

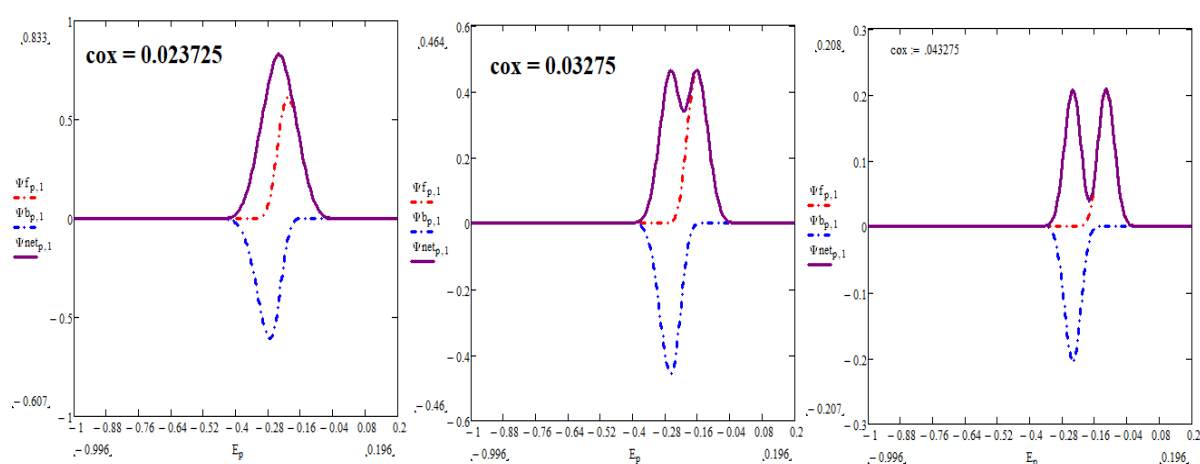
# Surface CE Mechanism with Second Order Chemical Step-Theoretical Analysis in Square-Wave Voltammetry

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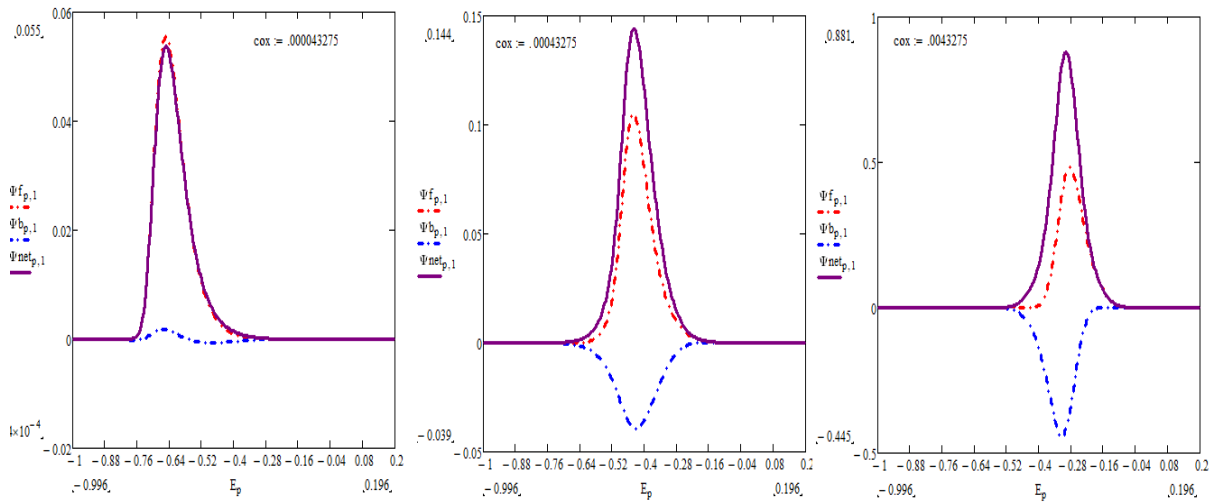
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## Abstract

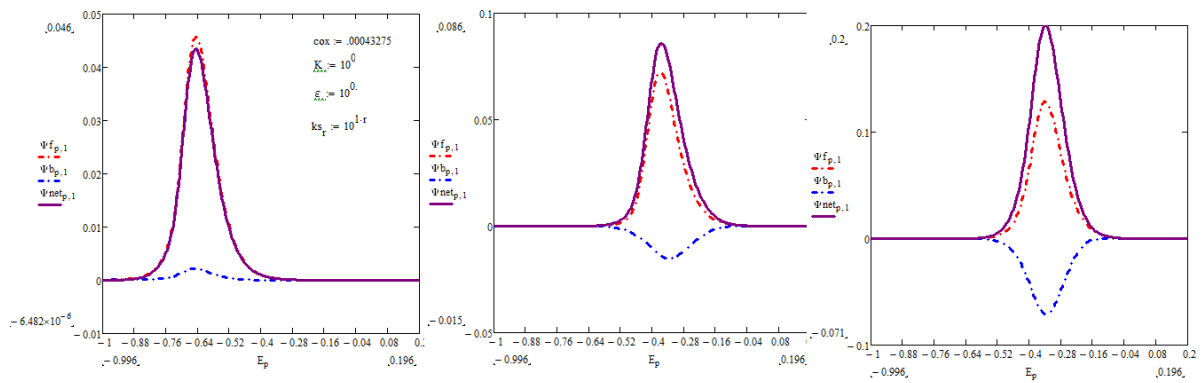
Electrochemical processes where the initial electrochemically active entities arise from chemical reactions between two molecules of a dormant reactant pertain to the second-order surface CE mechanism concerning the concentration of the starting agent. When the chemical reaction is reversible and the electron transfer step is quasi-reversible, the outcomes in square-wave voltammetry depend on the chemical rate parameter, the equilibrium constant for the chemical reaction, the electron transfer rate, and the starting concentration of electrochemically inert species in the voltammetric cell ( $c_{Ox}$ ). In this MATHCAD simulation file, we introduce a simulation procedure for this intricate model in the context of square-wave voltammetry for the very first time. We provide readers with insights on identifying this mechanism in actual experiments and on determining both kinetic and thermodynamic parameters pertinent to the chemical and electron transfer steps. This work can assist experimenters focused on protein-film voltammetry.



**Effect of the initial concentration  $c(Ox)$  to the Splitting phenomenon**  
 **$A+A \rightarrow B + 1e^- = C(ads)$  reaction:  $K_{eq}$  is 10000;  $K_{chem}$  is 0.01,  $k_s$  is 1000**  
 **$E_{sw}$  is 80 mV,  $dE$  is 4 mV,  $f$  is 10 Hz,  $\alpha$  is 0.5**



Effect of initial concentration  $c(\text{Ox})$  to the features of square-wave voltammograms in lower concentration range. Other conditions as in previous figure



Effect of standard rate constant of electron transfer

Es := 0.2   ΔE := 1.2   dE := 0.004   Esw := 0.08  
n := 1   F<sub>∞</sub> := 96500   R<sub>∞</sub> := 8.314   T := 298.15

r := 1..1

cox := .00243275

2C > --Ox + 1e = • Red

f := 10

ks<sub>r</sub> := 10<sup>2.5·r</sup>

kf := .1

kb := .1

epsilon := kf + kb

λ<sub>r</sub> :=  $\frac{ks_r}{f}$    K<sub>∞</sub> := 10<sup>2</sup>

λ<sub>r</sub> =

log( $\frac{ks}{f}$ ) =

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

α := 0.5

pot<sub>j</sub> := Es + Esw -  $\left[ \left( \text{ceil}\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + \text{if}\left(\frac{\text{ceil}\left(\frac{j}{25}\right)}{2} = \text{ceil}\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw \right) - dE \right]$

31.623

ε<sub>∞</sub> := 10<sup>4</sup>

λ<sub>r</sub> =

ε = 1 × 10<sup>4</sup>

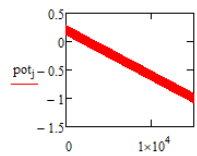
ε<sub>r</sub> =

31.623

log(z<sub>r</sub>) =

z :=  $\frac{\epsilon}{f}$

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



$\frac{0.099}{0.119} = 0.832$

$\frac{.239}{.252} = 0.948$

ε = 1 × 10<sup>4</sup>

z = 1 × 10<sup>3</sup>

SURFACE MONOMERIZATION MECHANISM  
in SWV APRIL 2023

10<sup>1.2</sup> = 15.849

Kchem za monomerizacii e golemo  
treba vlijanie na cox i Keq i na KET

Φ<sub>∞</sub> := n ·  $\frac{F}{R \cdot T}$  · pot<sub>j</sub>

log(z) = 3

ε<sub>r</sub> =

log(λ<sub>r</sub>) =

1.5

Ψ<sub>1,r</sub> =

Ψ<sub>1,r</sub> := λ<sub>r</sub> · e<sup>-α·Φ<sub>1</sub></sup> ·  $\frac{\text{cox}}{2+0}$  ·  $\left[ (1) \cdot \left[ 1 + \lambda_r \cdot e^{-\alpha \cdot \Phi_1} \cdot \frac{\text{cox} \cdot (K)}{(1+K) \cdot 2} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi_1} \cdot S_1 \cdot \text{cox}}{(1+K) \cdot z} \right]^2 + \frac{\lambda_r \cdot e^{(1-\alpha) \cdot \Phi_1}}{50} \right]^{-1}$

Ψ<sub>k,r</sub> :=  $\frac{\left[ \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi_k} \cdot (\text{cox})^2}{2+0} \cdot \left( 1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi_{j,r} \right) - \left[ \frac{(z)^{-1}}{1+K} \cdot \lambda_r \cdot \frac{(\text{cox})^2}{2+0} \cdot (-1) \cdot e^{-\alpha \cdot \Phi_k} \cdot \sum_{j=1}^{k-1} (\Psi_{j,r} \cdot S_{k-j+1}) - \frac{K}{1+K} \cdot \lambda_r \cdot \frac{(\text{cox})^2}{2+0} \cdot (-1) \cdot e^{-\alpha \cdot \Phi_k} \cdot \sum_{j=1}^{k-1} (\Psi_{j,r} \cdot S_{k-j+1}) \right] \right]}{\left[ \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi_k} \cdot 1}{2+0} \cdot \frac{(\text{cox})^2}{50} + 1 + \frac{(z)^{-1}}{1+K} \cdot \lambda_r \cdot (-1) \cdot \frac{(\text{cox})^2}{2+0} \cdot S_1 \cdot e^{-\alpha \cdot \Phi_k} + \frac{K}{1+K} \cdot \lambda_r \cdot (-1) \cdot \frac{(\text{cox})^2}{2+0} \cdot S_1 \cdot e^{-\alpha \cdot \Phi_k} \right] + \frac{\lambda_r}{50} \cdot e^{\Phi_k \cdot (1-\alpha)}}$



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