Voltammetry

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Cyclic Voltammetry in the Absence of Excess Supporting Electrolyte Offers Extra Kinetic and Mechanistic Insights: Comproportionation of Anthraquinone and the Anthraquinone Dianion in Acetonitrile**

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Voltammetry is normally performed in the presence of excess supporting electrolyte, which is deliberately added to screen electric fields and to compensate solution resistance. Voltammetric theory is then a simple "diffusion-only" problem. Several situations exist, however, in which kinetic and mechanistic information can be unobtainable or ambiguous under diffusion-only conditions. For example, stepwise two-electron reactions are commonly encountered in electrochemistry [Eqs. (1)–(3)].[1,2]

$$A + e^- \rightleftharpoons B \qquad E^{\ominus}_{f,A/B} \tag{1}$$

$$B + e^- \rightleftharpoons C \qquad E^{\ominus}_{f,B/C} \tag{2}$$

$$A + C \rightleftharpoons 2B \tag{3}$$

Comproportionation between species A and C is thermodynamically favorable when the reduction potential of the second step is more negative than that of the first step ($E^{\ominus}_{f,A/B} > E^{\ominus}_{f,B/C}$). Pioneering work by Andrieux and Savéant[3] has shown that conventional diffusion-only voltammetry is blind to comproportionation when both electron transfers are reversible and the diffusion coefficients of species A, B, and C are equal. Extreme differences of diffusion coefficients are required to distinguish whether or not comproportionation kinetics are significant on an experimental timescale.[4]

One possible approach is to perform the experiments in the presence of a very low concentration of supporting electrolyte (hereafter referred to as "low support"). In this case, unscreened Coulombic attraction or repulsion of the electroactive species may elevate or reduce its transport-controlled current depending on its charge, as observed voltammetrically.[5–7] This technique was introduced for electrochemical mechanism determination by Norton et al.,[8,9] and has been developed more recently by others.[10,11] Under low support, voltammetry varies with comproportionation rate because the electric field causes mass transport to be highly dependent on the charge of the rate-limiting species: the species responsible for a voltammetric process is distinguishable.

Several theories have been developed to account for electrochemistry at low support.[5,6,12–16] Most publications to date have only considered systems at steady state; this was the case for the EE studies (E stands for an electron-transfer step) noted above.[8–11] Work under transient conditions has been done exclusively for the E mechanism.[17] We have developed a simulation system for transient cyclic voltammetry which has been applied successfully to E processes[18,19] and admits extension to any mechanism. The simulation solves the dynamic Nernst–Planck–Poisson equations simultaneously for all chemical species and for potential, subject to a zero-field approximation.[20] Details are provided in the Supporting Information.

A dynamic theory allows study at a range of scan rates, which is good voltammetric practice and allows better determination of uniqueness of mechanistic fit and of kinetic parameters. Additionally, we can simulate finite kinetics and unequal diffusion coefficients. We find the comparison of theory and experiment(below) for the EE case to be excellent, across a range of scan rates, and so believe it is now possible to advocate weakly supported voltammetry as a tool for mechanism determination quantitatively and under much more general circumstances.

We consider the reduction of anthraquinone (AQ) in acetonitrile. Cyclic voltammetry was recorded at various scan rates in a well-supported solution (see the Experimental Section), and as expected two reversible reduction waves were observed.[21] The large separation between the reduction waves suggests that the comproportionation mechanism is thermodynamically viable. The results were compared with two simulations: one assuming no comproportionation and one assuming fast (diffusion-controlled) comproportionation, with the other parameters as in Table 1. Both simulations were in good agreement with experiment, over all scan rates (Figure 1). This is consistent with diffusion-only theory:[3] the simulations are indistinguishable since the diffusion coefficients of AQ, AQ^-, and AQ^{2-} are very similar in acetonitrile. Therefore, no information about the reaction mechanism could be obtained using conventional cyclic voltammetry.

Cyclic voltammograms were then recorded in a solution with a very low concentration of supporting electrolyte

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Table 1: Parameters used for simulations.

Parameter	Value	Reference
α_{AQ/AQ^-}	0.5	
$\alpha_{AQ^-/AQ^{2-}}$	0.5	
D_{AQ}	$2.1\times10^{-9}\,m^2\,s^{-1}$	
D_{AQ^-}	$1.7\times10^{-9}\,m^2\,s^{-1}$	
$D_{AQ^{2-}}$	$1.6\times10^{-9}\,m^2\,s^{-1}$	
D_{TBA^+}	$0.68\times10^{-9}\,m^2\,s^{-1}$	[26]
$D_{ClO_4^-}$	$2.35\times10^{-9}\,m^2\,s^{-1}$	[26]
$\varepsilon_{r,AN}$	37.5	[27]
k^0_{AQ/AQ^-}	$\geq 0.001\,m\,s^{-1}$	
$k^0_{AQ^-/AQ^{2-}}$	$\geq 0.001\,m\,s^{-1}$	
k_{comp}	0 or $>10^5\,m^3\,mol^{-1}\,s^{-1}$	

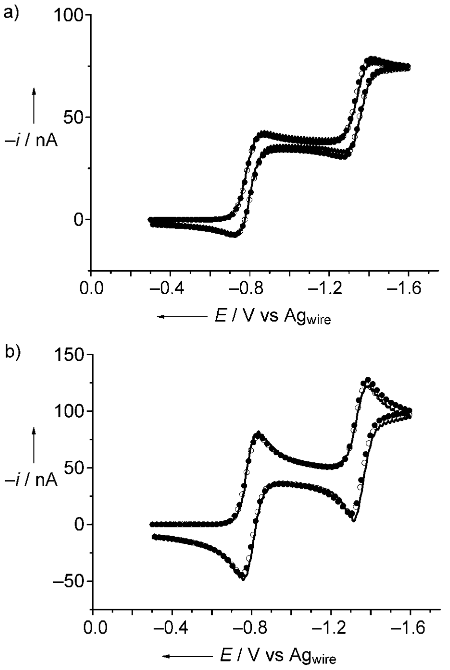

Figure 1. Comparison of experiment (——) and simulation (●: $k_{comp}=0\,m^3\,mol^{-1}\,s^{-1}$; ○: $k_{comp}>10^5\,m^3\,mol^{-1}\,s^{-1}$) at high support (1.25 mM AQ with 62.5 mM TBAP (tetra-*n*-butylammonium perchlorate)). Scan rates: a) $\nu=50\,mV\,s^{-1}$, b) $\nu=1000\,mV\,s^{-1}$.

(Experimental Section). The results with high and low support are compared in Figure 2. Under low support, each wave broadens due to uncompensated solution resistance, as expected;[18] additionally, the separation between the reduction waves increases due to ohmic potential drop and changes to the ionic strength of the solution. Since activity coefficients are not well known for this system, both reduction potentials are treated as "fitting parameters"; in practice the first wave is almost unchanged while the second wave is shifted by approximately −200 mV.

A considerable decrease in the magnitude of the second reduction wave is observed at low support. In the case with full support, both waves are of approximately equal size. The cyclic voltammograms were again compared with two simulations, one with fast comproportionation ($k_{comp}>10^5\,m^3\,mol^{-1}\,s^{-1}$) and one without comproportionation, as presented at Figure 3. It is evident that the simulation assuming fast comproportionation is in good agreement with experiment, but the simulation without comproportionation is not.

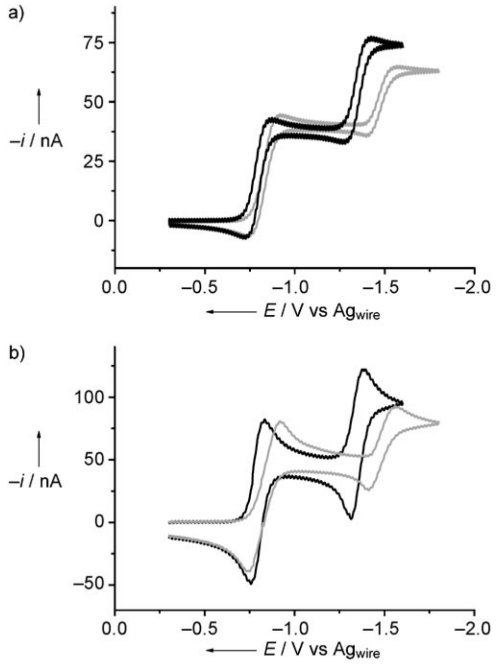

Figure 2. Comparison of experimental cyclic voltammetry at high (black line; 1.25 mM AQ with 62.5 mM TBAP) and low (gray line; 1.25 mM AQ with 0.7 mM TBAP) support. Scan rates: a) $\nu=50\,mV\,s^{-1}$, b) $\nu=1000\,mV\,s^{-1}$.

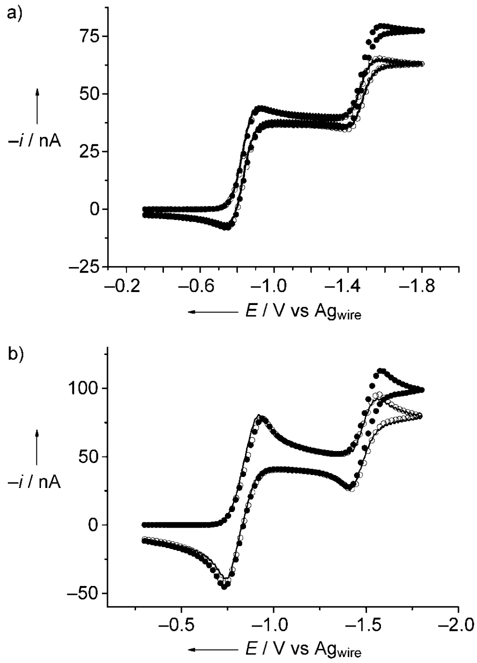

Figure 3. Comparison of experiment (——) and simulation (●: $k_{comp}=0\,m^3\,mol^{-1}\,s^{-1}$; ○: $k_{comp}>10^5\,m^3\,mol^{-1}\,s^{-1}$) at low support (1.25 mM AQ with 0.7 mM TBAP). Scan rates: a) $\nu=50\,mV\,s^{-1}$, b) $\nu=1000\,mV\,s^{-1}$.

We can explain the difference between the two simulations by examining concentration profiles after the second reduction wave for the diffusion-only case, which differ considerably even though the voltammograms are very similar (Figure 4). In the absence of comproportionation, the second reduction wave is rate-limited by diffusion of neutral AQ to the electrode surface, which gains two electrons at the electrode almost concertedly. With fast comproportionation, however, AQ is excluded from a reaction layer close to the electrode due to its fast reaction with the AQ^{2-} product. The second reduction wave is therefore rate-limited by diffusion of AQ^{-} to the electrode.

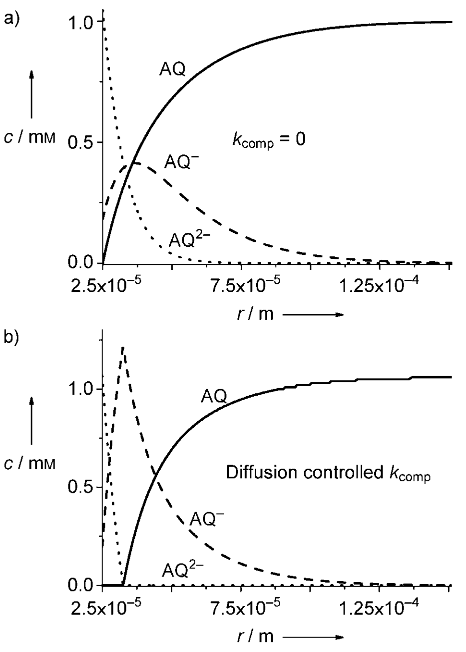

Figure 4. Simulated concentration profiles after the second reduction wave at high support (1.25 mM AQ with 62.5 mM TBAP).

As the concentration of supporting electrolyte decreases, an electric field arises close to the electrode, due to the charge introduced into the solution by electrolysis. The transport-controlled current is determined by the flux of an electroactive species to the electrode, which at low support may be altered depending on its charge.[6,7] In the absence of comproportionation, transport of neutral AQ is rate-limiting, which is unaffected by the electric field and so the current is unchanged. If comproportionation is fast, however, transport of AQ^{-} is rate-limiting, which is reduced by repulsion from the negatively charged reaction layer, and so the current is reduced. This is exactly what is observed experimentally; the good agreement between simulation assuming comproportion and experiment, at low support, demonstrates that the comproportionation reaction of AQ with its dianion is very fast ($k_{comp} > 10^{5}\,m^{3}\,mol^{-1}\,s^{-1}$) in acetonitrile. A fuller, more quantitative discussion is available in the Supporting Information.

In many cases, cyclic voltammetry under conventional fully supported conditions cannot unambiguously determine the electrochemical mechanism, as for the case studied here. In contrast, under weakly supported conditions the distinction is often unequivocal. It has been shown experimentally that comproportionation of anthraquinone in acetonitrile is fast. At low support, the contribution of migration to the current makes the gross difference between the charges of species experimentally much clearer than the subtle differences between diffusion coefficients. We have shown simulation and experiment to agree for transient voltammetry at a range of scan rates, and so we anticipate electrochemistry in solutions of variable ionic strength to become widely used in order to enhance the scope of voltammetry for detecting mechanistic pathways and their kinetic and thermodynamic parameters.

Experimental Section

Chemicals: Acetonitrile solvent (HPLC grade, Fisher Scientific), anthraquinone (AQ, $>97\,\%$, Strem Chemicals), tetra-*n*-butylammonium perchlorate (TBAP, $\geq 99\,\%$, Fluka). A three-electrode cell was used: the working electrode was a 25 μm radius mercury hemispherical electrode, prepared according to the literature procedure.[22,23] A silver wire was used as a reference electrode. All experimental measurements were recorded using a PG-STAT12 potentiostat (Autolab, Netherlands). All solutions were thoroughly degassed with N_2 before each experiment, and an inert atmosphere was maintained during the experiments. The diffusion coefficients of AQ, AQ^{-}, and AQ^{2-} were calculated by double and quadruple potential step chronoamperometry.[24,25] All solutions contained 1.25 mM AQ in acetonitrile; 62.5 or 0.7 mM TBAP was added for high and low support, respectively. Scan rates of 50, 100, 200, 500, and 1000 $mV\,s^{-1}$ were used.

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