Supplementary Material: Related to Paper: Protein-film Voltammetry of Two-step Electrode Enzymatic Reactions Coupled with an Irreversible Chemical Reaction of a Final Product – A Theoretical Study in Square-wave Voltammetry

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MATHCAD File for TWO-STEP SURFACE EECirr MECHANISM in SWV

$f := 10$ $r := 1..1$ $ks1_r := 1 \cdot r$

$EsI := 0.2$ $\Delta E := 0.8$ $dE := 0.004$ $Esw := 0.05$ $ks2 := 1$

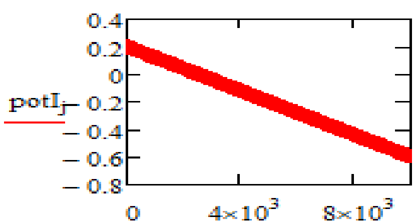
$EsII := 0.5$ $F := 96500$ $R := 8.314$ $T := 298.15$ $K1_r := \frac{ks1_r}{f}$

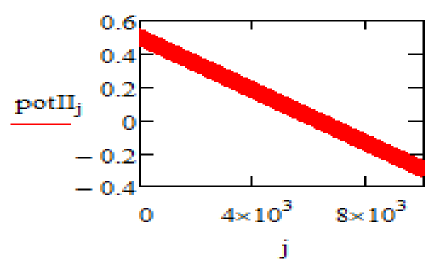
$n := 1$

$j := 1 .. \frac{\Delta E}{dE} \cdot 50$ $\alpha 1 := 0.5$ $\alpha 2 := 0.5$ $K2 := \frac{ks2}{f}$

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

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





$kc := 0.1$

$Kchem := \frac{kc}{f}$

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

$$M_j := e^{-Kchem \cdot \frac{j}{50}} - e^{-Kchem \cdot \frac{j+1}{50}}$$

$x := 0.001$

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$$\Psi I_{1,r} := \text{root}\left[\left[1 + \frac{K1_r \cdot e^{-\alpha 1 \cdot \Phi I_1}}{50} \cdot \left(1 + e^{\Phi I_1}\right)\right] \cdot x - \frac{K1_r}{50} \cdot e^{(1-\alpha 1) \cdot \Phi I_1} \cdot \left[\frac{x \cdot \frac{K2 \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50}}{1 + \frac{K2 \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50} \cdot \left(1 + e^{\Phi II_1}\right)}\right] - K1_r \cdot e^{-\alpha 2 \cdot \Phi I_1}, x\right] \qquad \textbf{(I)}$$

$$\Psi II_{1,r} := \frac{K2 \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50 + K2 \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right)} \cdot \Psi I_{1,r} + \frac{K2 \cdot e^{(-\alpha 2) \cdot \Phi II_1}}{50 + K2 \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right) + \frac{K2}{Kchem \cdot 50} \cdot e^{(1-\alpha 2) \cdot \Phi II_1} \cdot M_1} \qquad \textbf{(II)}$$

$x := 0.001$

$$\Psi I_{j,r} := \text{root}\left[x - K1_r \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \left[1 - \left[\frac{1}{50} \cdot \left(1 + e^{\Phi I_j}\right) \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r}\right) + \frac{e^{\Phi I_j}}{50} \cdot \left[\frac{1}{1 + e^{\Phi II_j}} \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r}\right) - \frac{50}{K2 \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j}\right)} \cdot \left[K2 \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \left[\frac{1}{50} \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r}\right) - \frac{1}{50} \cdot \left(1 + e^{\Phi II_j}\right) \cdot \left[\frac{50 \cdot x}{K1_r \cdot e^{(1-\alpha 1) \cdot \Phi I_j}} - 50 \cdot e^{-\Phi I_j} \cdot \left[1 - \frac{1}{50} \cdot \left(1 + e^{\Phi I_j}\right) \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r}\right)\right]\right]\right]\right]\right]\right]\right], x\right]$$

(III)

$$\Psi II_{j,r} := \frac{0.02K2 \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1}{1 + \frac{K2}{50} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j}\right)} \cdot \sum_{i=1}^{j} \Psi I_{i,r} + \frac{0.02K2 \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1 - \frac{K2}{50} \cdot e^{(-\alpha 2) \cdot \Phi II_j} \cdot \sum_{i=1}^{j-1} \Psi II_{i,r} - \frac{K2}{Kchem \cdot 1} \cdot e^{(1-\alpha 2) \cdot \Phi II_j} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot M_i\right)}{1 + \frac{K2}{50} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1 + \frac{K2}{Kchem \cdot 1} \cdot e^{(1-\alpha 2) \cdot \Phi II_j} \cdot M_1}$$

(IV)

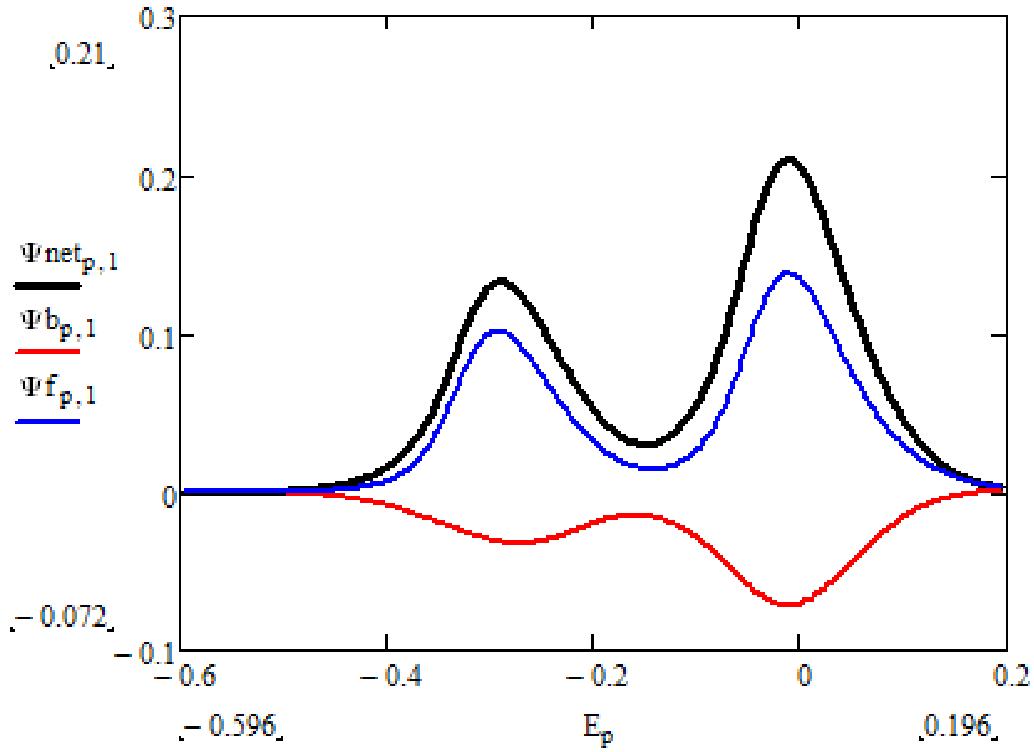
$$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$$

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

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

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

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


0.3
0.21
0.2
0.1
0
– 0.072
– 0.1
Ψnet$_{p,1}$
Ψb$_{p,1}$
Ψf$_{p,1}$
– 0.6
– 0.4
– 0.2
0
0.2
– 0.596
E$_p$
0.196

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