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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1 Theory Section

All symbols used in this paper are defined in Tables 1 and 2.

1.1 Reaction Mechanism

We consider a solution containing an electroactive species, A, which is capable of undergoing two, reversible, single electron reductions, forming species B and C respectively. These heterogeneous processes occur at a hemispherical electrode and imply an additional homogeneous comproportionation/disproportionation equilibrium

\[
A^{z_A} + e^- \rightleftharpoons B^{z_A-1} \quad E_{f,A/B}^{\circ}
\]

\[
B^{z_A-1} + e^- \rightleftharpoons C^{z_A-2} \quad E_{f,B/C}^{\circ}
\]

\[
A^{z_A} + C^{z_A-2} \rightleftharpoons 2B^{z_A-1} \quad K_{eqm} = \frac{k_{comp}}{k_{disp}}
\]

Species A is accompanied by a counterion, \(Y^{-z_A}\), and the solution is supported by a monovalent 1:1 inert salt, \(M^+X^-\). In this paper, \(z_A\) is relatively small and ion pairing is assumed to be completely absent in solution. The equilibrium constant for comproportionation, \(K_{eqm}\), varies as a function of the formal potentials for both of the heterogeneous steps, \(E_{f,A/B}^{\circ}\) and \(E_{f,B/C}^{\circ}\)

\[
K_{eqm} = \exp\left(\frac{F}{RT}(E_{f,A/B}^{\circ} - E_{f,B/C}^{\circ})\right)
\]

We examine the case \(E_{f,A/B}^{\circ} \gg E_{f,B/C}^{\circ}\): thermodynamically, the comproportionation reaction is favoured.
1.2 Mathematical Formulation

The concentration of each species varies in space and time according to the mass transport equations

\[
\begin{align*}
\frac{\partial C_A}{\partial t} &= D_A \left( \frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) + D_A z_A \left( \frac{\partial C_A \partial \phi}{\partial r} + C_A \frac{\partial^2 \phi}{\partial r^2} + C_A \frac{2 \partial \phi}{r \partial r} \right) - k_{\text{comp}} C_A C_C + k_{\text{disp}} C_B^2 \\
\frac{\partial C_B}{\partial t} &= D_B \left( \frac{\partial^2 C_B}{\partial r^2} + \frac{2}{r} \frac{\partial C_B}{\partial r} \right) + D_B (z_A - 1) \left( \frac{\partial C_B \partial \phi}{\partial r} + C_B \frac{\partial^2 \phi}{\partial r^2} + C_B \frac{2 \partial \phi}{r \partial r} \right) + 2k_{\text{comp}} C_A C_C - 2k_{\text{disp}} C_B^2 \\
\frac{\partial C_C}{\partial t} &= D_C \left( \frac{\partial^2 C_C}{\partial r^2} + \frac{2}{r} \frac{\partial C_C}{\partial r} \right) + D_C (z_A - 1) \left( \frac{\partial C_C \partial \phi}{\partial r} + C_C \frac{\partial^2 \phi}{\partial r^2} + C_C \frac{2 \partial \phi}{r \partial r} \right) - k_{\text{comp}} C_A C_C + k_{\text{disp}} C_B^2 \\
\frac{\partial C_M}{\partial t} &= D_M \left( \frac{\partial^2 C_M}{\partial r^2} + \frac{2}{r} \frac{\partial C_M}{\partial r} \right) + D_M z_M \left( \frac{\partial C_M \partial \phi}{\partial r} + C_M \frac{\partial^2 \phi}{\partial r^2} + C_M \frac{2 \partial \phi}{r \partial r} \right) \\
\frac{\partial C_X}{\partial t} &= D_X \left( \frac{\partial^2 C_X}{\partial r^2} + \frac{2}{r} \frac{\partial C_X}{\partial r} \right) + D_X z_X \left( \frac{\partial C_X \partial \phi}{\partial r} + C_X \frac{\partial^2 \phi}{\partial r^2} + C_X \frac{2 \partial \phi}{r \partial r} \right) \\
\frac{\partial C_Y}{\partial t} &= D_Y \left( \frac{\partial^2 C_Y}{\partial r^2} + \frac{2}{r} \frac{\partial C_Y}{\partial r} \right) + D_Y (-z_A) \left( \frac{\partial C_Y \partial \phi}{\partial r} + C_Y \frac{\partial^2 \phi}{\partial r^2} + C_Y \frac{2 \partial \phi}{r \partial r} \right)
\end{align*}
\]

Each equation is composed of three terms. The first quantifies diffusion, the second migration, and the third quantifies the homogeneous chemical reaction. Since species M, X and Y are chemically inert, the latter term in the respective mass transport equations is equal to zero. This system of 6 independent equations contains 7 unknowns: the concentration for each of the 6 species and an additional term for the potential. Consequently, the description of the problem is incomplete and a further relationship must be introduced. For this purpose, we invoke the Poisson equation

\[
\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = -\frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i 
\]

\[
= -\frac{F}{\epsilon_s \epsilon_0} [z_A C_A + (z_A - 1) C_B + (z_A - 2) C_C + z_M C_M + z_X C_X - z_A C_Y]
\]
This relationship follows from Maxwell’s equations; however, many workers have attempted to simplify the problem by invoking, instead, the electroneutrality approximation

\[ \sum_i z_i C_i = 0 \]  

(6)

In the experience of the present authors, this relationship, although well obeyed over the majority of simulation space, does not significantly increase simulation efficiency. It is therefore regarded in the presented work as an unnecessary, additional, approximation.

The mass transport equations and the Poisson equation can be solved in the region \( r_e \leq r \leq \infty \) subject to a set of boundary conditions. However, the problem is considerably simplified, without affecting the result, by defining a finite upper limit, \( r = r_{\text{max}} \). In this paper

\[ r_{\text{max}} = r_e + 6\sqrt{D_{\text{max}}t} \]  

(7)

where \( D_{\text{max}} \) is the diffusion coefficient of the fastest moving species in solution.\(^1\)

Beyond the point \( r = r_{\text{max}} \), all concentrations are temporally invariant and the flux of each species at can be set equal to zero at all times. In addition, it follows, from the Poisson equation combined with electroneutrality, that at \( r = r_{\text{max}} \)

\[ \frac{\partial^2 \phi}{\partial r^2} \bigg|_{r=r_{\text{max}}} + 2 \frac{\partial \phi}{r \partial r} \bigg|_{r=r_{\text{max}}} = 0 \]  

(8)

Integrating this equation subject to the condition \( \theta \to 0 \) as \( r \to \infty \) leads to a boundary condition for the potential at \( r = r_{\text{max}} \)

\[ \frac{\partial \phi}{\partial r} \bigg|_{r=r_{\text{max}}} = -\frac{\phi}{r} \]  

(9)

The complete set of boundary conditions for the problem are
\[ t = 0, \text{ all } r \]

\[ C_A = C_A^* \quad C_B = 0 \quad C_C = 0 \]

\[ C_Y = C_A^* \quad C_M = C_M^* \quad C_X = C_M^* \]

\[ \phi = 0 \]

\[ t > 0, \quad r = r_{\text{max}} \]

\[ \frac{\partial C_A}{\partial r} \bigg|_{r=r_{\text{max}}} = 0 \quad \frac{\partial C_B}{\partial r} \bigg|_{r=r_{\text{max}}} = 0 \quad \frac{\partial C_C}{\partial r} \bigg|_{r=r_{\text{max}}} = 0 \]

\[ \frac{\partial C_Y}{\partial r} \bigg|_{r=r_{\text{max}}} = 0 \quad \frac{\partial C_M}{\partial r} \bigg|_{r=r_{\text{max}}} = 0 \quad \frac{\partial C_X}{\partial r} \bigg|_{r=r_{\text{max}}} = 0 \]

\[ \frac{\partial \phi}{\partial r} \bigg|_{r=r_{\text{max}}} = -\frac{\phi}{r} \]

\[ t > 0, \quad r = r_{e} \]

\[ D_A \frac{\partial C_A}{\partial r} \bigg|_{r=r_{e}} = k_{0}^{0} A/B C_A,0 \exp \left( -\alpha_{A/B} \frac{F(E_{\text{app}} - E_{F_{A/B}} - \phi_{\text{PET}})}{RT} \right) \]

\[ -k_{0}^{0} A/B C_B,0 \exp \left( (1 - \alpha_{A/B}) \frac{F(E_{\text{app}} - E_{F_{A/B}} - \phi_{\text{PET}})}{RT} \right) \]

\[ D_B \frac{\partial C_B}{\partial r} \bigg|_{r=r_{e}} = -D_A \frac{\partial C_A}{\partial r} \bigg|_{r=r_{e}} - D_C \frac{\partial C_C}{\partial r} \bigg|_{r=r_{e}} \]

\[ D_C \frac{\partial C_C}{\partial r} \bigg|_{r=r_{e}} = -k_{0}^{0} B/C C_B,0 \exp \left( -\alpha_{B/C} \frac{F(E_{\text{app}} - E_{F_{B/C}} - \phi_{\text{PET}})}{RT} \right) \]

\[ +k_{0}^{0} B/C C_C,0 \exp \left( (1 - \alpha_{B/C}) \frac{F(E_{\text{app}} - E_{F_{B/C}} - \phi_{\text{PET}})}{RT} \right) \]

\[ D_M \frac{\partial C_M}{\partial r} \bigg|_{r=r_{e}} = 0 \]

\[ D_X \frac{\partial C_X}{\partial r} \bigg|_{r=r_{e}} = 0 \]

\[ D_Y \frac{\partial C_Y}{\partial r} \bigg|_{r=r_{e}} = 0 \]

The boundary condition at \( r = r_{e} \) invokes the ‘zero-field approximation’ which states that the double layer at the electrode surface is negligible in extent compared to the diffusion layer, such that the charge on the electrode is fully compensated at \( r \approx r_{e} \). This point is called the ‘plane of electron transfer’, PET. It follows from Gauss’s law that

\[ \frac{\partial \phi}{\partial r} \bigg|_{r=r_{e}} = 0 \quad (10) \]

For cyclic voltammetry, the applied potential, \( E_{\text{app}} \), varies as a function of time, \( t \), according to

\[ E_{\text{app}} = | - vt + E_{\text{start}} - E_{\text{vertex}} | + E_{\text{vertex}} \quad (11) \]
where $E_{\text{start}}$ and $E_{\text{vertex}}$ are the starting and vertex potentials respectively.

The flux at the surface of the electrode, $j$, is calculated using

$$ j = 2D_A \frac{\partial C_A}{\partial r} \bigg|_{r=r_u} + D_B \frac{\partial C_B}{\partial r} \bigg|_{r=r_u} $$

which may be related to the current, $i$

$$ i = -2\pi F r_e^2 j $$

### 1.3 Numerical Methods

The problem is readily formulated in terms of a conventional set of normalised parameters, defined in Table 2. This procedure reduces the number of solutions by amalgamating parameters that act as scaling factors into parameters that do not. The problem is discretised using the fully implicit finite difference method. The resulting nonlinear equations are solved using the Newton-Raphson method and the Thomas algorithm.²

It is known³ that when $K_{\text{comp}}$ is large, a singularity in the concentration gradient of species B exists at a time-dependent point $R_B$. It is therefore necessary to constructed a spatial mesh of high density close to the electrode surface and close to $R_B$. This can be achieved either by using a mesh that is uniformly dense³ or, more efficiently, by using a temporally dynamic mesh that adapts to changes in the concentration profile at each timestep.⁴⁻⁶ In the method of Amatore et al., the dynamically adaptive gridding techniques could handle any mechanism. In so doing, the authors sacrificed computational efficiency in favour of mechanistic generality. In the simulation used for this paper, a dynamically adaptive grid is used that is specifically tailored to the EE reaction, with comproportionation. The singularity in species B is only considered when $R_B > 1.1$. When $R_B < 1.1$, the mesh density close to the electrode is sufficient to resolve
the singularity caused by species B. Linear interpolations are used to calculate concentration profiles at successive timesteps. The variation in grid density during the voltammogram, when $K_{\text{comp}}$ is large, is shown in figure 1. The discretization is quantitatively expressed as

\[
R_0 = 0
\]

\[
R_j < \frac{R_B}{2} \quad R_j = R_{j-1} + \gamma_R (H(R_s - R_j)R_s + H(R_j - R_s)R_{j-1} - 1)
\]

\[
\frac{R_B}{2} < R_j < R_B \quad R_j = R_B - (R_B - R_{j-1} + \gamma_R (H(R_s - R_j + R_B)R_s + H(R_j + R_B - R_s)(R_B - R_{j-1}) - 1)
\]

\[
R_j > R_B \quad R_j = R_B + (R_{j-1} - R_B + \gamma_R (H(R_s - R_j - R_B)R_s + H(R_j - R_B - R_s)(R_{j-1} - R_B) - 1)
\]

where $H(x)$ is the Heaviside step function. The parameters are converged to yield $< 1\%$ error ($\gamma_R = 1 \times 10^{-2}$ and $R_s = 2 \times 10^{-3}$). The mesh density is considerably higher than that used in simple ‘diffusion only’ studies$^{7-9}$ owing to the extremely tight coupling between the electric field and the concentration profiles of the ionic species.$^{10,11}$ All simulations were programmed in C++ and run on a desktop computer (Intel Core2 Quad 2.4 GHz, 2 GB RAM), with running times of 30-60 minutes per voltammogram being typical.

1.4 Theoretical Results and Discussion

1.4.1 Preliminaries

The mechanism considered varies as a function of several parameters. Discussions in this section are based on a system in which $D_B' = D_C' = 1$, $z_A = 0$, $z_B = -1$, $z_C = -2$, $R_e = 2660$ and the electrode kinetics are reversible. The value of $R_e$ is derived from $C_A^* = 1$ mM, $r_e = 25$ $\mu$m and $\epsilon_s = 37.5$, which correspond to the experiments in acetonitrile considered in the experimental section.$^{12}$
Figure 2 shows schematic concentration profiles for which $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$ at the second peak. Trivially, when $K_{\text{comp}} = 0$, species A travels towards the electrode from bulk solution while species C travels away. Species B, formed in the first wave, has remained very close to the electrode and, consequently, is almost depleted at the second peak. The concentration profile when $K_{\text{comp}} = 10^8$ is more complicated. As before, during the second wave, all 3 electroactive species are present in solution. Species A travels towards the electrode from bulk solution while species C travels away. At an intermediate point in solution, a homogeneous comproportionation reaction occurs between species A and C leading to a maximum in the concentration of species B.

The comproportionation can be studied using cyclic voltammetry. During the second wave of the forward sweep, all three electroactive species (A, B and C) are present in appreciable quantities close to the electrode surface. It follows that the peak current for this wave ($J_{\text{peak2}}$) is the most sensitive measure of the rate constant, $K_{\text{comp}}$. As is conventional, this current is quoted relative to a baseline derived from the forward wave of the corresponding one electron process. This procedure is illustrated schematically in figure 3.

1.4.2 Effect of $c_{\text{sup}}$

Figure 4 shows $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of $c_{\text{sup}}$ and $K_{\text{comp}}$. When $c_{\text{sup}}$ is high, the ionic strength is sufficiently high at every point in solution to suppress potential gradients. In this region, migration does not occur and the voltammetry is purely diffusional. As explained in the introduction, the effects of $K_{\text{comp}}$ are not voltammetrically distinguishable under diffusion only conditions. This manifests in figure 4, as $J_{\text{peak2}} - J_{\text{baseline}}$ is invariant with $K_{\text{comp}}$ when $c_{\text{sup}}$ is high. Additionally, it is known that when $D'_B$ and $D'_C$ both close to unity, the value
of $K_{\text{comp}}$, though experimentally obtainable using voltammetry, is not unambiguous.\textsuperscript{14} As $c_{\text{sup}}$ decreases, the ionic strength in solution decreases and the potential gradient close to the electrode increases. Migration makes a progressively more significant contribution to mass transport. In every case, the current is given by:

$$J = D'_B \left( \frac{\partial c_B}{\partial R} \right)_0 + 2 \left( \frac{\partial c_A}{\partial R} \right)_0$$

(14)

When $\sigma = 10^3$, the timescale of the experiment is short and, during the second wave, $B$ is present in appreciable quantities close to the surface of the electrode when $K_{\text{comp}}$ large \textit{and} when $K_{\text{comp}}$ is small. Therefore, in both situations, as the value of $c_{\text{sup}}$ decreases the current decreases. When $c_{\text{sup}}$ is small, the current increases with decreasing $K_{\text{comp}}$. This occurs because the term in species $B$ is more important for the current when $K_{\text{comp}}$ is large, due to the higher concentration of species $B$ close to the electrode. Lower values of $c_{\text{sup}}$ are required to reach the self support limit as the scan rate increases. The ions of the supporting electrolyte move to nullify the effect of the potential gradient close to the electrode. As the scan rate decreases, the time over which the ions can adapt to a given potential at the electrode increases and the extent of this shielding effect becomes more significant.

When $\sigma = 10^{-3}$ and $K_{\text{comp}}$ is small, species $B$ is almost completely depleted and this contribution to the flux is negligible. The flux is given solely in terms of the uncharged species, $A$. Since $A$ is uncharged, its mass transport is independent of potential gradients in solution. As $c_{\text{sup}}$ decreases, $J_{\text{peak2}} - J_{\text{baseline}}$ is constant. In contrast, when $K_{\text{comp}}$ is large species $A$ is almost completely depleted close to the electrode and this contribution to the flux is negligible. The flux is given solely in terms of the charged species, $B$. Since $B$ is negatively charged, it is repelled by the negative charge at the surface of the electrode. As $c_{\text{sup}}$ decreases, the flux
of species B at the electrode surface, and \( J_{\text{peak2}} - J_{\text{baseline}} \), decreases. At very low values of \( c_{\text{sup}} \), the system begins to tend towards a limit in which the ionic strength of the solution varies as a function of only the electroactive species present in solution and its counter ion and products, and hence is independent of \( c_{\text{sup}} \). This is called the limit of ‘self support’\(^\text{15}\). The comproportionation reaction is most effectively studied at, or near, steady state because the charge on the ions close to the electrode changes with \( K_{\text{comp}} \) and leads to significant changes in the voltammetry at low support when migration is a significant form of mass transport.

1.4.3 Effect of \( D'_{\text{sup}} \)

Figure 5 shows \( J_{\text{peak2}} - J_{\text{baseline}} \) as a function of \( D'_{\text{sup}} \) (\( = D'_M = D'_X \)) and \( K_{\text{comp}} \). The surface is drawn for a situation in which \( c_{\text{sup}} = 1 \). This value represents a compromise between a support ratio low enough to allow comproportionation to be observed while allowing the effect of changing \( D'_{\text{sup}} \) to be probed. As explained above, \( J_{\text{peak2}} - J_{\text{baseline}} \) decreases as \( K_{\text{comp}} \) increases. As \( D'_{\text{sup}} \) increases, the ions of the supporting electrolyte can move more quickly and so are more effective at maintaining the electroneutrality in the solution: the proportion of migration that must occur from the electroactive species is smaller. As the scan rate increases, the time over which the ions can adapt increases and the rate at which the ions move becomes less significant. Therefore, when \( \sigma = 10^{-3} \), the voltammetry is insensitive to \( D'_{\text{sup}} \); in contrast, when \( \sigma = 10^3 \) the value of the value of \( J_{\text{peak2}} - J_{\text{baseline}} \) tends towards the limit of full support as \( D'_{\text{sup}} \) increases.

1.4.4 Effect of \( z_A \)

As explained in section 1.4.2, when \( z_A = 0 \), the presence of comproportionation is most easily measured at low scan rates and low support ratios. This conclusion is expected to hold in
other situations when \( z_A \neq 0 \). Figure 6 shows \( J_{\text{peak2}} - J_{\text{baseline}} \) as a function of \( c_{\text{sup}} \) and \( K_{\text{comp}} \). The surface is redrawn for different values of \( z_A \); the case for which \( z_A = 0 \) has already been considered in section 1.4.2. Since both heterogeneous processes are one electron transfers, the charges of the other species follow directly from \( z_A \). In each case, the charge on species A is balanced by a counterion of equal but opposite charge. The ionic strength of the solution, for a given \( c_{\text{sup}} \), changes between the surfaces for \( z_A \); however, it is still possible to identify meaningful trends in the \( z_A \) values.

In each case, when \( K_{\text{comp}} \) is close to zero, the value of \( J_{\text{peak2}} - J_{\text{baseline}} \) is determined solely by the flux of species A, from eqn 14. As \( c_{\text{sup}} \) decreases, the mass transport of species A becomes increasingly dictated by the potential gradient at the electrode surface. The reaction considered is a reduction and the electrode is negatively charged. Therefore, when \( z_A < 0 \), negative migration occurs and the value of \( J_{\text{peak2}} - J_{\text{baseline}} \) decreases with \( c_{\text{sup}} \); in contrast, when \( z_A > 0 \), positive migration occurs and the value of \( J_{\text{peak2}} - J_{\text{baseline}} \) increases with \( c_{\text{sup}} \). As pointed out in section 1.4.2, when \( z_A = 0 \), migration does not occur and the value of \( J_{\text{peak2}} - J_{\text{baseline}} \) does not vary with \( c_{\text{sup}} \).

When \( z_A = -1 \) and \( K_{\text{comp}} \) is very large, both species A and B are negatively charged and undergo negative migration close to the surface of the electrode. The difference between \( K_{\text{comp}} = 0 \) and \( K_{\text{comp}} = 10^8 \) is relatively small because each case, the flux determining species is negatively charged and mass transport is affected by negative migration.

When \( z_A = 1 \) and \( K_{\text{comp}} \) is very large, species B is neutral and is not affected by migration close the electrode surface. The difference between \( K_{\text{comp}} = 0 \) and \( K_{\text{comp}} = 10^8 \) is very large because in the former case, mass transport is affected by positive migration while, in the latter, mass transport is unaffected by migration. In this situation, it is even possible to
voltammetrically distinguish a wide range of intermediate values of $K_{\text{comp}}$, between $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$. The range lies approximately between $K_{\text{comp}} = 10^{-4}$ and $K_{\text{comp}} = 10^4$.

When $z_A = 2$ or 3, and $K_{\text{comp}}$ is very large, species B is positively charged and is affected by positive migration towards the electrode surface. The difference between $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$ is small because, in both cases, mass transport is affected by positive migration. The difference is less when $z_A = 3$ because the relative difference in charge between species A and B is lower.
2 Analysis of diffusion-only steady-state currents for comproportionation

In this section it is shown analytically that, for a hemisphere in fully supported media, the steady state $2e^-$ current when comproportionation is absent is equal to that when comproportionation is diffusional controlled, regardless of the values of $D_A$, $D_B$ and $D_C$.

The steady state $2e^-$ current in the absence of comproportionation can be trivially derived since $J_{ss} = 2$ for a $2e^-$ process.

\[ i = -\frac{FAD_A C_A^* J}{r_e} = -\frac{2FAD_A C_A^*}{r_e} \]  

(15)

The mechanism, in the presence of comproportionation, is

A + e$^- \rightleftharpoons$ B \hspace{1cm} (16)

B + e$^- \rightleftharpoons$ C \hspace{1cm} (17)

A + C \rightleftharpoons 2B \hspace{1cm} (18)

The corresponding concentration profile is shown schematically in figure 2. There is a reaction front, $r_{\text{front}}$, below which species A does not exist and above which species C does not exist.

The problem is solved in two parts: the first for $r \leq r_{\text{front}}$ and the second for $r \geq r_{\text{front}}$. The species names are given the subscripts “L” and “U” in the respective parts of the problem.

2.1 Inside reaction layer

The mass transport equations are

\[ C_{A,L} = 0 \]  

(19)
\[ \begin{align*}
D_B \left( \frac{\partial^2 C_{B,L}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{B,L}}{\partial r} \right) &= 0 \quad (20) \\
D_C \left( \frac{\partial^2 C_{C,L}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{C,L}}{\partial r} \right) &= 0 \quad (21)
\end{align*} \]

Integration of these equations leads to

\[ \begin{align*}
C_{A,L} &= 0 \quad (23) \\
C_{B,L} &= \frac{p_{B,L}}{r} + q_{B,L} \quad (24) \\
C_{C,L} &= \frac{p_{C,L}}{r} + q_{C,L} \quad (25)
\end{align*} \]

Where \( p_{B,L}, p_{C,L}, q_{B,L}, q_{C,L} \) are constants of integration. When \( r = r_e, C_{B,L} = 0 \). Therefore

\[ p_{B,L} + q_{B,L} = 0 \quad (27) \]

When \( r = r_e, \frac{D_C}{D_A} \nabla C_{C,L} = \frac{D_C}{D_B} \nabla C_{B,L} \). Therefore

\[ -\frac{D_C}{D_B} = \frac{p_{B,L}}{p_{C,L}} \quad (28) \]

When \( r = r_{\text{front}}, C_{C,L} = 0 \). Therefore

\[ \frac{p_{C,L}}{r_{\text{front}}} + q_{C,L} = 0 \quad (29) \]

### 2.2 Outside reaction layer

The mass transport equations are

\[ \begin{align*}
D_A \left( \frac{\partial^2 C_{A,U}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{A,U}}{\partial r} \right) &= 0 \quad (30)
\end{align*} \]
\[ D_B \left( \frac{\partial^2 C_{B,U}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{B,U}}{\partial r} \right) = 0 \]  
\[ C_{C,U} = 0 \]
\[ C_{C,U} = 0 \]  
(31)  
(32)  
(33)

Integration of these equations leads to

\[ C_{A,U} = \frac{p_{A,U}}{r} + q_{A,U} \]  
\[ C_{B,U} = \frac{p_{B,U}}{r} + q_{B,U} \]  
\[ C_{C,U} = 0 \]  
(34)  
(35)  
(36)

When \( r = r_{\text{front}} \), \( C_{A,U} = 0 \). Therefore

\[ \frac{p_{A,U}}{r_{\text{front}}} + q_{A,U} = 0 \]  
(38)

When \( r = r_{\text{front}} \), \( \nabla C_{A,U} = \frac{D_C}{D_A} \nabla C_{C,L} \). Therefore

\[ -\frac{p_{A,U}}{p_{C,L}} = \frac{D_C}{D_A} \]  
(39)

When \( r = r_{\text{front}} \), \( \frac{D_B}{D_A} \nabla C_{B,L} - \frac{D_B}{D_A} \nabla C_{B,U} = 2\nabla C_{A,U} \). Therefore

\[ \frac{D_B}{D_A} C_{B,L} - \frac{D_B}{D_A} C_{B,U} = 2p_{A,U} \]  
(40)

When \( r \to \infty \), \( C_{A,U} = C_{A}^* \). Therefore

\[ q_{A,U} = C_{A}^* \]  
(41)

When \( r \to \infty \), \( C_{B,U} = 0 \). Therefore

\[ q_{B,U} = 0 \]  
(42)
From this information it is possible to show that

\[ p_{B,L} = -\frac{D_A}{D_B} r_{\text{front}} \]  
(43)

\[ q_{B,L} = \frac{D_A}{D_B} r_{\text{front}} \]  
(44)

\[ p_{C,L} = \frac{D_A}{D_C} r_{\text{front}} \]  
(45)

\[ q_{C,L} = -\frac{D_A}{D_C} \]  
(46)

\[ p_{A,U} = -r_{\text{front}} \]  
(47)

\[ q_{A,U} = C^*_A \]  
(48)

\[ p_{B,U} = \frac{D_A}{D_B} r_{\text{front}} \]  
(49)

\[ q_{B,U} = 0 \]  
(50)

The current is given by

\[ i = -FAj \]  
(52)

\[ i = -FA \left( 2\nabla C_{A,L} + \frac{D_B}{D_A} \nabla C_{B,L} \right) \]  
(53)

\[ i = -FAD_A C^*_A r_{\text{front}} \]  
(54)

When \( r = r_{\text{front}} \), \( C_{B,U} = C_{B,L} \). It follows, from eqns 24 and 35 that

\[ r_{\text{front}} = 2r_e \]  
(55)

Therefore

\[ i = \frac{-2FAD_A C^*_A}{r_e} \]  
(56)

This is the same result as in the absence of comproportionation.
References


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{A/B}$</td>
<td>Transfer coefficient of A/B redox couple / unitless</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Concentration of species A / mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_{i,0}$</td>
<td>Surface concentration of species A / mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_i^*$</td>
<td>Bulk concentration of species A / mol m$^{-3}$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusion coefficient of species A / m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>Permittivity of free space (= 8.85 × 10$^{-12}$) / Fm$^{-1}$</td>
</tr>
<tr>
<td>$\epsilon_s$</td>
<td>Relative permittivity / unitless</td>
</tr>
<tr>
<td>$E_{\text{app}}$</td>
<td>Applied potential / V</td>
</tr>
<tr>
<td>$E_{f,A/B}^\circ$</td>
<td>Formal reduction potential of A/B redox couple / V vs. SCE</td>
</tr>
<tr>
<td>$i$</td>
<td>Current / A</td>
</tr>
<tr>
<td>$j$</td>
<td>Flux / mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{A/B}^0$</td>
<td>Electrochemical rate constant of A/B redox couple / m s$^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{comp}}$</td>
<td>Rate constant for comproportionation / m$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{disp}}$</td>
<td>Rate constant for disproportionation / m$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$K_{\text{eqm}}$</td>
<td>Equilibrium constant for com/dis-proportionation / unitless</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Potential / V</td>
</tr>
<tr>
<td>$\phi_{\text{PET}}$</td>
<td>Potential at the plane of electron transfer / V</td>
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<tr>
<td>$r$</td>
<td>Radial coordinate / m</td>
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<tr>
<td>$r_e$</td>
<td>Radius of the electrode / m</td>
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<td>$r_{\text{max}}$</td>
<td>Maximum value of $r$ / m</td>
</tr>
<tr>
<td>$t$</td>
<td>Time / s</td>
</tr>
<tr>
<td>$v$</td>
<td>Scan rate ($=</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Charge of species $i$ / unitless</td>
</tr>
</tbody>
</table>

Table 1: List of parameters.
<table>
<thead>
<tr>
<th>Normalised Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_i$</td>
<td>$\frac{C_i}{C_A^*}$</td>
</tr>
<tr>
<td>$c_{i,0}$</td>
<td>$\frac{C_{i,0}}{C_A^*}$</td>
</tr>
<tr>
<td>$D'_i$</td>
<td>$\frac{D_i}{D_A}$</td>
</tr>
<tr>
<td>$J$</td>
<td>$-i/(2\pi FC_A^* D_A r_e)$</td>
</tr>
<tr>
<td>$K^0$</td>
<td>$k^0 r_e/D_A$</td>
</tr>
<tr>
<td>$K_{comp}$</td>
<td>$\frac{k_{comp} C_A^* r_e^2}{D_A}$</td>
</tr>
<tr>
<td>$K_{disp}$</td>
<td>$\frac{k_{disp} C_A^* r_e^2}{D_A}$</td>
</tr>
<tr>
<td>$\theta_{app}$</td>
<td>$\frac{F(E_{app} - E_{app}^o)}{RT}$</td>
</tr>
<tr>
<td>$\theta_{PET}$</td>
<td>$\frac{F(E_{PET} - E_{PET}^o)}{RT}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$\frac{r}{r_e}$</td>
</tr>
<tr>
<td>$R_e$</td>
<td>$r_e \sqrt{\frac{F \Delta C_A}{RT \epsilon_o}}$</td>
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<tr>
<td>$\sigma$</td>
<td>$\frac{r_e^2 F}{D_A RT} \frac{\partial E_{app}}{\partial t}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$\frac{D \Delta t}{r_e^2}$</td>
</tr>
</tbody>
</table>

Table 2: List of normalised parameters.
Figure 1: Schematic representation of the spatial grid as a function of $\theta_{app}$. The corresponding voltammogram is shown for comparison.
Figure 2: Schematic concentration profiles for $K_{\text{comp}} = 10^{-8}$ and $10^8$. The general shape of each profile is invariant to the kinetic and thermodynamic parameters simulated.
Figure 3: Schematic voltammograms for 1 electron, $A + e^- \rightleftharpoons B$, and two electron, $A + 2e^- \rightleftharpoons B + e^- \rightleftharpoons C$, processes. The procedure for calculating baseline corrected currents for the second peak, $J_{\text{peak}2} - J_{\text{baseline}}$, is shown.
Figure 4: $J_{\text{peak}2} - J_{\text{baseline}}$ as a function of $c_{\text{sup}}$ and $K_{\text{comp}}$ for $\sigma = 10^{-3}$ and $10^{3}$. 
Figure 5: $J_{\text{peak}2} - J_{\text{baseline}}$ as a function of $D_{\text{sup}}'$ = $D_{\text{M}}'$ = $D_{X}'$ and $K_{\text{comp}}$ for $\sigma = 10^{-3}$ and $10^{3}$. 
Figure 6: $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of $c_{\text{sup}}$ and $K_{\text{comp}}$ for $z_A = -1, 1, 2$ and $3$. 