Simulation of Diffusional EEC' Mechanism in Square-Wave Voltammetry

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Abstract

When a chemical reaction is associated to the last product of a two-step successive electrochemical diffusional mechanism, while causing regeneration of the intermediate electrochemically active compound (generated in the first electron transfer step), then the name of this mechanism in electrochemical terminology is ***EEC' mechanism***. In this work, for the first time this complex mechanism is solved under conditions of square-wave voltammetry, and the entire simulation MATHCAD file is provided for free. The voltammetric patterns of this mechanism are function of the electron transfer coefficients related to both electron transfer steps, of the kinetics of electron transfer of both electron transfer steps, and of the kinetics of regenerative chemical reaction. Plenty of interesting situation can be simulated at this mechanism, depending on the formal redox potentials of both electron transfer steps. Importance of this mechanism is found in the redox behavior of enzymes whose electrochemical transformation occurs in two successive steps.

TWO STEP DIFFUSIONAL EEC'cat Mechanism in SWV---Tocen 21 Oct 2023

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

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

$KII := 10^{.75}$

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

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

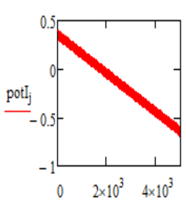
$\alpha 2 := 0.5 \quad \alpha 1 := 0.5$

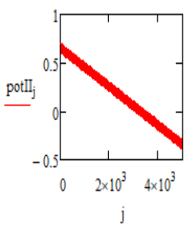
$\log(KI_r) = 0.75$

$KI_1 = 5.623$

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

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





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

$z := 100.000000500$

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

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

$x := 0.001$

z e kataliticki parametar vo ovoj model povrzan so hemiska regeneracija na reaktant od vtor elektrohemiski cekor

$$\Psi I_{1,r} := \frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_1}}{1 + KI_r\cdot\frac{2}{\sqrt{\pi\cdot 50}}\cdot M1_1\cdot e^{-\alpha 1\cdot\Phi I_1} + KI_r\cdot\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}\cdot M1_1}$$

$$\Psi II_{1,r} := \frac{KII\cdot\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\Psi I_{1,r}\cdot M1_1}{1 + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{1\cdot\Phi II_1\cdot(-\alpha 2)} + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{1\cdot\Phi II_1\cdot(1-\alpha 2)}}$$

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

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

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

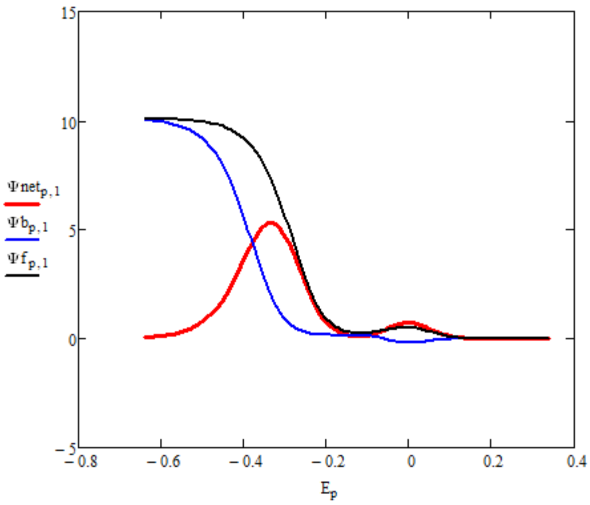
$$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$$

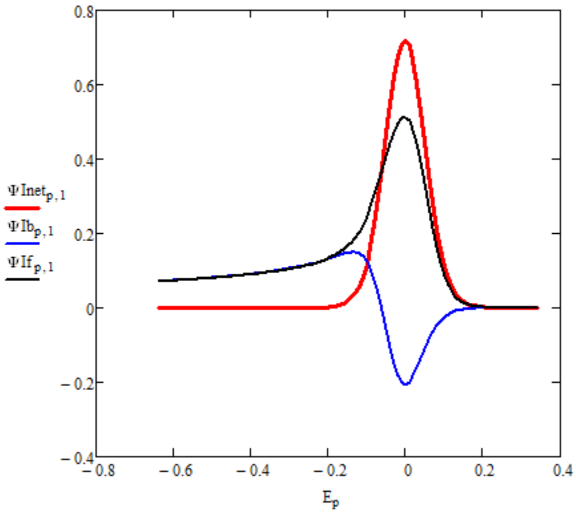
$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

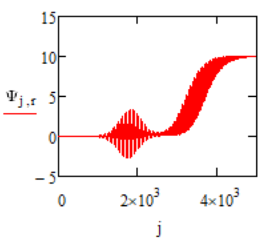
$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,\imath}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

$E_p := EsI - p \cdot dE$

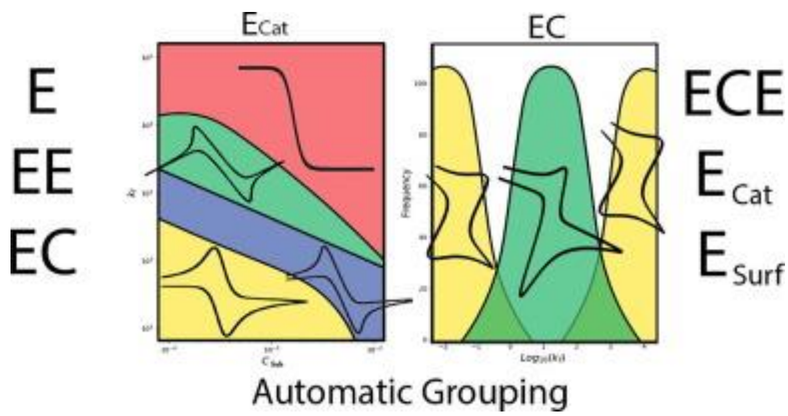
$\Psi b_{p,r} := \Psi_{50 \cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1) \cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$

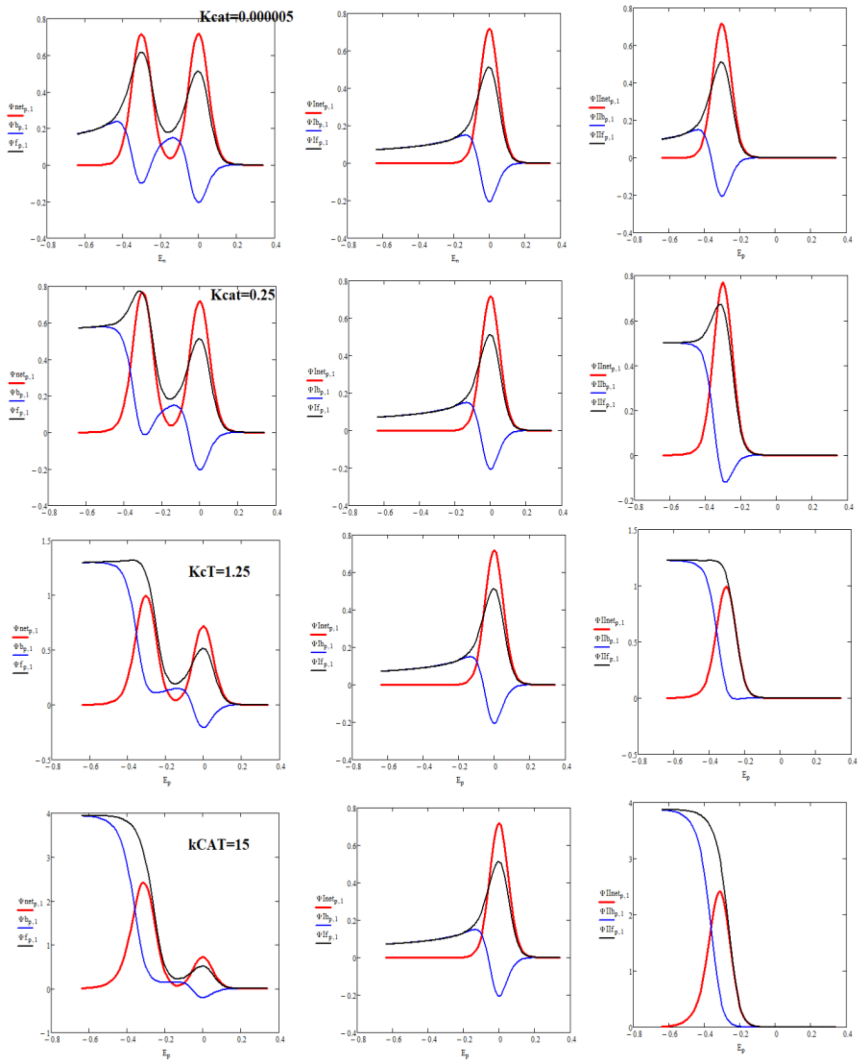






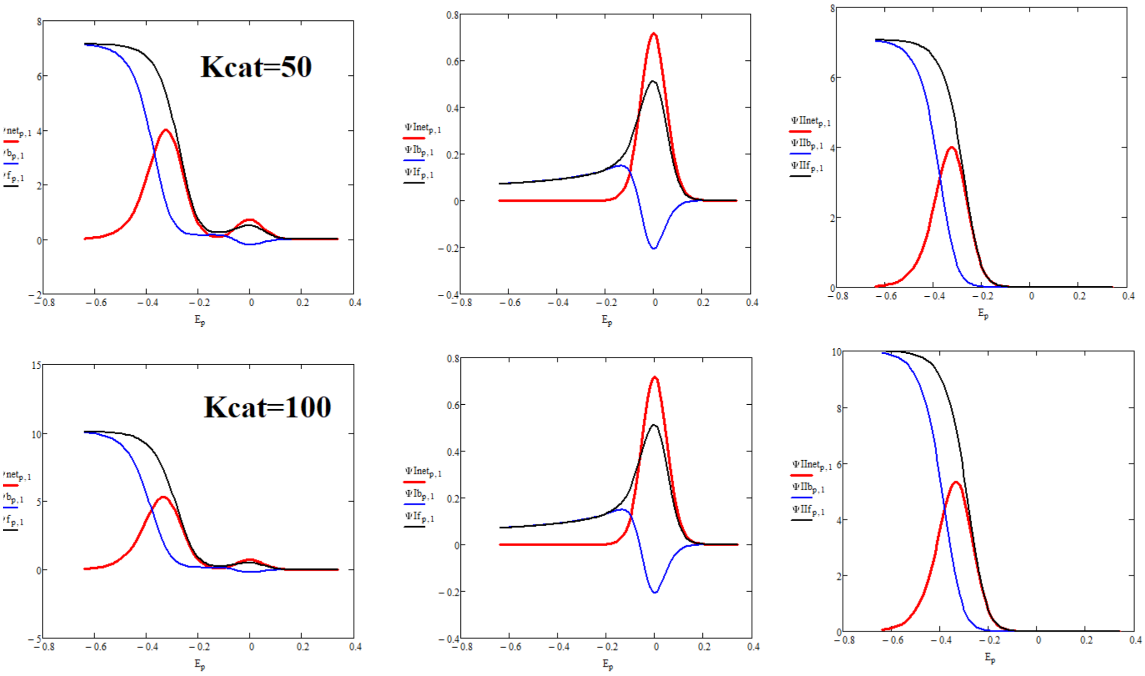
$\Psi f_{p,1} =$	$\Psi b_{p,1} =$	$\Psi net_{p,1} =$
$9.208 \cdot 10^{-6}$	$-1.879 \cdot 10^{-6}$	$1.109 \cdot 1$
$1.322 \cdot 10^{-5}$	$-3.312 \cdot 10^{-6}$	$1.654 \cdot 1$
$1.931 \cdot 10^{-5}$	$-5.159 \cdot 10^{-6}$	$2.447 \cdot 1$
$2.836 \cdot 10^{-5}$	$-7.781 \cdot 10^{-6}$	$3.614 \cdot 1$
$4.175 \cdot 10^{-5}$	$-1.16 \cdot 10^{-5}$	$5.335 \cdot 1$
$6.155 \cdot 10^{-5}$	$-1.721 \cdot 10^{-5}$	$7.875 \cdot 1$
$9.078 \cdot 10^{-5}$	$-2.546 \cdot 10^{-5}$	$1.162 \cdot 1$
	$-3.762 \cdot 10^{-5}$	





EEC'CAT MECHANISM IN SWV

A+1e-=B+1e-=C + Y = B



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