# Protein-Film Voltammetry of a Surface EC'EC' Mechanism-Effect of Regenerative Reaction Associated to the Second Electron Transfer Step in Systems with Inverted Formal Redox Potentials


***Rubin Gulaboski***

***Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia***



**Abstract:** As many lipophilic redox enzymes often undergo electrochemical transformation in two consecutive electron transfer steps, it is very common that so-called scenario of "inverted formal redox potentials" that makes only one peak to appear in the voltammograms. Here we elaborate a a scenario of a protein-film voltammetry of an EC'EC' mechanism of systems with inverted potentials, and we show how this mechanism can be elucidated by simple variation of the rate of the regenerative reaction associated to the 2nd electron transfer step. This is first model that predicts recognition of redox enzymes with inverted potentials by exploring the surface EC'EC' model in SWV.


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

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

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

$KI_r := 10^{95 \cdot r}$

$KII := 10^{95}$

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

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

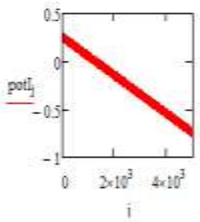
$\lambda := .004001246$

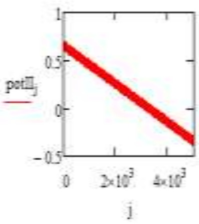
λ e kineticki parametar na regenerativna hemiska reakcija povrzana so prv elektroden cekor

$KI_1 = 8.913$

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

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




$z := .004$

z e kataliticki regenerativen hemiski parametar povrzan so vtor cekor

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

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

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

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

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

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

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

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

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

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

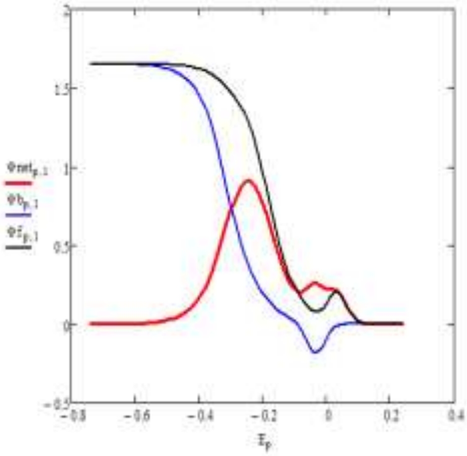
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

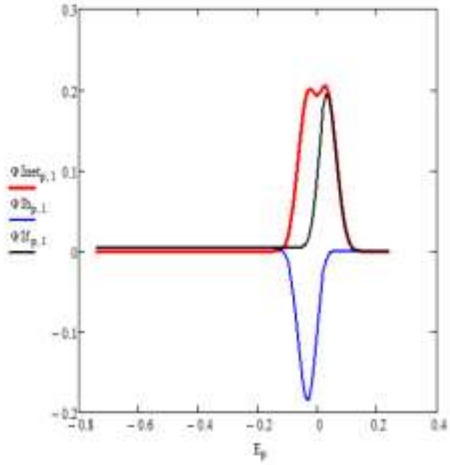
$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

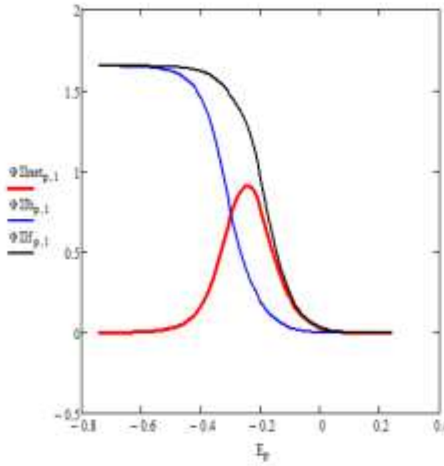
$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

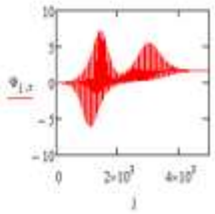
$E_p := EsI - p \cdot dE$

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



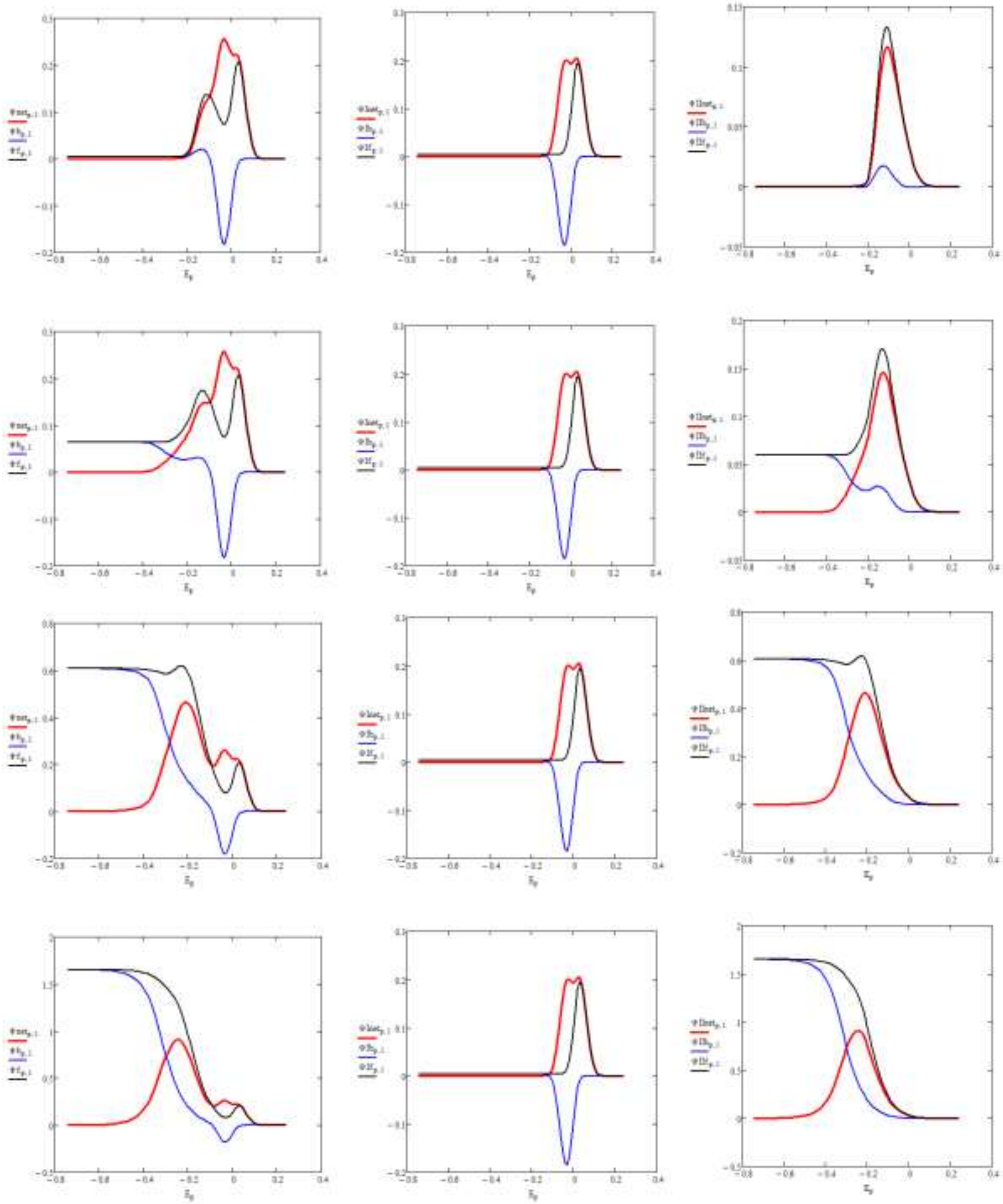




$\Psi f_{p,1} =$ $\Psi b_{p,1} =$ $\Psi net_{p,1} =$ $E_p =$

## Scenario with fast rate of electron transfer of first step and slow rate of electron transfer of second electron transfer step-System with Inverted Formal Redox potentials



**Effect of the rate of the regenerative chemical step coupled to second electron transfer, in conditions of moderate rate of catalytic reaction associated to first electron transfer step.**

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