Effect of the Frequency to the Features of a Diffusional EC'EC' Mechanism in Square-Wave Voltammetry

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Abstract: As two-step consecutive electron transfer mechanisms are common to the electrochemical transformation of many water-soluble redox proteins and enzymes under physiological conditions, it is a real challenge to model such systems when two regenerative steps are coupled to both electron transfer steps. In this work we show how the frequency of the square-wave potential signal affects the features of both voltammetric peaks. This scenario can be used to recognize such a complex mechanism, especially when both electron transfer step occur at same potential.

TWO STEP DIFFUSIONAL EC'EC'cat Mechanism in SWV--new version 23 04 2024
Effect of SW frequency

$f := 10$

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.65 \quad r := 1..1$

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

$KI_r := 10^{.75 \cdot r} \quad KII := 10^{.75}$

$kc1 := 100 \quad kc2 := 200$

λ i z se definirani kako odnos na Kc1/f i kc2/f

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

$\alpha 2 := 0.5 \quad \alpha 1 := 0.5 \quad \log(KI_r) =$

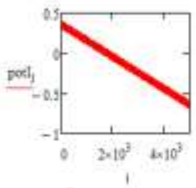
$\lambda := 2.40612400001$

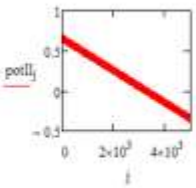
$KI_1 = 5.623$

λ e kineticki parametar na ireverzibilna hemiska reakcija povrzana so prv elektroden cekor

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

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





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

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

$z := 5.5001$

z e katalticki parametar vo ovoj model povrzan so vtor cekor

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

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

$x := 0.001$

$$\Phi I_{1,r} := \frac{\frac{KI_r}{1} \cdot e^{-\alpha 1 \cdot \Phi I_1} - 0}{1 + KI_r \cdot \lambda^{-.5} \cdot A_1 \cdot e^{-\alpha 1 \cdot \Phi I_1} + 1 \lambda^{-.5} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)} \cdot A_1}$$

$$\Phi II_{1,r} := \frac{\lambda^{-.5} KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{1 + \frac{KII \cdot MI_1 \cdot 2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_1} \left(1 + e^{\Phi II_1}\right)} \cdot \Phi I_{1,r} \cdot A_1$$

$\Phi I_{1,1} = 6.168 \times 10^{-6}$

$\Phi II_{1,1} = 0$

$$\Psi I_{j,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} - KI_r \cdot \frac{1}{\sqrt{\lambda}} \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - KI_r \cdot \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right)}{1 + KI_r \cdot \frac{2}{\sqrt{\lambda}} \cdot A_1 \cdot e^{-\alpha 1 \cdot \Phi I_j} + \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot A_1 \cdot KI_r}$$

$$_{r} := \frac{KII \frac{1}{\sqrt{\lambda}} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - KII \frac{0}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - \frac{0}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot MI_{j-i+1}\right) - \frac{1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 + KII \frac{A_1 \cdot 0}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} + \frac{0 MI_1}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)}}$$

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

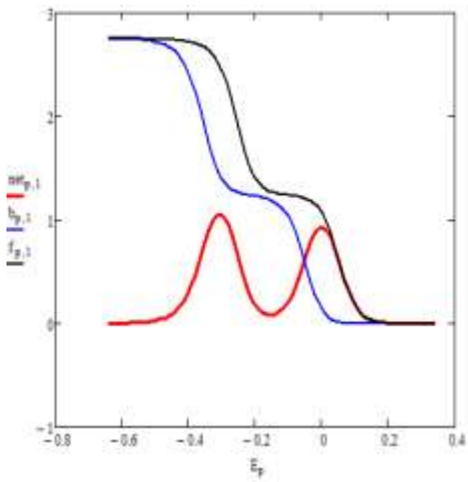
$:= 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

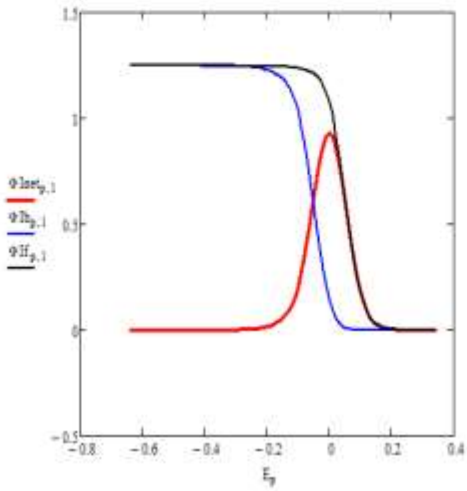
$If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

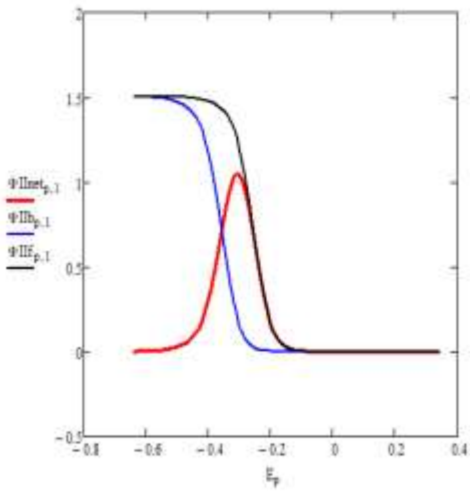
$_{p,r} := \Psi II_{50 \cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

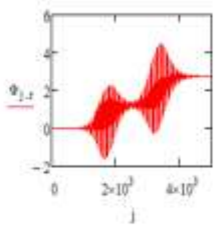
$\cdot Esl - p \cdot dE$

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

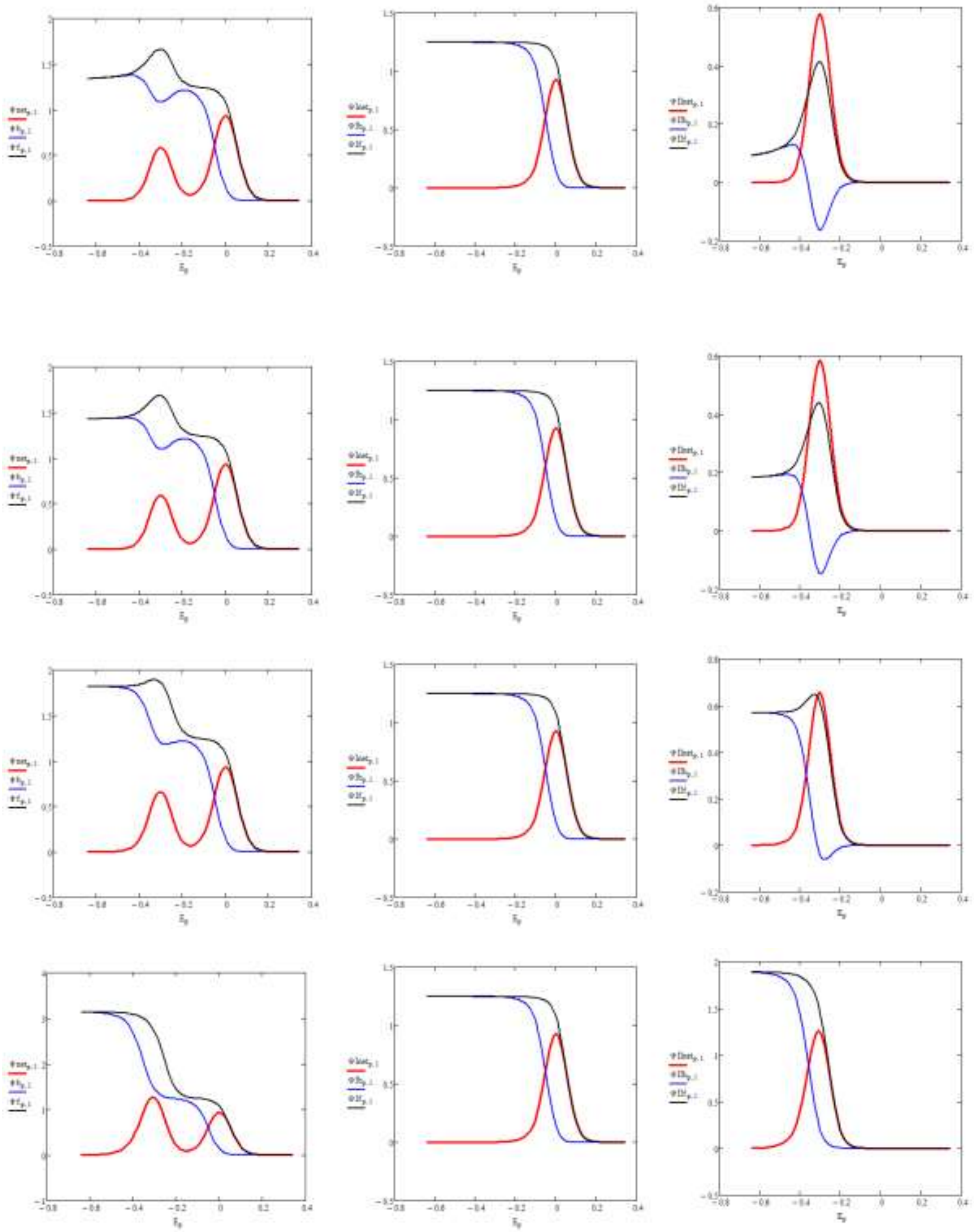








$\Psi f_{p,1} =$ $\Psi b_{p,1} =$ $\Psi net_{p,1} =$ $E_p =$



Effect of the rate of catalytic reaction (expressed via the magnitude of SW frequency) associated to the second step to the features of forward, backward and net voltammetric peaks, in conditions of fast rates of electron transfer steps of both electron transfers and fast catalytic rate of first electron transfer step

(SW frequency changes from 200 Hz to 10 Hz going from the voltammograms from the top to the bottom of the voltammetric patterns, respectively)

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