pH-Dependent Charge Trapping by Quinones Electrostatically Bound in an Electrode-Confined Benzylviologen Polymer

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Anthraquinone-2,6-disulfonate, 2,6-AQ, and anthraquinone-2-sulfonate, 2-AQ, have been electrostatically bound in an electrode-confined N,N'-bis[p-(trimethoxysilyl)benzyl]-4,4'-bipyridinium-based polymer, (BPQ^{2+/+})_n. Under all conditions in aqueous electrolyte it appears that charge transport via the quinone redox system, AQ/AQH₂, is too slow to allow direct access to all quinone centers in the polymer. Generally, all quinone centers are electrode accessible only via the BPQ^{2+/+} redox mediator. At pH 6.5 the electrochemistry of [(BPQ²⁺)_n·(AQ)_m]_{surf} is approximately the superposition of the AQ solution electrochemistry and the electrochemistry of surface-confined (BPQ^{2+/+})_n examined separately. At pH 1.0 the reduction potential of AQ shifts positive and (BPQ^{2+/+})_n can only mediate the reduction of AQ to the 2e⁻/2H⁺ reduced form, AQH₂, remains trapped in analogy to previous reports of charge trapping in bilayer systems. The trapped charge is released from the [(BPQ²⁺)_n·(AQ)_m]_{surf} system by a sudden increase in pH which changes the thermodynamics to allow oxidation of the AQH₂ by the BPQ²⁺.

We wish to report results showing pH-dependent charge trapping¹⁻³ by anthraquinone-2,6-disulfonate, 2,6-AQ, and anthraquinone-2-sulfonate, 2-AQ, electrostatically bound⁴⁻⁷ in a redox-active, surface-confined polymer derived from hydrolysis of N,N'-bis[*p*-(trimethoxysily])benzyl]-4,4'-bipyridinium, I.^{7b,8}



Scheme I illustrates what is meant by charge trapping by the electrostatically bound quinones at low pH: reducing equivalents are "trapped" in the polymer in the sense that the reduced form of the quinone, AQH₂, does not release its electrons to the electrode when the electrode is moved to a potential where the oxidation of AQH₂ should occur thermodynamically. Thus the charge-trapping phenomena at low pH is associated with the ability to reduce the BPQ²⁺ to BPQ⁺ and the quinone, AQ, to AQH₂, (1), $[(BPQ^{2+})_{n} \cdot (AQ)_{m}] + (n + 2m)e^{-} + 2mH^{+} \rightarrow$

$$[(BPQ^+)_n (AQH_2)_m]$$
 (1)

while oxidation only leads to withdrawal of the ne^- from the BPQ⁺ to regenerate BPQ²⁺, (2). The result is that $2me^-$ are "trapped"

$$[(BPQ^+)_n (AQH_2)_m] \rightarrow [(BPQ^{2+})_n (AQ)_m] + ne^- \quad (2)$$

in the electrostatically bound AQH₂ centers. The charge-trapping phenomenon is pH dependent, because the AQ/AQH₂ system is only electrochemically accessible via the BPQ^{2+/+} mediator. The mediated reduction and oxidation are both possible at pH's where $E^{\circ'}(AQ/AQH_2) \sim E^{\circ'}(BPQ^{2+/+})$, but at low pH's where the AQH₂ is a much weaker reducing agent, only the mediated reduction process, (1), is energetically and kinetically viable. Scheme II summarizes the energetics for the low- and high-pH regimes.

The significant new finding with the $[(BPQ^{2+}), (AQ)_m]$ system is that the electrostatically bound quinones trap charge as effectively as polymer-modified electrodes involving either bilayer assemblies,^{1,2} or so-called "homogeneous bilayers".⁹⁻¹¹ Electrostatic binding of the charge-trapping quinone in the polymeric viologen redox mediator in our system represents a simplification of the bilayer and homogeneous bilayer schemes, since the need for synthesis of covalently linked polymers or production of pinhole-free bilayers is eliminated. The use of electrostatically bound AQ to trap charge allows study of a wide range of charge-trapping systems, owing to the ease of varying the viologen/quinone ratio.

Below pH 8, $(BPQ^{2+})_n$ undergoes two, one-electron, pH-insensitive reductions at ~-0.5 and ~-0.9 V vs SCE, while AQ









in solution is reduced in a $2e^{-}/2H^{+}$, pH-dependent process¹² occurring over the range $E^{\circ\prime} = \sim -0.08$ and $\sim -0.4 \text{ V}^{13}$ between

(1) (a) Abruña, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. J. Am. Chem. Soc. **1981**, 103, 1. (b) Vining, W. J.; Surridge, N. A.; Meyer, T. J. J. Phys. Chem. **1986**, 90, 2281.

(4) Ohsaka, T.; Oyama, N.; Takahira, Y.; Nakamura, S. J. Electroanal. Chem. 1988, 247, 339.

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⁽²⁾ Denisevich, P.; William, K. W.; Murray, R. W. J. Am. Chem. Soc. 1981, 103, 4727.

⁽³⁾ Wrighton, M. S.; Palmore, T. R.; Hable, C. T.; Crooks, R. M. The Fourth International Kyoto Conference on New Aspects of Organic Chemistry, in press.

 ^{(5) (}a) Oyama, N.; Anson, F. C. J. Electrochem. Soc. 1980, 127, 247. (b)
 Oyama, N.; Shimomura, T.; Shigehara, K.; Anson, F. C. J. Electroanal. Chem. 1980, 112, 271.

⁽⁶⁾ Kuo, K.; Murray, R. W. J. Electroanal. Chem. 1982, 131, 37.
(7) (a) Bruce, J. A.; Wrighton, M. S. J. Am. Chem. Soc. 1982, 104, 74.

^{(7) (}a) Bruce, J. A.; Wrighton, M. S. J. Am. Chem. Soc. 1982, 104, 74.
(b) Dominey, R. N.; Lewis, T. J.; Wrighton, M. S. J. Phys. Chem. 1983, 87, 5345.



Figure 1. Cyclic voltammetry of a glassy C electrode modified with $(BPQ^{2+})_n$ (~2×10⁻⁸ mol/cm²) and then soaked for 30 min in a 25 mM solution of either 2-AQ or 2,6-AQ. The first two scans are shown for 2-AQ and 2,6-AQ at pH 6.5 and pH 1. The insets show the cyclic voltammetry of 3 mM AQ in aqueous solution (solid line) and surface-confined (BPQ²⁺)_n (dotted line) scanned separately at a C electrode. (a) 2-AQ in 0.1 M K₂HPO₄/KH₂PO₄, pH 6.5. $E^{\circ\prime}(2-AQ/2-AQH_2) = -0.46 \text{ V}; E^{\circ\prime}((BPQ^{2+/+})_n) = -0.49 \text{ V}.$ (b) 2-AQ in 0.1 M HCl, pH 1.0. $E^{\circ\prime}(2-AQ/2-AQH_2) = -0.16 \text{ V}; E^{\circ\prime}((BPQ^{2+/+})_n) = -0.46 \text{ V}.$ (c) 2,6-AQ in 0.1 M K₂HPO₄/KH₂PO₄, pH 6.5. $E^{\circ\prime}(2,6-AQ/2,6-AQH_2) = -0.41 \text{ V}; E^{\circ\prime}((BPQ^{2+/+})_n) = -0.49 \text{ V}.$ (d) 2,6-AQ in 0.1 M HCl, pH 1.0. $E^{\circ\prime}(2,6-AQ/2,6-AQH_2) = -0.09 \text{ V}; E^{\circ\prime}((BPQ^{2+/+})_n) = -0.46 \text{ V}.$ The scan rate in all cases is 50 mV/s, and the potentials are versus SCE.

pH 1 and 6.5, respectively. The insets of Figure 1 show the electrochemical response of electrode-confined $(BPQ^{2+/+})_n$ and solution 2-AQ and 2,6-AQ in aqueous electrolyte at pH 1.0 and 6.5. In our experiments $(BPQ^{2+})_n$ is electrochemically grown onto the surface of a C disk (~3 mm in diameter), a Au foil (~7 × 11 mm), or indium tin oxide coated glass (~7 × 9 mm) electrode by a procedure previously described,^{7b} until integration of the cyclic voltammogram indicates coverage of ~1-2 × 10⁻⁸ mol/cm². The polymer-modified electrode is then soaked in a 25 mM solution of 2-AQ or 2,6-AQ until maximum uptake of the AQ by the cationic polymer is achieved. Optical spectroscopic, X-ray photoelectron spectroscopic, and electrochemical analysis of [$(BPQ^{2+})_n \cdot (2-AQ)_m$] and [$(BPQ^{2+})_n \cdot (2,6-AQ)_m$] indicate that

maximum charge compensation of BPQ^{2+} by 2-AQ or 2,6-AQ occurs within 10 min. After uptake of AQ the electrode is removed, rinsed thoroughly with H₂O, and placed into a buffered, degassed, aqueous electrolyte solution for electrochemical characterization.

Figure 1 shows the cyclic voltammetry for C electrodes, modified with $[(BPQ^{2+})_{n}(2-AQ)_{m}]$ or $[(BPQ^{2+})_{n}(2,6-AQ)_{m}]$, at pH 6.5 and pH 1.0. Evidence for the presence of electroactive AQ in the $(BPQ^{2+})_n$ polymer comes from the observation that the integral of the cyclic voltammogram increases after uptake of AQ. At pH 6.5, $E^{\circ'}(AQ/AQH_2)$ is similar to $E^{\circ'}$ of $(BPQ^{2+/+})_n$, as shown by the close position of the cyclic voltammetry waves in the insets of Figure 1. Under these conditions $(BPQ^{2+/+})_n$ can mediate both the reduction and oxidation of the quinones. Figure 1a,c shows that a single, persistent wave is observed which is approximately the superposition of the AQ \Rightarrow AQH₂ and $(BPQ^{2+})_n \rightleftharpoons (BPQ^+)_n$ voltammetry when measured independently. The integrals of the cyclic voltammogram before and after uptake of AQ show significant, but not complete, charge compensation of the cationic sites by AQ. Typically, for the C electrodes we find 50-75% of the cationic sites to be compensated by the sulfonate anions. Accordingly, 2-AQ is typically present at a concentration twice that of 2,6-AQ. Optical spectroscopic and electrochemical characterization of $[(BPQ^{2+})_n \cdot (2,6-AQ)_m]$ show that all 2,6-AQ detected optically is also electroactive. From the cyclic voltammetry there is little loss (\sim 7%) of, for example, 2,6-AQ from the $(BPQ^{2+})_n$ -coated electrodes in 30 min in dilute $(\leq 0.1 \text{ M})$ electrolyte (KCl, HCl, etc.) solutions.

The charge-trapping phenomenon illustrated in Scheme I is found for $[(BPQ^{2+})_n(2-AQ)_m]$ and $[(BPQ^{2+})_n(2,6-AQ)_m]$ at low pH's, Figure 1b,d, due to the fact that at low pH $E^{\circ\prime}(AQ/AQH_2)$ shifts positive of $E^{\circ\prime}(BPQ^{2+/+})$. On the first negative scan there is a large cathodic current which corresponds to the reduction of $(BPQ^{2+})_n$ plus the reduction of AQ mediated by $(BPQ^+)_n$, (1). Upon scan reversal, however, only the current corresponding to oxidation of $(BPQ^+)_n$ is observed, (2). The cathodic current in the second scan results from reduction of $(BPQ^{2+})_n$ and a small amount of the total bound AQ directly accessible by the electrode. Current resulting from direct oxidation of electrode-accessible AQH₂ is observed as a broad wave on the positive sweep.

Our interpretation of the result at pH 1 is that $(BPQ^{2+/+})_n$ mediated oxidation of AQH₂ proceeds slowly, if it all, since this process is thermodynamically uphill. It seems likely that most of the electrostatically bound AQH₂ is isolated from the electrode surface, since the oxidation of AQH₂ at a naked C electrode occurs more negative than the positive potential limit of the scans shown in Figure 1. Results for 2-AQ and 2,6-AQ with respect to charge trapping are the same, except the trapped charge is about twice as high for 2-AQ. We expect this result, since the concentration of the monoanionic 2-AQ in the polymer is typically twice that of the dianionic 2,6-AQ for the $(BPQ^{2+})_n$ polymer.

We are able to show persistent charge trapping by doing pH jump (acidic to basic) experiments following charge trapping.¹¹ For pH jump experiments, rotating C disk electrodes (~3-mm diameter) were coated with $[(BPQ^{2+})_n \cdot (2,6-AQ)_m]$ as described above. The electrode was placed into a 0.1 M HCl solution and rotated at 1000 rpm. At the beginning of the experiment the electrode potential was stepped to -0.6 V to fully reduce 2,6-AQ and $(BPQ^{2+})_n$, and 12 s later the potential was stepped to +0.2 V to oxidize $(BPQ^+)_n$, leaving trapped charge in the form of 2,6-AQH₂. At variable times later the pH of the solution was raised by addition of base to the solution which releases trapped charge by moving the reduction potential of $2,6-AQ/2,6-AQH_2$ into a region where 2,6-AQH₂ is thermodynamically capable of reducing $(BPQ^{2+})_n$, Schemes I and II. The results of these experiments are shown in Figure 2. Figure 2a demonstrates that significant charge is released following the pH jump after holding just a few seconds at +0.2 V. Figures 2b and 2c show the amount of charge released by a pH jump 10 and 30 min after charge trapping. It is apparent from the shape of the current response after adding base that it is difficult to reproducibly change the pH of the film. We have developed a better method for repro-

⁽⁸⁾ Lewis, T. J.; White, H. S.; Wrighton, M. S. J. Am. Chem. Soc. 1984, 106, 6947.

⁽⁹⁾ Smith, D. K.; Lane, G. A.; Wrighton, M. S. J. Am. Chem. Soc. 1986, 108, 3522.

⁽¹⁰⁾ Smith, D. K.; Lane, G. A.; Wrighton, M. S. J. Phys. Chem. 1988, 92, 2616.

⁽¹¹⁾ Smith, D. K.; Tender, L. M.; Lane, G. A.; Licht, S.; Wrighton, M. S. J. Am. Chem. Soc., in press.

⁽¹²⁾ Ksenzhek, O. S.; Petrova, S. A.; Oleinik, S. V.; Kolodyazhnyi, M. V.; Moskovskii, V. Z. Elektrokhimiya 1977, 13, 182.

⁽¹³⁾ All E° values were estimated by averaging the potentials of peak cathodic and peak anodic current.



Figure 2. (a-c) Demonstration of charge release by a pH jump experiment. A glassy C rotating disk electrode was modified with $(BPQ^{2+})_n$ (~2.5 × 10⁻⁸ mol/cm²) and then soaked in 25 mM AQ for 45 min. The electrode was rotated at 1000 rpm in 10 mL of 0.1 M HCl. The electrode potential was first stepped to -0.6 V for 12 s to fully reduce AQ to AQH₂ and $(BPQ^{2+})_n$ and then stepped to 0.2 V to oxidize $(BPQ^{+})_n$. 2 mL of 2 M KOH was added at the time indicated in the figure to release the stored charge. The measured pH at the end of the experiment was ~13. (d) pH jump for a glassy C electrode modified with $(BPQ^{2+})_n$ only.

ducible, local pH changes that show reproducible charge release upon raising the pH, and the details will be reported elsewhere. However, in the present work the charge under the peaks is in reasonable agreement with optical experiments which also show about one-third of the charge remains trapped after 30 min. Figure 1d shows the control experiment for a pH jump for a $(BPQ^{2+})_n$ -coated electrode containing no AQH₂ or AQ and that there is negligible current following the pH jump.

To summarize, we have demonstrated that electrostatic binding of sulfonated quinones into $(BPQ^{2+/+})_n$ can be persistent in aqueous electrolytes. The $[(BPQ^{2+})_n \cdot (AQ)_m]$ system represents a "homogeneous bilayer", similar in concept to conventional bilayers^{1,2} and covalently assembled homogeneous bilayers.^{9–11} The electrostatically bound systems are capable of trapping charge for at least 30 min. The mechanism for the slow leakage of charge is unknown, but is likely a result of a small amount of O_2 or other oxidizing impurities which can rapidly oxidize AQH₂.^{14,15} The charge-trapping phenomenon at low pH is due to the ability of the $(BPQ^{2+/+})_n$ to mediate the reduction of bound AQ, but not the oxidation of AQH_2 . Critically, charge transport in the polymer via AQ/AQH_2 self-exchange occurs slowly,^{16,17} if at all, meaning that the bulk of the AQ/AQH_2 is only accessible via the unidirectional $(BPQ^{2+/+})_n$ mediator. Interestingly, there is a recent report of an electroactive quinone, alizarin red S, electrostatically bound in a polymer.⁴ That the alizarin red S is electroactive whereas the quinone in $[(BPQ^{2+})_n (AQ)_m]$ is not, is likely a consequence of the difference in the rate of physical diffusion of the anionic quinone in the host polycation.

The charge-trapping phenomenon for $[(BPQ^{2+})_n (AQ)_m]$ is essentially the same as that found for polymers derived from monomers consisting of covalently linked viologen and quinone redox centers. Obviously, the synthesis via electrostatic binding is simpler than the assembly of multicomponent monomers and yet the same essential function is achieved: pH-dependent charge trapping. Experiments are now under way to study the charge trapping for a wide range of compositions, since the ratio of quinone to viologen is easily adjusted. Moreover, the electrostatic binding suggests many other charge-trapping systems, including ones which will be chemically sensitive to species other than H⁺. Perhaps the most intriguing finding in the present work is that the quinone can actually be the dominant constituent of the redox polymer in the sense that for 2-AQ we have been able to produce films having a ratio of 2-AQ to BPQ²⁺ of up to 1.5 to 1. Thus, there is the prospect of trapping larger amounts of charge per unit mass and volume. Experiments are now directed toward study of 2-AQ electrostatically bound into a more highly charged mediator system to determine the factors governing maximum density of deliverable stored charge.

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- (16) Laviron, E. J. Electroanal. Chem. 1984, 169, 29.
- (17) Laviron, E. J. Electroanal. Chem. 1986, 208, 357.

⁽¹⁴⁾ Smith, D. K.; Wrighton, M. S. Unpublished results.

⁽¹⁵⁾ Calabrese, G. C.; Buchanan, R. M.; Wrighton, M. S. J. Am. Chem. Soc. 1983, 105, 5594.