so on.3–5 On the other hand, another view for the PPD structure has been proposed. The solubility to ten common organic solvents, the structural identifications by NMR and IR spectroscopies, and the elemental analysis indicate that the backbone of PPD has not ladder but 1,4-substituted benzenoid-quinoid structure.6 Oxidative dimerization of oPD leads to 2,3-diaminophenazine (DAP), however, the trimmer obtained by the oxidation of oPD has no phenazine ring,7 suggesting that the structure (Scheme 2) is actually valid. Thus, the structure of PPD is not yet fully identified so far.

To form the ladder like polymer with extensively linear conjugation is an attractive subject8 and one strategy is the electropolymerization of the aromatic diamines that already contains phenazine unit in themselves. The molecular structure of DAP seems to satisfy the above requirement. There are enormous number of papers which deals with the electropolimerization of oPD,1 whereas those of DAP appear to be relatively small.9–12 The earlier work was the electropolimerization of DAP into poly(2,3-diaminophenazine) (PDAP) on glassy carbon and platinum working electrodes in perchloric acid and the properties for photoelectrochemical and electron transfer mediator reactions were investigated.9–15 Euler et al. indicated that the effect of atmosphere and light during the electrochemical formation of PDAP.11 Malitesta et al. proposed the formation mechanism and the structure of PDAP films electrophysically polymerized on platinum electrodes from the measurement of QCM and X-ray photo spectroscopy, which contained the branched polymer with 1,2-coupling mechanism.15 However, there seems to be few report which treats the redox properties of DAP and the corresponding electropolymerized product in organic solvents. In this study, we present the redox chemistry of DAP monomer and polymerized products either in acidic aqueous or acetonitrile solutions using continuous- and single-sweep cyclic voltammetries.

2. Experimental

The reagents for the electrochemical measurements were 2,3-diaminophenazine (Aldrich, Scheme 3), lithium perchlorate (LiClO₄, Wako pure Chemicals), perchloric acid (HClO₄, Wako), methanesulfonic acid (MSA, Wako), and acetonitrile (infinity pure grade, 99.8%, Wako). All chemicals were reagent grade and used without further purification. Solutions were prepared with Millipore water (>18 MΩ) or acetonitrile of highly pure grade. Cyclic voltammograms with continuous- or single-potential sweeps were performed using a computer-controlled potentiostat (ALS/DY 2323, BAS) under an argon atmosphere at laboratory temperature (25°C). Before the measurements, pure argon gas was bubbled directly into the cell in order to remove oxygen, and during the measurement argon gas was flushed over the cell solution. The measurements...
were carried out in a three-electrode cell configuration. Glassy carbon working electrodes (GC with 1.0 mm diameter, BAS) was polished with lapping film sheets (3M) and then sonicated in Millipore water prior to each measurement. A Pt wire and an Ag/AgCl (3 mol dm$^{-3}$ (M) NaCl) electrode with a salt bridge were the auxiliary and reference electrodes for the measurement in the aqueous solutions. For acetonitrile solutions as an electrolyte, an Ag wire was used as a quasi-reference electrode.

3. Results and Discussion

Figure 1 shows a typical cyclic voltammogram obtained at a GC disk electrode in an aqueous solution containing 0.2 M HClO$_4$ and 0.75 mM DAP. Potential sweep at 50 mV s$^{-1}$ was repeated continuously between +1.2 and −0.4 V vs. Ag/AgCl reference electrode for 20 cycles. The voltammograms contain irreversible oxidation peaks and a chemically reversible redox peak with small shoulder that increases as the successive potential sweeps. In the first forward sweep of the potential from +0.25 V, the broad and irreversible anodic peaks were appeared around at +0.85 and +1.05 V, which corresponded to the oxidation of the monomer compound, probably its protonated amino groups. During the first reverse sweep, the well-defined cathodic peak was observed and coupled oxidation peak was obtained in the second reversed sweep. These phenomena observed in the initial potential sweep are similar to those of oPD case, except the oxidation current at higher potential is comparable to the current of redox couple at lower potential. As the sweep rate was repeated up to 20 cycles, the current response of the redox couple at −0.2 V and the reduction pre-peak around at −0.1 V developed markedly and the latter became sharp, demonstrating the formation of the redox active polymeric products (PDAP) on the electrode surface. Reduction pre-peak did not overlap with the main reduction peak.

After the electrolysis described above, the electrode was withdrawn and thoroughly washed with Millipore water and then transferred into a 0.2 M HClO$_4$ aqueous solution in the absence of DAP to investigate the redox properties of PDAP. In Fig. 2(a), the voltammogram was shown where the initial electrode potential was held at +0.25 V for 60 s and then the potential sweep started to the positive direction, reversed at +1.2 V. During the potential sweep into negative direction, sharp reduction peak was observed and followed by the ill-defined broad reduction peaks. In the second positive sweep, only one oxidation peak was appeared around at −0.2 V, which seemed to be coupled with the broad peaks of reduction. The above redox properties have yet to be reported in the preceding studies of DAP electropolymerization.$^{9,22}$ In oPD electropolymerization studies, one could sometimes find such a reduction pre-peak or splitting reduction peak,$^{11,13,14}$ however, there were no interpretation for this kind of phenomena to our best of knowledge. Figures 2(b) and 2(c) show the cyclic voltammograms where the initial potential sweep goes to the negative direction. After holding the potential at +0.25 V for 60 s (current almost zero) and then starting the sweep to the negative direction, the reduction peak at less negative potential was not so remarkable [Fig. 2(b)] compared to that in Fig. 2(a), whereas the potential holding of initial at +0.6 V for 60 s made the corresponding reduction peak enhanced [Fig. 2(c)]. These phenomena indicate that there seems to be redox active portions in PDAP, whose oxidation potential is between +0.25 and +0.6 V and its oxidized form might generate marked and sharp reduction peak.

The potential sweep rate dependence of the cyclic voltammograms of PDAP deposited GC electrode was investigated in 0.2 M HClO$_4$ aqueous solution. An initial potential was set to +0.6 V that was held for 60 s and then potential was swept to −0.5 V. A typical result of such measurements is shown in Fig. 3. Reduction current peaks around at −0.2 and −0.4 V, and defined oxidation peak at −0.2 V were observed. As the sweep rates decreased, well-defined reduction pre-peaks were shifted to positive direction. From the graphical integration of the voltammogram at 5 mV s$^{-1}$, surface concentration of electroactive site, $\Gamma$, was estimated to be $(1.42/n) \times 10^{-7}$ mol cm$^{-2}$ where $n$ is a stoichiometric number of electrons involved in the electrode reaction. If we assumed $n$ to be 2,$^{9}$ $\Gamma$ would be $7.1 \times 10^{-9}$ mol cm$^{-2}$. 

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**Figure 1.** Cyclic voltammogram of 0.75 mM DAP in aqueous solution containing 0.2 M HClO$_4$ with a GC electrode at the sweep rate of 50 mV s$^{-1}$ in the range of potential between −0.4 and +1.2 V.

**Figure 2.** Cyclic voltammograms obtained with PDAP deposited GC electrode in aqueous solution containing 0.2 M HClO$_4$ at the sweep rate of 50 mV s$^{-1}$ from the initial potentials; +0.25 V (a, b), and +0.6 V (c). The direction of potential sweep is; positive (a), and negative (b, c).

**Figure 3.** Cyclic voltammograms obtained with PDAP deposited GC electrode in aqueous solution containing 0.2 M HClO$_4$ at the sweep rate of 200, 100, and 50 mV s$^{-1}$. 

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Figure 4. Cyclic voltammogram of 1.0 mM DAP in acetonitrile containing 0.2 M LiClO₄ and 0.1 mM MSA with a GC electrode at the sweep rate of 50 mV s⁻¹ in the range of potential between −0.75 and +0.85 V.

Figure 5. Cyclic voltammograms obtained with PDAP deposited GC electrode in acetonitrile containing 0.2 M LiClO₄ and 0.1 mM MSA at the sweep rate of 200, 100, and 50 mV s⁻¹.

Figure 6. Cyclic voltammograms obtained with PDAP deposited GC electrode in aqueous solution containing 0.2 M HClO₄ at the sweep rate of 200, 100, and 50 mV s⁻¹.

Figure 7. Cyclic voltammograms obtained with PDAP deposited GC electrode in aqueous solution containing 0.2 M HClO₄ at the sweep rate of 50 mV s⁻¹ from the initial potentials; +0.25 V (a), and +0.6 V (b).

The solubility of DAP into concentrated acidic solution is not sufficient under room temperature compare to that of oPD. To investigate the effect of solvent, the use of acetonitrile with organic acid was attempted as a electrolytic solution for electrode reactions of DAP. Figure 4 indicates a typical cyclic voltammogram obtained at a GC disk electrode in acetonitrile containing 0.2 M LiClO₄, 0.1 mM MSA and 1.0 mM DAP. Potential sweep at 50 mV s⁻¹ was started at 0 V, and repeated between +0.85 and −0.75 V vs. Ag wire quasi-reference electrode for 20 cycles. Compared to the aqueous solution case, the redox properties in Fig. 4 is not distinct from those in Fig. 1. Current at higher potential is relatively small and cathodic peaks at −0.45 and −0.65 V decrease as potential cycling is repeated. This phenomenon suggests that the electropolymORIZATION mechanism in acetonitrile is different from that in acidic aqueous solution. In the same manner as electropolymORIZATION in acidic aqueous solution, the electrode was taken out of the cell and thoroughly washed and then transferred into an electrolytic solution in the absence of DAP. Figure 5 shows cyclic voltammograms of PDAP deposited electrochemically in acetonitrile solution, where the sweep rates are changed from 200 to 50 mV s⁻¹. Electrolytic solution is acetonitrile containing 0.2 M LiClO₄ and 0.1 mM MSA. An initial potential was hold at +0.6 V vs. Ag wire for 60 s and the electrode potential was swept to the negative direction. Chemically reversible coupled redox response probably due to phenazine moiety was observed, however, no faradaic current was appeared if no MSA was added. Up to 10 mM MSA concentration, the shape of voltammogram remained unaltered. These current-potential curves account for very small response due to phenazine site in Fig. 4. Figure 6 indicates cyclic voltammograms of PDAP deposited electrochemically in acetonitrile solution. The measurements were carried out in 0.2 M HClO₄ aqueous solution. An initial potential was hold at +0.6 V vs. Ag/AgCl for 60 s and the electrode potential was swept to the negative direction. The voltammetric waves were obtained as well-defined shape. The separation of the primary cathodic and anodic peak currents is relatively small, indicating that the electrode reaction has the characteristics of an adsorbed species. From the graphical integration of the voltammogram at 5 mV s⁻¹, surface concentration of electroactive site, $\Gamma$, was estimated to be $(5.90/n) \times 10^{-10}$ mol cm⁻². The $\Gamma$ value corresponds to $2.9 \times 10^{-9}$ mol cm⁻², assuming $n$ value to be 2.

The effect of initial potential on the voltammograms are confirmed and indicated in Fig. 7. When the potential was swept from less positive potential at +0.25 V (a), reduction pre-peak did not appear appreciably and the initial potential at +0.6 V generated a pronounced reduction pre-peak (b). These phenomena indicate that the redox properties of PDAP deposited either in aqueous or in acetonitrile are similar despite that reversibility, namely wave shapes are quite different.

From XPS and theoretical calculation, molecular structure of PDAP electropolymerized in aqueous solution was reported that it contains both branched and ladder moieties. Our result of DAP redox properties in acetonitrile suggests that the electropolymORIZATION mechanism in acetonitrile is different from that in acidic aqueous solution and that enables monolayer like wave shape in perchloric acid solution. Though the amount of electroactive moiety in Fig. 6 is less than that in Fig. 3, PDAP deposited in acetonitrile shows simple current-potential curve and the structure might be few branched than that deposited in acidic aqueous solution. The structural evaluations of PDAP electropolymerized in aqueous and acetonitrile solutions are underway.
4. Conclusion

Electrode reaction of DAP in acidic aqueous solutions showed similar properties to oPD case, however, that of PDAP was more complicated redox response. The magnitude of reduction pre-peak depends on the initial potential at which sweep starts, indicating that there might be another redox active site on PDAP whose oxidation potential is at between +0.25 and +0.6 V. Electrode reaction of DAP in acetonitrile with methanesulfonic acid differs greatly from that in aqueous solution in the lacking of defined current peak despite the current decreases as sweep cycle continues. In spite of the above electrodeposition response, current-potential curve of PDAP formed in acetonitrile has the characteristics of adsorption species with small peak separation and nearly symmetric wave shape.

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References