Effect of Potential Step (dE) of Potential Signal to the Splitting Net-Peak Phenomena of a Surface EC'EC' Mechanism in Square-Wave Voltammetry

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Abstract: As electrochemical transformation of various redox enzymes often takes place in two consecutive steps, it is quite difficult to modeling such systems under voltammetric conditions. In couple of our previous works, we presented the voltammetric results of a surface EC'EC' mechanism in square-wave voltammetry, considering both electron transfer steps to be very fast and happening at potentials separated more than 200 mV. The effect of the potential step (dE) in such scenario is presented in this work that can help in better understanding of this complex electrode mechanism,

TWO STEP SURFACE EC'EC'cat Mechanism in SWV--new version 01 04 2024 OK-Effect of potential step dE

$EsI := 0.25$ $\Delta E := 1$ $dE := 0.01$ $Esw := 0.05$ $EsII := 0.55$ $r := 1..1$

$n := 1$ $F := 96500$ $R := 8.314$ $T := 298.15$ $KI_r := 10^{5 \cdot r}$

$KII := 10^{5}$

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

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

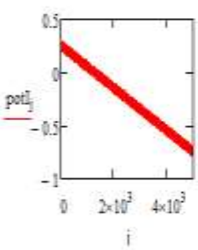
$\lambda := .04001246$

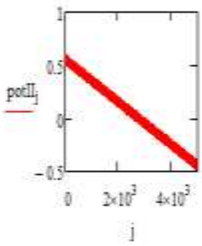
$$potI_j := EsI + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$KI_1 = 3.162$

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

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





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

$z := .04094$

z e kataliticki regenerativen hemiski parametar povrzan so vtor cekor

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

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

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

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

$\Psi I_{1,1} = 1.17 \times 10^{-3}$

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

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

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

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

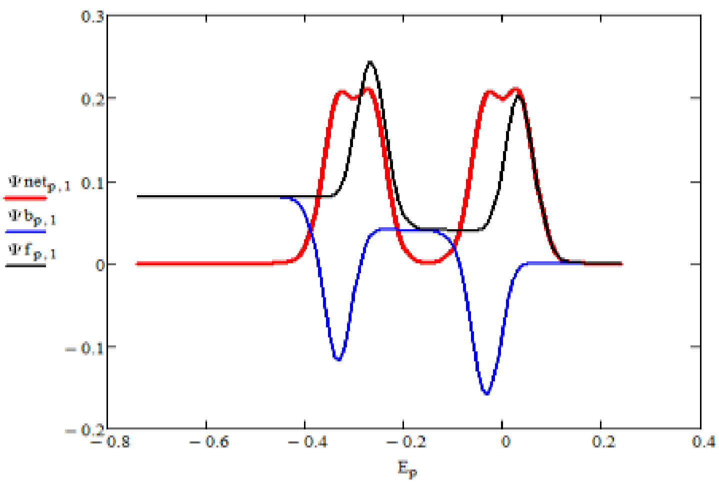
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

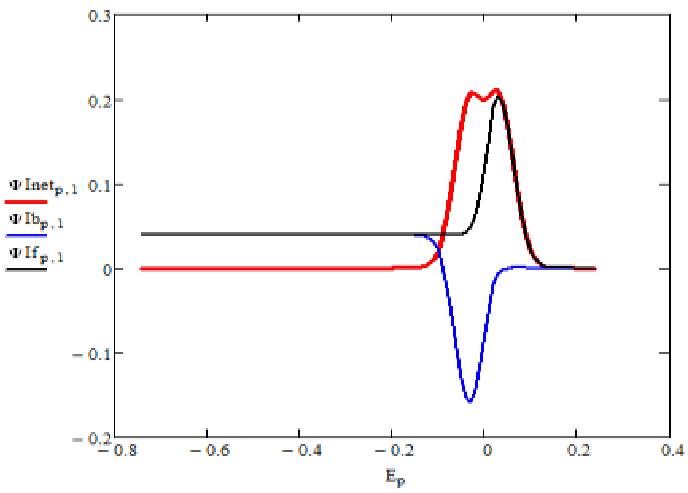
$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

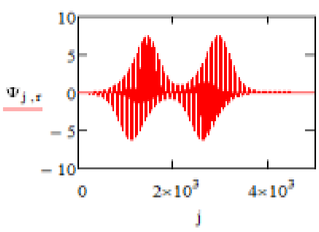
$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,1}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

$E_p := EsI - p \cdot dE$

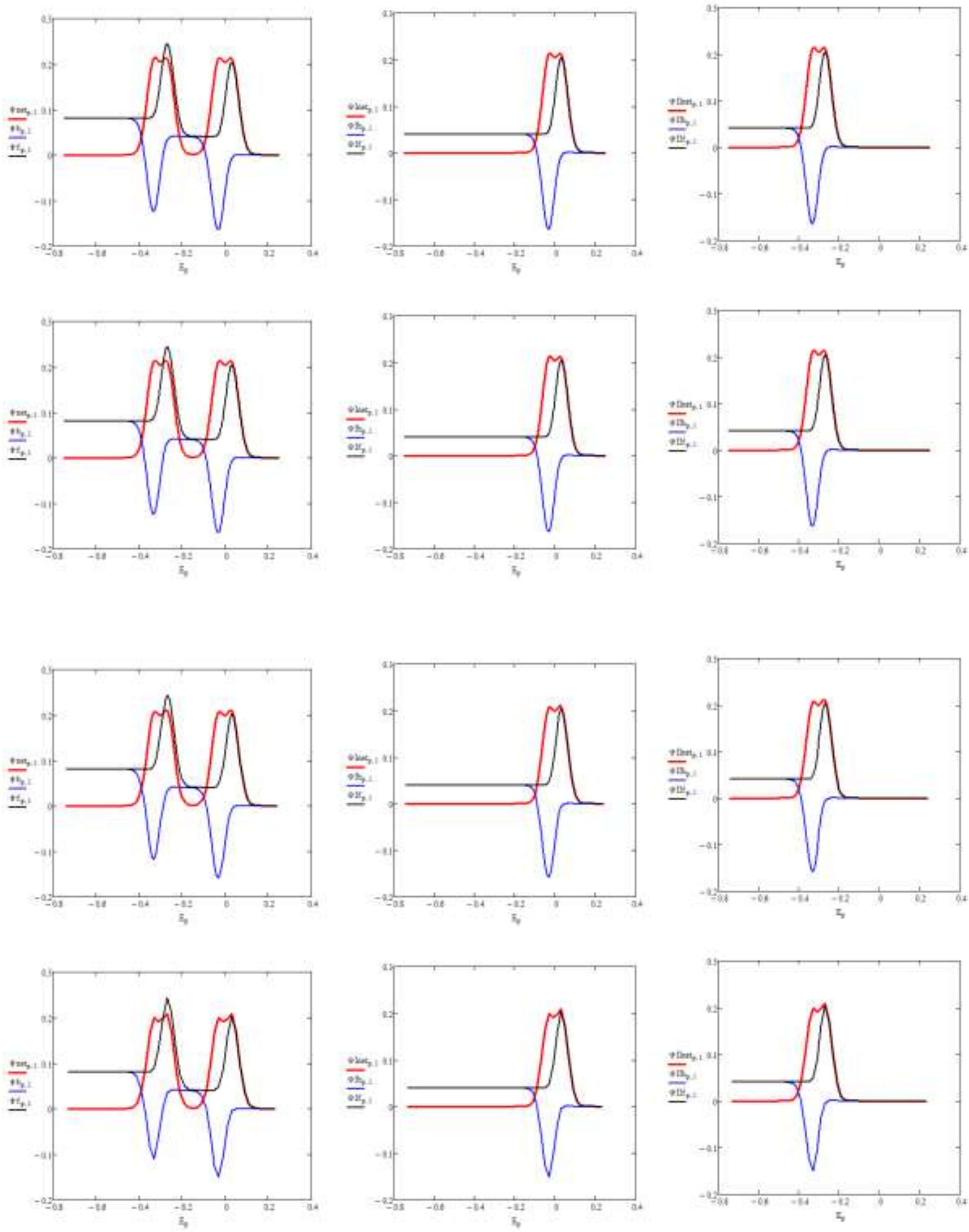
$\Psi b_{p,r} := \Psi_{50 \cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1) \cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$







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



Effect of the SW potential step (dE) to the both voltammetric peaks, in conditions of fast rates of electron transfer steps moderate rate of both chemical regenerative reactions.

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