THEORETICAL MODEL IN CYCLIC VOLTAMMETRY OF AN ELECTRODE REACTION OF WATER-SOLUBLE REDOX ENZYMES ASSOCIATED WITH REVERSIBLE REGENERATIVE STEP-MATHCAD SIMULATION FILE for Studying kinetics and thermodynamics of Enzyme-Substrate and Drug-Drug interactions

Sofija Petkovska, Rubin Gulaboski

Abstract

In our recent work published in Croatica Chemica Acta 92 (4) (2019) 1-8 we reported on a new theoretical model of a diffusional EC‘ mechanism associated with reversible regenerative step. Model is suitable for assessing the kinetic and themrodynamic parameters relevant to hydrophilic enzymes (as citochromes) and hydrophilic substrates. The features of simulated voltammetric patterns are function of parameters related to the electrode reaction (standard rate constant of electron transfer, number of exchanged electrons, electron transfer coefficient), and they additionally depend on the kinetic and thermodynamic of regenerative reaction. We provide the readers entire simulation protocol in MATHCAD for calculation of theoretical cyclic voltammograms. Model is also relevant to study many hydrophilic drug-drug interactions. In the work published in Analytical and Bioanalytical Electrochemistry 12 (2020) 345-364, we provide a large set of experimental results relevant to drug-drug and drug-DNA interactions evaluated from the models we present in that work.

$$tac := 0.01 \qquad \tau := 0.01 \qquad D := 0.000005$$

$$el := 2 \qquad \alpha := 0.5 \qquad ks := 0.02 \qquad kc := 0.01 \qquad d := \frac{\tau}{25}$$

$$Es := -0.4 \qquad Ef := 0.4 \qquad \Delta E := Ef - Es \qquad dE := 0.004 \qquad s := 1 .. \frac{tac}{d} \qquad KET := \frac{ks \cdot \tau^{0.5}}{D^{0.5}}$$

$$m := \frac{\tau}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d} \qquad n := \frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{\tau}{d}\right) \qquad Keq := 0.01$$

$$Kcatalytic := kc \cdot \tau$$

$$E_m := Es + \left(\mathrm{ceil}\left(\frac{m - \frac{\tau}{d}}{25}\right) \cdot dE - dE\right) \qquad k := 1 .. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d}\right) \qquad Kcatalytic := 10^{-1.5}$$

$$E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d}\right)}{25}\right] \cdot dE - dE\right]$$

$$R := 8.314 \qquad F := 96500$$

$$T := 298$$

$$\Phi ac := \frac{el \cdot F}{R \cdot T} \cdot Ef \qquad \Phi_m := \frac{el \cdot F}{R \cdot T} \cdot E_m \qquad \Phi_n := \frac{el \cdot F}{R \cdot T} \cdot E_n \qquad S_k := \mathrm{erf}\left(\frac{\sqrt{Kcatalytic} \cdot \sqrt{k}}{\sqrt{50}}\right) - \mathrm{erf}\left(\frac{\sqrt{Kcatalytic} \cdot \sqrt{k - 1}}{\sqrt{50}}\right)$$

$$\Psi_s := \frac{KET \cdot e^{-\alpha \cdot \Phi ac}}{1 + KET \cdot e^{-\alpha \cdot \Phi ac} \cdot \left(1 + e^{\Phi ac}\right) \cdot \frac{S_1 \cdot Keq}{Kcatalytic \cdot (1 + Keq) \cdot 25} + KET \cdot e^{-\alpha \cdot \Phi ac} \cdot \left(1 + e^{\Phi ac}\right) \cdot \frac{S_1 \cdot 1}{25 \cdot (1 + Keq)}}$$

EC catalytic mechanism with reversible regenerative reaction

Symbols and abbreviations

KET-is dimensionless kinetic parameter of electron transfer

ks -is standard rate constant of electron transfer

ks - is rate constant of catalytic reaction

Keq - is equilibrium constant of regenerative chemical reaction

Kcatalytic - is dimensionless catalytic parameter

D - is diffusion coefficient

α - is electron transfer coefficient

el - is number of electrons

τ - is time frame of potential steps in cyclic staircase voltammetry

d - is the time increment

dE - is potential step height

Es - is starting potential

EF - is final potential

Em and En are potential ramps of cathodic and anodic scan, respectively

R- is gas constant

T - is thermodynamic temperature

Φm Φac and Φn are dimensionless potentials

Ψ is dimensionless current

Sk is numerical integration factor

ΔE is potential frame

Ψc is cathodic current

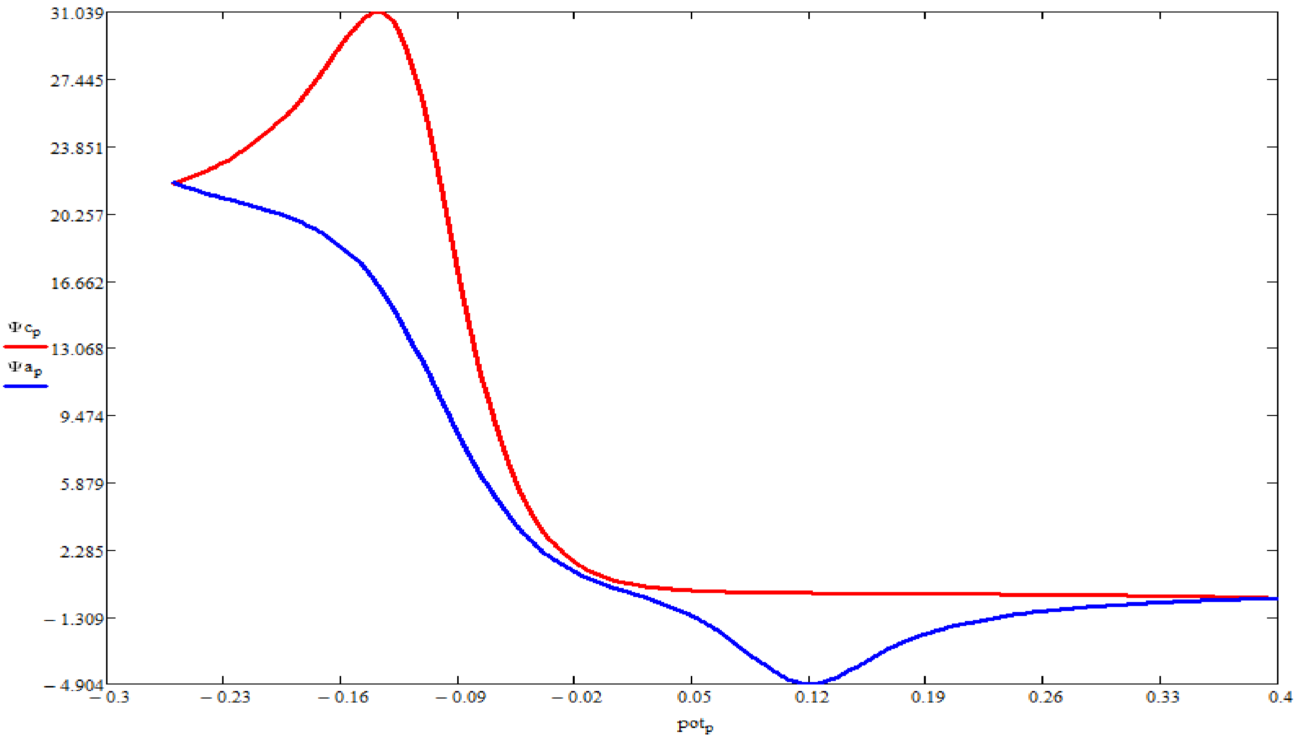
Ψa is anodic current

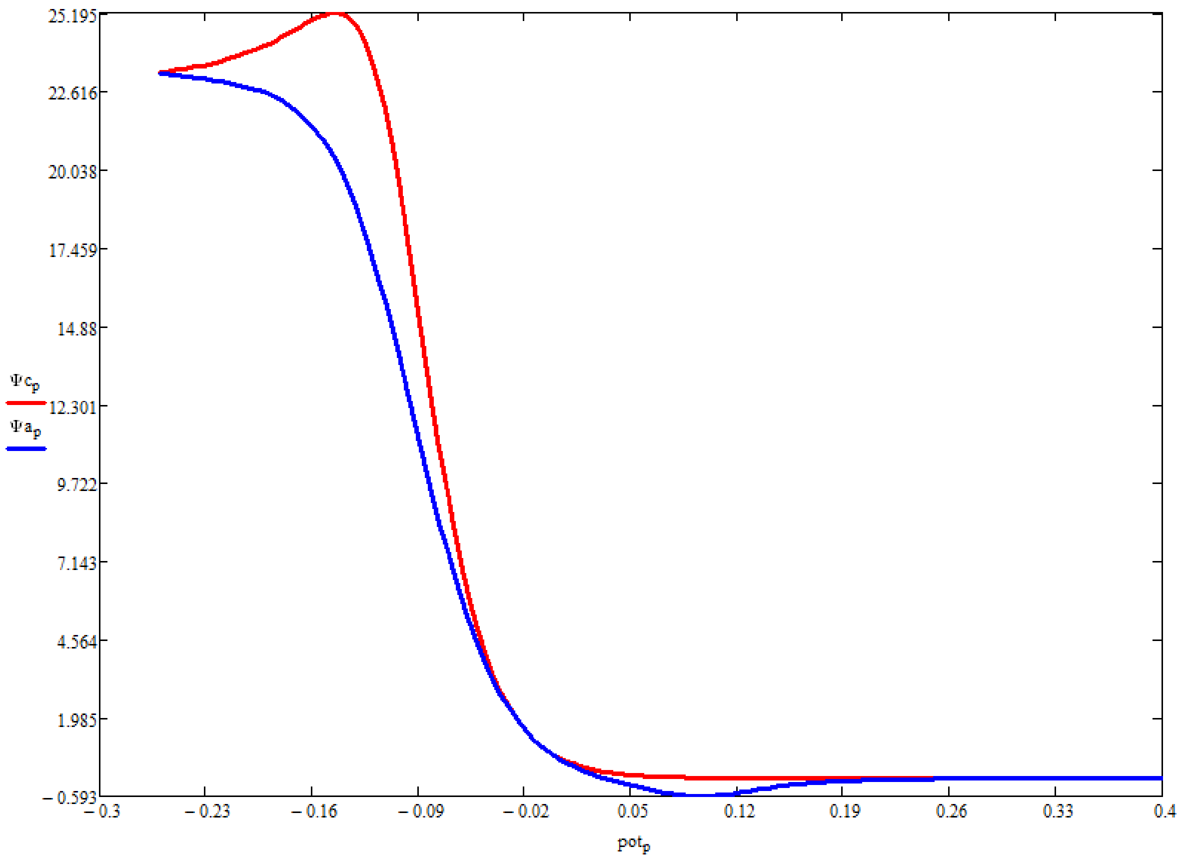
$$\Psi_m := \frac{KET\cdot e^{-\alpha\cdot\Phi_m}\cdot\left[1-\frac{\left(1+e^{\Phi_m}\right)\cdot Keq}{Kcatalytic\cdot(1+Keq)\cdot 25}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S_{m-j+1}\right)-\frac{\left(1+e^{\Phi_m}\right)\cdot 1}{25\cdot(1+Keq)}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S_{m-j+1}\right)\right]}{1+KET\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot\frac{S_1\cdot Keq}{Kcatalytic(1+Keq)\cdot 25}+KET\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot\frac{S_1\cdot 1}{25(1+Keq)}}$$

$$\Psi_n := \frac{KET\cdot e^{-\alpha\cdot\Phi_n}\cdot\left[1-\frac{\left(1+e^{\Phi_n}\right)\cdot Keq}{Kcatalytic\cdot(1+Keq)\cdot 25}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S_{n-j+1}\right)-\frac{\left(1+e^{\Phi_n}\right)\cdot 1}{25\cdot(1+Keq)}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S_{n-j+1}\right)\right]}{1+KET\cdot e^{-\alpha\cdot\Phi_n}\cdot\left(1+e^{\Phi_n}\right)\cdot\frac{S_1\cdot Keq}{Kcatalytic(1+Keq)\cdot 25}+KET\cdot e^{-\alpha\cdot\Phi_n}\cdot\left(1+e^{\Phi_n}\right)\cdot\frac{S_1\cdot 1}{25(1+Keq)}}$$

$p := 35 .. \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi)_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$ $\quad pot_p := Es + p\cdot dE$

$\Psi c_p := (\Psi)_{\left[\left[\frac{\Delta E}{dE}\cdot 2+\left(\frac{\tau}{25\cdot d}\right)\right]-p\right]\cdot 25}$

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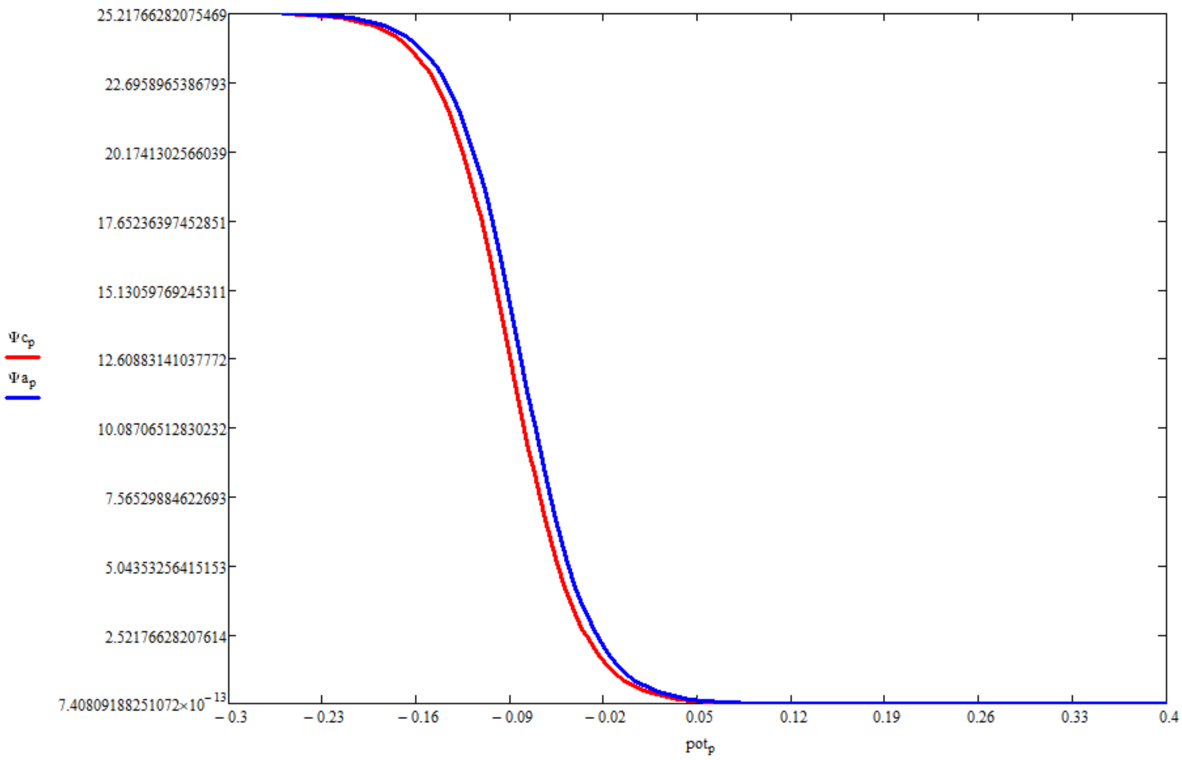
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Ψc_p
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REFERENCES

1. S. Petkovska**, R. Gulaboski**, *Croatica Chemica Acta* 92 (4) (2019) 1-8.

2. **R. Gulaboski**, P. Kokoskarova, S. Petkovska, *Analytical and Bioanalytical Electrochemistry* 12 (2020) 345-364

3. **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.
4. **R. Gulaboski**, Theoretical contribution towards understanding specific behaviour of "simple" protein-film reactions in square-wave voltammetry", ***Electroanalysis,*** 31 (2019) 545-553
5. **Gulaboski R**. in Electrochemical Dictionary, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2008 (2nd Edition in 2012)

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 2[nd] Edition

7. 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. 2[nd] Edition, 2015

8. **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.
9. **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.**
10. 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
11. **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 .**
12. 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
13. 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* 32 (2020) 333-344.**
14. V. Mirceski, D. Guziejewski, L. Stojanov, **R. Gulaboski,** Differential Square-Wave Voltammetry, ***Analytical Chemistry*** 91 (2019) 14904-14910.
15. **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. ***Bioelectrochemistry*** 111 (2016) 100-108.

16. **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.
17. H H. Haeri, 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. ***Molecular Physics*** *114 (2016) 1856-1866.*
18. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.
19. **R. Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochim. Acta***, *167 (2015) 219-225.*
20. 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
21. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.
22. 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.
23. **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.
24. **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.
25. B. Sefer, **R. Gulaboski** and V. Mirceski, Electrochemical deposition of gold at liquid–liquid interfaces studied by thin organic film-modified electrodes, ***J. Solid State Electrochem*** 16 (2012) 2373-2381.
26. V. Mirceski, S. Hocevar, B. Ogorevc, **R. Gulaboski** and I. Drangov, "Diagnostics of Anodic Stripping Mechanisms under Square-Wave Voltammetry Conditions Using Bismuth Film Substrates" ***Anal. Chem***. 84 (2012) 4429-4436.
27. 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.
28. 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.
29. **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.
30. **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.
31. **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.
32. **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.

33. **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.
34. **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.
35. **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.
36. 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.

37. **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.

38. **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.

39. **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.

40. 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.

41. 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.

42. 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.

43. 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.

44. **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.

45. **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.

46. **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.

47. 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.

48. 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.

49. **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.

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

51. **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.

52. 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**.**

53. 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.

54. 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.

55. **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.

56. 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.

57. 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.

58. **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", ***Electroanal.*** 14 (2002) 345-354.

59. V. Mirčeski and **R. Gulaboski**, “Adsorptive Stripping Voltammetric Behavior of Probucole. Experimental and Theoretical Treatment ”, ***Mikrochim. Acta***, **138** (2002) 33.

60. 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.

61. **R. Gulaboski**, I. Spirevska, L. Soptrajanova and R. Slavevska, “Square-wave Voltammetric Method for Determination of FUmaric and Maleic Acid-Determination of Fumaric Acid in Wine”, ***Anal. Lett.*** 34 (2001) 1719-1731.

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

63. **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.

64. **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

65. F. Scholz, **R. Gulaboski**, V. Mirčeski, P. Langer, „Quantification of the chiral recognition in electrochemically driven ion transfer across the interface water/chiral liquid.” ***Electrochem. Commun**.,* 4 (2002) 659-662.

66. 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.

67. Š. Komorsky-Lovrić, K. Riedl, **R. Gulaboski**, V. Mirčeski and F. Scholz, “Determination of Standard Gibbs Energies of Transfer of Organic Anions across the Water/Nitrobenzene Interface” ***Langmuir***, 18 (2002), 8000-8005.

68. **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.

69. 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.

70. B. Jordanoski, V. Mirčeski and **R. G**ulaboski, „Square-Wave Voltammetric Determination of Sulpiride“, ***Portugal. Electrochim. Acta****,* 17 (1999) 243-253.

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

72. V. Mirčeski, **R. Gulaboski**, S. Petrovska-Jovanović and K. Stojanova, „Characterization of the Redox Reaction of V(V) in Ammonia Buffers with Square-Wave Voltammetry“, ***Portugal. Electrochim. Acta****,* 19 (2001) 25-41