Protein-Film Voltammetry of Two-Step Mechanism with Reversible Intermediate Chemical Reaction-Theoretical Consideration in Square-Wave Voltammetry

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SURFACE ECrevE Mechanism
MATHCAD Simulation file

$EsI := 0.25 \quad \Delta E := 0.8 \quad dE := 0.004 \quad Esw := 0.05 \quad EsII := 0.45$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \alpha := 0.5$

$ks1 := 0.5$

$ks2 := 0.5$

$f := 5.0$

$KI := \frac{ks1}{f} \qquad \varepsilon := 0.05$

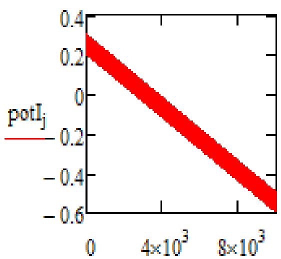
$KII := \frac{ks2}{f} \qquad U := 10.00$

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

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

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

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



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

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

$x := 0.001$

DEFINITIONS of the parameters used in the file:

EsI---is standard redox potential of first electron transfer
EsII--is standard redox potential of second electron transfer
dE is potential 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 rated parameter defined as ε=(kf+kb)
λ=Kchem-is a dimensionless chemical kinetic 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
ks1 and ks2----are standard rate constants of electron transfer of first and second electron transfer step respectively
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
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

$x := 0.001$

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

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

$x := 0.001$

$$\Psi I_j := \frac{1KI \cdot e^{-\alpha \cdot \Phi I_j} - \frac{KI}{50} \cdot e^{-\alpha \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \Psi I_i - \frac{KI \cdot U}{1 + U} \lambda^{-1} \cdot e^{\Phi I_j \cdot (1-\alpha)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot M_i\right) - \frac{\lambda^{-1} \cdot KI}{1 + U} \cdot e^{(1-\alpha) \cdot \Phi I_j} \cdot 1 \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot M_i\right)}{1 + \frac{KI}{50} \cdot e^{-\alpha \cdot \Phi I_j} + \frac{KI \cdot U}{1 + U} \lambda^{-1} \cdot e^{\Phi I_j \cdot (1-\alpha)} \cdot M_1 + \frac{\lambda^{-1}}{1 + U} \cdot e^{(1-\alpha) \cdot \Phi I_j} \cdot M_1}$$

$$\Psi II_j := \frac{\frac{KII}{50} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \Psi I_i - KII \cdot \frac{1 \cdot U}{1 + U} \lambda^{-1} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_i \cdot M_j\right) - \frac{KII}{50} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j}\right) \cdot \sum_{i=1}^{j-1} \Psi II_i}{1 + \frac{KII}{50} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j}\right) + KII \cdot \frac{1 \cdot U}{1 + U} M_1 \cdot \lambda^{-1} \cdot e^{-\alpha \cdot \Phi II_j}}$$

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

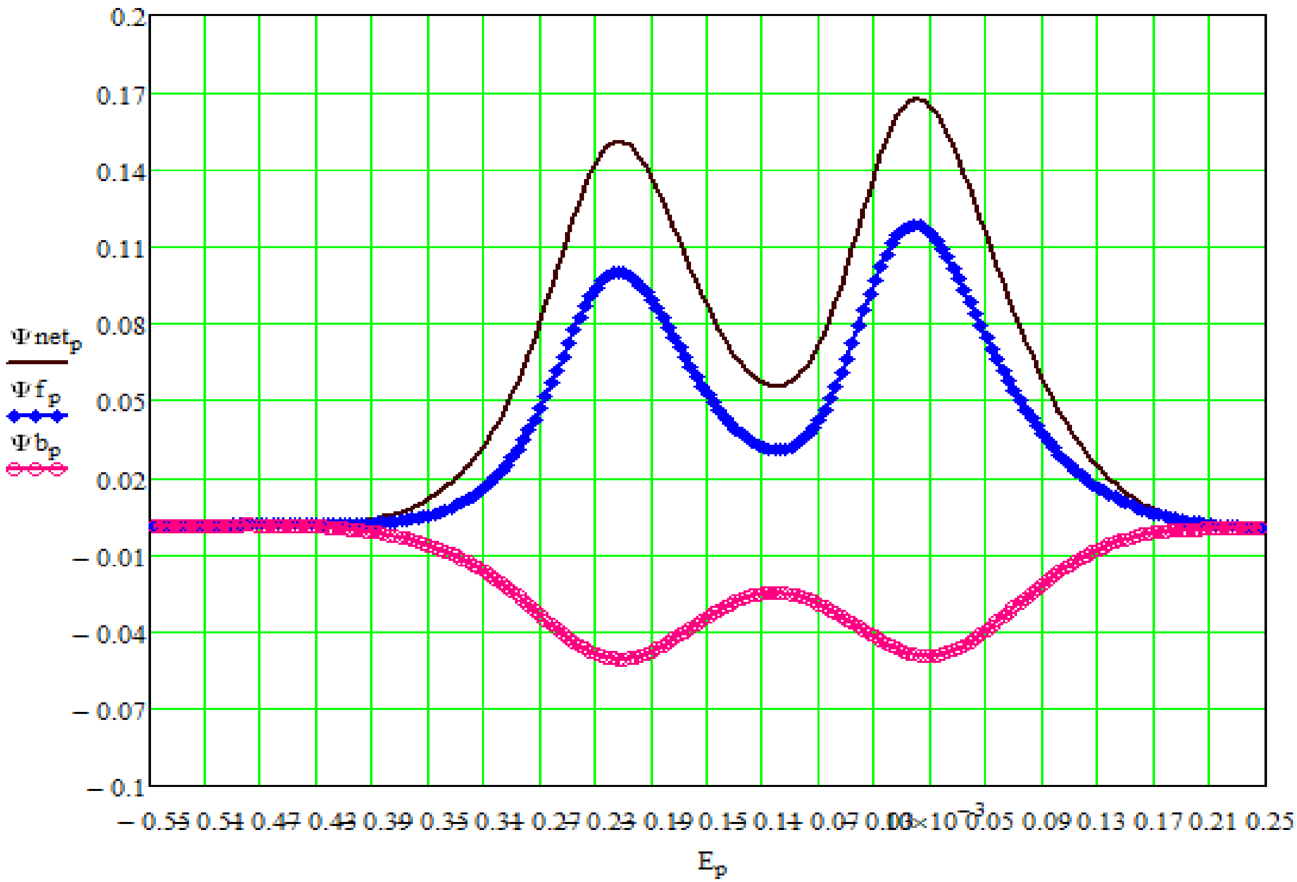
$$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$$

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

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

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

$$E_p := EsI - p\cdot dE \qquad \Psi net_p := \Psi Inet_p + \Psi IInet_p$$



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