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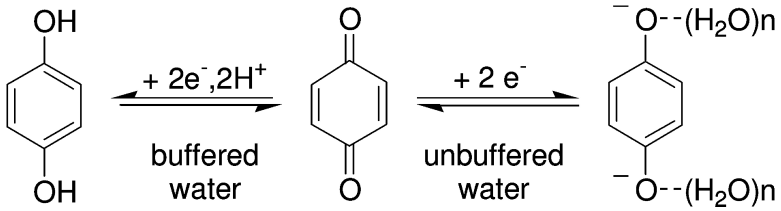

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Voltammetry of Quinones in Unbuffered Aqueous Solution: Reassessing the Roles of Proton Transfer and Hydrogen Bonding in the Aqueous Electrochemistry of Quinones

May Quan, Daniel Sanchez, Mark F. Wasylkiw, and Diane K. Smith*

Contribution from the Department of Chemistry and Biochemistry, San Diego State University, San Diego, California 92182-1030

Received June 13, 2007; E-mail: dsmith@sciences.sdsu.edu

Abstract: Cyclic voltammetry studies are reported for two representative quinones, benzoquinone and 2-anthraquinonesulfonate, in buffered and unbuffered aqueous solution at different pH's. While the redox reaction of quinones in buffered water is well described as an overall 2 e^-, 2 H^+ reduction to make the hydroquinone, a much better description of the overall reaction in unbuffered water is as a 2 e^- reduction to make the strongly hydrogen-bonded quinone dianion, which will exist in water as an equilibrium mixture of protonation states. This description helps to unify quinone electrochemistry by bridging the apparent gap between the redox chemistry of quinones in water and that in aprotic organic solvents, where quinones undergo two sequential 1 e^- reductions to form the quinone dianion.

Introduction

Quinones are one of the most important and well-studied examples of organic redox couples.[1−3] They are well-represented in biological electron transport processes, playing key roles, for example, in the photosynthetic reaction center[4] and in mitochondrial ATP synthesis.[5] Man has also found a number of uses for quinones, such as dyes[6] and as oxidizing and reducing agents in industrial[7] and laboratory scale chemical synthesis.[8] In addition, a number of quinones have also been found to have medicinal properties, including antibiotic, antimicrobial, and anticancer activity.[8,9] From a fundamental standpoint, quinones have played an important role in developing our current understanding of organic redox chemistry.[10] Indeed they have been studied throughout the development of the instrumentation and theory behind modern electroanalytical techniques from polarography[11] to rapid scan voltammetry with ultra-microelectrodes.[12]

Given all the attention that quinones have received it may seem surprising that there is a significant part of their redox chemistry that has not been well studied, but this is in fact the case. While there have been hundreds of electrochemical studies of quinones in aqueous solutions over the past 100+ years, almost all of these have been done in pH buffered solutions. Only a handful have been done in unbuffered aqueous solution.[13−22] The assumption appears to be that either the electrochemistry of quinones in unbuffered aqueous solutions will be very similar to that observed in buffered solutions or that the electrochemistry in unbuffered solutions is not well-defined and therefore will lead to results that are difficult to interpret.

The latter belief stems largely from thinking that the redox chemistry of quinones in aqueous solution is always best described as shown in Scheme 1a, as a 2 e^-, 2 H^+ reaction giving the hydroquinone as the final product. Based on the above equation, reduction of quinones in aqueous solution consumes protons. Therefore, in the absence of buffer, reduction of the quinone will cause the pH near the electrode to increase, creating an "effective pH" near the electrode which is greater than that

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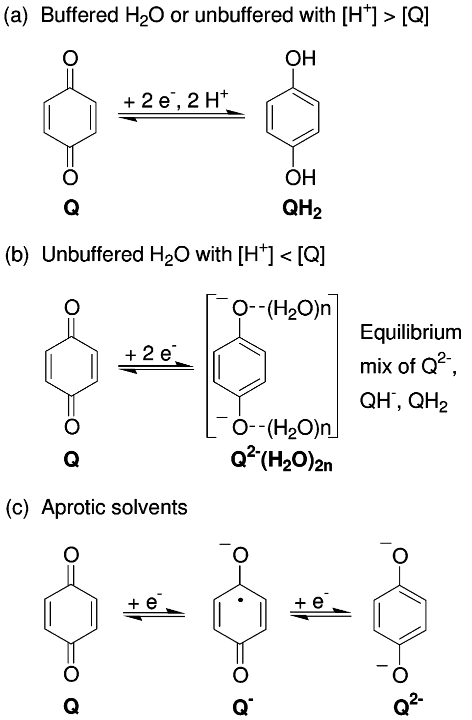
Scheme 1. Quinone Redox Reactions



in the bulk.[23] Furthermore, since protons are part of the overall redox process, the redox potential is pH dependent, moving to more negative potentials as the pH increases. This means the redox potential for this process will be changing as the reduction proceeds in the unbuffered solution, clearly a rather messy situation and one that inevitably leads rather quickly to the conclusion that pH buffered solutions should be used.

The above logic is not necessarily incorrect, although it certainly is not a very productive way of thinking about the redox chemistry of quinones in unbuffered aqueous solution. Nonetheless, it is definitely true that the pH will change at the electrode surface when quinones or hydroquinones are reduced or oxidized in unbuffered aqueous solution. For this reason, the presence of acidic or basic species, such as the components in a buffer solution, will have a strong influence on the observed electrochemistry. We will present evidence to this effect in this paper. However, this was actually nicely demonstrated almost 70 years ago by Müller,[13] who showed in an early polarographic study that the voltammetry of quinhydrone (a 1:1 complex of benzoquinone and benzohydroquinone) changed dramatically as the buffer was diluted. Müller concluded his paper with an exhortation that polarographic studies should be conducted in well buffered solutions. This plea was echoed the following year by Kolthoff and Lingane,[24] who, in the first edition of their influential book on polarography, noted that it was difficult to compare results of the early polarographic studies of organic compounds because many were done in unbuffered or poorly buffered solutions.

While the above works will largely go unread by current electrochemists, their conclusions have become standard practice, with the result that most electrochemical studies of redox couples with acid−base functionality have been done in buffered aqueous solutions since that time. There is, of course, still good reason for this. However, this does not mean that studies in unbuffered aqueous solution should not be done. The point of this work is not only to show that the electrochemistry of quinones in unbuffered aqueous solutions is easily understood but also to argue that it is necessary to do so in order to develop a complete understanding of how the redox chemistry varies with solvent.[25]

Examination of the few reports[13−22] on quinone electrochemistry in unbuffered aqueous solution that have appeared in the literature shows good consistency in the experimental results, but the interpretations of these results differ. An observation common to all the studies is that when the proton concentration is comparable to the quinone concentration, two voltammetric waves are observed. The wave at more positive potentials is universally interpreted as being due to the 2 e^-, $2H^+$ reaction shown in Scheme 1a. However, interpretation of the more negative wave is varied. Some Authors interpret this also with Scheme 1a, with the protons coming from either water or hydroquinone.[13−15,17] Others are more circumspect. Bailey and Ritchie,[16] for example, suggest it likely corresponds to production of a “deprotonated form of the hydroquinone”. More recently, Shim and Park[19,20] have argued that it is due to 1 e^- reduction to form the quinone radical anion. Wang and co-workers[21] disputed this interpretation suggesting, instead, that it is due to 2 e^- reduction to form the quinone dianion. Forster and Kelly[22] also came to the same conclusion as Wang in a study of quinone monolayers adsorbed on Hg electrodes.

Our interpretation of this wave is most consistent with this latter view in that we believe the overall reaction largely corresponds to 2 e^- reduction to form the dianion, Q^{2-}. However, characterizing the reaction as just Q/Q^{2-} is an oversimplification. We will argue that a better description is that shown in Scheme 1b, an overall 2 e^- reaction to give the strongly hydrogen-bonded dianion, Q^{2-}, which, due to its basicity, will exist in water as a mixture of Q^{2-}, protonated anion, QH^-, and hydroquinone, QH_2. The exact distribution will depend on the pK_a’s of the particular hydroquinone and the total concentration of quinone species. With *p*-quinones under typical voltammetric conditions (1 mM concentration), the principal component of the mixture will be QH^-, followed by Q^{2-}. QH_2 will be the minor constituent of the mixture.

The use of Scheme 1b to describe the redox chemistry of quinones in unbuffered aqueous solution is significant for several reasons. First, unlike Scheme 1a, it actually describes the pH-dependence of the observed redox potentials for quinones in unbuffered water. Second, and perhaps most importantly, it bridges the apparent gap between the electrochemistry of quinones in protic solvents, in which Scheme 1a has generally been believed to be operative, and the electrochemistry of

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(23) This argument is nicely expressed by Bailey and Ritchie in their 1985 paper, ref 16, but it goes back much further, at least to Muller’s 1940 paper, ref 13.

(24) Kolthoff, I. M.; Lingane, J. J. *Polarography*; Interscience: New York, 1941; p 344.

(25) Studies like this are rare with organic redox couples, but there are more examples with inorganic couples. A very nice recent example is the following study by Bond, Weld and co-workers looking at the redox chemistry of an iron-substituted polyoxotungstate: Guo, S.-X.; Feldberg, S. W.; Bond, A. M.; Callahan, D. L.; Richardt, P. J. S.; Wedd, A. G. *J. Phys. Chem. B* **2005**, *109*, 20641−20651. This study also demonstrates that, in addition to understanding solvent effects, studies in unbuffered solution can also be useful for sorting out mechanistic details. This is because the distribution of intermediates and products will be different in the absence of buffer, making the voltammetry sensitive to different parameters. In the above paper, digital simulation of the CVs in the unbuffered solution allowed determination of parameters that the studies in the buffered solutions could only place an upper limit on.

quinones in aprotic solvents. Under these conditions, quinones are well-known to undergo two successive 1 e$^-$ reductions, first to form the radical anion and then the dianion, as shown in Scheme 1c. Finally, Scheme 1b points out the important role that intermolecular hydrogen-bonding plays in making quinones a 2 e$^-$ redox couple in aqueous solution, a point that, although perhaps obvious in retrospect, has to our knowledge not been specifically discussed in the literature.

Experimental Section

Reagents and Solutions. All chemicals were purchased from commercial sources as reagent grade or better. 1,4-Benzoquinone, BQ, was further purified by sublimation. The Na salt of 2-anthraquinonesulfonic acid, AQS, was recrystallized from ethanol.

Aqueous electrolyte solutions were prepared using deionized water run through a Barnstead Easypure UV system to remove organics. Buffer solutions of various pH's (all 0.10 M ionic strength in buffer) were prepared using the following mixtures: sodium acetate + HCl (pH 4 to 5.5), "bis-tris" (2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol) + HCl (pH 5.5 to 7), "tris" (tris(hydroxymethyl)aminomethane) + HCl (pH 7.5 to 9), Na_2CO_3 + $NaHCO_3$ (pH 9 to 10.5), Na_3PO_4 + HCl (pH 11 to 12.5), and NaOH (pH 13). The Henderson−Hasselbalch equation, along with the mass balance equation and ionic strength definitions, was used to estimate the concentration of buffer component(s) needed to give 0.10 M ionic strength after pH adjustment. Concentrated HCl was then added to a solution of appropriate concentration(s) until the desired pH (as measured by a pH electrode) was reached. For the "unbuffered" solutions, the pH, monitored with a pH electrode, was adjusted by adding 6 M HCl or NaOH solutions to the thoroughly degassed aqueous electrolyte solution.

General Voltammetry Procedures. Cyclic voltammetry (CV) experiments were performed with a PAR Model 263 digital potentiostat using the Model 270 electrochemistry software package. The acquisition mode was set to "ramp" in order to simulate an analogue experiment. All measurements were conducted under N_2 in a jacketed, one-compartment cell with a glassy carbon disk working electrode (∼2 mm diameter), a Pt wire counter electrode, and an SCE reference electrode. For most of the experiments a combination pH-reference electrode with temperature probe (Fisher Accuflow double junction pH/ATC electrode) was also inserted in the cell to monitor the pH and temperature. Temperature was controlled at 25 °C by using a circulating water bath to run warmed water through the outer cell jacket. The glassy carbon electrode was cleaned immediately before each experiment by polishing with 0.25 μm diamond polishing compound, then rinsing with copious amounts of DI water, followed by a second polish with a 0.05 μm alumina slurry and a final rinse with DI water.

For BQ, CV's were run with 1 mM solutions in 0.50 M KCl/H_2O. With AQS, CVs were run with 0.5 mM solutions in 0.20 M KCl/H_2O (unbuffered) or 0.10 M KCl/H_2O (buffered at $I = 0.10$ M to give a total $I = 0.20$ M). In initial experiments in the unbuffered solutions, HCl(aq) or NaOH(aq) was added directly to the quinone solution in the cell in order to adjust the pH. However, this method lead to results that were inconsistent with those from the buffered solutions. Specifically the apparent half-wave potential, $E_{1/2,\text{ app}}$, reached a minimum between pH 11.5 and 12 and then started to move more positive as the pH was increased further. This is likely because $E_{1/2,\text{ app}}$ is sensitive to both the quinone concentration and the total ionic strength of the solution. In order to reach the high pH's, enough NaOH solution had to be added that both the volume and total ionic strength of the quinone solution changed appreciably. Much improved results were obtained by making separate quinone solutions for each pH using electrolyte solution that had already been set to the desired pH with NaOH and by decreasing the KCl concentration at the higher pH's to ensure that [KCl] + [NaOH] = 0.20 M.

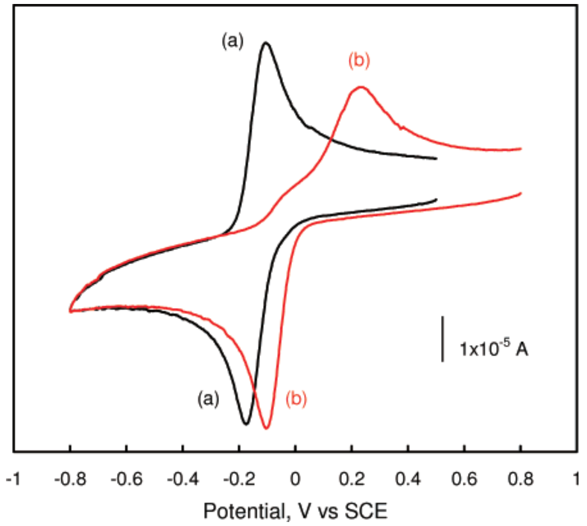

Figure 1. (a) CV of BQ in unbuffered pH 7.2 water. (b) CV after addition of KH_2PO_4/K_2HPO_4 to make a pH 7.2 buffered solution in the same cell. 100 mV/s scan rate with a glassy carbon working electrode.

Results

Cyclic Voltammetry of Benzoquinone and Hydroquinone in Buffered and Unbuffered Neutral Water. The substantial difference between the electrochemistry of quinones in buffered and unbuffered aqueous solution is illustrated in Figure 1 with cyclic voltammograms (CVs) of 1,4-benzoquinone (BQ) in unbuffered aqueous solution (scan a) and after addition of buffer components (KH_2PO_4, K_2HPO_4) to the cell to give a buffered solution of exactly the same pH (7.2) as the original solution (scan b). In the original unbuffered solution, a single reversible-looking redox process is observed with an apparent half-wave potential, $E_{1/2,\text{ app,}}$ equal to −0.139 V vs SCE. Addition of the buffer components has a dramatic effect; not only does the $E_{1/2,\text{ app}}$ move positive by 0.20 V, there is also a huge increase in the peak-to-peak separation (from 74 mV to 334 mV). Both of these changes are clear indications that fundamentally different redox chemistries are occurring in the two solutions. The shift to a more positive potential in the buffered solution indicates that the reduction is easier thermodynamically in the presence of the buffer, but the large increase in peak-to-peak separation indicates that the overall process is kinetically much slower. Almost identical behavior is observed when Tris/TrisHCl is used as the buffer, so these effects are not due to the chemical nature of the buffer. Furthermore, a qualitatively similar behavior is observed with 2-anthraquinone sulfonate (AQS) indicating that this behavior is not unique to BQ.

Additional evidence that different redox chemistry is occurring with BQ in buffered and unbuffered solutions of the same pH is obtained by doing a similar experiment starting with hydroquinone, BQH_2, Figure 2. If BQH_2 is the product of BQ reduction, then the peak potentials in the CV should be the same as those observed for BQ. This, indeed, is close to what is observed in the buffered solutions. Comparison of Figure 1, scan (b) to Figure 2, scan (b) shows that the potential of the cathodic peak for BQ is almost exactly the same as that observed for BQH_2 in the buffered solutions. The anodic peaks occur at slightly different potentials, but given the irreversibility of the

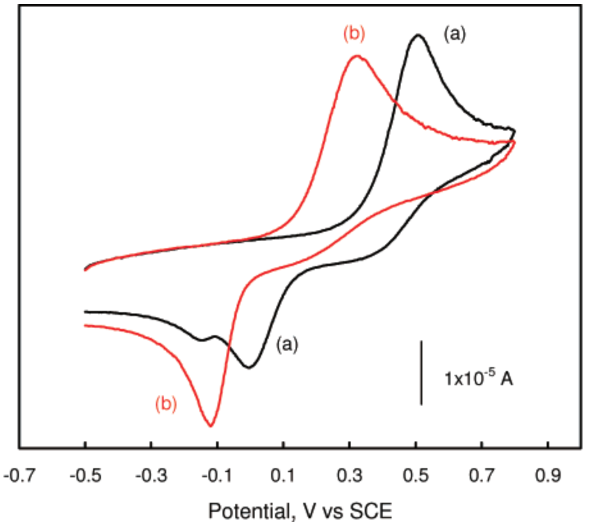

Figure 2. (a) CV of BQH_2 in unbuffered pH 7.2 water. (b) CV after addition of KH_2PO_4/K_2HPO_4 to make a pH 7.2 buffered solution in the same cell. 100 mV/s scan rate with a glassy carbon working electrode.

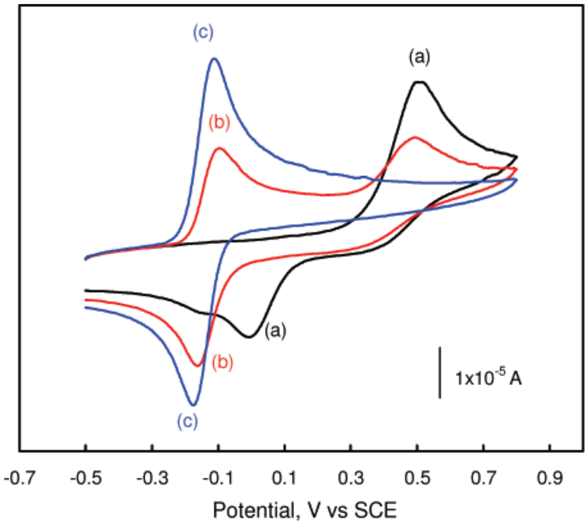

Figure 3. (a) CV of BQH_2 in unbuffered water. (b) CV after addition of 1 equiv of OH^- (from $Ca(OH)_2$) to the cell. (c) CV after addition of a total of 2 equiv of OH^- to the cell. 100 mV/s scan rate with a glassy carbon working electrode.

CV waves,[26] the peaks are close enough to agree with the very well-established fact that BQ and BQH_2 are directly coupled in buffered solutions at neutral pH.

On the other hand, in unbuffered aqueous solution the electrochemistry of BQH_2 (Figure 2, scan a) is completely different than that of BQ (Figure 1, scan a). Unlike the reversible process observed for BQ in unbuffered aqueous solution, a chemically and electrochemically irreversible oxidation is observed for BQH_2. This shows that BQH_2 is not a product of BQ reduction under these conditions and, therefore, that Scheme 1a does not describe the actual redox reaction of BQ in unbuffered neutral water.

Despite the clear differences in the electrochemistry of both BQ and BQH_2 in unbuffered and buffered neutral solution, there is one important similarity — the CV peak heights on the forward scans. This indicates that the same number of electrons are involved. Given that the interconversion between BQ and BQH_2 that is observed in buffered solution is a 2 e^- process, the redox reactions occurring in the unbuffered solutions also must involve 2 e^-'s.[27]

So, if BQ is still reduced by 2 e^- in unbuffered water, but BQH_2 is not the product, what is? The identity of the actual product can be confirmed by doing the simple experiment shown in Figure 3. Scan (a) in Figure 3 is once again that of BQH_2 in unbuffered neutral water. Addition of 1 equiv of OH^- to the solution to give nominally BQH^-, scan (b), causes the original irreversible oxidation peak of BQH_2 to decrease by approximately half and a new reversible wave to appear at more negative potentials. Addition of another equivalent of OH^- to give BQ^{2-}, scan (c), causes the reversible wave to double in size and the oxidation peak for BQH_2 to disappear completely. This new reversible wave that appears in the BQ^{2-} solution is very close to the same potential and shows the same kinetic characteristics as those observed for BQ in the unbuffered solution. This provides very strong evidence that the redox couple seen in both unbuffered solutions is BQ/BQ^{2-}, i.e., the half reaction described in Scheme 1b.[28]

Cyclic Voltammetry of 2-Anthraquinonesulfonate in Unbuffered Water at Different pH's. Further support that Scheme 1b best describes the redox chemistry of quinones in unbuffered water comes from examining the pH dependence of the voltammetry of quinones. For these studies we have focused on 2-anthraquinone sulfonate, AQS, since it is more stable at basic pH's than BQ. However, similar qualitative behavior has been observed by us and Bailey and Ritchie[16] for BQ.

Simple manipulation of the Nernst equation shows that the observed redox potential for an m H^+, n e^- redox couple will change $-m/n$(59 mV)/pH unit at 25 °C. So, under conditions where quinones undergo a 2 e^-, 2 H^+ reduction, a plot of $E_{1/2,\mathrm{app}}$ vs pH should give a slope of -59 mV/pH unit up to pH $=$ pK_{a1} for QH_2. At higher pH's the product will be QH^-, meaning the reaction is now 1 H^+, 2 e^- and the slope will decrease to -30 mV/pH unit. This will continue up to pK_{a2} of QH_2. At this point, the product becomes Q^{2-}, the reaction becomes 0 H^+/2 e^- and the slope of the $E_{1/2,\mathrm{app}}$ vs pH plot becomes 0.

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(26) The peak potentials varied slightly from experiment to experiment almost certainly due to variations in the condition of the glassy carbon surface. It is known that the rates of quinone reduction in water are very sensitive to the condition of the electrode surface: White, J. H.; Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem.* **1985**, *185*, 331−8.

(27) Strong support for an overall 2 e^- process comes from some of the other studies of benzoquinone in unbuffered aqueous solution in which steady-state voltammograms were produced. For example, in Müller's 1940 polarographic study (ref 13) in which the concentration of buffer was varied, the maximum limiting current was the same at all buffer concentrations, indicating that the same number of electrons were involved. Robertson and Pendley (ref. 17) observed 54 years later similar behavior and came to the same conclusion when they measured the steady-state voltammograms of BQ in the presence of small concentrations of sulfuric acid with 5 micron diameter Pt microelectrodes. In addition, although they do not actually show the data, Wang and co-workers (ref 21) state that they confirmed that the reaction was 2 e^- using a rotating disk electrode, another steady-state technique.

(28) It is interesting to note that only the two waves are observed in this experiment; there is no intermediate CV wave corresponding to BQH^-. This behavior is consistent with rapid protonation equilibria. Although BQH^- will be the major species produced with 1 equiv of OH^-, small amounts of the other protonation states have to also be present at equilibrium. Since Q^{2-} will be the easiest to oxidize, it is oxidized first. This removes these ions from the mixture, causing some of the QH^- to dissociate to Q^{2-} and H^+ in order to re-establish equilibrium. This Q^{2-} is then oxidized, more QH^- dissociates, and so on, until half of the original QH^- has been oxidized and half an equivalent of H^+ has been produced. These H^+'s will have combined with the remaining QH^- to make QH_2 which is oxidized at the more positive potential.

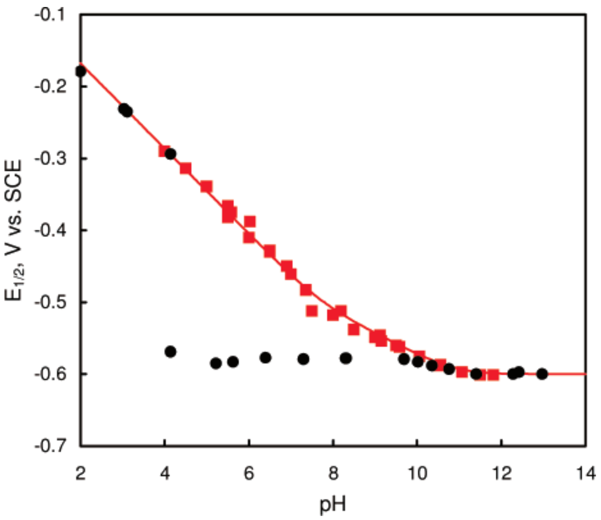

Figure 4. $E_{1/2}$ (from CV) vs pH data for AQS in buffered and unbuffered aqueous solutions. (Red squares) $E_{1/2}$ values in buffered aqueous solutions ($I = 0.2$ M). (Red line) Best fit of experimental data to eq 1, corresponding to $E^{\circ\prime}$ of AQS/AQS^{2-} = −0.600 V vs SCE, pK_{a1} of AQSH$_2$ = 7.68 and pK_{a2} = 10.92. (Black circles) $E_{1/2}$ values for 0.50 mM AQS in unbuffered solutions of various pH's (I = 0.2 M).

Quinones, including BQ[16] and AQS,[16,29−32] are well-known to follow the expected $E_{1/2,\mathrm{app}}$ vs pH behavior in buffered aqueous solutions. Our data for AQS from CV experiments in buffered solutions are shown in Figure 4 (red squares). In line with expectations, we observe a slope of −60 mV/pH unit between pH 4 and 7.5, a slope of −28 mV/pH unit between pH 8 and 10.5, and a slope of 0 mV/pH unit above pH 11.3.

The complete relationship between $E_{1/2}$ and the proton concentration, $C_{\mathrm{H+}}$, at 25 °C is given by eq 1,[32] where $E^{\circ\prime}$ is the formal potential and the K'_{a}'s are the nonthermodynamic (concentration-based) acid dissociation constants. Fitting the data from buffered solutions in Figure 4 to this equation using nonlinear least-squares regression[33] gives the solid red line, which corresponds to $E^{\circ\prime}_{\mathrm{Q/Q^{2-}}} = -0.600$ V vs SCE, pK_{a1} = 7.68, and pK_{a2} = 10.92.[34] These values agree well with other literature values for the pK_a's of AQSH$_2$.[35]

$$E_{1/2,\mathrm{app}} = E^{\mathrm{O}'}_{\mathrm{Q/Q^{-2}}} + 0.0296\ \mathrm{V} * \log\left(1 + \frac{C_{\mathrm{H+}}}{K'_{\mathrm{a2}}} + \frac{C^2_{\mathrm{H+}}}{K'_{\mathrm{a1}}K'_{\mathrm{a2}}}\right) \quad (1)$$

Quite different pH-dependent CV behavior is observed for AQS in unbuffered aqueous solution. Figure 5 shows CVs of 0.5 mM AQS at different pH's in unbuffered 0.2 M KCl solution. At pH's where the H$^+$ concentration is greater than the Q concentration (scans a and b), one quasi-reversible CV wave is observed. The $E_{1/2}$ of this wave is pH-dependent and occurs at essentially the same potential as that in buffered solutions of the same pH, indicating that it represents the 2 e$^-$, 2 H$^+$ reduction, Scheme 1a. However, when the pH is increased so that the H$^+$ concentration is close to the Q concentration, the CV now shows two waves (scan c). The more positive wave occurs at the potential expected for the Q/QH$_2$ couple, but a new wave appears at a more negative potential. The appearance of the two waves is easy to understand in that under these conditions there will not be enough protons around to fully reduce Q to QH$_2$. This process, which is thermodynamically more favorable, occurs first. But, once the available H$^+$'s are consumed, the remainder of the Q will be reduced at more negative potentials. As the pH is increased further, the pH-dependent wave at more positive potentials disappears entirely, and the wave at more negative potentials becomes the only wave (scans d and e). As noted in the Introduction, this behavior has been observed in all previous voltammetric studies of quinones in unbuffered aqueous solutions.[13−22] Typically it has been explained by a combination of Scheme 1a and the "effective pH" argument as described in the Introduction. Our alternative explanation is that under these conditions the reaction switches to Scheme 1b.

Consistent with the stoichiometry of Scheme 1b, the more negative wave is approximately independent of pH over a wide range, black dots in Figure 4. However, careful inspection of this data shows that there is actually a small change in the $E_{1/2}$ at basic pH's. This region is enlarged in Figure 6, showing that there is an approximately −20 mV shift toward a more negative potential centered between pH 10 and 12. This can be explained qualitatively by Scheme 1b in that the product of the redox reaction, Q^{2-}, is stated to exist as a thermodynamic mixture of protonation states in the unbuffered solution. The overall reaction is therefore more explicitly described by eqs 2, 3, and 4, with the first base dissociation, eq 3, having the most effect on the redox equilibrium. Under conditions where the bulk OH$^-$ concentration is small compared to that of Q, eqs 3 and 4 act to remove Q^{2-}. This will make it easier to reduce Q, and the observed redox potential will be shifted positive of $E^{\circ\prime}$ for the Q/Q^{2-} couple. From Le Chatelier's principle, as the OH$^-$ concentration becomes significant relative to the Q concentration, the equilibrium position for eqs 3 and 4 will shift left. These equilibria will then have less effect on the overall reaction, so the observed redox potential will move negative toward $E^{\circ\prime}$ for the Q/Q^{2-} couple.

$$\mathrm{Q} + 2\mathrm{e}^- \leftrightarrow \mathrm{Q}^{2-} \quad (2)$$

$$\mathrm{Q}^{2-} + \mathrm{H_2O} \leftrightarrow \mathrm{QH}^- + \mathrm{OH}^- \quad (3)$$

$$\mathrm{QH}^- + \mathrm{H_2O} \leftrightarrow \mathrm{QH_2} + \mathrm{OH}^- \quad (4)$$

The above effect provides a nice means to test the quantitative validity of our description of the overall reaction in unbuffered

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(33) The nonlinear least squares regression fit was accomplished using the Levenberg−Marquardt method as implemented in PsiPlot V 8.11.
(34) It should be noted that there is an error in pK_a values measured in this fashion introduced by combining voltammetric $E_{1/2}$ values with potentiometric pH values (those measured with a pH electrode). The former are inherently concentration sensitive due to their dependence on a current measurement, whereas the latter are inherently activity dependent. Equation 1 is rigorously correct with formal potentials and proton concentrations. The problem is simply that we are actually measuring proton activity. However, if the ionic strength is constant, the error in the pH should be constant and equal to log of the activity coefficient for protons at the ionic strength used. For this work, the error is essentially self-correcting because our main use of these pK_a values is to calculate the expected $E_{1/2}$ in unbuffered solution as a function of the activity dependent pH's.
(35) The following pK_a's have been determined for AQSH$_2$. All values are at 25 °C unless otherwise noted. The ionic strength, if given, is in parentheses. pK_{a1}: 7.2 (I = 1, ref 16), 7.65 (30 °C, I = 0.2, ref 31), 7.97 (Broadbent, A. D.; Melanson, R. J. *Can. J. Chem.* **1975**, *53*, 3757−60), 8 (ref 32), 8.16 (ref 29), 8.65 (I = 0.1, ref 30). pK_{a2}: 9.28 (ref 29), 10.9 (I = 1, ref 16), 11.05 (I = 0.1, ref 30), 11.05 (30 °C, I = 0.2, ref 31), 11.08 (Broadbent and Melanson), 11.3 (ref 32).

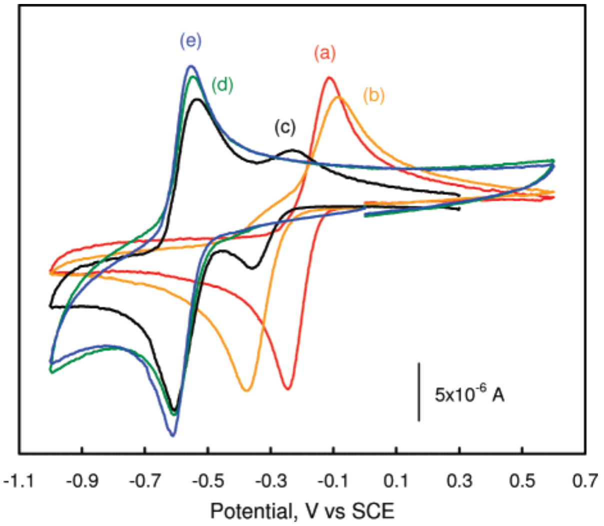


Figure 5. CVs of 0.5 mM AQS in unbuffered aqueous solution of various pH's: (a) pH = 2.00, (b) pH = 3.03, (c) pH = 4.14, (d) pH = 6.40, (e) pH = 8.46. 100 mV/s scan rate with a glassy carbon working electrode.

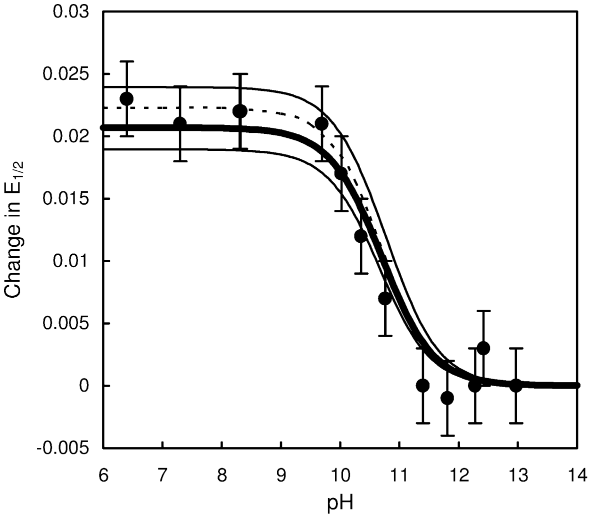
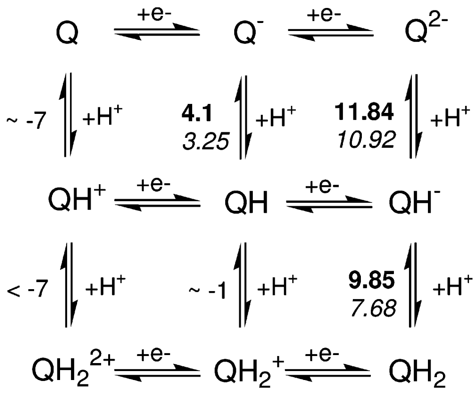


Figure 6. $\Delta E_{1/2}$ vs pH data for AQS in unbuffered aqueous solution. $\Delta E_{1/2} = E_{1/2,\,\mathrm{app}} - E^{\circ\prime}_{Q/Q^{2-}}$. $E^{\circ\prime}_{Q/Q^{2-}} = -0.600$ V vs SCE from the fit to the buffered data in Figure 4. (Circles) Experimental data. Error bars are calculated based on an uncertainty of ±2 mV in the E_p values used to calculate $E_{1/2,\,\mathrm{app}}$ from the CV data. (Thick line) Theoretical $\Delta E_{1/2}$ values calculated using eqs 5 and 6, and $K'_b = 8.31 \times 10^{-4}$ M, determined from the fit to the buffered data in Figure 4. (Dashed lines) 95% Confident limits based on the uncertainty in the K'_b value from the regression analysis. High value: $K'_{b1} = 1.15 \times 10^{-3}$ M; Low value $K'_b = 6.49 \times 10^{-4}$ M. (Dashed line) $\Delta E_{1/2}$ values calculated using both K'_{b1} and K'_{b2}values as explained in the Supporting Information.

Scheme 2. Nine-Membered Square Scheme for Quinones with Known and Estimated pK_a's of BQ (bold) and AQS (italic)



solution. If we assume reaction 4 will not have a significant effect, it is straightforward to develop the mathematical relationship between the observed potential shift and the bulk pH by using the Nernst equation for reaction 2, the K'_b expression for reaction 3, and the appropriate mass balance equations. The $E_{1/2}$ condition is also needed, which occurs when the total concentration of oxidized species at the electrode surface equals the total concentration of reduced species. Using all of the above, $E_{1/2,\mathrm{app}}$ can be related to the equilibrium concentration of OH$^-$ at the electrode surface, $C_{\mathrm{OH}-}$, by eq 5.[36] $C_{\mathrm{OH}-}$ is given by eq 6 as a function of the total quinone concentration, C_{Qtot}, the bulk OH$^-$ concentration, $C^*_{\mathrm{OH}-}$, and K'_b. Using these two equations and the experimentally determined K'_{b1} (8.3×10^{-4} M, from the pK_{a2} of AQSH$_2$ determined from the fit to the buffered data in Figure 4) gives the thick line shown in Figure 6, which is in reasonable agreement with the experimental $E_{1/2}$ values. An even better fit can be obtained by including the second base dissociation reaction, dashed line in Figure 6.[37]

$$E_{1/2,\mathrm{app}} = E^{\circ\prime} + \frac{RT}{2F}\ln\left(1 + \frac{K'_b}{C_{\mathrm{OH}-}}\right) \tag{5}$$

$$C_{\mathrm{OH}-} = \frac{-K'_b + C^*_{\mathrm{OH}-} + \sqrt{(K'_b - C^*_{\mathrm{OH}-})^2 + 2K'_b(2C^*_{\mathrm{OH}-} + C_{\mathrm{Qtot}})}}{2} \tag{6}$$

Discussion

Literature Support for the Q/Q^{2-} Reaction in Unbuffered Aqueous Solution. The conclusion that the redox chemistry of quinones in unbuffered water follows Scheme 1b is in full agreement with known thermodynamic information about the possible species involved in the reaction. Some of these values are given in the nine-membered square shown in Scheme 2, which is typically used to summarize the possible electrode reactions (listed horizontally) and proton-transfer reactions (listed vertically) that are likely involved in quinone redox chemistry.[1-3,38] Focusing first on the proton-transfer equilibria, quinones themselves (top left corner of Scheme 2) are extremely weak bases. The pK_a for the protonated benzoquinone, QH$^+$, has been estimated to be -7.[39] The pK_a of the diprotonated species, QH$_2$$^{2+}$, would be even smaller. This means that, in either a buffered or an unbuffered aqueous solution of neutral pH, the reactant in the overall reaction is almost certainly Q and not any of the other protonated forms shown in the left column of Scheme 2.

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[36] The complete derivation of eqs 5 and 6 are given in the Supporting Information.

[37] The algebra is more complex if the second base dissociation is included. In this case, the relationship between $E_{1/2}$ and the equilibrium concentration of OH$^-$ at the electrode surface is given by an equation analogous to eq 1, except with the K'_a's converted to K'_b's and $C_{\mathrm{H}+}$ converted to $C_{\mathrm{OH}-}$. Derivation of the expression for the equilibrium concentration of OH$^-$ at the electrode follows the same logic as that used for eq 6, except because of the second base dissociation, a quartic (fourth order) equation results instead of a quadratic. The exact equations along with an outline of their derivation are given in the Supporting Information.

[38] Jacq, J. *Electrochim. Acta* **1967**, *12*, 1345−71.

[39] Laviron, E. *J. Electroanal. Chem.* **1984**, *164*, 213−27.

Since our results, and those of others,[13,17,21,22] show that the overall reaction involves two electrons in both buffered and unbuffered aqueous solutions, the possible products, assuming only protonation reactions, are those shown in the right column of Scheme 2. Unlike the starting quinone, all of these species have acid−base character in aqueous solution: Q^{2-} is a pretty good base, QH_2 is a weak acid, and QH^- will have both weak base and weak acid character. Using the pK_a's for QH_2 and QH^- given in Scheme 2,[40] in a well buffered solution at pH 7, 99.9% of the doubly reduced BQ will be in the QH_2 form and 83% of AQS will be in the QH_2 form. Therefore, under these conditions, even for the less basic AQS, the overall redox reaction is nicely described as in Scheme 1a. In contrast, in the unbuffered neutral solution, using the same pK_a's and 1 mM quinone, the calculated pH of the solution at the electrode surface after $2e^-$ reduction is 10.97 with a distribution of 11.1% Q^{2-}, 82.6% QH^-, and 6.3% QH_2. For AQS, the pH would be 10.77, with 41.4% Q^{2-}, 58.5% QH^-, and 0.1% QH_2.[41] Note that, in both cases, unlike the buffered solution, the hydroquinone QH_2 is the minor product. Furthermore, although the primary product for both quinones at 1 mM is QH^-, the best single reaction to describe the overall reaction in an unbuffered solution is still eq 2, since this predicts the correct proton content of the product mixture. One simply needs to understand that due to its basicity "Q^{2-}" will exist in water as a mixture of protonation states, as indicated in Scheme 1b.

In addition to proton-transfer equilibria, the use of Scheme 1b to describe the overall reduction of quinones in unbuffered water also has implications with regard to the electron-transfer equilibria in Scheme 2. Namely, if the reaction is accurately described as 2 e^-, the redox potentials for the two electron-transfer steps across the top row must be either inverted ($E°$ of $Q^-/Q^{2-} > E°$ of Q/Q^-) or close enough in potential that the two processes overlap to produce the one CV wave that is observed experimentally. In fact, the latter is known to be the case.

For BQ, the difference in redox potential between the individual electron-transfer reactions can be calculated from the equilibrium constant for the comproportionation reaction, eq 7. K for this reaction is related to the difference in potentials for the 1 e^- transfer steps, as shown in eq 8 (at 25 °C). Using the experimentally determined K_c of 4.2,[42] the difference in potential for BQ is −37 mV. For AQS, differences of −32 mV[31] and −36 mV[30] have been determined from analysis of the shape of redox titration and polarographic curves, respectively, at high pH. In both cases, although potential inversion is not observed, the potentials are close enough that only one CV wave will be observed.

$$Q + Q^{2-} \leftrightarrow 2Q^- \tag{7}$$

$$\log K_c = \frac{(E°_{Q/Q^-} - E°_{Q^-/Q^{2-}})}{0.0592\ \mathrm{V}} \tag{8}$$

Further support for the appropriateness of Scheme 1b comes from experimental observations (UV/vis[19] and ESR[20,21]) that the BQ radical anion, Q^-, is formed upon reduction of BQ in unbuffered aqueous solutions but not in pH 7 buffered solutions. As suggested by Wang and co-workers,[21] the radical likely results from the comproportionation reaction between the Q^{2-} formed at the electrode and Q coming from the bulk solution, eq 7. This reaction requires that a substantial concentration of Q^{2-} exist at the electrode surface, something that would be true in unbuffered solution but not in buffered solution at neutral pH.

Kinetic Differences between BQ Reduction in Buffered and Unbuffered Aqueous Solution. As shown in Figure 1, in addition to the thermodynamic differences between the reduction of quinones in buffered and unbuffered solutions, there is also very clearly a kinetic difference. The much larger peak-to-peak separations observed in the buffered solution indicates that the reaction, although thermodynamically more favorable, is kinetically much slower in the buffered solutions at neutral pH. It is well-known that the kinetics of quinone reduction are strongly pH-dependent in buffered solution.[1,2] This phenomena can be seen in Figure 5, scans (a) and (b). The solutions are unbuffered, but since the pH is such that $[H^+] > [Q]$, the behavior is the same as that in buffered solutions. Clearly there is a large increase in the peak-to-peak separation going from pH 2 to 3, indicating that the reaction is much slower at pH 3.

Laviron addressed the pH dependence of quinone reduction in a series of papers in which he explored the mathematics of square schemes that have chemical steps at equilibrium.[43−46] This is likely the case for protonation equilibria in aqueous solution, and he applied his analysis specifically to the example of BQ reduction.[39] In general, Laviron showed that when the protonations are at equilibrium, each overall electron transfer in square schemes behaves as a simple electron transfer with an apparent $E°$ that depends on the $E°$'s of each electron-transfer step, the pK_a's and the pH, and an apparent standard heterogeneous electron-transfer rate constant, $k°$, that depends on the $k°$'s of each electron-transfer step, the pK_a's, and the pH. Applying this analysis to the case of BQ reduction, he was able to fit the pH dependence of the apparent $k°$'s with reasonable values for the various parameters.

Qualitatively, one can conclude from Lavirons analysis that at pH's where the overall reaction is moving in a net diagonal direction[47] through the square, the overall rate of the reaction will be slower than that at pH's where the reaction is moving horizontally across the scheme. This is because under these conditions the proton transfer will be shifting the equilibrium potential for the overall reaction by a large amount. In order for the overall reaction to occur at equilibrium, current will need to flow at potentials significantly prior to the $E°$ for the actual electron-transfer step. This requires inherently fast electron-transfer rates. If electron transfer is not inherently fast, and this is generally the case with quinones in aqueous solution, then significant current will not flow until the electrode potential is significantly past the $E°$ for the overall reaction. In effect, the

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[40] AQSH$_2$ pK_a's are from this study. BQ pK_a's at $I = 0.65$: Baxendale, J. H.; Hardy, H. R. *Trans. Faraday Soc.* **1953**, *49*, 1140−4.

[41] The pH and % distributions were calculated using the spreadsheet program described in the following: Fresier, H. *Concepts & Calculations in Analytical Chemistry, A Spreadsheet Approach*; CRC Press: Ann Arbor, MI, 1992; Chapter 4.

[42] Bishop, C. A.; Tong, L. K. J. *J. Am. Chem. Soc.* **1965**, *87*, 501−5.

[43] Laviron, E. *J. Electroanal. Chem.* **1981**, *124*, 1−7.

[44] Laviron, E. *J. Electroanal. Chem.* **1981**, *124*, 9−17.

[45] Laviron, E. *J. Electroanal. Chem.* **1983**, *146*, 1−13.

[46] Laviron, E. *J. Electroanal. Chem.* **1983**, *146*, 15−36.

[47] To clarify, "net diagonal direction" means stepwise e^- transfer, followed by H^+ transfer, or the reverse. The actual diagonal reaction would be a concerted e^-, H^+ transfer reaction, which Laviron's theory does not consider. There is much current interest in such reactions, but we are not aware of any evidence presented so far that they are involved in aqueous quinone redox chemistry.

rapid protonation equilibria further stresses any underlying kinetic limitations to electron transfer, resulting in even less reversible behavior.

The inherent kinetic problem in the buffered solution is actually nicely illustrated by the data in Figure 1. At pH 7.2, the mechanism of BQ reduction in buffered solution is believed to be electron transfer, proton transfer, electron transfer, proton transfer.[48] This means in order for the protonation equilibria to shift the potential, the electron has to be transferred first. The position of the cathodic peak in the CV in the unbuffered solution (Figure 1a) indicates the potential this would occur in aqueous solution in the absence of the buffer. Proton transfer does cause current to flow positive of this value as indicated by the more positive cathodic peak in the buffered solution (Figure 1b), but the potential of this peak is still considerably negative of the $E_{1/2}$ for the CV wave, indicating a significant overpotential for the reduction in the buffered solution.

From the above discussion the electrode reaction should be faster in the unbuffered solution if, under these conditions, the reaction is primarily moving horizontally across the top row of Scheme 2. This is the mechanism implied by eq 1, although it is not required for the equilibrium calculations we have done to be correct. In truth, our experimental results do not address the issue of mechanism directly, but the faster kinetics in the unbuffered solution do support this mechanism. Further insight into this issue can be gained from a more detailed application of Laviron's theory as given in the Supporting Information. Using the standard notation for electrode mechanisms where "E" stands for an electron-transfer step and "C" stands for a chemical step, this analysis supports our contention that the mechanism for quinone reduction in unbuffered neutral water is most likely EEC, with the C step being the base dissociation of Q^{2-}.

Putting All the Pieces Togther. Relevance of This Work to a Comprehensive, "Pan-Solvent", Understanding of Quinone Electrochemistry. Descriptions of quinone redox chemistry are typically divided into two categories: behavior in water, in which the overall reaction is described as 2 e^-, 2 H^+ to give QH_2 (Scheme 1a), and behavior in aprotic organic solvents, in which the overall reaction is described as two 1 e^- transfers to give Q^{2-} (Scheme 1c). However, this work shows that Scheme 1a is not a universal description of quinone electrochemistry in water. In fact, it is only applicable to the special cases when the proton concentration is greater than the quinone concentration or the proton concentration is fixed by addition of a large excess of weak acid and base (the buffer components). The latter creates a situation that is quite different from that with just water plus electrolyte and for which there is typically no direct analogy in aprotic solvents. Therefore, it is not really appropriate to compare the behavior of quinones in aprotic solvents to that in buffered water; the comparison that should be made is between the behavior of quinones in aprotic solvents and the behavior in unbuffered water. When this comparison is made, the redox chemistries are actually quite similar. In both cases the mechanism appears to be primarily EE to form Q^{2-}. Due to the greater acidity of water compared to aprotic solvents, protonation of Q^{2-} does occur in water, but this latter equilibrium only has a minor effect on the overall potential as shown in Figures 4 and 6.

Role of Hydrogen Bonding versus Proton Transfer. There is a general perception that the differences in electrochemistry between quinones in aprotic and those in protic solvents are due to the occurrence of proton-transfer reactions in protic solvents. Certainly, it is commonly recognized among electrochemists that protonation of the 1 e^- product, Q^-, will produce a species that is easier to reduce than the starting quinone, leading to a 2 e^- reaction with potential inversion ($E°$ of $QH/QH^- > E°$ of Q/Q^-).[49] However, as discussed above, protonation of the radical intermediate, Q^-, is unlikely a major pathway in unbuffered neutral water. If one agrees with the argument that the behavior of quinones in aprotic solvents should be compared to their behavior in unbuffered water, then the fundamental difference between the redox behaviors of quinones in aprotic solvents and water is NOT proton transfer. This is because the underlying difference in the redox chemistry, the one that leads to one CV wave versus two, is the potential difference between the two electron-transfer steps. In aprotic solvents this is large enough that two well-defined CV waves are observed. In unbuffered water these values are not inverted, but they are close enough, independent of proton transfer, that the two electron transfers merge into one CV wave.

So why are $E°$ of Q/Q^- and $E°$ of Q^-/Q^{2-} so close in water? In many respects the behavior observed in aprotic solvents is more reasonable since, from electrostatic arguments, it should be harder to add an electron to a species that is already negatively charged. The fact that the $E°$'s are so close in water must mean that Q^{2-} in water is strongly stabilized relative to Q^-. The large dielectric constant and greater polarity of water compared to those of aprotic solvents are certainly part of the explanation. However, as Peover noted 45 years ago when comparing the behavior of quinones in water to that of quinones in acetonitrile: "The outstanding difference in the properties of the two solvents is the capacity of water (and hydroxylic solvents generally) for hydrogen bonding."[50]

Peover's comment was directed at explaining differences in the Q/Q^- redox potential between the two solvents, but it is reasonable to expect that hydrogen bonding would have an even greater effect on the Q^-/Q^{2-} redox potential. In fact, there is abundant experimental evidence to show that this is the case. It has been known for 50 years that addition of water to solutions of quinones in aprotic solvents causes $E°'$ of Q^-/Q^{2-} to move positive.[51-57] $E°'$ of Q/Q^- also moves positive, but by a much smaller amount, so the two $E°'$'s move closer together as the

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(48) This is the mechanism originally proposed by Vetter based on analysis of Tafel plots for BQ/BQH_2 at different pH's: Vetter, K. J. *Z. Elektrochem.* **1952**, *56*, 797−806. Other workers disputed this mechanism; see ref 1 for a summary. However, Laviron (ref 39) re-examined Vetter's data based on his theory and came to the same conclusion as Vetter for neutral pH.

(49) This concept was originally proposed by Hoijtink for aromatic radical anions based on Huckel-type molecular orbital calculations: Hoitjink, G. J.; van Schooten, J.; de Boer, E.; Aalbersberg, W. Y. *Recl. Trav. Chim.* **1954**, *73*, 355−375. It has long been recognized to be true for quinone radical anions as well; see: Peover, M. E. *Electroanal. Chem.* **1967**, *2*, 1−51. Recent high level computations support the conclusion that the QH radical will be an unstable intermediate in the Q to QH_2 conversion in both the gas phase and water: Johnsson Wass, J. R. T.; Ahlberg, E.; Panas, I.; Schiffrin, D. J. *J. Phys. Chem. A* **2006**, *110*, 2005−2020.

(50) Peover, M. E. *J. Chem. Soc.* **1962**, 4540−9.

(51) Wawzonek, S.; Berkey, R.; Blaha, E. W.; Runner, M. E. *J. Electrochem. Soc.* **1956**, *103*, 456−9.

(52) Kolthoff, I. M.; Reddy, T. B. *J. Electrochem. Soc.* **1961**, *108*, 980−5.

(53) Cauquis, G.; Marbach, G. *Bull. Soc. Chim. Fr.* **1971**, 1908−16.

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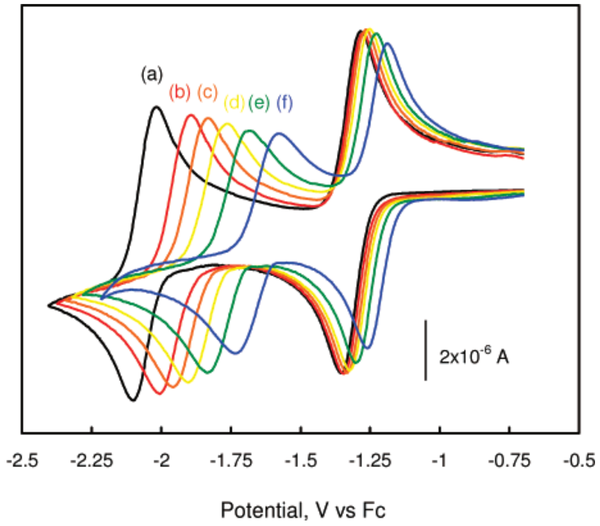

Figure 7. CVs of anthraquinone in 0.1 M NBu_4PF_6/DMF after addition of water: (a) 0% H_2O, (b) 0.5% H_2O, (c) 1% H_2O, (d) 2% H_2O, (e) 4% H_2O, (f) 8% H_2O. 100 mV/s with a Au working electrode.

water content increases. This is shown in Figure 7 for addition of water to a DMF solution of anthraquinone. With even larger additions, the two waves will actually merge.[54,58] In the past, this behavior was often explained by protonation of Q^{2-} by water,[3,50−53,56] although in 1971 Hayano and Fujihira[54] suggested that the positive shift was likely due to hydrogen bonding, and several other workers noted that the observed behavior was not consistent with protonation.[57,58] In an important 1997 paper, Gupta and Linschitz[59] examined the cyclic voltammetry of a number of benzoquinones of different basicities in the presence of a several alcohols of different acidities. They argued, based on pK_a's and solvent effects, that behavior such as that seen in Figure 7, where the second wave shifts positive while remaining reversible, is indeed due to hydrogen bonding and not proton transfer. A number of subsequent studies with different quinones by Gonzalez, Gonzalez and co-workers have lent further credence to this conclusion.[60−63]

The current study also offers support for the hydrogen bond explanation for the shift in the Q^-/Q^{2-} wave seen in Figure 7. The successful fit of the data in Figure 6 shows that even in water, where acid−base reactions would be expected to be the most rapid and the most favorable, protonation of Q^{2-} by water only has a minor effect on the observed redox potential. It certainly cannot explain the large potential shifts observed in Figure 7.

Of course, one could also ask if protonation of Q^{2-} causes only a small shift in potential, how can a relatively weak interaction like a hydrogen bond produce such large shifts? The answer, in part, is that more than one hydrogen bond is clearly involved. Based on the three lone pairs on each oxygen in the dianion, at least six strong-to-moderate strength hydrogen bonds are possible. In several of the studies with alcohols and quinones, the number of associated molecules has been evaluated by analyzing the shift in potential of the second wave with concentration of the hydrogen donor.[59,60,62,63] The number varies depending on the nature and concentration of hydrogen donor and quinone, but up to six ligands have been indicated by this type of analysis.

The ~0.75 V positive shift required to cause the two anthraquinone waves in Figure 7 to overlap corresponds to ~72 kJ of stabilization for Q^{2-} over Q^- or , assuming six hydrogen bonds, −12 kJ per hydrogen bond. Therefore, ignoring entropy effects, the two waves would overlap if, on average, the strength of a hydrogen bond between water and Q^{2-} was 12 kJ larger than a hydrogen bond between water and Q^-. It is difficult to come up with a completely appropriate comparison, but the strength of a water−water hydrogen bond has been determined to be 15.5 kJ, and that of a water-hydroxide hydrogen bond, to be 112 kJ.[64] This corresponds to a 96.5 kJ increase between a water hydrogen bonded to an uncharged oxygen and that to a −1 charged oxygen. Given this, it does not seem unreasonable that the strength of a hydrogen bond between water and Q^{2-} would be at least 12 kJ larger than that of a hydrogen bond between water and Q^-.

Of course, hydrogen bonds are not the only possible source of Q^{2-} stabilization relative to Q^- in water. Another possibility is nonspecific solvation due to the greater polarity and larger dielectric constant of water compared to those of polar aprotic solvents like DMF. The magnitude of this effect can be estimated by using the Born equation which calculates $\Delta G°$ for ion solvation based on only nonspecific electrostatic interactions with the solvent. Following Evans and Hu,[65] the Born equation can be used to calculate $\Delta G°$ of the comproportionation reaction, eq 7, for anthraquinone in the two different solvents. This is directly related to the difference in potential between the two electron-transfer steps, $\Delta E = E°_{Q/Q^-} - E°_{Q^-/Q^{2-}}$. With this logic, simple manipulation of the equations given by Evans and Huo leads to eq 9, in which N_A = Avogadro's number, e_0 = charge on an electron (1.602×10^{-19} C), F = Faraday's constant (96 485 C/mol), e_0 = permittivity of free space (8.854×10^{-12} C V^{-1} m^{-1}), r = apparent radius of the reactant in meters, and D = the dielectric constants of the two solvents. The apparent spherical radius for anthraquinone can be estimated from the molecular weight of anthraquinone assuming a density of 1.25 g/mL.[65] This gives a value of 4.04×10^{-10} m. Plugging in $D_{H_2O} = 78.3$ and $D_{DMF} = 36.7$ into eq 9 gives $\Delta E_{H_2O} - \Delta E_{DMF} = -52$ mV. This indicates that nonspecific electrostatic interactions should also help to bring the two quinone waves closer together in water compared to DMF, but they likely account for only a small fraction of the observed effect.

$$\Delta E_{H_2O} - \Delta E_{DMF} = \frac{N_A e_0^{\,2}}{4\pi F \epsilon_0\, r}\left(\frac{1}{D_{H_2O}} - \frac{1}{D_{DMF}}\right) \qquad (9)$$

Given all of the above, it is reasonable to conclude that the major reason the two quinone $E°$'s are close enough in water that a single voltammetric wave is observed is, as indicated in Scheme 1b, strong hydrogen bonding between the quinone dianion and water molecules. Thus, arguably, the fundamental

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difference between quinone electrochemistry in water and polar, aprotic solvents is not proton transfer but hydrogen bonding.

Conclusions

In summary, this study shows that the redox chemistry of quinones in unbuffered water is both qualitatively and quantitatively described by Scheme 1b, that is, as a 2 e^- reduction to give the strongly hydrogen-bonded quinone dianion, which exists in solution as a thermodynamic mixture of protonation states. This conclusion helps to unify quinone redox chemistry by bridging the apparent gap between the electrochemistry of quinones in nonaqueous solution, where quinones undergo two sequential 1 e^- reductions to give the dianion, and that in buffered aqueous solution where they undergo an overall 2 e^-, 2 H^+ reduction to give the hydroquinone. This study also helps to point out the important role that hydrogen bonding to water undoubtably plays in the aqueous electrochemistry of quinones.

More generally, we believe this work also demonstrates the need to examine the electrochemistry of redox couples with acid−base functionality in unbuffered as well as buffered aqueous solution, in order to come to a full understanding on the role of solvent in the redox chemistry. There has been a historical reluctance to do these types of studies based on the general belief that the results will be difficult to interpret if pH is not controlled. However, this example clearly shows that this is not necessarily the case.

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Supporting Information Available: (1) Derivation of eqs 5 and 6, plus the related equations that include the second base dissociation of Q^{2-}. (2) Mechanism discussion based on a more detailed application of Laviron's theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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