Two Step Diffusional EE Mechanism Associated with Irreversible Regenerative Reaction to First Electrode Step-MATHCAD Simulation Protocol

Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

Abstract

Redox transformation of many water-soluble redox proteins occurs via two step electrochemical process. In such systems, where often an irreversible chemical process of regenerative nature is associated to the product of first redox electrode transformation. In our most recent work, we have developed a theoretical model for simulating this complex electrode mechanism in square-wave voltammetry, and we offer for free the entire simulation protocol. This is the first theoretical model solved mathematically for this complex electrode mechanism that is very important to understand the features of complex electrochemical transformations in enzymatic voltammetry

TWO STEP DIFFUSIONAL EC'E Mechanism in SWV---this is EE diffusional mechanism with regenerative irreversible reaction associated with the product of first electrode transformation

$EsI := 0.35 \quad \Delta E := 1.2 \quad dE := 0.01 \quad Esw := 0.055 \quad EsII := 0.7 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{0.1 \cdot r} \quad KII := 10^{0.1}$

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

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

$\log(KI_r) =$ $\boxed{0.1}$

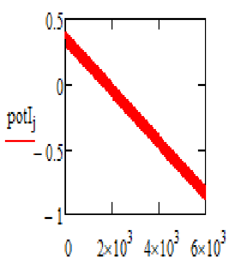
$\lambda := 000.003$

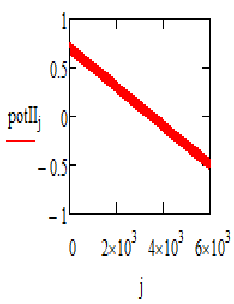
$KI_1 = 1.259$

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

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

$\gamma := .000000100$





$U := 00.0000001$

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

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

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

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

$$\Psi II_{1,r} := \frac{\frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{1+\frac{KII\cdot M1_1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)}\cdot \Psi I_{1,r} + \frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1} - \frac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot 0 - \frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot\frac{U}{(1+U)\cdot 1}\cdot 0 - \frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot 0}{1+\frac{2\cdot KII\cdot M1_1\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}+\frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot\frac{U\cdot M1_1}{(1+U)\cdot 1}+\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot M_1}\cdot 1$$

$\Psi I_{1,1} = 6.141\times 10^{-8}$

$\Psi II_{1,1} = 4.978\times 10^{-7}$

$x := 0.001$

$$\Psi I_{j,r} := \frac{\frac{KI_r}{1}\cdot 1\cdot e^{-\alpha 1\cdot \Phi I_j} - \frac{KI_r\cdot\lambda^{-1}\cdot\frac{2}{\sqrt{4}}}{1}\cdot e^{-\alpha 1\cdot \Phi I_j}\cdot\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right) - \frac{KI_r}{1}\lambda^{-1}\cdot\frac{2}{\sqrt{4}}\cdot e^{\Phi I_j\cdot(1-\alpha 1)}\cdot\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right)}{1+\frac{KI_r\cdot\lambda^{-1}\cdot A_1}{\frac{2}{\sqrt{4}}}\cdot e^{-\alpha 1\cdot \Phi I_j} + 1\lambda^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha 1)}\cdot A_1\cdot\frac{\frac{1}{\sqrt{4}}}{\sqrt{4}}}$$

$$\Psi II_{j,r} := \frac{\frac{\frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot \Phi II_j}}{1+0}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right) - KII\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right) - \frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{1\cdot \Phi II_j\cdot(1-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)}{1+\frac{KII\cdot\frac{2\cdot M1_1}{\sqrt{\pi\cdot 50}}}{1}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}$$

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

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

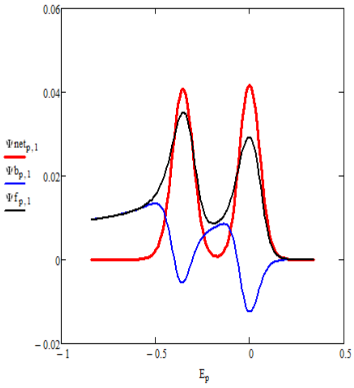
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

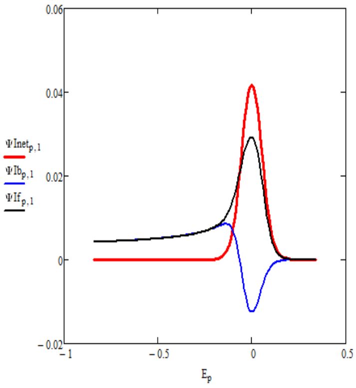
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,1}$ $\Psi IIf_{p,r} := \Psi II_{(p+1}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

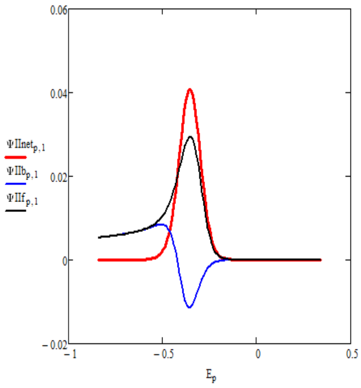
$E_p := EsI - p\cdot dE$

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

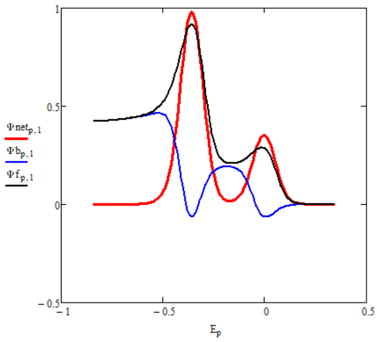
$_{,r} := \Psi_{50\cdot p+25,r} \quad \Psi I_{p,r} := \Psi_{(p+1)\cdot 5(} \quad \Psi net_{p,r} := \Psi I_{p,r} - \Psi b_{p,r}$

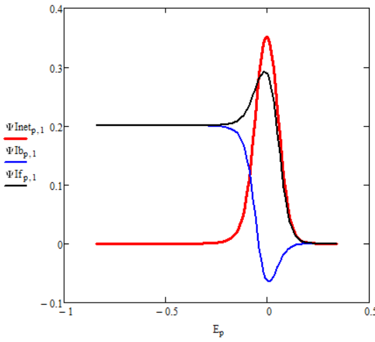


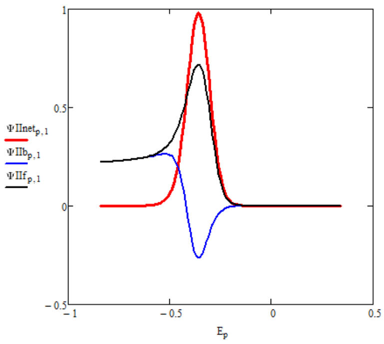


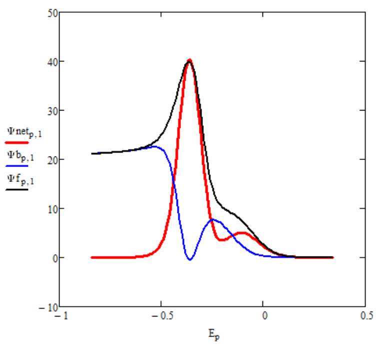


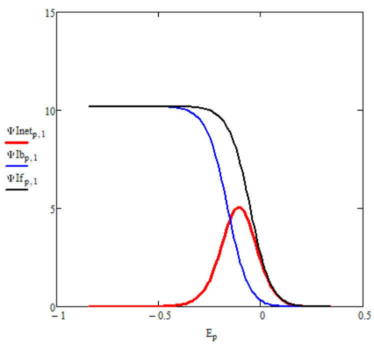
$_{,r} := \Psi_{50\cdot p+25,r} \quad \Psi I_{p,r} := \Psi_{(p+1)\cdot 5(} \quad \Psi net_{p,r} := \Psi I_{p,r} - \Psi b_{p,r}$

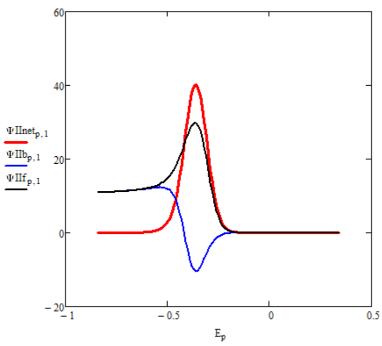


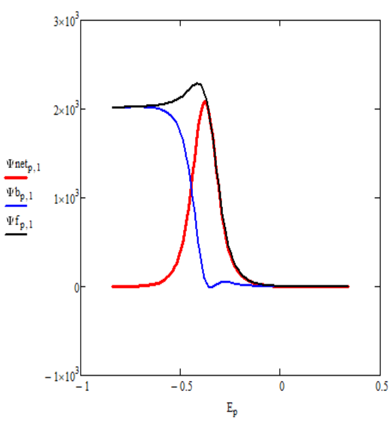


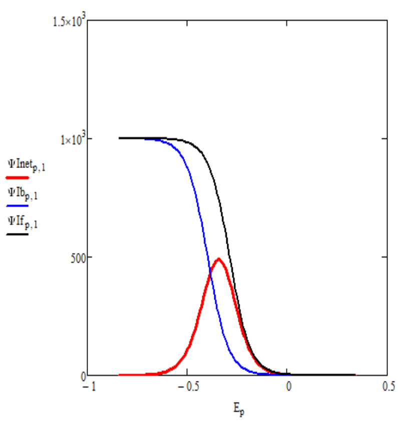


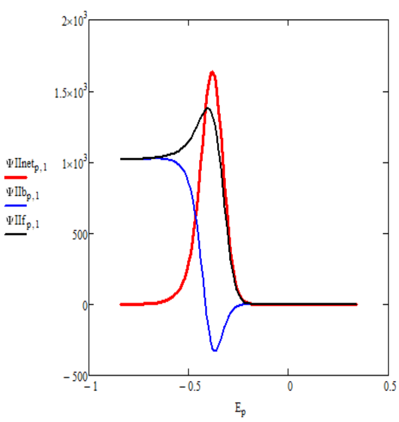












REFERENCES

1. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435
2. B. Sefer, R. Gulaboski, V. Mirceski, ***Journal of Solid State Electrochemistry*** 16 (2012) 2373-2381.
3. V. Mirceski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (2002) 813-818
4. R. Gulaboski, V. Mirceski, S. Mitrev, ***Food Chemistry*** 138 (2013) 116-121
5. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435
6. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842
7. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, ***Cell Calcium*** 43 (2008) 615-621
8. V. Mirceski, R. Gulaboski, ***Bulletin of the Chemists and Technologists of Macedonia*** 18 (1999) 57-64.
9. R. Gulaboski, C. M. Pereira, ***Electroanalytical Techniques and Instrumentation in Food Analysis***; in Handbook of Food Analysis Instruments (2008) 379-402.
10. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, ***Journal of Physical Chemistry B*** 110 (2006) 12530-12538.
11. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, ***Analytical Chemistry*** 91 (2019) 14904-14910.
12. V. Mirceski, R. Gulaboski, F. Scholz, ***Journal of Electroanalytical Chemistry*** 566 (2004) 351-360.
13. R. Gulaboski, V. Mirceski, S. Mitrev, ***Food Chemistry*** 138 (2013) 116-121
14. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842
15. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, ***Cell Calcium*** 43 (2008) 615-621
16. R. Gulaboski, V. Mirceski, F. Scholz, ***Amino Acids*** 24 (2003) 149-154

17. V. Mirceski, R. Gulaboski, ***Croatica Chemica Acta*** 76 (2003) 37-48.

18. F. Scholz, R. Gulaboski, ***Faraday Discussions*** 129 (2005) 169-177.

19. V. Mirceski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (2002) 814-819.

20. R. Gulaboski, K. Caban. Z. Stojek, F. Scholz, ***Electrochemistry Communications*** 6 (2004) 215-218.

21. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, ***Electroanalysis*** 31 (2019) 2488-2506

22. V. Mirceski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (2002) 814-819