<u>Supplementary Material to work</u>: *Distinction between Film Loss and Enzyme Inactivation in Protein-Film Voltammetry-A Theoretical Study in Cyclic Staircase Voltammetry*

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$$m := \frac{tac}{d} + 1 .. \frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d}$$

$$n := \frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d} + 1 .. \left(\frac{\Delta E}{dE}\cdot 25\cdot 2 + \frac{tac}{d}\right)$$

$$ks := 10^{1.6995}$$

$$E_m := Es + \left(\mathrm{ceil}\left(\frac{m - \frac{tac}{d}}{25}\right)\cdot dE - dE\right)$$

$$\alpha := 0.5$$

$$s := 1 .. \frac{tac}{d}$$

$$Ket := \frac{ks\cdot\tau}{1}$$

$$Ket = 1.001$$

$$E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d}\right)}{25}\right]\cdot dE - dE\right]$$

$$\frac{dE}{\tau} = 0.2$$

$$Kchem := \frac{kc\cdot\tau}{1}$$

$$el := 1$$

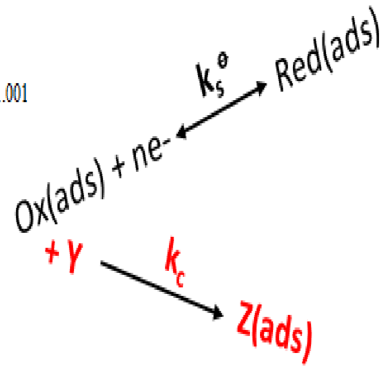
$$k := 1 .. 2\cdot\left(\frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d}\right)$$

$$Kchem = 3$$

$$S_k := e^{\frac{Kchem}{25}\cdot(-k)} - e^{\frac{Kchem}{25}\cdot(-k+1)}$$

$$F := 96500 \qquad T := 298 \qquad R := 8.314$$

Coupled to Initial Redox Form in Protein-Film Cyclic Voltammetry



$$\Phi_m := el\cdot\frac{F}{R\cdot T}\cdot\left(E_m\right) \qquad b_n := el\cdot\frac{F}{R\cdot T}\cdot\left(E_n\right) \qquad \Phi ac := el\cdot\frac{F}{R\cdot T}\cdot Es$$

$$\Psi 1_1 := \frac{Ket\cdot e^{-\alpha\cdot\Phi_1} - \left[Ket\cdot e^{-\alpha\cdot\Phi_1}\cdot\frac{\left(1+e^{\Phi_1}\right)}{25}\cdot 0 + \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi_1}\cdot 1\cdot S_1}{1+0}\right]}{1 + \frac{Ket\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)}{25} - \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi_1}\cdot 1\cdot S_1}{1+0}}$$

$$\Psi 1_s := \frac{Ket\cdot e^{-\alpha\cdot\Phi ac} + \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi ac}\cdot 1}{1}\cdot\sum_{j=1}^{s-1}\left(\Psi 1_j\cdot S_{s-j+1}\right) - Ket\cdot e^{-\alpha\cdot\Phi ac}\cdot\frac{\left(1+e^{\Phi ac}\right)}{25}\cdot\sum_{j=1}^{s-1}\Psi 1_j}{1 + \frac{Ket\cdot e^{-\alpha\cdot\Phi ac}\cdot\left(1+e^{\Phi ac}\right)}{25} - \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi ac}\cdot 1\cdot S_1}{1+0}}$$

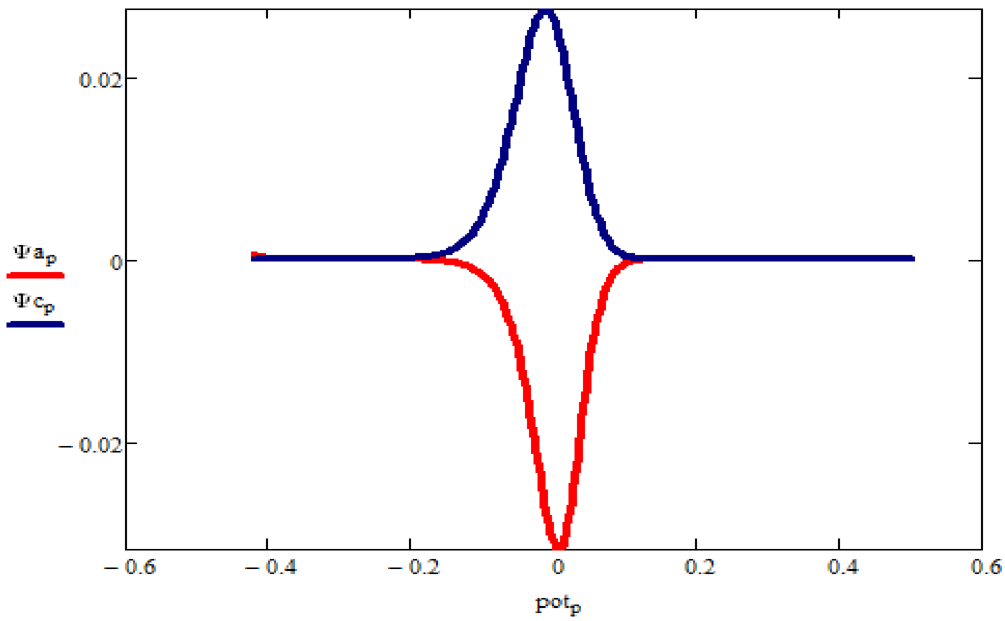
Definitions and Meanings of the Symbols

τ is the duration of potential steps
ks is standard rate constant of electron transfer
α is electron transfer coefficient
el is number of exchanged electrons
dE is potential step
Em is potential of reduction ramp
En is potential of oxidation ramp
T is thermidynamic teperature
R is universal gas constant
kc is rate constant of irreversible chemical rection
Ket is dimensionless kinetic electrode parameter
Kchem is dimensionless kinetic chemical parameter
Sk is numerical integration factor
Es is starting potential
Φ is dimensionless potentials
F is the Faraday constant
Ψ is dimensionless current
Φm is cathodic potential ramp
bn is anodic potential ramp

$$\Psi 1_m := \frac{Ket \cdot e^{-\alpha \cdot \Phi_m} + \frac{Kchem^1 \cdot e^{-\alpha \cdot \Phi_m}}{1+0} \cdot \sum_{j=1}^{m-1} \left(\Psi 1_j \cdot S_{m-j+1}\right) - Ket \cdot e^{-\alpha \cdot \Phi_m} \cdot \frac{\left(1+e^{\Phi_m}\right)}{25} \cdot \sum_{j=1}^{m-1} \Psi 1_j}{1 + \frac{Ket \cdot e^{-\alpha \cdot \Phi_m} \cdot \left(1+e^{\Phi_m}\right)}{25} - \frac{Kchem^1 \cdot e^{-\alpha \cdot \Phi_m} \cdot 1 \cdot S_1}{1+0}}$$

$$\Psi 1_n := \frac{Ket \cdot e^{-\alpha \cdot b_n} + \frac{Kchem^1 \cdot e^{-\alpha \cdot b_n} \cdot 1}{1} \cdot \sum_{j=1}^{n-1} \left(\Psi 1_j \cdot S_{n-j+1}\right) - Ket \cdot e^{-\alpha \cdot b_n} \cdot \frac{\left(1+e^{b_n}\right)}{25} \cdot \sum_{j=1}^{n-1} \Psi 1_j}{1 + \frac{Ket \cdot e^{-\alpha \cdot b_n} \cdot \left(1+e^{b_n}\right)}{25} - \frac{Kchem^1 \cdot e^{-\alpha \cdot b_n} \cdot 1 \cdot S_1}{1}}$$

$p := 20 .. \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi 1)_{\left(\frac{\tau}{d \cdot 25}+p\right)} \cdot 25$ $\quad \Psi c_p := (\Psi 1)_{\left[\left[\frac{\Delta E}{dE} \cdot 2+\left(\frac{\tau}{25 \cdot d}\right)\right]-p\right]} \cdot 25$ $\quad pot_p := Es + p \cdot dE$



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