Effect of Square-Wave Amplitude to the Splitting Net-Peak Phenomena of a Surface EC'EC' Mechanism in Square-Wave Voltammetry

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Abstract: While many redox enzymes undergo electrochemical transformation in two consecutive steps, there is always a need to make mathematical models for such systems under voltammetric conditions in order to get insight into their kinetics and thermodynamics. In this work, we present 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 square-wave amplitude in such scenario reveals aspects that can lead not only to mechanistic revelations, but also provides mean for kinetic determinations.

TWO STEP SURFACE EC'EC'cat Mechanism in SWV—new version 01 04 2024 OK-Effect of SW amplitude

$EsI := 0.25 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.16 \quad EsII := 0.55 \quad r := 1..1$

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

$KII := 10^{5}$

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

$\alpha 2 := 0.5$

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

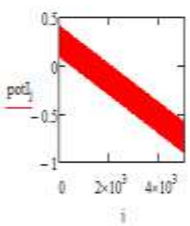
$\lambda := .04001246$

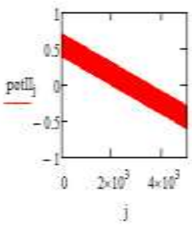
$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$KI_1 = 3.162$

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

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





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

$z := .04094$

z e kataliticki regenerativen hemiski parametar povrzan so vtor cekor

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

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

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

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

$\Psi I_{1,1} = 1.821 \times 10^{-5}$

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

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

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

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

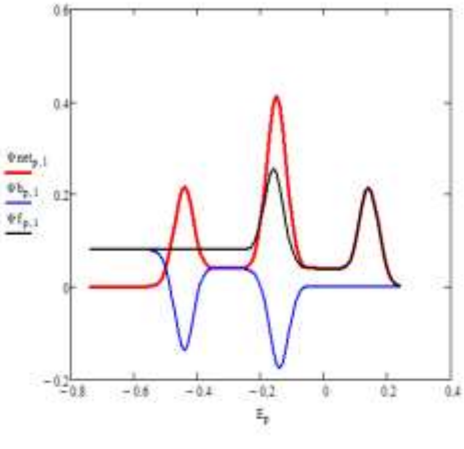
$$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$$

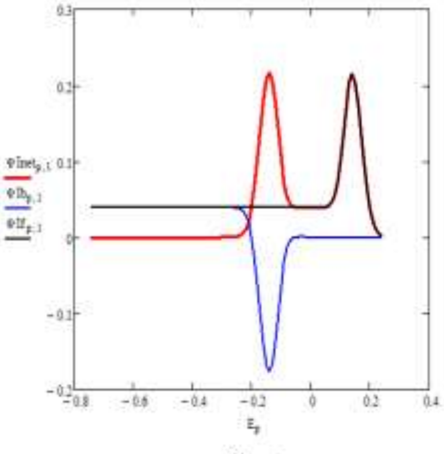
$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

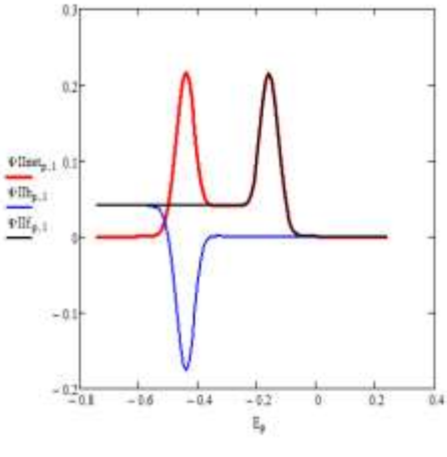
$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

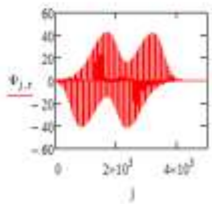
$E_p := Esl - p \cdot dE$

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

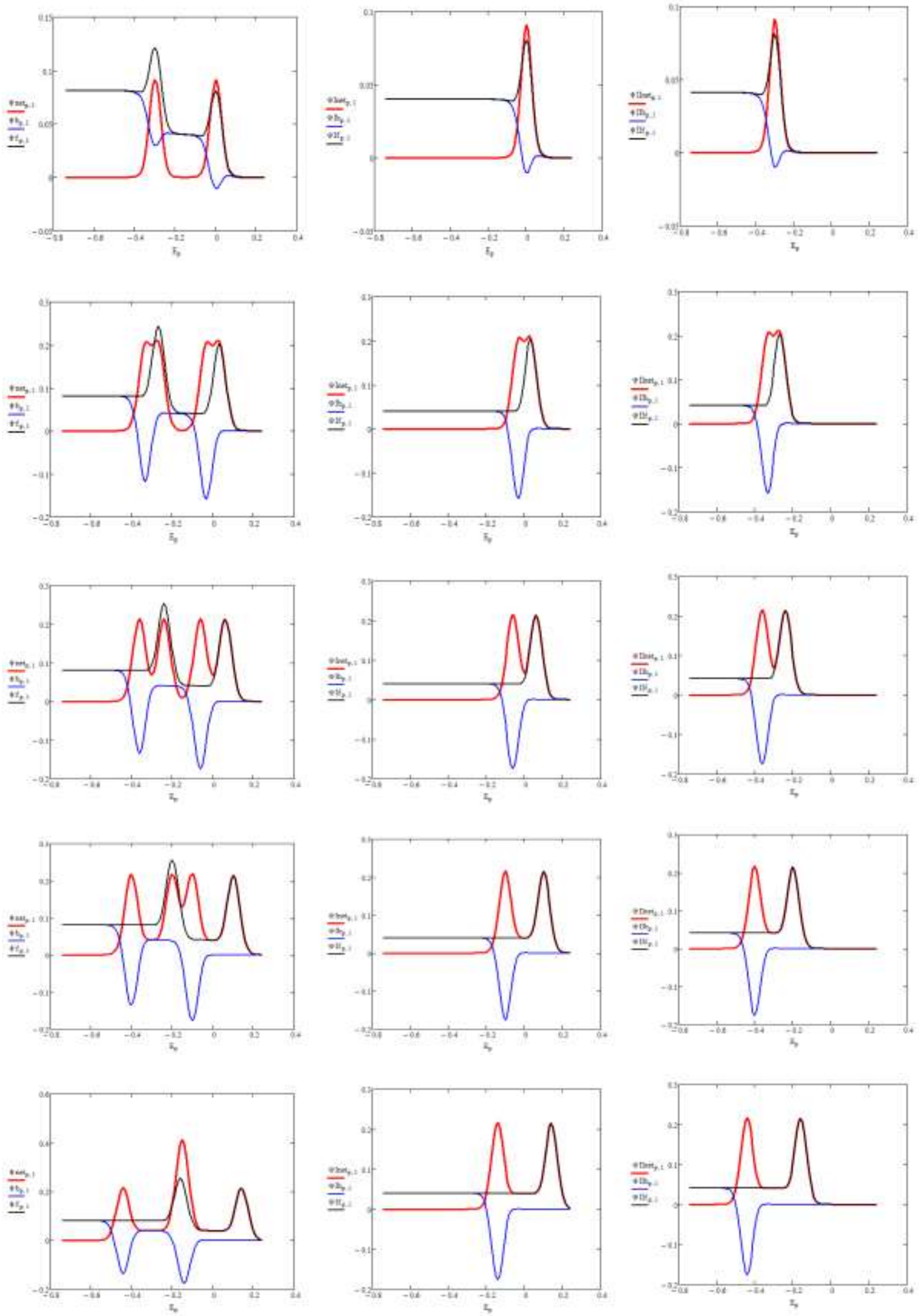








$\Psi f_{p,1} =$ $\Psi b_{p,1} =$ $\Psi net_{p,1} =$ $E_p =$



Effect of the SW amplitude 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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