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Supplementary Materials

Theoretical Analysis of Two-step EEC′ Mechanism in Square-Wave Voltammetry: Application to Water Soluble Redox Systems with Inverted Potentials

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MATHCAD simulation protocol
TWO STEP DIFFUSIONAL EEC' Mechanism in Squate-wave voltammetry

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.65$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15$

$r := 1..1 \quad KI_r := 10^{.75 \cdot r} \quad KII := 10^{.75}$

$j := 1..\frac{\Delta E}{dE} \cdot 50$

$$\mathrm{Ox} + e^- \rightleftharpoons \mathrm{Int} \quad (k_{s,1};\ \alpha_1) \qquad (a)$$

$$\mathrm{Int} + e^- \rightleftharpoons \mathrm{Red} \quad (k_{s,2};\ \alpha_2) \qquad (b)$$

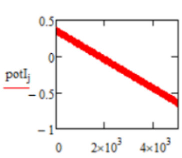
$$\mathrm{Red} + \mathrm{Y} \rightarrow \mathrm{Int} + \mathrm{S}\ (k_c) \qquad (c)$$

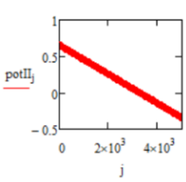
$\alpha 1 := 0.5$

$\alpha 2 := 0.5$

$$potI_j := EsI + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

$$potII_j := EsII + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$





$z := .50000500$

z is catalytic parameter (Kchem in our model)

$M1_j := \sqrt{j} - \sqrt{j-1}$

$$\Phi I_j := n\cdot\frac{F}{R\cdot T}\cdot potI_j \quad \Phi II_j := n\cdot\frac{F}{R\cdot T}\cdot potII_j$$

$$B_j := \left(1 - \mathrm{erfc}\left(\sqrt{\frac{z}{50\times 1}\cdot j}\right)\right) - \left[1 - \mathrm{erfc}\left[\sqrt{\frac{z}{50\times 1}\cdot(j-1)}\right]\right]$$

$$\Psi I_{1,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_1}}{1 + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot M1_1 \cdot e^{-\alpha 1 \cdot \Phi I_1} + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)} \cdot M1_1}$$

$$\Psi II_{1,r} := \frac{KII \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \Psi I_{1,r} \cdot M1_1}{1 + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_1 \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_1 \cdot (1-\alpha 2)}}$$

$$\Psi I_{j,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} - KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right)}{1 + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot M1_1 \cdot e^{-\alpha 1 \cdot \Phi I_j} + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot M1_1}$$

$$\Psi II_{j,r} := \frac{KII \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - \frac{1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)}}$$

$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$

$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

$E_p := EsI - p \cdot dE$

$\Psi b_{p,r} := \Psi_{50 \cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1) \cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$