Theory of Diffusional Two-Step Electrochemical Mechanism associated with Regenerative Chemical Reaction to the First Electron Transfer and Reversible Chemical Reaction to the Product of Second Electron transfer Step-EC'ECrev Mechanism in Square-Wave Voltammetry

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Abstract

For the first time, the theory of diffusional EC'ECrev mechanism is considered under conditions of square-wave voltammetry. The voltammetric features of the first electron transfer are function of the catalytic parameter, alongside to the kinetic of the corresponding electron transfer. The second step is initiated by the first electron transfer, and it is additionally complicated by reversible follow up chemical reaction to the product of second transfer step. The voltammetric features of the second SW peak are function of equilibrium constant, and the chemical rate parameter, next to the parameters of electrode kinetics. This model opens up a way to study the redox behavior of many water soluble redox enzymes, whose transformation takes place in two subsequent steps.

TWO STEP DIFFUSIONAL EC'ECrev Mechanism in SWV---
this is EE diffusional mechanism with regenerative irreversible reaction associated with the product of first electrode transformation and reversible follow up chemical reaction associated with the product of the second electron transfer step

$EsI := 0.35$ $\Delta E := 1$ $dE := 0.01$ $Esw := 0.05$ $EsII := 0.75$ $r := 1..1$

$n := 1$ $F := 96500$ $R := 8.314$ $T := 298.15$ $KI_r := 10^{.75\cdot r}$ $KII := 10^{.75}$

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

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

$\lambda := .32050000000001000$

λ e hemiski kataliticki parametar povrzan so prv elektrohemiski cekor

$KI_1 = 5.623$

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

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

+Y

$A + 1e = B + 1e = C + K = D$ EC'ECrev

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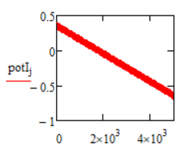
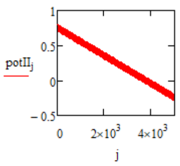




$$M1_j := \sqrt{\frac{j}{1}} - \sqrt{\frac{j-1}{1}}$$

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

$z := 3.6769500$ z e hem parametar na follow up chem reakcija povrzana so intermed step

L e konst na ramnoteza na hem follow up

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

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

$x := 0.001$

$L := 10$

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

$$\Psi II_{1,r} := \frac{\lambda^{-0.5} KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{1 + \frac{KII\cdot M1_1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\left(1 + e^{\Phi II_1}\right)}\cdot\Psi I_{1,r}\cdot A_1$$

$\Psi I_{1,1} = 6.082\times 10^{-6}$

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

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

$$\Psi II_{j,r} := \frac{KII\,\lambda^{-0.5}\cdot e^{\Phi II_j\cdot(-\alpha 2)}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right) - KII\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right) - \frac{2}{\sqrt{\pi\cdot 50}}\,\frac{KII}{1+L}\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot B_{j-i+1}\right) - \frac{L}{\left(\sqrt{z}\right)\cdot(1+L)}KII\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot B_{j-i+1}\right)}{1 + KII\cdot\frac{2\cdot M1_1}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left(1+e^{\Phi II_j}\right) + \frac{2B_1}{\sqrt{\pi\cdot 50}}\,\frac{KII}{1+L}\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)} + \frac{LB_1}{\sqrt{z}}\,\frac{KII}{1+L}\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}}$$

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

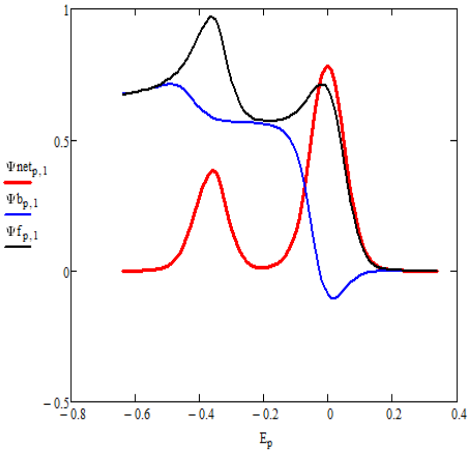
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

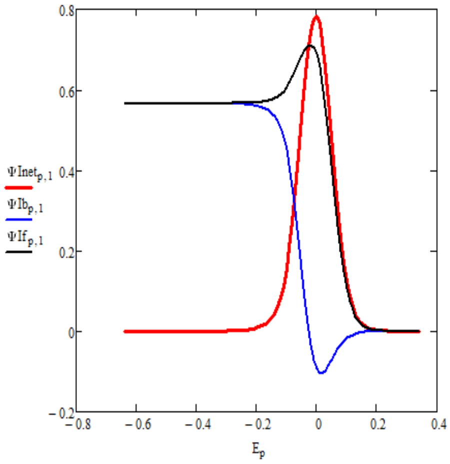
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

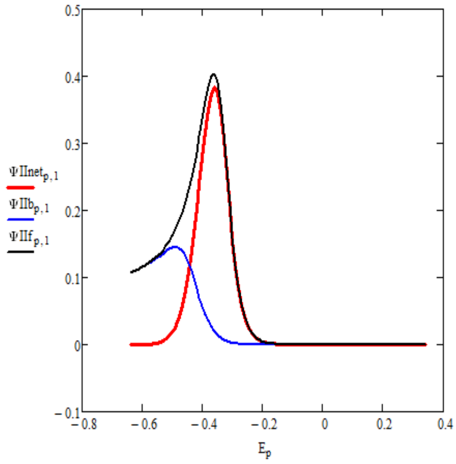
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

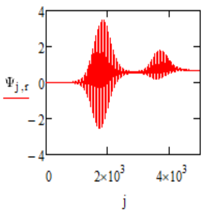
$E_p := EsI - p\cdot dE$

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

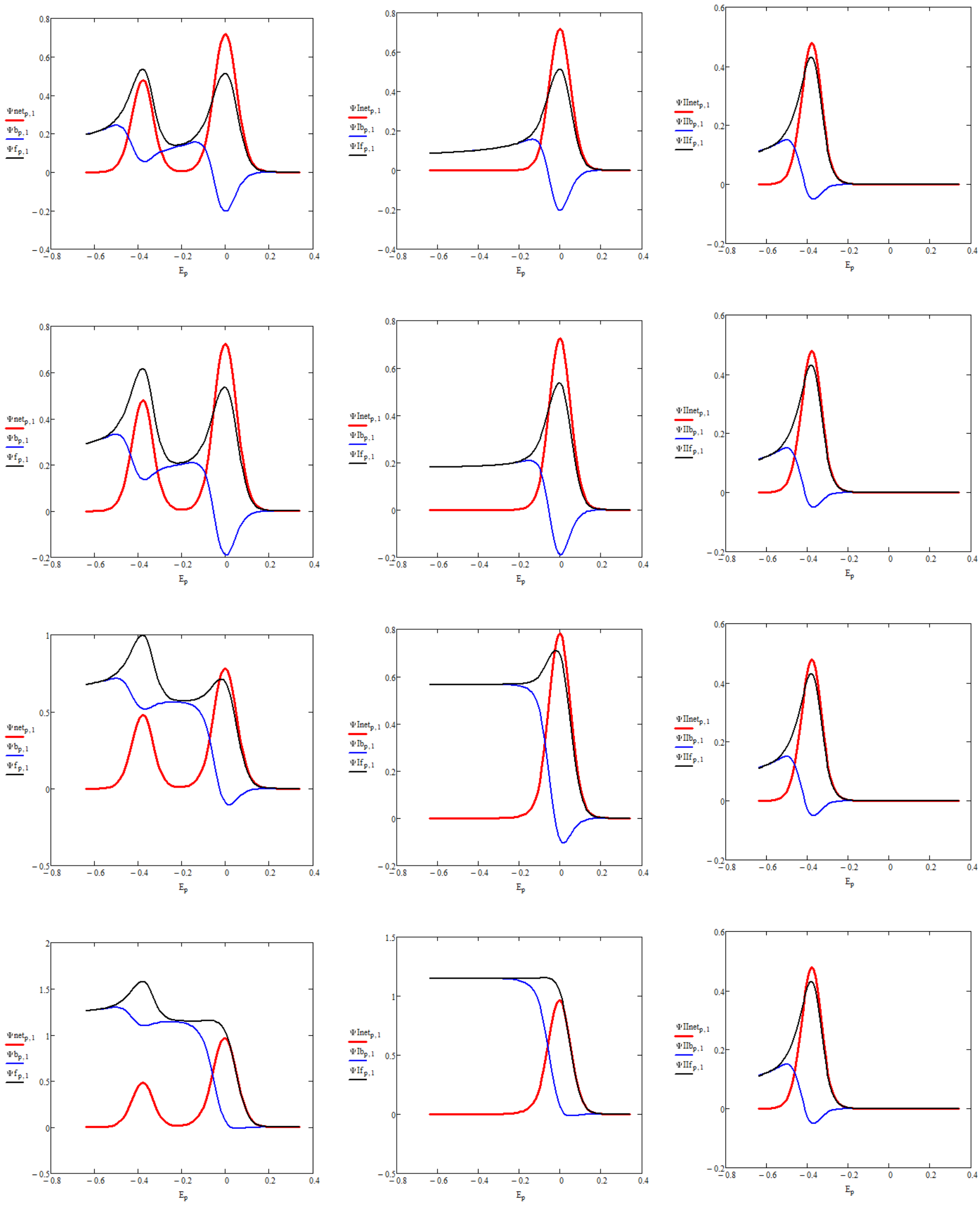




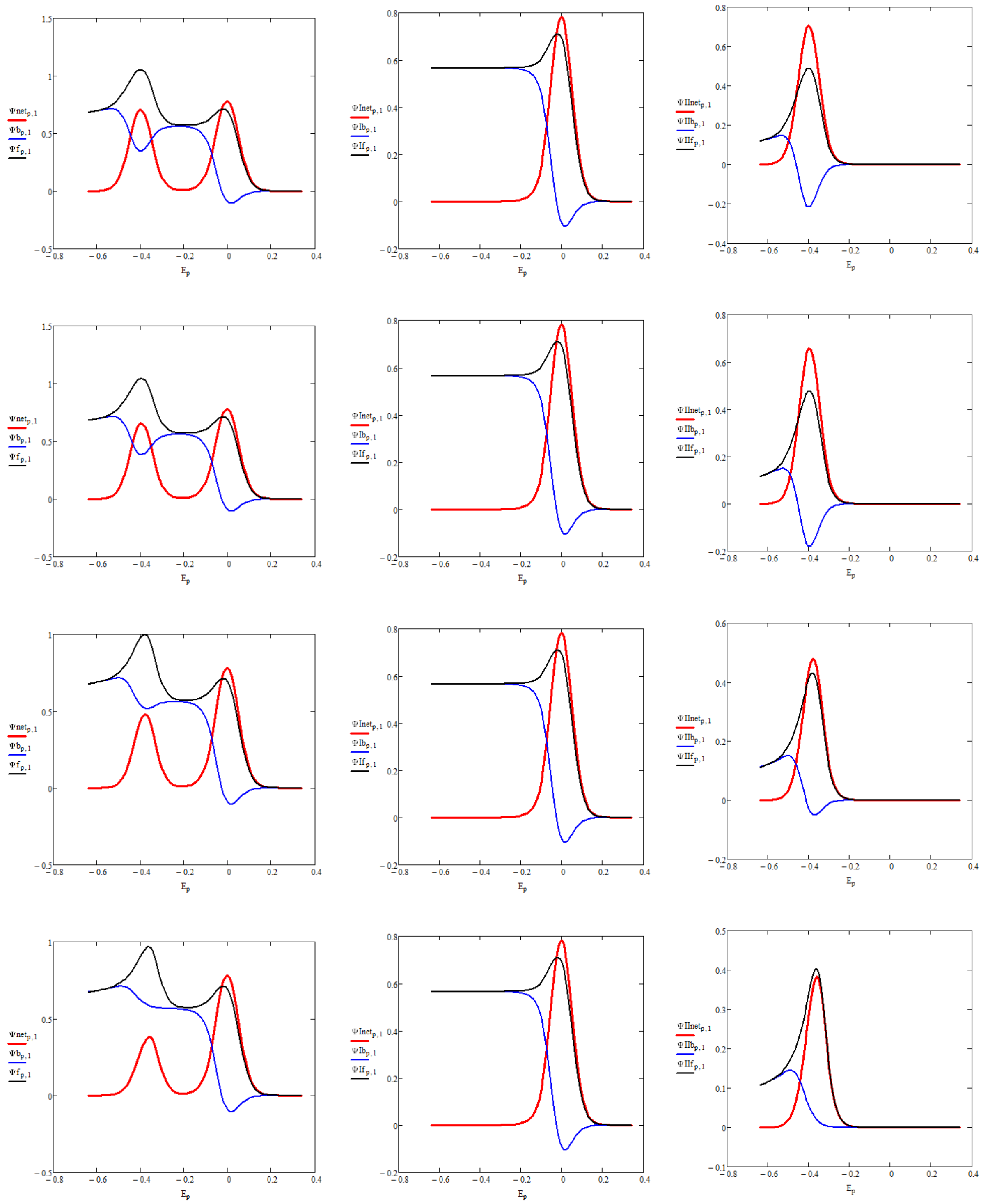




$\Psi f_{p,1} =$ $\Psi b_{p,1} =$ $\Psi net_{p,1} =$ $E_p =$



Effect of the rate of the regenerative chemical step, in conditions of moderate chemical reaction of the follow up chemical reaction associated to the second electrochemical step.



Effect of the rate of the follow up chemical reaction, in conditions of moderate catalysis to the first electrochemical step.

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