Effect of Kinetics of Electron Transfer to Splitting Phenomenon of a Surface EC’EC’ Mechanism Calculated at Moderate Rate of Regenerative Reactions

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Abstract

The net SWV splitting phenomenon is unique feature for surface confined electrode mechanisms characterized with very fast rates of electron transfer step. Two s0-called surface electrode mechanism is a platform of electrochemical consideration of many lipophilic redox enzymes. Since many of these enzymes undergo electrochemical transformation in two consecutive electron transfer steps, while being regenerated by defined substrates, it was of outmost importance to develop a model of so-called EC’EC mechanism under conditions of protein-film voltammetry. In this work, for the first time the MATHCAD simulation platform is presented of surface EC’EC’ mechanism.

TWO STEP SURFACE EC'EC'cat Mechanism in SWV---new version 19 03 2024 OK

$EsI := 0.25 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.65 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{.95 \cdot r}$

$KII := 10^{.95}$

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

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

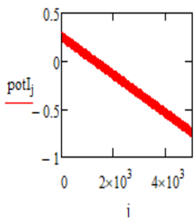
$\lambda := .004001246$

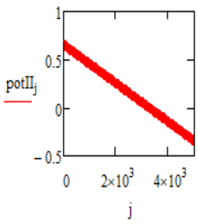
$KI_1 = 8.913$

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

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

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





$z := .004$

z e kataliticki regenerativen hemiski parametar povrzan so vtor cekor

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

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

$$B_j := e^{-z \cdot \frac{j}{50}} - e^{-z \cdot \frac{j+1}{50}}$$

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

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

$\Psi I_{1,1} = 3.295 \times 10^{-3}$

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

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

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

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

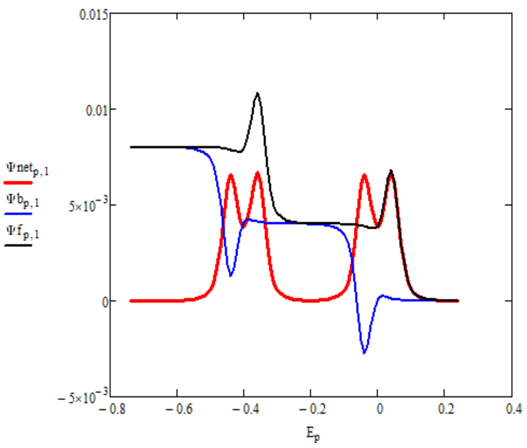
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

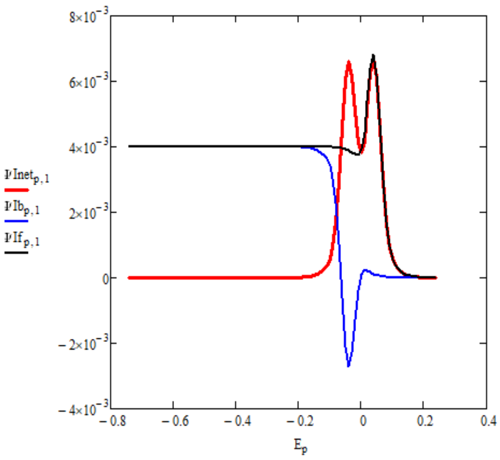
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

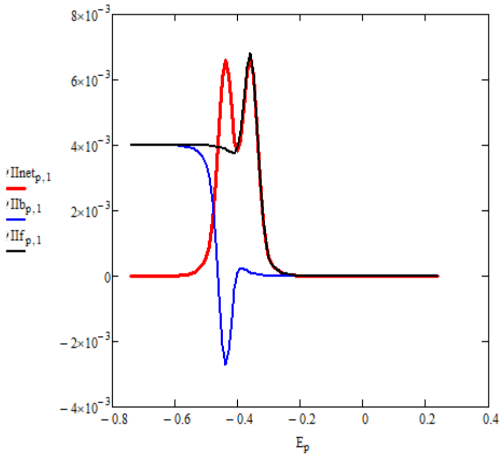
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

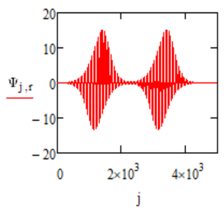
$E_p := EsI - p \cdot dE$

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

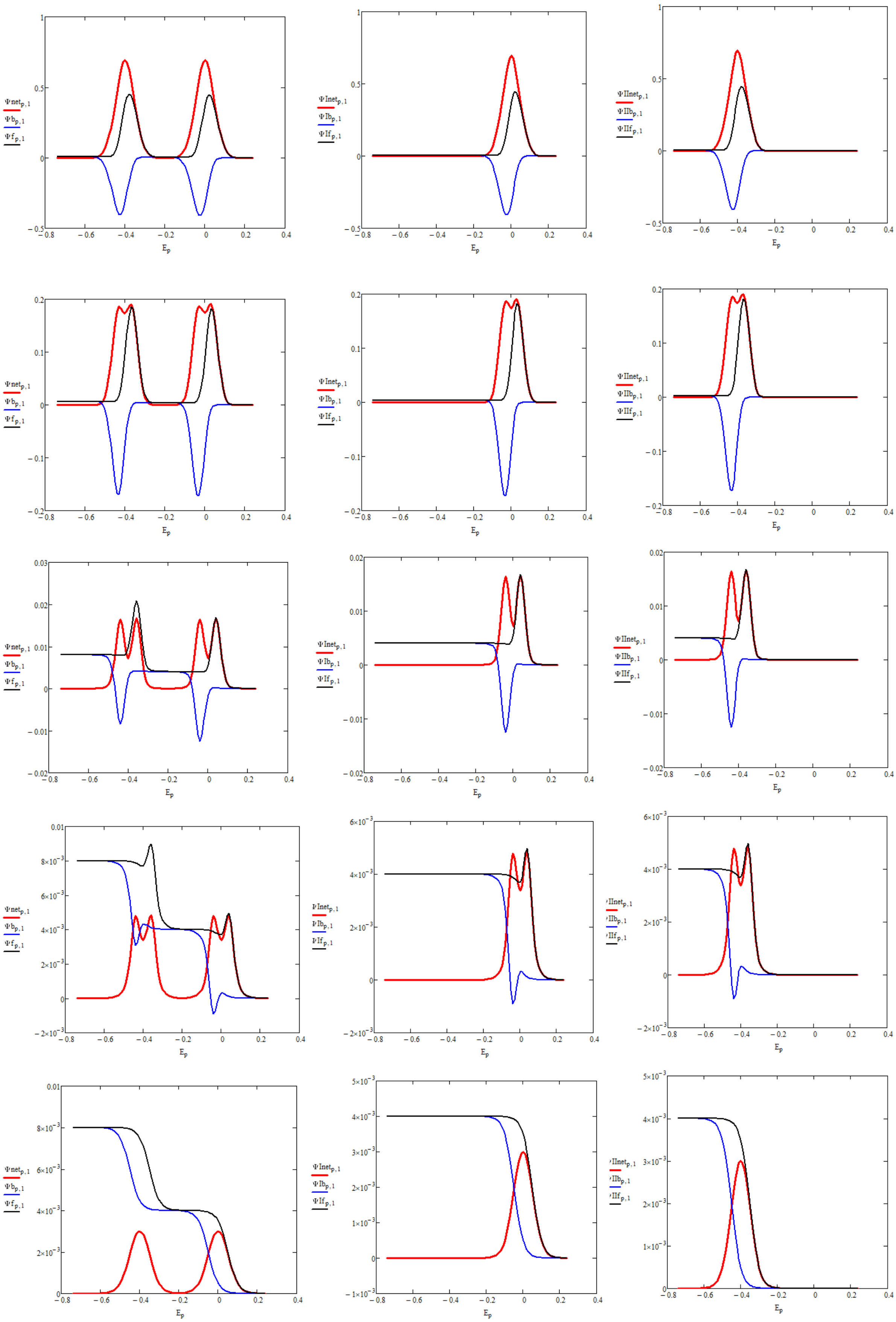








$\Psi f_{p,1} =$ $\Psi b_{p,1} =$ $\Psi net_{p,1} =$ $E_p =$



Effect of the rate of the regenerative chemical step coupled to both electron transfers, in conditions of moderate fast and very fast electron transfer steps.

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