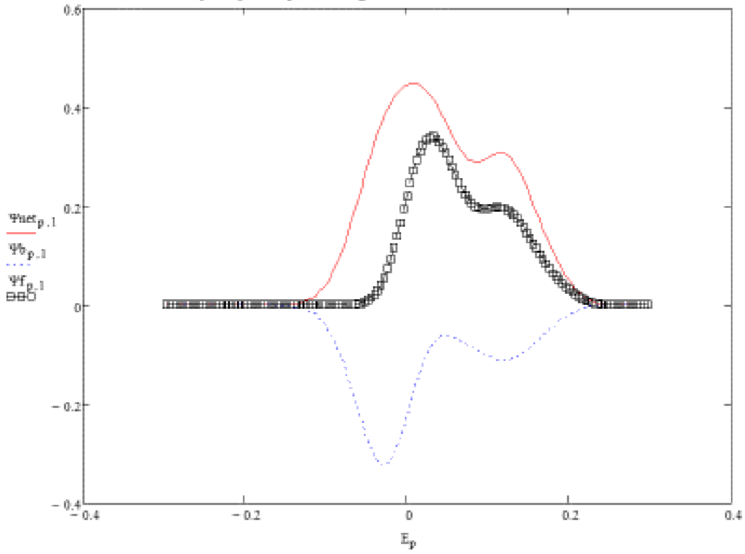
THEORETICAL MODEL OF A TWO-STEP SURFACE EECrev MECHANISM
SWV APPROACH TO SEPARATE BOTH ELECTRON TRANSFER STEPS
WHEN BOTH HAPPEN AT SAME POTENTIAL

-For Keq smaller than 1.0, we adjust the value of Kchemical that will displace Peak II towards more positive potentials, and we can distinguish this Complex mechanism only by adjusting the concentration of the susbtrate Y



Additional Supplementary Material Related to work:
Milkica Janeva, Pavlinka Kokoskarova, Viktorija Maksimova, **Rubin Gulaboski**, Square-wave voltammetry of two-step surface redox mechanisms coupled with chemical reactions-a theoretical overview, ***Electroanalysis, 31 (2019) 1488-1506***
doi: *10.1002/elan.201900416*

IMPORTANT TO KNOW: *SURFACE EECrev MECHANISM In SWV*

The peak at MORE NEGATIVE POTENTIALS at 0.0V IS THE Oxidation-Reduction process of the FIRST ELECTRON TRANSFER STEP,
WHILE the PEAK AT MORE POSITIVE POTENTIALS is the Oxidation-Reduction Process of the Second Process that got Displaced to More POSITIVE POTENTIALS by INCREASING THE RATE OF CHEMICAL REACTION that is COUPLED TO THE SECOND ELECTRON TANSFER STEP.
STARTING POSITION IS A SINGLE PEAK THAT INITIALLY, IN ABSENCE OF CHEMICAL REACTION, EXISTS AS A SINGLE PROCESS AT POTENTIAL of 0.00 V. From that STARTING POSITION WE CHANGE THE RATE OF THE CHEMICAL REACTION AND WE INDUCE DISPLACEMENT OF THE SECOND ELECTRON TRANSFER STEP TOWARDS MORE POSITIVE POTENTIALS, WHILE THE FIRST PROCESS IS NOT AFFECTED BY THE RATE OF CHEMICAL REACTION AND IT STAYS AT SAME POSITION.

We provide here entire simulation file

SURFACE TWO-STEP EECrev MECHANISM
with BOTH ELECTRON TRANSFER STEPS TAKING PLACE
AT SAME POTENTIAL-APPROACH TO RESOLVE IVERLAPPER PEAKS IN SWV

$EsI := 0.3 \quad \Delta E := 0.6 \quad dE := 0.004 \quad Esw := 0.05 \quad EsII := 0.3 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{0.35 \cdot r}$

$KII := 10^{-3}$

KI = ks1/f ---e konst na brz na prenos na elektroni kaj prviot
KII = ks2/f e konst na brzina na prenos na elektroni kaj vtori

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

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

$\log(KI_r) =$ 0.35

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

$KII = 1.995$

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

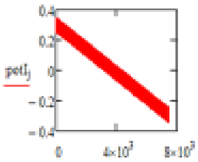
$\gamma := 0.12$

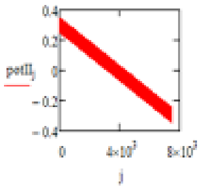
Ova γ e bezdimenzionalen kineticki parametar na hemisk
γ = ε/f = (kf+kb)/f

U e konstanta na ramnoteza definirana kako U = kf/kb

$U := 100.10000010001$

kf-konst na brzina na direktna hemiska reakcija
kb-konst na brzina na povratna hemiska reakcija





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

$$M_j := e^{-\gamma \cdot \frac{j}{50}} - e^{-\gamma \cdot \frac{j+1}{50}}$$

$x := 0.001$

$$\Phi I_{1,r} := root\left[\left[1 + \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_1}}{50} \cdot \left(1 + e^{\Phi I_1}\right)\right] \cdot x - \frac{KI_r}{50} \cdot e^{(1-\alpha 1) \cdot \Phi I_1} \cdot \left[\frac{x \cdot \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50}}{1 + \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50} \cdot \left(1 + e^{\Phi II_1}\right)}\right] - KI_r \cdot e^{-\alpha 2 \cdot \Phi I_1}, x\right]$$

$$UII_{1,r} := \frac{\Phi I_{1,r}\cdot\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}}{1+\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}\cdot\left(1+e^{\Phi II_1}\right)}$$

$$\Phi II_{1,r} := \frac{1KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50+1KII\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)}\cdot\Phi I_{1,r}+\frac{\frac{UKII}{1+U}\cdot e^{(-\alpha 1)\cdot\Phi II_1}-\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{1}\cdot 0}{50+KII\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)+\frac{UKII}{(1+U)\cdot 50}\cdot e^{(1-\alpha 2)\cdot\Phi II_1}\cdot M_1}+\frac{\frac{1\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot\Phi II_1}\cdot 0}{50+KII\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)+\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot\Phi II_1}\cdot M_1}$$

$\Phi I_{1,1} = 5.902\times 10^{-5}$

$\Phi II_{1,1} = 1.165\times 10^{-6}$

$x := 0.001$

$$\Phi I_{j,r} := \mathrm{root}\left[x-KI_r\cdot e^{-\alpha 1\cdot\Phi I_j}\cdot\left[1-\left[\frac{1}{50}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left(x+\sum_{i=1}^{j-1}\Phi I_{i,r}\right)+\frac{e^{\Phi I_j}}{50}\cdot\left[\frac{1}{1+e^{\Phi II_j}}\cdot\left(x+\sum_{i=1}^{j-1}\Phi I_{i,r}\right)-\frac{50}{KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\left[KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left[\frac{1}{50}\cdot\left(x+\sum_{i=1}^{j-1}\Phi I_{i,r}\right)-\frac{1}{50}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[\frac{50x}{KI_r\cdot e^{(1-\alpha 1)\cdot\Phi I_j}}-50\cdot e^{-\Phi I_j}\cdot\left[1-\frac{1}{50}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left(x+\sum_{i=1}^{j-1}\Phi I_{i,r}\right)\right]\right]\right]\right]\right]\right], x\right]$$

$$\Phi II_{j,r} := \frac{0.02KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot 1}{50+1\frac{KII}{50}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot 1\cdot\left(1+e^{\Phi II_j}\right)}\cdot\sum_{i=1}^{j}\Phi I_{i,r}+\frac{1KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot 1-\frac{\frac{1KII}{50}\cdot e^{(-\alpha 2)\cdot\Phi II_j}\cdot 1}{1}\cdot\sum_{i=1}^{j-1}\left(\Phi II_{i,r}\cdot 1\right)-\frac{\frac{1UKII}{\gamma\cdot(1+U)}\cdot e^{(1-\alpha 2)\cdot\Phi II_j}\cdot 1}{1}\cdot\sum_{i=1}^{j-1}\left(\Phi II_{i,r}\cdot M_i\right)-\frac{1\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot\Phi II_j}\cdot 1\cdot\sum_{i=1}^{j-1}\left(\Phi II_{i,r}\cdot M_i\right)}{1+\frac{1KII}{50}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot 1+\frac{1UKII}{\gamma\cdot(1+U)}\cdot e^{(1-\alpha 2)\cdot\Phi II_j}\cdot M_j+\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot\Phi II_j}\cdot M_j\cdot 1}\cdot 1$$

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

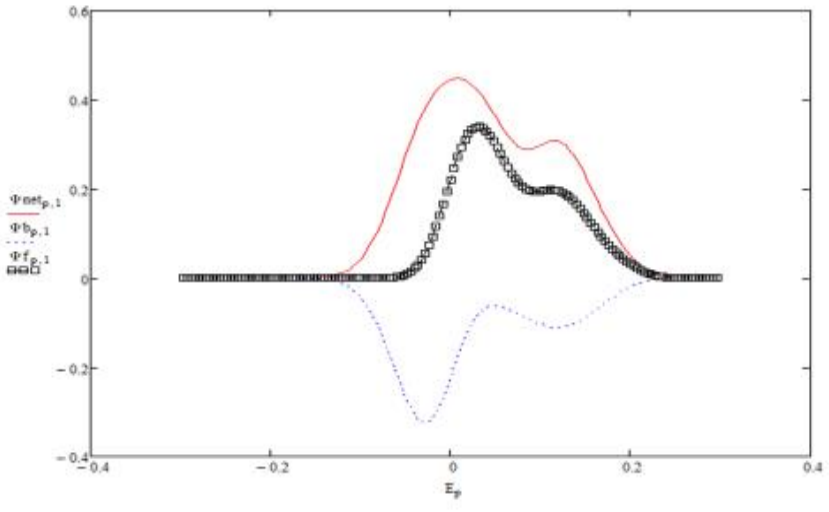
$$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$$

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

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

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

$$E_p := Esl - p\cdot dE$$



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