Theory of Diffusional ECirrECat Mechanism in Square-Wave Voltammetry

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Abstract

For the first time, the theory of two-step electrochemical mechanism, in which the product of second electrochemical step is produced via chemical transformation from the product of first electrochemical step, and additionally involved in a regenerative irreversible chemical step is solved under conditions of square-wave voltammetry. While the entire MATHCAD file to simulate voltammograms of the so-called "ECirrECat" mechanism is presented, hints are given that can bring experimentalists a step closer to recognize this mechanism. The elaborated mechanism is met in the redox chemistry of many water-soluble enzymes and proteins, such as cytochromes for example.

TWO STEP DIFFUSIONAL ECirrEC'cat Mechanism in SWV---Tocen 17 sept 2023

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.004 \quad Esw := 0.05$

$EsII := 0.65 \quad r := 1..1$

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

$KII := 10^{.75}$

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

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$

$\log(KI_r) = 0.75$

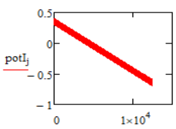
$KI_1 = 5.623$

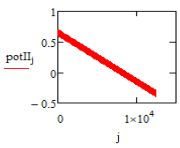
$\lambda := .450000$

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

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

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





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

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

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

$z := 50.0500$

z e kataliticki parametar vo ovoj model povrzan so vtor cekor

L e konst na ramnoteza na hem follow up

$L := 100.000001000$

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

$x := 0.001$

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

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

$\Psi I_{1,1} = 6.087 \times 10^{-6}$

$\Psi II_{1,1} = 9.165 \times 10^{-12}$

$$\Psi I_{j,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} - KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - KI_r \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right)}{1 + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot M1_1 \cdot e^{-\alpha 1 \cdot \Phi I_j} + \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot A_1 \cdot KI_r}$$

$$\Psi II_{j,r} := \frac{KII \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - KII \frac{1}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - \frac{0}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot M1_{j-i+1}\right) - \frac{1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 + KII \frac{A_1 \cdot 1}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} + \frac{0 M1_1}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z}) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)}}$$

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

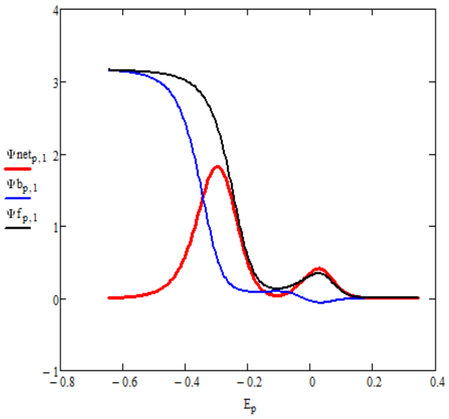
$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$

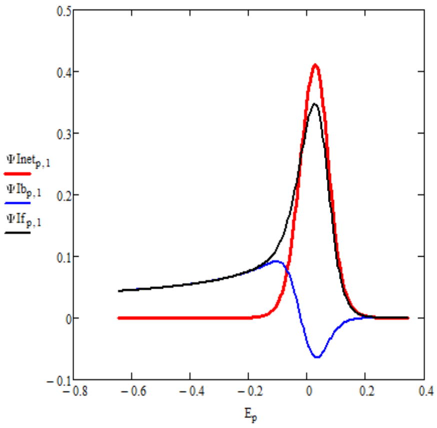
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

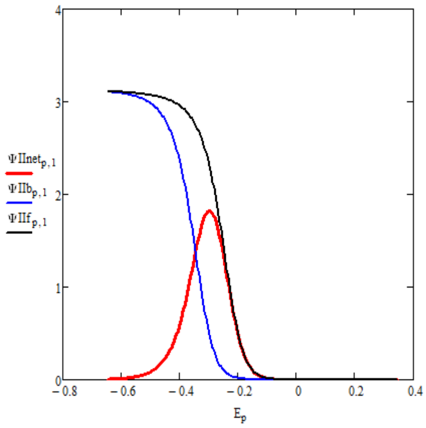
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,1}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

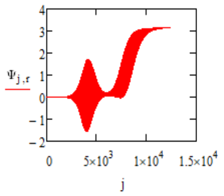
$E_p := EsI - p\cdot dE$

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









$\Psi f_{p,1} =$

$1.058\cdot 10^{-5}$
$1.232\cdot 10^{-5}$
$1.437\cdot 10^{-5}$
$1.678\cdot 10^{-5}$
$1.96\cdot 10^{-5}$
$2.29\cdot 10^{-5}$
$2.676\cdot 10^{-5}$
$3.127\cdot 10^{-5}$
$3.653\cdot 10^{-5}$
$4.269\cdot 10^{-5}$
$4.988\cdot 10^{-5}$
$5.828\cdot 10^{-5}$
$6.809\cdot 10^{-5}$

$\Psi b_{p,1} =$

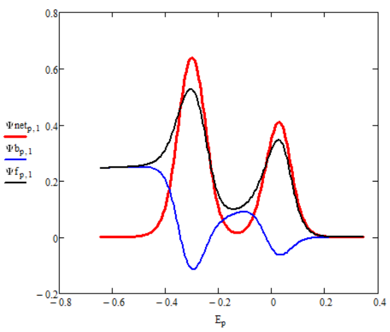
$-1.333\cdot 10^{-6}$
$-1.808\cdot 10^{-6}$
$-2.192\cdot 10^{-6}$
$-2.593\cdot 10^{-6}$
$-3.044\cdot 10^{-6}$
$-3.563\cdot 10^{-6}$
$-4.167\cdot 10^{-6}$
$-4.87\cdot 10^{-6}$
$-5.691\cdot 10^{-6}$
$-6.65\cdot 10^{-6}$
$-7.77\cdot 10^{-6}$
$-9.078\cdot 10^{-6}$
$-1.061\cdot 10^{-5}$
$-1.239\cdot 10^{-5}$

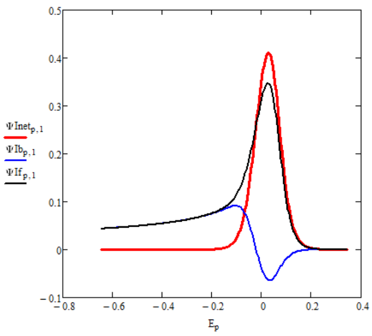
$\Psi net_{p,1} =$

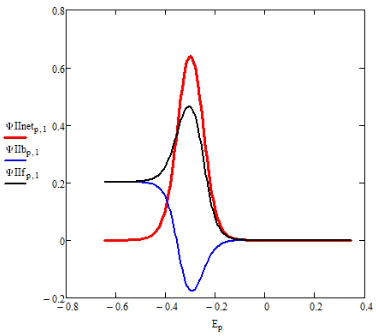
$1.051\cdot 10^{-5}$
$1.239\cdot 10^{-5}$
$1.451\cdot 10^{-5}$
$1.696\cdot 10^{-5}$
$1.983\cdot 10^{-5}$
$2.317\cdot 10^{-5}$
$2.707\cdot 10^{-5}$
$3.163\cdot 10^{-5}$
$3.696\cdot 10^{-5}$
$4.318\cdot 10^{-5}$
$5.046\cdot 10^{-5}$
$5.896\cdot 10^{-5}$
$6.889\cdot 10^{-5}$

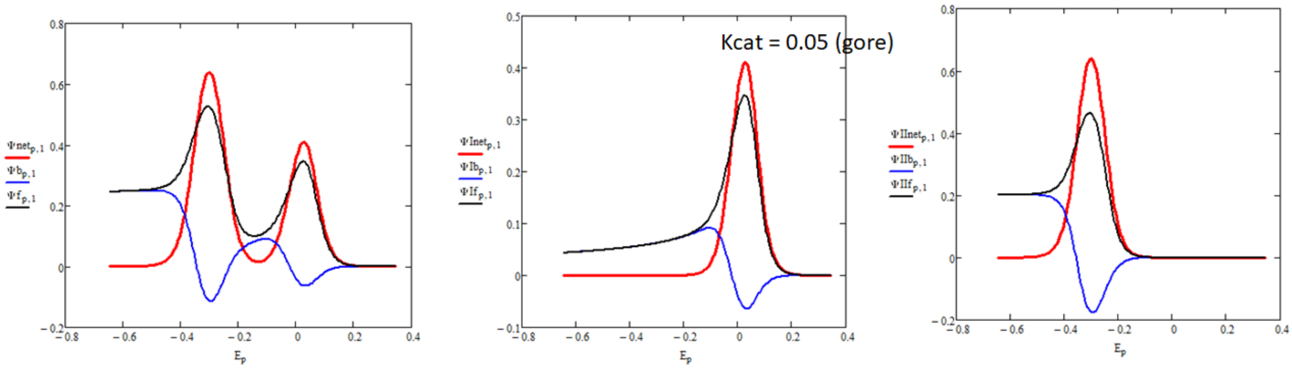
$E_p =$

0.346
0.342
0.338
0.334
0.33
0.326
0.322
0.318
0.314
0.31
0.306
0.302
0.298

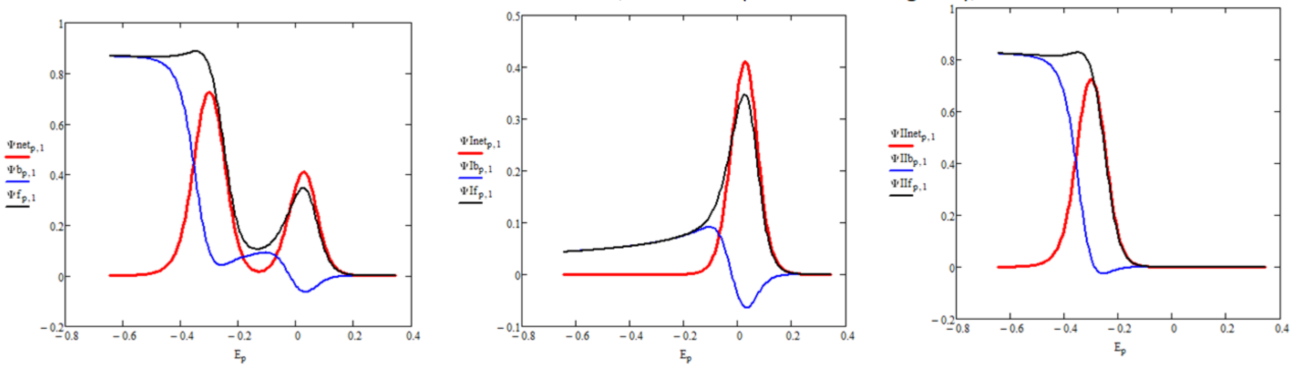


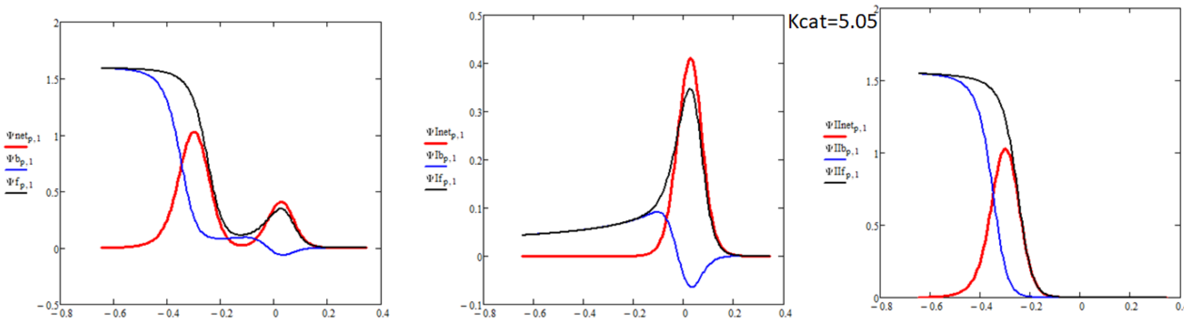


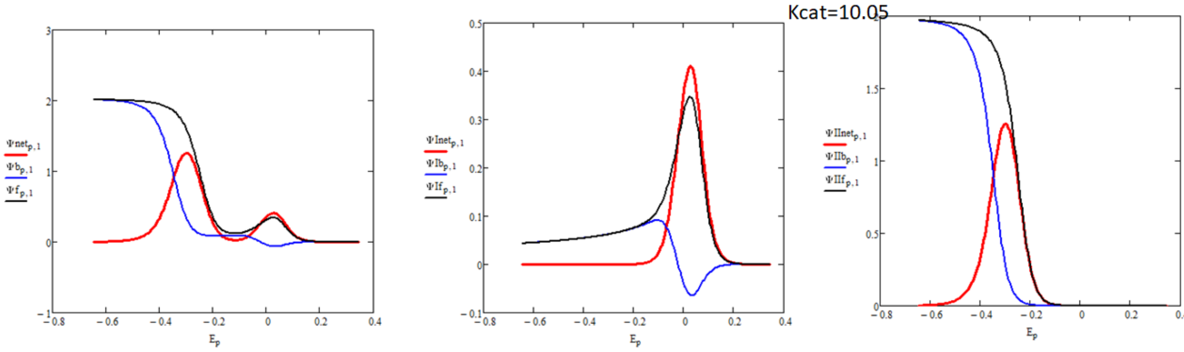


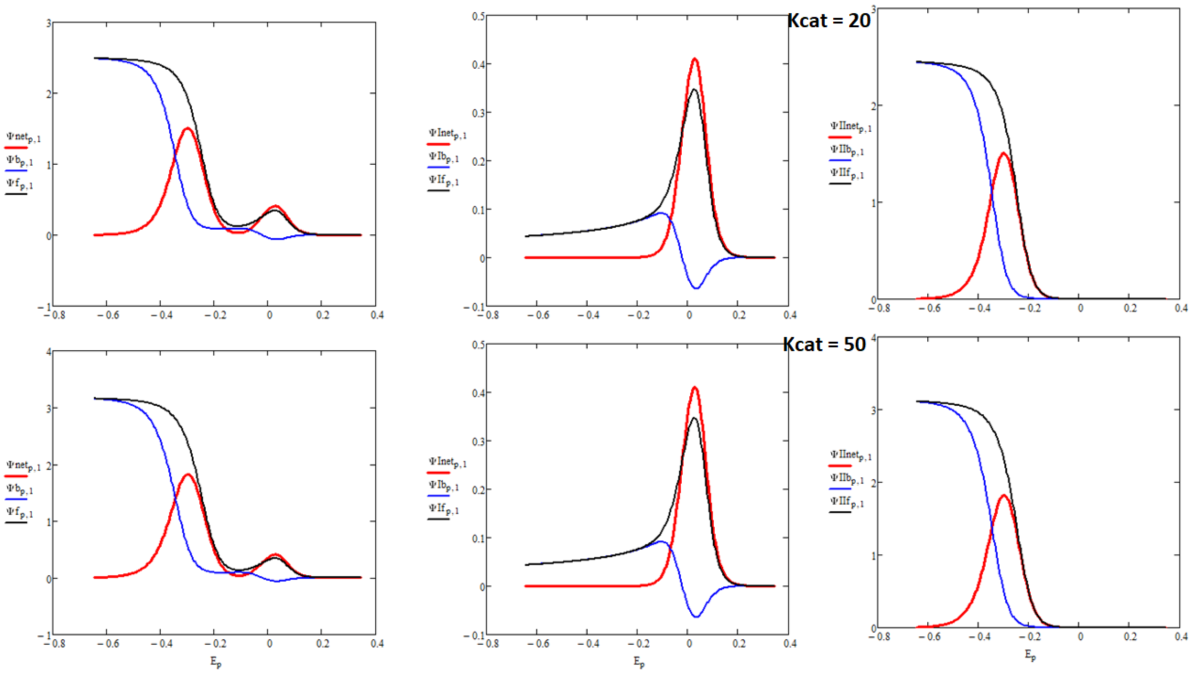


ECirrEC'—Kchem =0.45; Kcat =1.05 (dolni voltammogrami); Ket1=Ket2=5.62








Kcat = 20
Kcat = 50
Ψnet p,1
Ψb p,1
Ψf p,1
ΨInet p,1
ΨIb p,1
ΨIf p,1
ΨIInet p,1
ΨIIb p,1
ΨIIf p,1
E p

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