Square-wave Voltammetry of Surface Electrode Mechanisms with Non-Unity Stoichiometry-Simulation Protocol in MATHCAD

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Abstract

Many metal ions and other physiologically active systems undergo electrochemical transformation in a fashion that is different from 1:1 stoichiometry. Cu II ions, and H+ ions, for example, are typical systems whose reduction happens in non-unity stoichiometry. As we know, reduction of H+ ions at platinum electrode goes via redox scheme

2H+ + 2e- = H2gas (dissolved in the Pt)

We present in this simulation model for the first time simulation procedure of 2:1 stoichiometry under conditions of square-wave voltammetry. As expected, the peak potential of SWV voltammetric patterns of such systems is sensitive to analyte concentration, shifting for -59 mV in negative direction per decadic increase of c(H+). In addition, other SW voltammetric parameters are also affected by the analyte concentrations of 2:1 stoichiometric systems. This model is suitable for studying metal-ligand complexes of many transient metal ions, but also of many drugs that undergo direct 2 electron transformation, as the quinones in aqueous media, for example. A general explicit solution of all non-stochiometry mechanisms for diffusional systems is published in recent work in Journal of Electroanalytical Chemistry. Here we present model only for 2:1 specific surface stoichiometry.

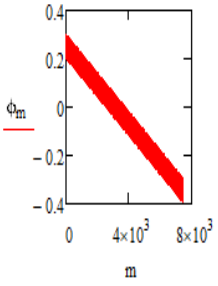
$Es := 0.25$ $\Delta E := 0.004$ $Esw := 0.05$

$m := 1..\frac{0.6}{\Delta E}\cdot 50$

$$relativenpot_m := \left[\left(ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right)\cdot\Delta E + if\left(\frac{ceil\left(\frac{m}{25}\right)}{2} = ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - \Delta E\right]$$

$\phi_m := Es + Esw - relativenpot_m$

$\alpha := 0.5$



$F := 96500$ $n := 2$ $R := 8.314$ $T := 273.15$ $i := 1..1$

$\gamma_i := 10^{-5.0003+i\cdot 0}$ $\lambda_i := 10^{-0.25\cdot i}$

$k := 1..\frac{0.6}{\Delta E}\cdot 50$ $M_{k,i} := e^{-\frac{\gamma_i}{50}\cdot(k-1)} - e^{-\frac{\gamma_i}{50}\cdot(k)}$

$\log(\gamma_i) =$ -5.0003

$\log(\lambda_i) =$ -0.25

$\Phi_m := \frac{n\cdot F}{R\cdot T}\cdot\phi_m$

SIMPLE SURFACE MECHANISM
with Non-Unity Stoichiometry
2Ox(ads) +ne- = Red(ads)
with both Ox and Red adsorbed
Ox(ads) +ne- = Red(ads)
λ is dimensionless kinetic parameter related to electron transfer step defined as λ = ks/f
ΔE is step potential
Esw is square-wave amplitude
Φ is dimensionless potential
k is counter
I is symbol of dimensionless current

$$I_{1,i} := \lambda_i\cdot e^{-\alpha\cdot\Phi_1}\cdot\left[1+\lambda_i\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)\cdot R^{-1}\right]^{-1}$$

$$I_{m,i} := \lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left[1-\left(1+e^{\Phi_m}\right)\cdot R^{-1}\cdot\sum_{j=1}^{m-1} I_{j,i}\right]\cdot\left[1+\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot R^{-1}\right]^{-1}$$

Povrsinska reakcija
SURFACE Mechanism
OX(ads) + ne = Red(ads)

$\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_1}\right)^2$

$$I_{m,i} := \lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left[1-\left(1+e^{\Phi_m}\right)\cdot R^{-1}\cdot\sum_{j=1}^{m-1} I_{j,i}\right]\cdot\left[1+\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot R^{-1}\right]^{-1}$$

Povrsinska reakcija
SURFACE Mechanism
OX(ads) + ne = Red(ads)

$$\Psi_{1,i} := \frac{1\cdot\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_1}\right)^2}{1+\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_1}\right)^2\cdot\left(1+e^{\Phi_1}\right)\cdot\frac{M_{1,i}}{\gamma_i}}$$

$$\Psi_{m,i} := \frac{1\cdot\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\right)^2 - \left[\left[\frac{1+e^{\Phi_m}}{\gamma_i\cdot 2}\cdot\sum_{j=1}^{m-1}\left[\Psi_{j,i}\cdot M_{(m-j)+1,i}\right]\right]\cdot\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\right)^2\right]}{1+\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\right)^2+e^{\Phi_m}\cdot\frac{M_{1,i}}{2\cdot\gamma_i}\cdot\left(\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\right)^2}$$

SURFACE 2Ox(adsorbed) +2e- = Red(adsorbed)
if γ parameter is smaller than 0.00001, then this mechanism describes the non-unity stochiometry surface 2A+ne- = B mechanism met by many metal ions and hydrogen ions reduction at Pt electrode

$p := 0..\frac{0.6}{\Delta E} - 1$ $E_p := Es - p\cdot\Delta E$

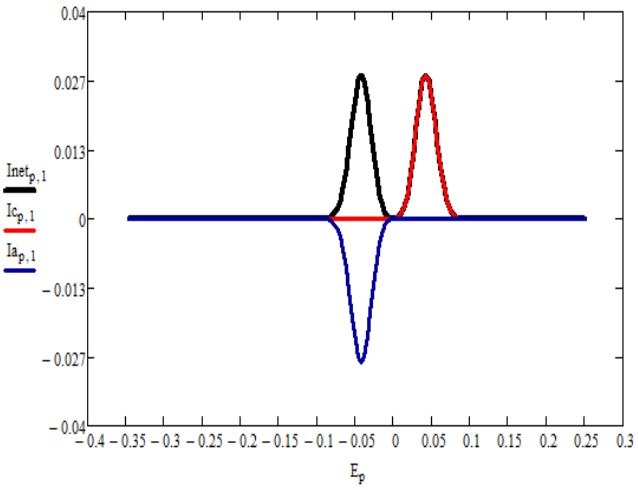
$Ia_{p,i} := I_{50\cdot p+25,i}$ $Ic_{p,i} := I_{(p+1)\cdot 50,i}$ $Inet_{p,i} := Ic_{p,i} - Ia_{p,i}$

$\Psi a_{p,i} := \Psi_{50\cdot p+25,i}$ $\Psi c_{p,i} := \Psi_{(p+1)\cdot 50,i}$ $\Psi net_{p,i} := \Psi c_{p,i} - \Psi a_{p,i}$

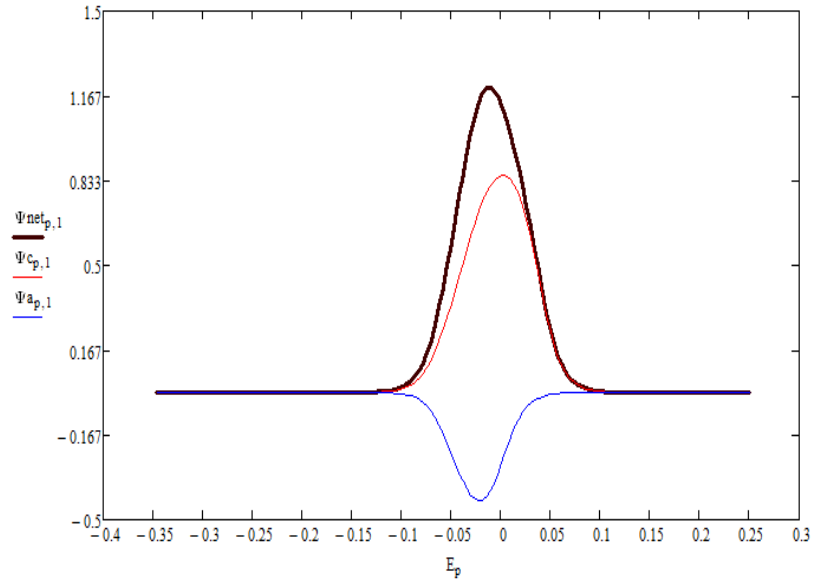
$p := 0 .. \frac{0.6}{\Delta E} - 1 \quad E_p := Es - p \cdot \Delta E$

$Ia_{p,i} := I_{50 \cdot p + 25, i} \quad Ic_{p,i} := I_{(p+1) \cdot 50, i} \quad Inet_{p,i} := Ic_{p,i} - Ia_{p,i}$

$\Psi a_{p,i} := \Psi_{50 \cdot p + 25, i} \quad \Psi c_{p,i} := \Psi_{(p+1) \cdot 50, i} \quad \Psi net_{p,i} := \Psi c_{p,i} - \Psi a_{p,i}$



SW Voltammogram of a SIMPLE Surface Mechanism



SW Voltammogram of a 2Ox(ads) + ne- = B(ads) mechanism with 2:1 stoichiometry

REFERENCES

1. **Gulaboski R**. in Electrochemical Dictionary, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2008 (2nd Edition in 2012)
2. **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.
3. S. Petkovska**, R. Gulaboski**, *Croatica Chemica Acta* 92 (4) (2019) 1-8.
4. **R. Gulaboski**, P. Kokoskarova, S. Petkovska, *Analytical and Bioanalytical Electrochemistry* 12 (2020) 345-364
5. **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.
6. **R. Gulaboski**, Theoretical contribution towards understanding specific behaviour of “simple” protein-film reactions in square-wave voltammetry”, ***Electroanalysis,*** 31 (2019) 545-553
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. **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.**
9. 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
10. **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 .**
11. 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
12. 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.**
13. V. Mirceski, D. Guziejewski, L. Stojanov, **R. Gulaboski,** Differential Square-Wave Voltammetry, ***Analytical Chemistry*** 91 (2019) 14904-14910.
14. **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.

15. **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*.*
16. 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.*
17. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.
18. **R. Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochim. Acta***, *167* (*2015) 219-225.*
19. 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
20. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.
21. 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.
22. **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.
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 Discussions*** 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