Supplementary Material
ORIGINAL PAPER

Surface ECE mechanism in protein film voltammetry—a theoretical study under conditions of square-wave voltammetry

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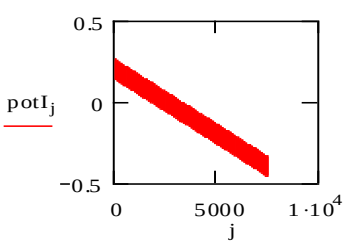
$EsI := 0.2 \quad \Delta E := 0.6 \quad dE := 0.004 \quad Esw := 0.06 \quad EsII := 0.35$

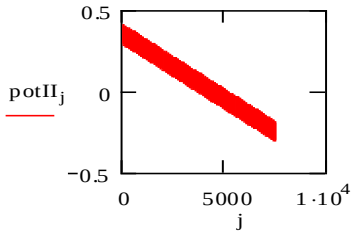
$n := 2 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \alpha := 0.5$

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

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

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





$ks1 := 1 \quad ks2 := 1 \quad f := 10 \quad kf := 0.00001$ kf is a chemical rate constant of pseudo-first order

$K1 := \frac{ks1}{f} \quad K2 := \frac{ks2}{f} \quad \lambda := \frac{kf}{f}$ λ is a dimensionless chemical parameter

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

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

$$\Psi I_1 := \frac{K1\cdot e^{-\alpha\cdot\Phi I_1}}{1 + \frac{K1}{50}\cdot e^{-\alpha\cdot\Phi I_1} + K1\lambda^{-1}\cdot e^{\Phi I_1\cdot(1-\alpha)}\cdot M_1}$$

$$\Psi II_1 := \frac{\left(\Psi I_1\cdot\frac{K2}{50}\cdot e^{-\alpha\cdot\Phi II_1}\right) - K2\cdot\lambda^{-1}\cdot e^{-\alpha\cdot\Phi II_1}\cdot\Psi I_1\cdot M_1}{1 + \frac{K2\cdot e^{-\alpha\cdot\Phi II_1}}{50}\cdot\left(1 + e^{\Phi II_1}\right)}$$

The equations (1) and (2) are recursiv formulas for the SURFACE ECE MECHANISM

$$\Psi I_j := \frac{K1\cdot e^{-\alpha\cdot\Phi I_j} - \frac{K1}{50}\cdot e^{-\alpha\cdot\Phi I_j}\cdot\sum_{i=1}^{j-1}\Psi I_i - K1\lambda^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha)}\cdot\sum_{i=1}^{j-1}\Psi I_i\cdot M_j}{1 + \frac{K1}{50}\cdot e^{-\alpha\cdot\Phi I_j} + K1\lambda^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha)}\cdot M_1} \qquad (1)$$

$$\Psi II_j := \frac{\frac{K2}{50}\cdot e^{-\alpha\cdot\Phi II_j}\cdot\sum_{i=1}^{j-1}\Psi I_i - K2\lambda^{-1}\cdot e^{-\alpha\cdot\Phi II_j}\cdot\sum_{i=1}^{j-1}\Psi I_i\cdot M_j - \frac{K2}{50}\cdot e^{-\alpha\cdot\Phi II_j}\cdot\left(1 + e^{\Phi II_j}\right)\cdot\sum_{i=1}^{j-1}\Psi II_i}{1 + \frac{K2}{50}\cdot e^{-\alpha\cdot\Phi II_j}\cdot\left(1 + e^{\Phi II_j}\right)} \qquad (2)$$

By Ψj is assigned current for the SURFACE ECE Mechanism

SIMPLE SURFACE REDOX REACTION

$z := 2$

$$\phi I_j := z \cdot \frac{F}{R \cdot T} \cdot potI_j$$

$$II_1 := \frac{K1 \cdot e^{-\alpha \cdot \phi I_1}}{1 + \frac{K1 \cdot e^{-\alpha \cdot \phi I_1} \cdot \left(1 + e^{\phi I_1}\right)}{50}}$$

$$II_j := \frac{K1 \cdot e^{-\alpha \cdot \phi I_j} - K1 \cdot e^{-\alpha \cdot \phi I_j} \cdot \frac{\left(1 + e^{\phi I_j}\right)}{50} \cdot \sum_{i=1}^{j-1} II_i}{1 + \frac{K1 \cdot e^{-\alpha \cdot \phi I_j} \cdot \left(1 + e^{\phi I_j}\right)}{50}}$$

$\Psi_j := \Psi I_j + \Psi II_j$

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

$\Psi If_p := \Psi I_{(p+1) \cdot 50}$ $\Psi Ib_p := \Psi I_{50 \cdot p + 25}$ $\Psi Inet_p := \Psi If_p - \Psi Ib_p$

$\Psi IIb_p := \Psi II_{50 \cdot p + 25}$ $\Psi IIf_p := \Psi II_{(p+1) \cdot 50}$ $\Psi IInet_p := \Psi IIf_p - \Psi IIb_p$

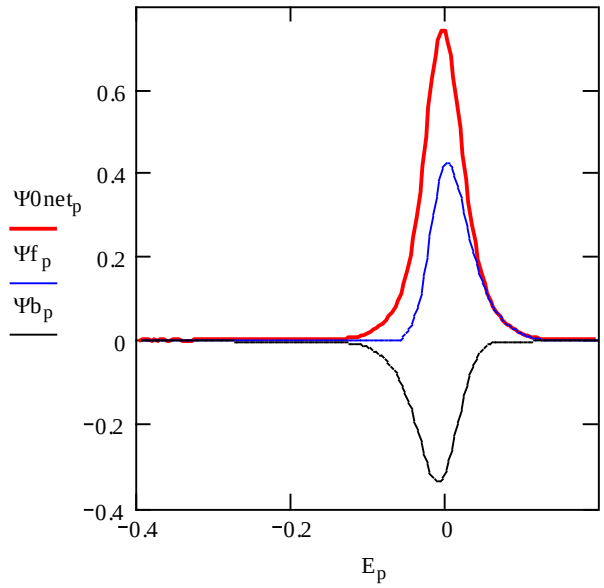
$\Psi b_p := \Psi_{50 \cdot p + 25}$ $\Psi f_p := \Psi_{(p+1) \cdot 50}$ $\Psi net_p := \Psi f_p - \Psi b_p$

$E_p := EsI - p \cdot dE$ $\Psi 0net_p := \Psi Inet_p + \Psi IInet_p$ FOR ECE MECHANISM

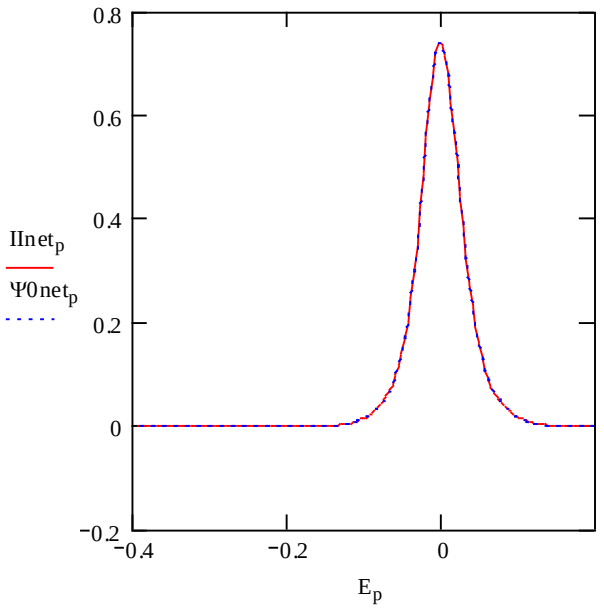
$IIf_p := II_{(p+1) \cdot 50}$

$IIb_p := II_{50 \cdot p + 25}$

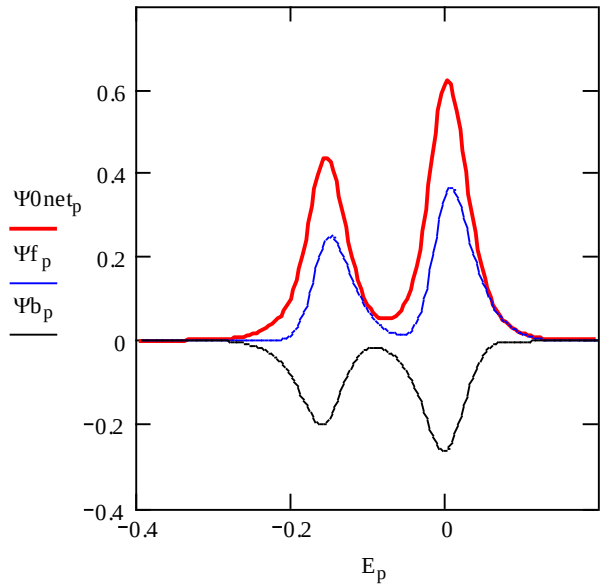
$IInet_p := IIf_p - IIb_p$ FOR SIMPLE SURFACE REDOX REACTION



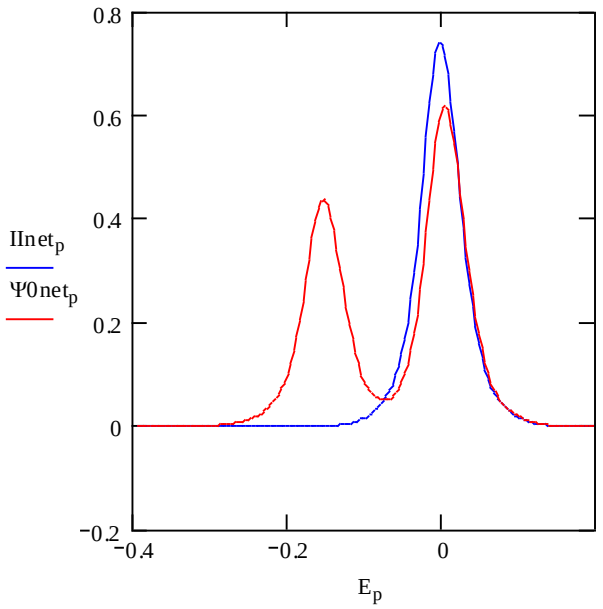
Voltammogram of surface ECE mechanism
Est(II) - Est(I) = -150 mV
K1 = K2 = 0.1
This voltammogram is simulated for small value of the chemical rate constant
λ = 0.000001.



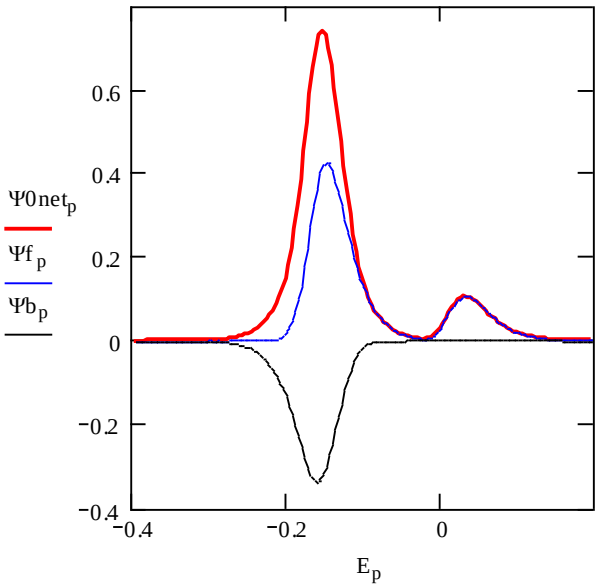
Voltammograms of surface ECE mechanism from previous case (blue line) and that of simple surface reaction (red line)
The simple surface reaction is simulated for the value of the kinetic parameter
K = 0.1



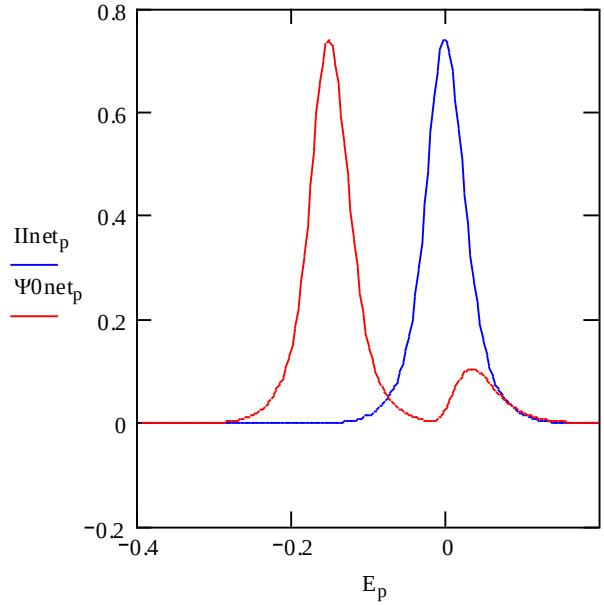
Voltammogram of surface ECE mechanism
Est(II) - Est(I) = -150 mV
K1 = K2 = 0.1
This voltammogram is simulated for moderate value of the chemical rate constant
$\lambda = 0.01$.



Voltammograms of surface ECE mechanism from the case above (red line) and that of simple surface reaction (blue line
The simple surface reaction is simulated for the value of the kinetic parameter
K = 0.1



Voltammogram of surface ECE mechanism
Est(II) - Est(I) = -150 mV
K1 = K2 = 0.1
This voltammogram is simulated for big value of the chemical rate constant
λ = 1



Voltammograms of surface ECE mechanism from the case above (red line) and that of simple surface reaction (blue line
The simple surface reaction is simulated for the value of the kinetic parameter
K = 0.1