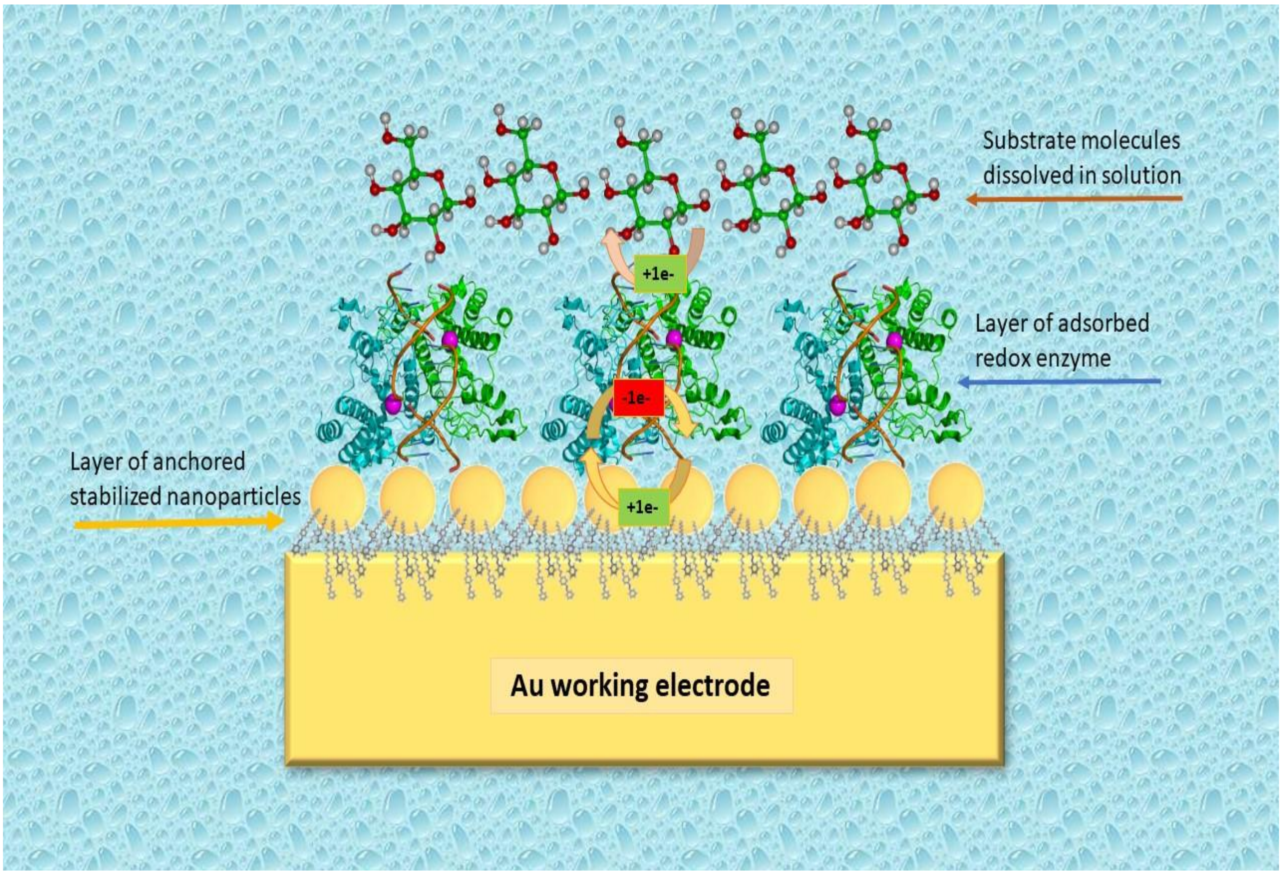
THEORY OF ENZYMATIC REACTIONS IN CYCLIC SQUARE-WAVE VOLTAMMETRY: MATHCAD SIMULATION PROTOCOL

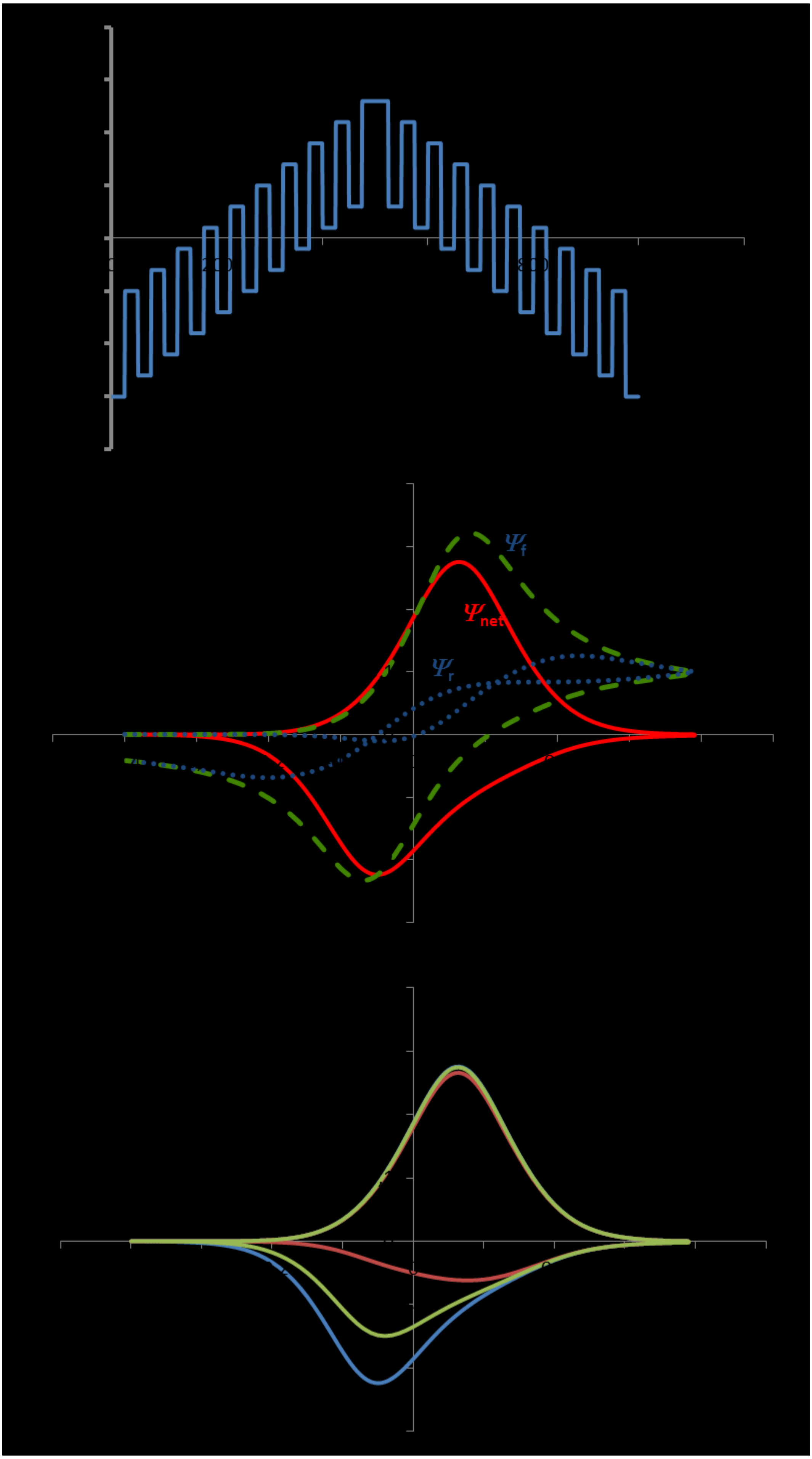
Rubin Gulaboski

Goce Delcev University Stip, Macedonia

Abstract

Protein-film voltammetry is seens as simplest methodology designed to study electrochemical features of lipophilic redox enzymes. By adsorbing a given redox enzyme on working electrode surface, it is possible to recognize the mechanism of action of many important proteins. Moreover, one can get access to relevant thermodynamic and kinetic parameters, which might reveal important chemical and physiological aspects of many enzyme-substrate interactions. Understanding the electrochemical behavior of redox enzymes contributes to a better understanding of many metabolisms in living systems. In addition, it also brings important information for designing of specific biosensors, simple medical devices, and bio-fuel cells. In this work, we present a working protocol in MATHCAD to simulate enzymatic reactions of lipophilic redox enzymes in cyclic square-wave voltammetry. This is a novel technique that is a hybrid between the cyclic and the square-wave voltammetry, especially suitable to evaluate mechanisms, kinetics and thermodynamics of surface confined molecules. We present the readers a full MATHCAD file for simulation of these reaction mechanism in Cyclic square-wave voltammetry. This MATHCAD FILE will be of help to experimentalists working in area of enzymatic voltammetry and surface redox mechanisms.




0
200
800
Ψ_f
Ψ_{net}
Ψ_r

This is the MATHCAD working file for simulation Cyclic SW Voltammograms

PROTEIN-FILM CYCLIC
Square-Wave Voltammetry
MATHCAD MODEL FILE
for SURFACE CE MECHANISM

Model is suitable for A(ads) + ne- = B(ads) protein film
Redox enzymes as
Cytochromes Hem-containing proteins
Glucosoxidase, Cytochromes, Metaloenzymes

$Es := 0.4$

$Ef := -0.4$

$r := 1..1$

$\Delta E := Es - Ef - Ef + Es$

$dE := 0.004$

$Esw := 0.05$

$n := 2$

$F := 96500$

$R := 8.314$

$T := 298.15$

$\Delta E = 1.6$

$$j := 1..\frac{\frac{\Delta E}{2}}{dE} \cdot 50$$

$\alpha := 0.5$

$f := 10$

$ks_r := 10^{1.2965r}$

$kf := 5$

$kb := 5$

$\varepsilon := kf + kb$

$$\lambda_r := \frac{ks_r}{f}$$

$K := 10^{-0.2}$

$K = 0.631$

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

$\varepsilon := 10^{0.4}$

$\lambda_r =$

$\boxed{1.979}$

$\varepsilon = 2.512$

$\varepsilon_r =$

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

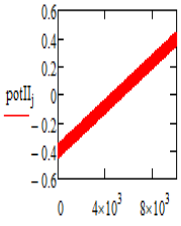
$$\log\left(\frac{ks}{\varepsilon_r} \cdot K\right) =$$

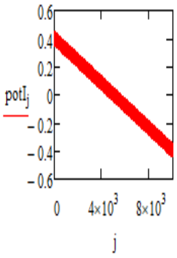
$z = 0.251$

$\log(z_r) =$

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

$$k := 1..\frac{\frac{\Delta E}{2}}{dE} \cdot 50$$





$$S_k := e^{\frac{z}{50}\cdot(-k)} - e^{\frac{z}{50}\cdot(-k+1)}$$

$\varepsilon = 2.512$

$z = 0.251$

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

$\log(\lambda_1) = 0.296$

$10^{1.2} = 15.849$

$$L_u := e^{\frac{z}{50}\cdot(-u)} - e^{\frac{z}{50}\cdot(-u+1)}$$

$\log(z) = -0.6$

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

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

$\varepsilon_r =$

$\log(\lambda_r) =$

$\boxed{0.296}$

$\Psi_{1,r} =$

$$\Psi I_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot \frac{K}{(1+K) \cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot S_1}{(K+1) \cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha) \cdot \Phi I_1}}{50}\right]^{-1}$$

$$\Psi I_{k,r} := \frac{\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_k} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi I_{j,r}\right) - (z)^{-1} \cdot \lambda_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi I_k} \cdot \sum_{j=1}^{k-1} \left(\Psi I_{j,r} \cdot S_{k-j+1}\right) - \frac{\lambda_r}{50} \cdot e^{\Phi I_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \Psi I_{j,r}}{\left(\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_k} \cdot K}{1+K} \cdot \frac{1}{50}\right) + 1 + (z)^{-1} \cdot \lambda_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi I_k} + \frac{\lambda_r}{50} \cdot e^{\Phi I_k \cdot (1-\alpha)}}$$

$$\Psi II_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot \frac{K}{(1+K) \cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot S_1}{(K+1) \cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha) \cdot \Phi II_1}}{50}\right]^{-1}$$

$$\Psi II_{k,r} := \frac{\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_k} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi II_{j,r}\right) - (z)^{-1} \cdot \lambda_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi II_k} \cdot \sum_{j=1}^{k-1} \left(\Psi II_{j,r} \cdot S_{k-j+1}\right) - \frac{\lambda_r}{50} \cdot e^{\Phi II_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \Psi II_{j,r}}{\left(\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_k} \cdot K}{1+K} \cdot \frac{1}{50}\right) + 1 + (z)^{-1} \cdot \lambda_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi II_k} + \frac{\lambda_r}{50} \cdot e^{\Phi II_k \cdot (1-\alpha)}}$$

$$\Psi T_{k,r} := \Psi I_{k,r} + \Psi II_{k,r}$$

$$p := 1 .. \frac{\frac{\Delta E}{2}}{dE} - 1$$

$$\Psi Af_{p,r} := \Psi I_{(p+1) \cdot 50,r} \qquad \Psi Ab_{p,r} := \Psi I_{50 \cdot p+25,r}$$

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

$$\Psi Bb_{p,r} := \Psi II_{50 \cdot p+25,r} \qquad \Psi Bf_{p,r} := \Psi II_{(p+1) \cdot 50,r}$$

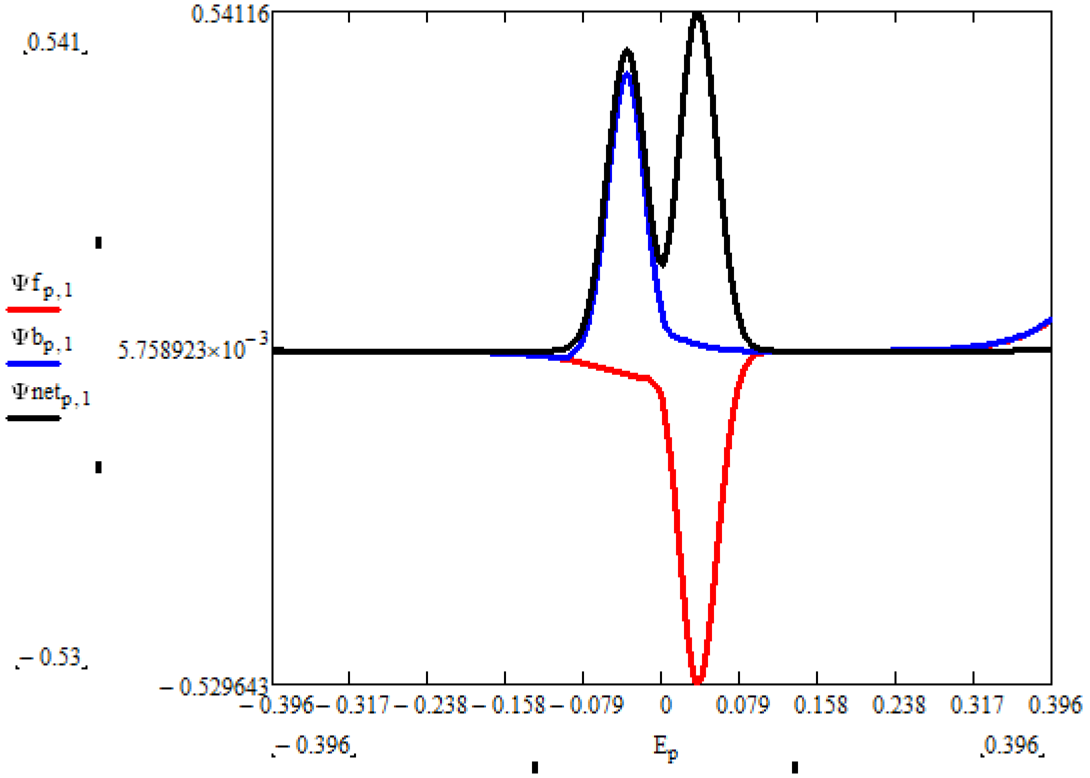
$$\Psi Bnet_{p,r} := \Psi Ab_{p,r} - \Psi Bb_{p,r}$$

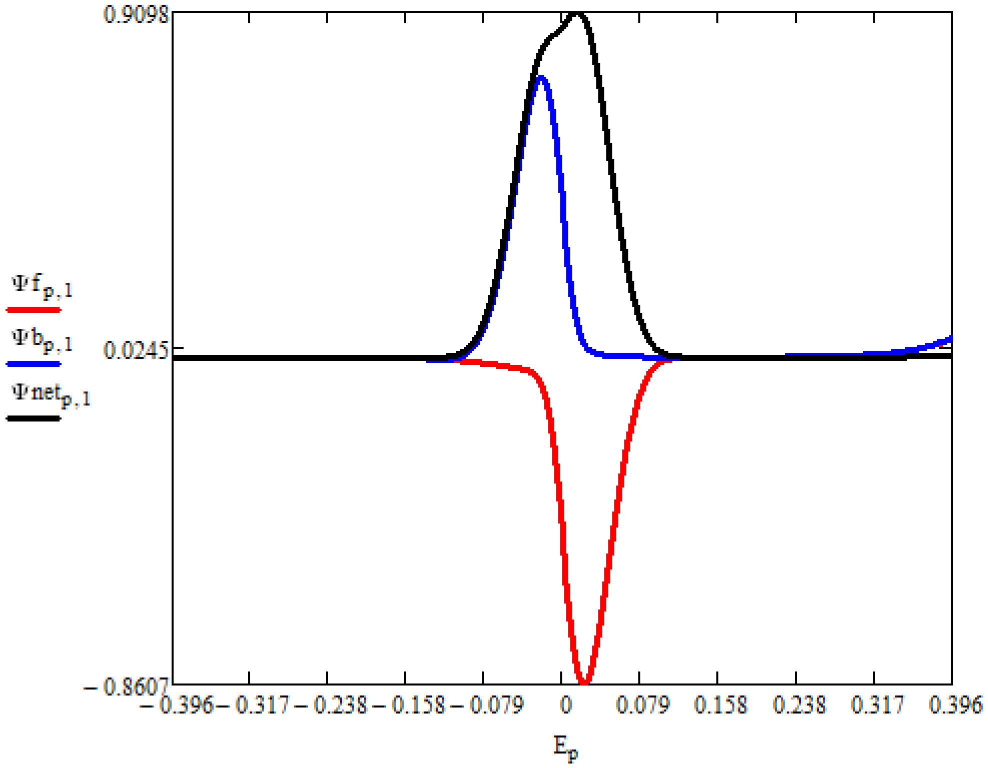
$$\Psi b_{p,r} := \Psi Bb_{p,r} - \Psi Ab_{p,r}$$

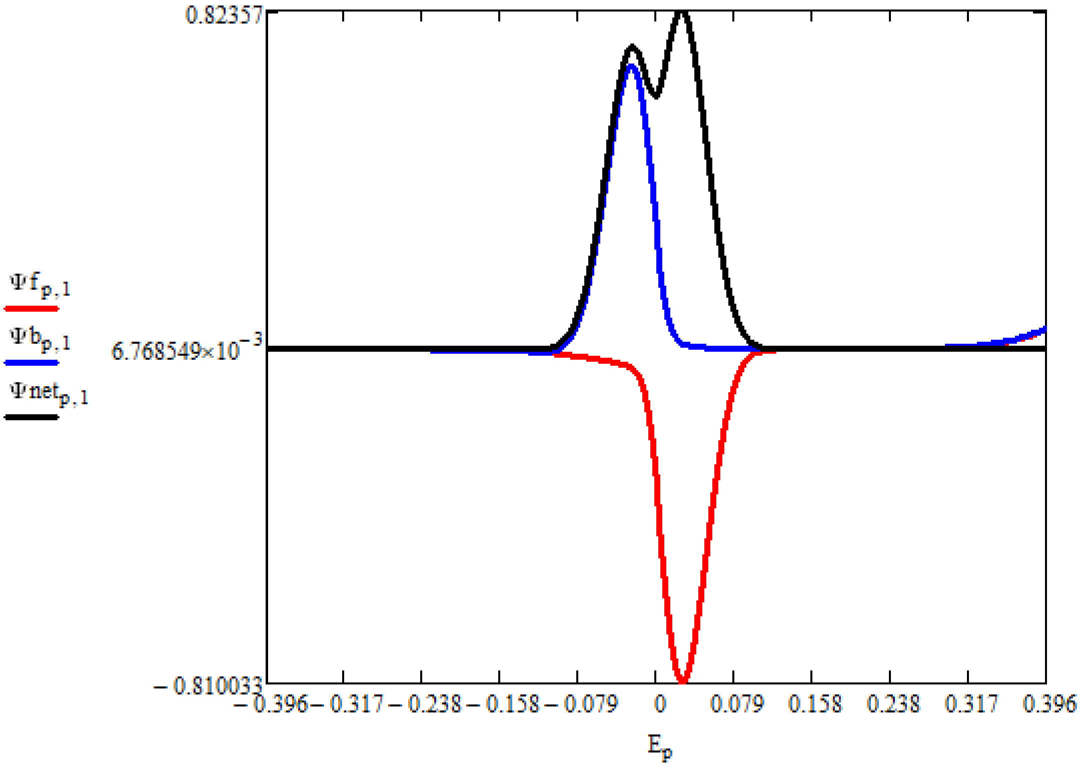
$$\Psi f_{p,r} := \Psi Bf_{p,r} - \Psi Af_{p,r}$$

$$\Psi Anet_{p,r} := \Psi Af_{p,r} + \Psi Bf_{p,r}$$

$$\Psi net_{p,r} := \Psi b_{p,r} - \Psi f_{p,r}$$




0.9098
0.0245
− 0.8607
− 0.396
− 0.317
− 0.238
− 0.158
− 0.079
0
0.079
0.158
0.238
0.317
0.396
E_p
$\Psi f_{p,1}$
$\Psi b_{p,1}$
$\Psi net_{p,1}$


0.82357
6.768549×10^{-3}
− 0.810033
− 0.396
− 0.317
− 0.238
− 0.158
− 0.079
0
0.079
0.158
0.238
0.317
0.396
E_p
$\Psi f_{p,1}$
$\Psi b_{p,1}$
$\Psi net_{p,1}$

REFERENCES

1. V. Mirceski, S Komorsky Lovric, M. Lovric, Square-wave voltammetry, Theory and Application, 2007.
2. **R. Gulaboski** and L. Mihajlov, "Catalytic mechanism in successive two-step protein-film voltammetry—heoretical study in square-wave voltammetry", ***Biophys. Chem.***155 (2011) 1-9.
3. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, Protein-film voltammetry: a theoretical study of the temperature effect using square-wave voltammetry., ***Biophys. Chem***. 137 (2008) 49-55.
4. **R. Gulaboski**, Surface ECE mechanism in protein film voltammetry—a theoretical study under conditions of square-wave voltammetry, ***J. Solid State Electrochem***. 13 (2009) 1015-1024.
5. Scholz, F.; Schroeder U.; **Gulaboski R**, *Electrochemistry of Immobilized Particles and Droplets*, Springer Verlag, New York, pp. 1-269, 2005

6. **Gulaboski, R.** Pereira, C. M. In Electrochemical Methods and Instrumentation in Food Analysis, in Handbook of Food Analysis Instruments, Otles, S. (ed.) Taylor & Francis, 2008 and 2015 2nd Edition

7. **R. Gulaboski**, Theoretical contribution towards understanding specific behaviour of “simple” protein-film reactions in square-wave voltammetry”, ***Electroanalysis,*** 31 (2019) 545-553
8. **R. Gulaboski,** P. Kokoskarova, S. Petkovska, Time independent methodology to assess Michaelis Menten constant by exploring electrochemical-catalytic mechanism in protein-film cyclic staircase voltammetry, ***Croat. Chem. Acta***, 91 (2018) 377-382.
9. V. Mirceski, D. Guziejewski, L. Stojanov, **R. Gulaboski,** Differential Square-Wave Voltammetry, ***Analytical Chemistry*** (2019) https://pubs.acs.org/doi/abs/10.1021/acs.analchem.9b03035.
10. Scholz, F, Schroeder U, **Gulaboski R**, A Domenech-Carbo, *Electrochemistry of Immobilized Particles and Droplets, Experiments with Three-phase Electrode,* Springer Verlag, New York, pp. 2nd Edition, 2015

11. **R. Gulaboski**, V. Mirceski, R. Kappl, M. Hoth, M. Bozem, "Quantification of Hydrogen Peroxide by Electrochemical Methods and Electron Spin Resonance Spectroscopy" ***Journal of Electrochemical Society,*** 166 (2019) G82-G101.
12. **Rubin Gulaboski**, Valentin Mirceski, Milivoj Lovric, Square-wave protein-film voltammetry: new insights in the enzymatic electrode processes coupled with chemical reactions, ***Journal of Solid State Electrochemistry***, 23 (**2019) 2493-2506.**
13. 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*** *https://onlinelibrary.wiley.com/doi/10.1002/elan.201900416*
14. **Gulaboski Rubin**, Milkica Janeva, Viktorija Maksimova, **"**New Aspects of Protein-film Voltammetry of Redox Enzymes Coupled to Follow-up Reversible Chemical Reaction in Square-wave Voltammetry***", Electroanalysis***, 31 (2019) **946-956 .**
15. P. Kokoskarova, M. Janeva, V. Maksimova, **R. Gulaboski,** "Protein-film Voltammetry of Two-step Electrode Enzymatic Reactions Coupled with an Irreversible Chemical Reaction of a Final Product-a Theoretical Study in

Square-wave Voltammetry", ***Electroanalysis 31*** (**2019**) 1454-1464, DOI: 10.1002/elan.201900225

16. P. Kokoskarova, **R. Gulaboski**, Theoretical Aspects of a Surface Electrode Reaction Coupled with Preceding and Regenerative Chemical Steps: Square-wave Voltammetry of a Surface CEC' Mechanism**, *Electroanalysis* (2019)**doi.org/10.1002/elan.201900491 https://onlinelibrary.wiley.com/doi/10.1002/elan.201900491
17. **R. Gulaboski,** I. Bogeski, P. Kokoskarova, H. H. Haeri, S. Mitrev, M. Stefova, Marina, J. Stanoeva-Petreska, V. Markovski, V. Mirceski, M. Hoth, and R. Kappl, *New insights into the chemistry of Coenzyme Q-0: A voltammetric and spectroscopic study.* ***Bioelectrochem.*** 111 (2016) 100-108.
18. **R. Gulaboski,** V. Markovski, and Z. Jihe, *Redox chemistry of coenzyme Q—a short overview of the voltammetric features*, ***J. Solid State Electrochem*.** 20 (2016) 3229-3238.
19. Haeri, Haleh H. I. Bogeski, **R. Gulaboski,** V. Mirceski, M. Hoth, and R. Kappl, *An EPR and DFT study on the primary radical formed in hydroxylation reactions of 2,6-dimethoxy-1,4-benzoquinone.* ***Mol. Phys****.* 114 (2016) 1856-1866.
20. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.
21. **R. Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochim. Acta***, *167 (2015) 219-225.*

22. V. Mirceski, A. Aleksovska, B. Pejova, V. Ivanovski, B. Mitrova, N. Mitreska and **R. Gulaboski**, Thiol anchoring and catalysis of Gold nanoparticles at the liquid-liquid interface of thin-organic film modified electrodes", ***Electrochem Commun***. 39 (2014) 5-8
23. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.
24. V. Mirceski, **R. Gulaboski**, M. Lovric, I. Bogeski, R. Kappl and M. Hoth, Square-Wave Voltammetry: A Review on the Recent Progress, ***Electroanal.*** 25 (2013) 2411–2422.
25. **R. Gulaboski**, I. Bogeski, V. Mirčeski, S. Saul, B. Pasieka, H. H. Haeri, M. Stefova, J. Petreska Stanoeva, S. Mitrev, M. Hoth and R. Kappl, "Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers" ***Sci. Reports***, 3 (2013) 1-8.
26. **R. Gulaboski**, V. Mirceski, I. Bogeski and M. Hoth, „Protein film voltammetry: electrochemical enzymatic spectroscopy. A review on recent progress„ ***J. Solid State Electrochem.*** 16 (2012) 2315-2328.
27. **R. Gulaboski,** P. Kokoskarova and S. Mitrev, "Theoretical aspects of several successive two-step redox mechanisms in protein-film cyclic staircase voltammetry" ***Electrochim. Acta*** 69 (2012) 86-96.
28. I. Bogeski, **R. Gulaboski***, R. Kappl, V. Mirceski, M. Stefova, J. Petreska and M. Hoth, „Calcium Binding and Transport by Coenzyme Q„ ***J. Am. Chem. Soc.*** 133 (2011) 9293-9303.
29. I. Bogeski, R. Kappl, C. Kumerow, **R. Gulaboski**, M. Hoth and B. A. Niemeyer "Redox regulation of calcium ion channels: Chemical and physiological aspects, ***Cell Calcium*** **50** (2011) 407-423.
30. **R. Gulaboski**, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garrau, V. Lippolis and A. F. Silva, Coupling of Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for Probing the Thermodynamics of Facilitated Ion Transfer Reactions Exhibiting Chemical Kinetic Hindrances, ***J. Phys. Chem. C*** 112 (2008) 153-161.
31. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, A new rapid and simple method to determine the kinetics of electrode reactions of biologically relevant

compounds from the half-peak width of the square-wave voltammograms., ***Biophys. Chem***. 138 (2008) 130-137.

32. **R. Gulaboski**, C. M. Pereira, M. N. D. S. Cordeiro, M. Hoth and I. Bogeski, Redox properties of the calcium chelator Fura-2 in mimetic biomembranes. ***Cell Calcium*** 43 (2008) 615-621.
33. **R. Gulaboski**, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa and A. F. Silva, Probing of the Voltammetric Features of Graphite Electrodes Modified with Mercaptoundecanoic Acid Stabilized Gold Nanoparticles, ***J. Phys. Chem.*** *C* 112 (2008) 2428-2435.
34. V. Mirceski, **R. Gulaboski**, I. Bogeski and M. Hoth, Redox Chemistry of Ca-Transporter 2-Palmitoylhydroquinone in an Artificial Thin Organic Film Membrane, ***J. Phys. Chem. C*** 111 (2007) 6068-6076.

35. **R. Gulaboski**, F. Borges, C. M. Pereira, M. N. D. S. Cordeiro, J. Garrido and A. F. Silva, Voltammetric insights in the transfer of ionizable drugs across biomimetic membranes: recent achievements., **Comb. Chem. High Throughput Screen.** 10 (2007) 514-526.

36. **R. Gulaboski**, V. Mirčeski, M. Lovrić and I. Bogeski, "Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry." ***Electrochem. Commun***. 7 (2005) 515-522.

37. **R. Gulaboski**, M. N. D.S. Cordeiro, N. Milhazes, J. Garrido, F. Borges, M. Jorge, C. M. Pereira, I. Bogeski, A. Helguera Morales**,** B. Naumoski and A. F. Silva, "Evaluation of the lipophilic properties of opioids, amphetamine-like drugs, and metabolites through electrochemical studies at the interface between two immiscible solutions. ***Anal. Biochem***. 361 (2007) 236-243.

38. M. Jorge, **R. Gulaboski**, C. M. Pereira and M. N. D. S. Cordeiro, Molecular dynamics study of nitrobenzene and 2-nitrophenyloctyl ether saturated with water", ***Mol. Phys.*** 104 (2006) 3627-3634.

39. M. Jorge, **R. Gulaboski**, C. M. Pereira and M. N. D. S. Cordeiro "Molecular dynamics study of 2-nitrophenyl octyl ether and nitrobenzene." ***J. Phys. Chem. B*** 110 (2006) 12530-12538.

40. M. Chirea, V. Garcia-Morales , J. A. Manzanares, C, M. Pereira and A. F: Silva "Electrochemical characterization of polyelectrolyte/gold nanoparticle multilayers self-assembled on gold electrodes." ***J. Phys. Chem. B*** 109 (2005) 21808-21817.

41. V. Mirčeski and **R. Gulaboski**, "Simple electrochemical method for deposition and voltammetric inspection of silver particles at the liquid-liquid interface of a thin-film electrode." ***J. Phys. Chem. B*** 110 (2006) 2812-2820.

42. **R. Gulaboski**, V. Mirčeski, C. M. Pereira, M. N. D. S. Cordeiro, A. F Silva, F. Quentel, M. L'Her and M. Lovrić, "A comparative study of the anion transfer kinetics across a water/nitrobenzene interface by means of electrochemical impedance spectroscopy and square-wave voltammetry at thin organic film-modified electrodes." ***Langmuir*** 22 (2006) 3404-3412.

43. **R. Gulaboski**, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski, E. Fereira, D. Ribeiro, M. Chirea and A. F. Silva, "Electrochemical study of ion transfer of acetylcholine across the interface of water and a lipid-modified 1,2-dichloroethane." ***J. Phys. Chem. B*** 109 (2005) 12549-12559.

44. **R. Gulaboski**, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski and A. F. Silva "Enzymatic formation of ions and their detection at a three-phase electrode" ***J. Solid State Electrochem*.** 9 (2005) 469-474.

45. F. Scholz and **R. Gulaboski** "Determining the Gibbs energy of ion transfer across water-organic liquid interfaces with three-phase electrodes." ***Chem. Phys. Chem***., 6 (2005) 1-13.

46. F. Scholz and **R. Gulaboski** "Gibbs energies of transfer of chiral anions across the interface water/chiral organic solvent determined with the help of three-phase electrodes." ***Faraday Discussions*** 129 (2005) 169-177.

47. **R. Gulaboski**, A. Galland, G. Bouchard, K. Caban, A. Kretschmer, P.–A. Carrupt, H. H. Girault and F. Scholz, A Comparison of the Solvation Properties of 2-Nitrophenyloctyl Ether, Nitrobenzene, and *n*-Octanol as Assessed by Ion Transfer Experiments" ***J. Phys. Chem*. *B*.** 108 (2004) 4565-4572.

48. **R. Gulaboski** and F. Scholz, "Lipophilicity of Peptide Anions: An Experimental Data Set for Lipophilicity Calculations", ***J. Phys. Chem*. *B***. 107 (2003) 5650-5657.

49. **R. Gulaboski**, K. Caban, Z. Stojek and F. Scholz, "The determination of the standard Gibbs energies of ion transfer between water and heavy water by using the three-phase electrode approach", ***Electrochem. Commun***. 6 (2004) 215-218.

50. V. Mirčeski, **R. Gulaboski** and F. Scholz, "Square-wave thin-film voltammetry: influence of uncompensated resistance and charge transfer kinetics", ***J. Electroanal. Chem*.** 566 (2004) 351-360**.**

51. F. Scholz, **R. Gulaboski** and K. Caban, "The determination of standard Gibbs energies of transfer of cations across the nitrobenzene|water interface using a three-phase electrode.", ***Electrochem. Commun***., 5 (2003) 929-934.

52. G. Bouchard, A. Galland, P.-A. Carrupt, **R. Gulaboski**, V. Mirčeski, F. Scholz and H. Girault, "Standard partition coefficients of anionic drugs in the *n*-octanol/water system determined by voltammetry at three-phase electrodes**"**, ***Phys. Chem. Chem. Phys***. 5 (2003) 3748-3751.

53. **R. Gulaboski**, V. Mirčeski, Š. Komorsky-Lovrić and M. Lovrić, "Square-Wave Voltammetry of Cathodic Stipping Reactions. Diagnostic Criteria, Redox Kinetic Measurements, and Analytical Applications", ***Electroanal.*** 16 (2004) 832-842.

54. V. Mirčeski and **R. Gulaboski**, "A Theoretical and Experimental Study of Two-Step Quasireversible Surface Reaction by Square-Wave Voltammetry" ***Croat. Chem. Acta*** 76 (2003) 37-48.

55. V. Mirčeski and **R. Gulaboski**, "The surface catalytic mechanism: a comparative study with square-wave and staircase cyclic voltammetry ", ***J. Solid State Electrochem***. 7 (2003) 157-165.

56. **R. Gulaboski**, V. Mirčeski and Š. Komorsky-Lovrić, "Square-Wave Voltammetry of a Second Order Cathodic Stripping Process Coupled by Adsorption of the Reacting Ligand", ***Electroanalysis*** 14 (2002) 345-354.

57. V. Mirčeski, M. Lovrić and **R. Gulaboski**, “Theoretical and experimental study of the surface redox reaction involving interactions between the adsorbed particles.under conditions of square-wave voltammetry.”, ***J. Electroanal. Chem***., 515 (2001) 91-99.

58. V. Mirčeski and **R. Gulaboski**, “Surface Catalytic Mechanism in Square-Wave Voltammetry”, ***Electroanalysis*** 13 (2001) 1326-1334.

59. **R. Gulaboski**, K. Riedel and F. Scholz, **“**Standard Gibbs energies of transfer of halogenate and pseudohalogenate ions, halogen substituted acetates, and cycloalkyl carboxylate anions at the water|nitrobenzene interface**”**, ***Phys. Chem. Chem. Phys***. 5 (2003) 1284-1289.

60. **R. Gulaboski**, V. Mirčeski and F. Scholz, “Determination of the standard Gibbs energies of transfer of cations and anions of amino acids and small peptides across the water nitrobenzene interface.”, ***Amino Acids***, 24 (2003) 149-154

61. V. Mirčeski, **R. Gulaboski** and F. Scholz, “Determination of the standard Gibbs energies of transfer of cations across the nitrobenzene|water interface utilizing te reduction of Iodine in an immobilized dropplett“ ***Electrochem. Commun***., 4 (2002) 814-819.

62. **R. Gulaboski**, V. Mirčeski and F. Scholz, “An electrochemical method for determination of the standard Gibbs energy of anion transfer between water and n-octanol” ***Electrochem. Commun*.** 4 (2002) 277-283.

63. V. Mirčeski, **R. Gulaboski** and I. Kuzmanovski, “Mathcad-a Tool for Numerical Calculation of Square-Wave Voltammograms”, ***Bull. Chem. Technol. Macedonia*,** 18 (1999) 57-64.

64. V. Mirčeski, **R. Gulaboski**, B. Jordanoski and Š. Komorsky-Lovrić, „Square-wave voltammetry of 5-fluorouracil “, ***J. Electroanal. Chem****.,* 490 (2000) 37-47.