Resolving a Consecutive Two-Step Electrochemical Transformation of Water-Soluble Redox Enzymes with Inverted Potentials-A Theory of Diffusional EEC' Mechanism in Square-Wave Voltammetry

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Abstract: Consecutive electron transfer steps involve a series of sequential redox reactions where electrons are successively transferred to a specific redox-active center within a protein structure. One of the key functions of consecutive electron transfer steps in water-soluble proteins is in energy metabolism and electron transport chains. For systems with inverted potentials, voltammetry gives a single peak in which both electron transfers are hidden. In this model, we show that the diffusional EEC' mechanism provides an elegant approach to distinguish the two step electrochemical transformation of enzymes with inverted potential. This can be achieved by changing the rate of the catalytic (regenerative) reaction only.

TWO STEP DIFFUSIONAL EC'EC'cat Mechanism in SWV—new version 15 04 2024

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

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

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

$KII := 10^{.75}$

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

$\alpha 2 := 0.5$

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

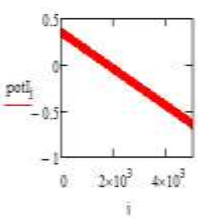
$\lambda := 2.40612400001$

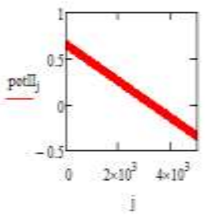
$KI_1 = 5.623$

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

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

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





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

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

$z := 3.5001$

z e kataliticki parametar vo ovoj model povrzan so vtor cekor

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

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

$x := 0.001$

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

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

$\Psi I_{1,1} = 6.166 \times 10^{-6}$

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

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

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

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

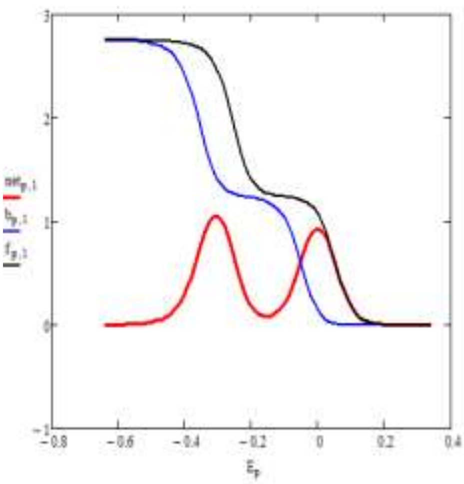
$:= 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

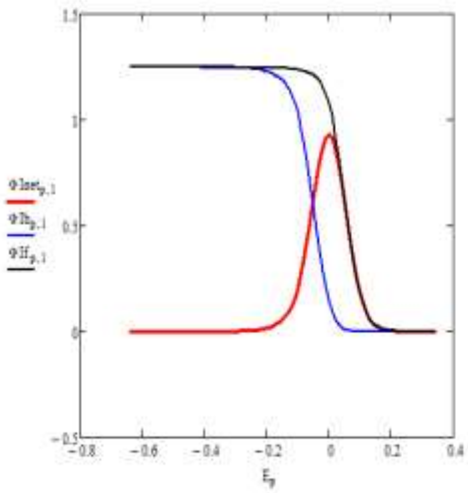
$If_{p,r} := \Psi I_{(p+1) \cdot 50,r} \quad \Psi Ib_{p,r} := \Psi I_{50 \cdot p+2} \quad \Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

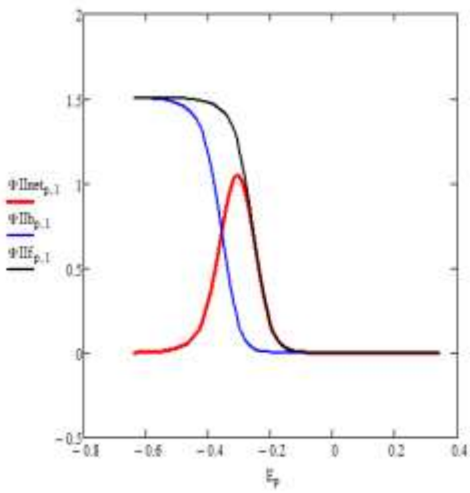
$_{p,r} := \Psi II_{50 \cdot p+25,r} \quad \Psi IIf_{p,r} := \Psi II_{(p+1)} \quad \Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

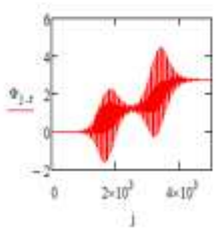
$\cdot Esl - p \cdot dE$

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

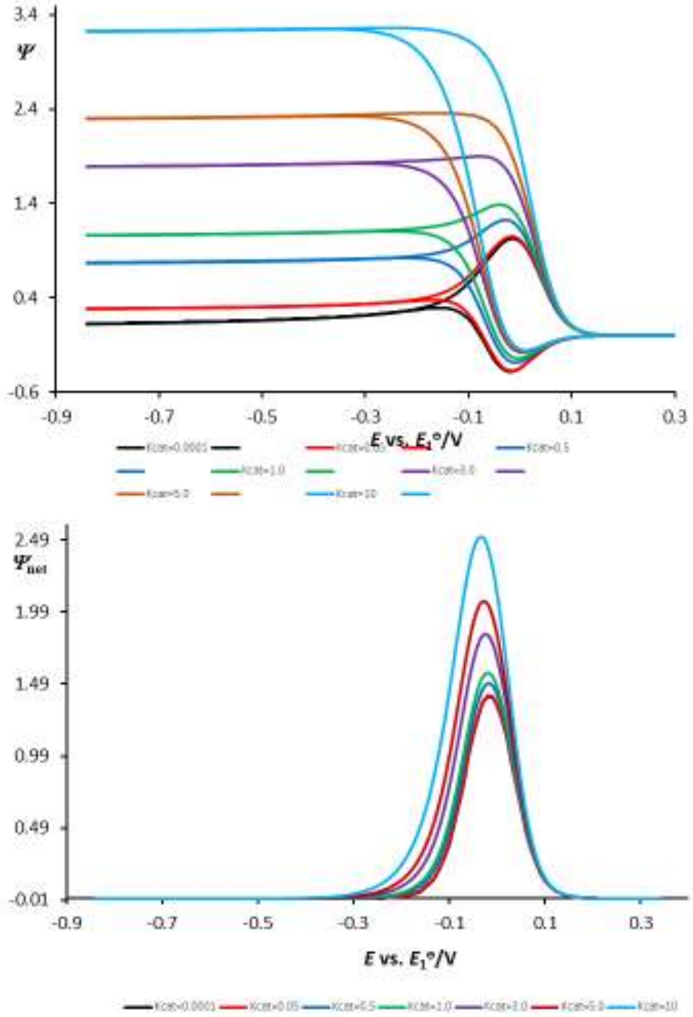




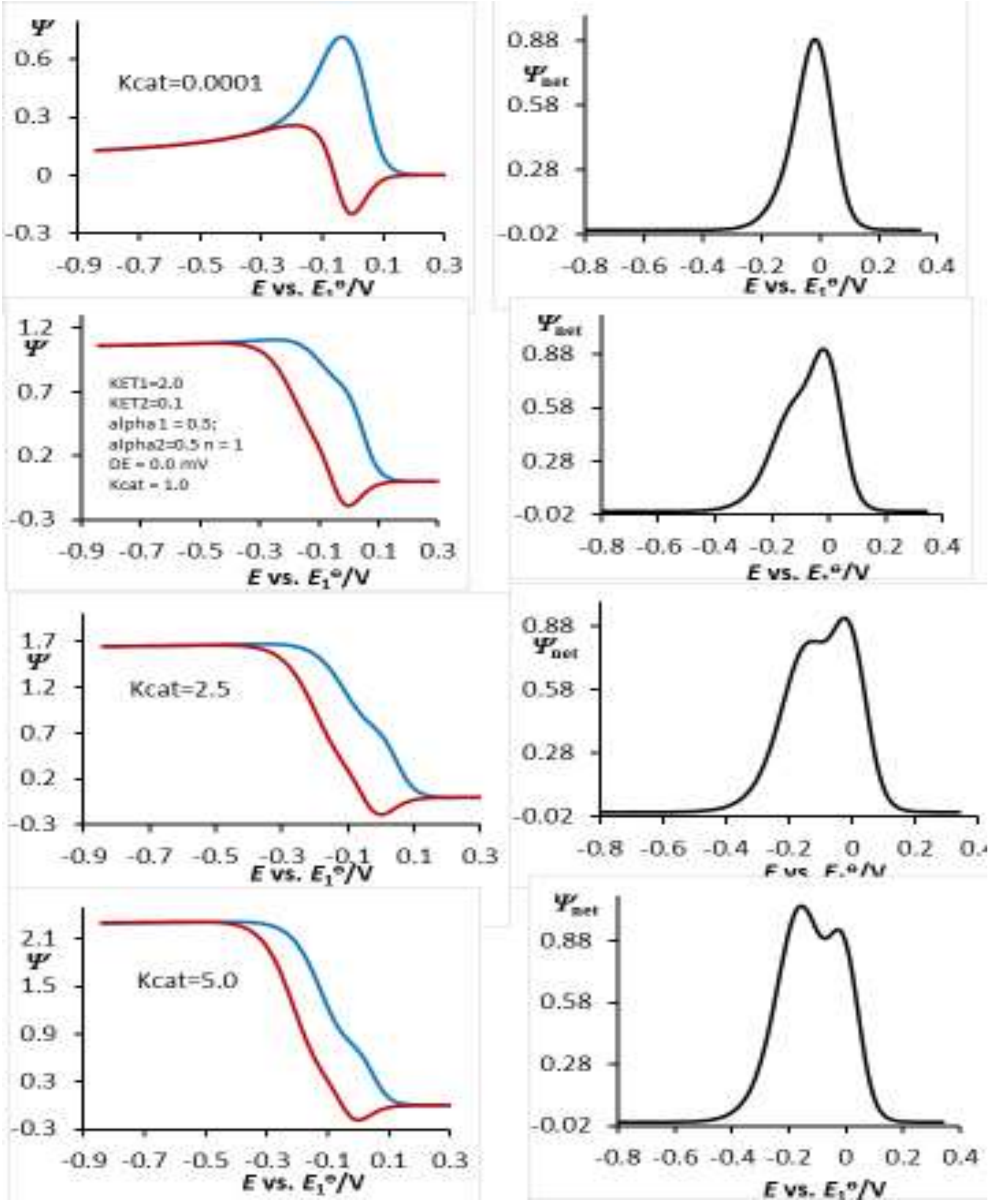




$\Psi f_{p,1} =$ $\Psi b_{p,1} =$ $\Psi net_{p,1} =$ $E_p =$



Effect of the rate of catalytic reaction to the features of forward, backward and net voltammetric peaks, in conditions of fast rates of electron transfer steps of both electron transfers of systems with inverted potentials.



Effect of the rate of catalytic reaction to the features of forward, backward (left patterns) and net voltammetric peaks (right patterns), in conditions of fast rate of electron transfer step of first electrochemical reaction and moderate rate of electron transfer of second electrochemical reaction in systems with inverted potentials.

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