SUPPLEMENTARY MATERIAL---SWV of TWO STEP DIFFUSIONAL EECrev Mechanism---MATHCAD File

$f := 10$

$EsI := 0.2 \quad \Delta E := .6 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.4 \quad r := 1..1$

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

$KI_r := 10^{0.5 \cdot r} \quad KI_1 = 3.162$

$KII := 10^{0.5} \quad KII = 3.162$

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$

$\varepsilon := 1000000$

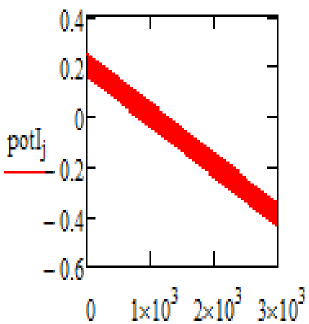
$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

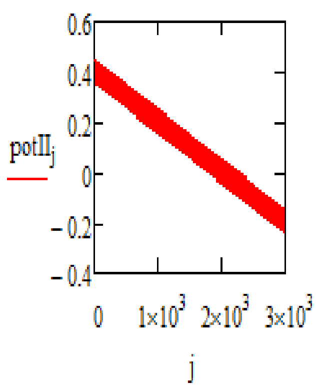
$\gamma := \frac{\varepsilon}{f}$

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

$\gamma := 10.00100$

$U := 100.05000001$





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

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

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

$x := 0.001$

EsI---is standard redox potential of first electron transfer
EsII--is standard redox potential of second electron transfer
dE is step increment
Esw is SW amplitude
f is SW frequency
ΔE is potential window
α is electron transfer coefficient
n--is number of electrons exchanged
ε is chemical rate parameter
KI = ks1/(Df)0.5 ---is dimensionless electrode parameter of first electron transfer
KII = ks2/(Df)0.5 --is dimensionless electrode parameter of second electron transfer
γ = Kchem = ε/f = (kf+kb)/f---is dimensionless chemical rate parameter
U = Keq = equilibrium constant of chemical reaction defined as = kf/kb
kf-rate constant of forward chemical step
kb-rate constant of backward chemical step
ΨI is dimensionless current of first electron transfer step
ΨII is dimensionless current of second electron transfer step
Ψ is overal dimensionless current
M1j --is numerical integration factor
Mj --is numerical integration factor
j--number of potential pulses
ΦIj and ΦIIj are dimensionless potentials
F is Faraday constant
R is universal gas constant
T is thermodynamic temperature

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$x := 0.001$

$$\Psi I_{1,r} := \mathrm{root}\left[\left[1+\frac{KI_r\cdot e^{-\alpha 1\cdot \Phi I_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi I_1}\right)\right]\cdot x-\frac{KI_r}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot e^{(1-\alpha 1)\cdot \Phi I_1}\cdot\left[\frac{x\cdot\dfrac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}}{1+\dfrac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi II_1}\right)}\right]-KI_r\cdot e^{-\alpha 2\cdot \Phi I_1},x\right]$$

$\Psi I_{1,1} = 3.662\times 10^{-4}$

$$\Psi II_{1,r} := \frac{\dfrac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{1+\dfrac{KII\cdot M1_1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)}\cdot \Psi I_{1,r}+\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}-\dfrac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot 0-\dfrac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot\dfrac{U}{(1+U)\cdot 1}\cdot 0-\dfrac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot 0}{1+\dfrac{2\cdot KII\cdot M1_1\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}+\dfrac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot\dfrac{U\cdot M1_1}{(1+U)\cdot 1}+\dfrac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot M_1}\cdot 1$$

$x := 0.001$

$\Psi II_{1,1} = 1.426\times 10^{-7}$

$$\Psi I_{j,r} := \mathrm{root}\left[x-\frac{KI_r\cdot e^{-\alpha 1\cdot \Phi I_j}}{M1_1}\cdot\left[1-\left[\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]+\frac{e^{\Phi I_j}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left[\frac{1}{1+e^{\Phi II_j}}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]-\frac{\sqrt{\pi\cdot 50}\cdot 0.5}{KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\left[KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left[\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]-\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left(1+e^{\Phi II_j}\right)\cdot\left[\frac{\sqrt{\pi\cdot 50}\cdot 0.5\cdot x}{KI_r\cdot e^{(1-\alpha 1)\cdot \Phi I_j}}-\sqrt{\pi\cdot 50}\cdot 0.5\cdot e^{-\Phi I_j}\cdot\left[1-\frac{1}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]\right]\right]\right]\right]\right]\right]\right],x\right]$$

$$\Psi II_{j,r} := \frac{\dfrac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot \Phi II_j}}{1+\dfrac{KII\cdot 1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)+\frac{\dfrac{2}{\sqrt{\pi\cdot 50}}\cdot KII\,e^{-\alpha 2\cdot \Phi II_j}-\dfrac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_j}}{\sqrt{\pi\cdot 50}}\cdot\displaystyle\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)-\dfrac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_j}}{\sqrt{\pi\cdot 50}}\cdot\dfrac{1}{(1+U)\cdot 1}\cdot\displaystyle\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)-\dfrac{KII\cdot U}{(1+U)\cdot\gamma}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot\displaystyle\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M_{j-i+1}\right)}{1+\dfrac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot M1_1}{\sqrt{\pi\cdot 50}}+\dfrac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_j}}{\sqrt{\pi\cdot 50}}\cdot\dfrac{1\cdot M1_1}{(1+U)\cdot 1}+\dfrac{KII\cdot U}{(1+U)\cdot\gamma}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot M_1}\cdot 1$$

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

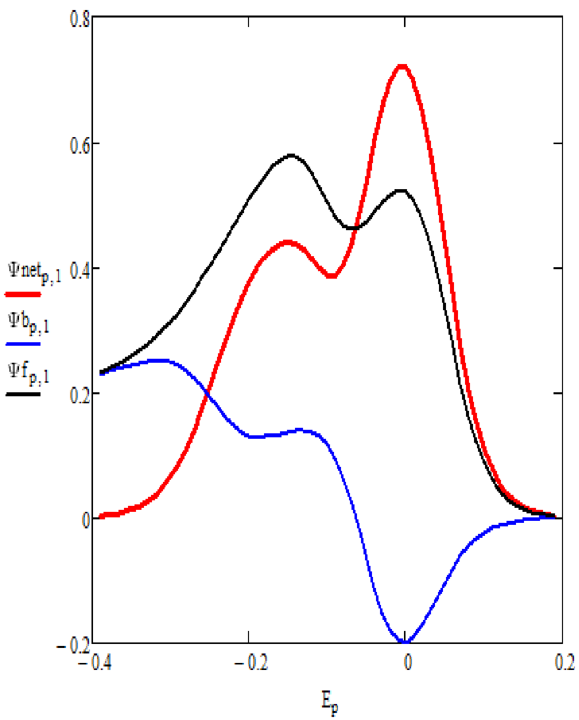
$$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$$

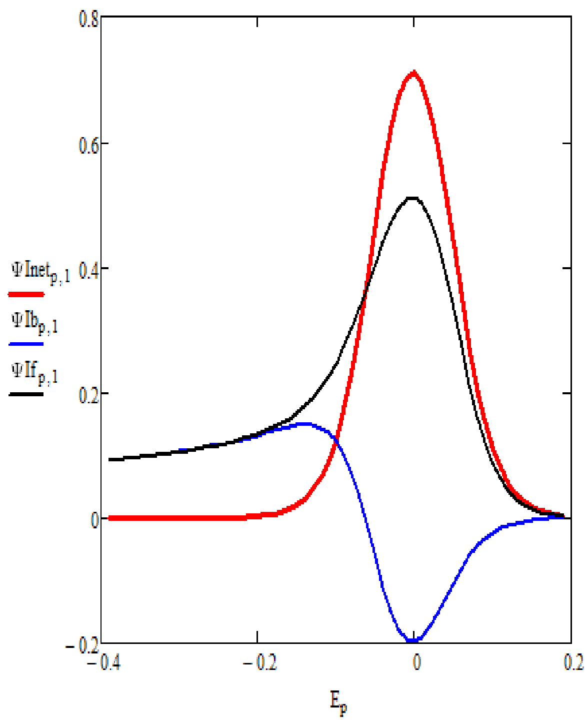
$$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r} \quad \Psi Ib_{p,r} := \Psi I_{50\cdot p+2} \quad \Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$$

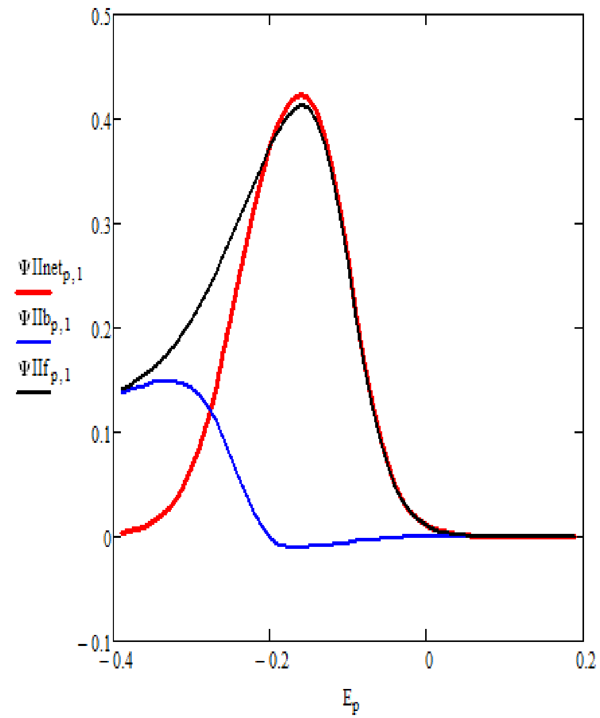
$$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,\,r} \quad \Psi IIf_{p,r} := \Psi II_{(p+1)\cdot} \quad \Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$$

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

$$E_p := EsI - p\cdot dE$$







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