SURFACE $C_{rev}E$ MECHANISM IN SQUARE WAVE VOLTAMMETRY-MATHCAD SIMULATION PROTOCOL

Rubin Gulaboski, Valentin Mirceski, Milivoj Lovric

Abstract

Surface reaction of dissociation of an electrochemically inactive compound „A" leads to generation of reactive species "Ox" that can undergo electron transfer at the working electrode surface. If all participants of the electrode reaction are strongl adsorbed at the working electrode surface, we designate this mechansim as a SURFACECE Mechanism. The reaction scheme of this mechanism met in many physiological systems is as follow

A --→ Ox(adsorbed) + ne- = Red(adsorbed)

SW voltammetric patterns are function of the electron transfer parameter related to the electrode reaction, but they also depend on the kinetic and thermodynamic parameters related to the chemical step. The entire interplay of all parameters leads to very specific voltammograms, whose feature can reveal important kinetic and thermodynamic parameters relevant to the physiological systems of interest. Electrode transformation of many transient metal ion, drugs, lipophilic enzymes, fat-soluble vitamins and lipophilic metal-Ligand complexes follow this pathway. We provide the readers methods on how to access all thermodynamic and kinetic parameters relevant for this particular mechanism.

$Es := 0.25 \quad \Delta E := 0.6 \quad dE := 0.004 \quad Esw := 0.05$

$n := 2 \quad F := 96500 \quad R := 8.314 \quad T := 298.15$

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

$r := 1..1$

$f := 10$

$ks_r := 10^{0.9r}$

$kf := 5$

$kb := 5$

$\varepsilon := kf + kb$

$f_r =$

$\alpha := 0.5$

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

$\lambda_r := \frac{ks_r}{f} \quad K := 10^{-2}$

$K = 0.01$

$\varepsilon := 10^1$

$\varepsilon = 10$

$\varepsilon_r =$

$\lambda_r =$

0.794

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

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

$\log\left(\frac{ks}{f_r}\right) =$

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

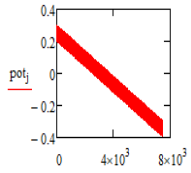
$z = 1$

$\log(z_r) =$

$\lambda_r =$

0.794

Pri Keq of 0.01 i kinet na elektrodna reakcija lambvda od 1.778...da se napravi analiza pri cepenjeto od Kchem od 100 do 0.001--sliki



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

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

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

$z = 1$

$10^{1.2} = 15.849$

$\log(z) = 0$

$\log(\lambda_1) = -0.1$

$\log(\lambda_r) =$

-0.1

$\varepsilon_r =$

$\Phi_j := n \cdot \frac{F}{R \cdot T} \cdot pot_j$

$\Psi_{1,r} =$

Pri Konst na ramnoteza od Keq = 1, da se napravi analiza Kvazimax pri z-hem parametar od 0.2 do 1

$$\Psi_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi_1} \cdot \frac{K}{(1+K) \cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi_1} \cdot S_1}{(K+1) \cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha) \cdot \Phi_1}}{50}\right]^{-1}$$

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

THEORETICAL MODEL IN SQUARE-WAVE VOLTAMMETRY
of a SURFACE CE (Chemical-Electrochemical) Mechanism

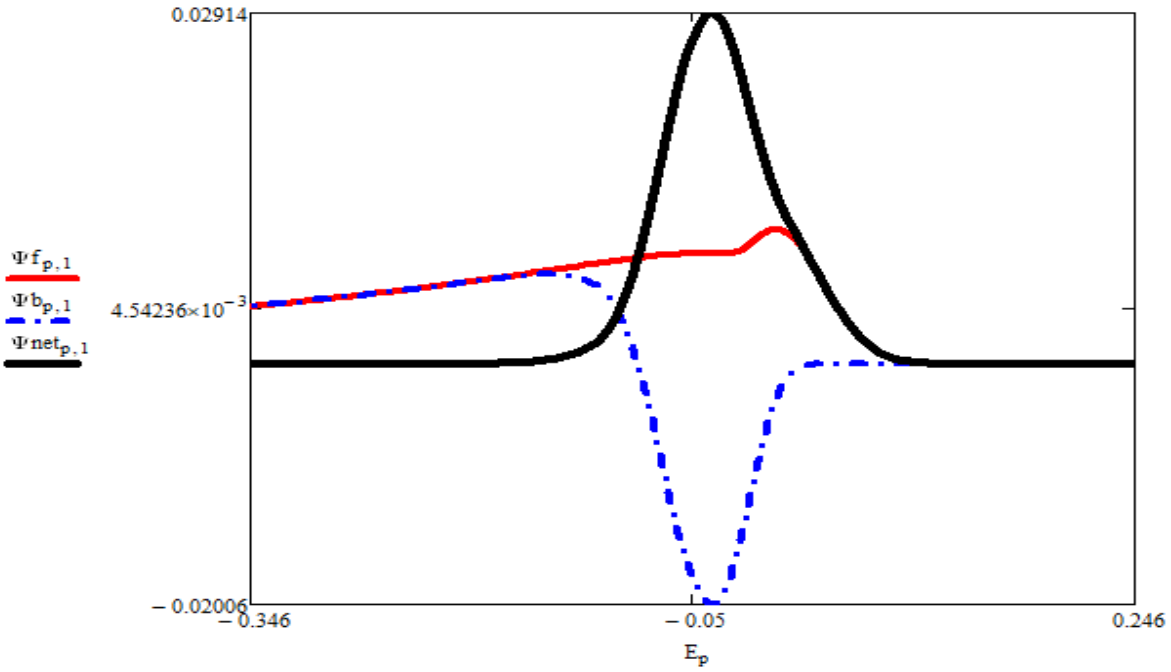
kf and kb are rate constants of forward and backward chemical steps
K is the eqiulibrium constant of chemical step
ks is standard rate constant of electrode reaction
λ is dimensionless kinetic parameter related to electron transfer step
z is dimensionless chemical kinetic parameter
S is integration factor
F is Faraday constant
R is universal gas constant
Φ is dimnesionless potential
dE is potential step
Es is starting potential
f is SW frequency
Ψ is dimensionless current
α is electron transfer coefficient
Esw is the square-wave amplitude

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

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

$E_p := Es - p \cdot dE$

$\exp\left(\frac{96480}{8.314 \cdot 30}\right) = 9.833 \times 10^{167}$



$E_p =$

0.246
0.242
0.238
0.234
0.23
0.226
0.222
0.218
0.214
0.21

LITERATURE

1. **R. Gulaboski**, Theoretical contribution towards understanding specific behaviour of “simple” protein-film reactions in square-wave voltammetry”, ***Electroanalysis,*** 31 (2019) 545-553
2. **Rubin Gulaboski,** P. Kokoskarova, S. Petkovska, Analysis of drug-drug interactions with cyclic voltammetry-an overview of relevant theoretical models and recent experimental achievements. **Analytical and Bioanalytical Electrochemistry, 12 (2020) 345-364.**
3. **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 .**
4. **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.**
5. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.
6. 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***
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. 2nd Edition, 2015
8. Scholz, F.; Schroeder U.; **Gulaboski** R, *Electrochemistry of Immobilized Particles and Droplets*, Springer Verlag, New York, pp. 1-269, 2005
9. **Gulaboski R**. in Electrochemical Dictionary, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2008 (2nd Edition in 2012)
10. V. Mirceski, S. Komorsky Lovric, M. Lovric, Square-wave voltammetry, theory and application, Springer 2007.
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. 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*** **(2019)**doi.org/10.1002/elan.201900491 https://onlinelibrary.wiley.com/doi/10.1002/elan.201900491
14. **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.

15. 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.
16. **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.
17. **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.
18. 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.
19. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.
20. **R. Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochim. Acta***, *167* (*2015) 219-225.*
21. 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
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**, 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.
24. 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.
25. 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.
26. 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.
27. 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.
28. **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.
29. **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.
30. **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.
31. **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.
32. **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.

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

36. **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.

37. **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.

38. **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.

39. 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.

40. 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.

41. 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.

42. 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.

43. **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.

44. **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.

45. **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.

46. 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.

47. 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 Discuss.,*** 129 (2005) 169-177.

48. **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.

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

50. **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.

51. 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**.**

52. 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.

53. 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.

54. **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.

55. 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.

56. 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.

57. **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.

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

59. 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.

60. **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.

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

62. **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.

63. **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

64. 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.

65. 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.

66. 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.

67. **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.

68. 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.

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

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

71. 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