Supplementary Material related to paper: Surface ECE mechanism in SWV

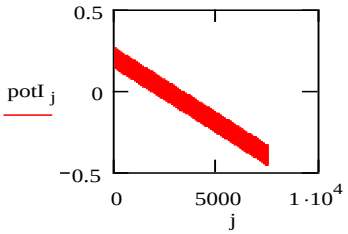
$EsI := 0.2$ $\Delta E := 0.6$ $dE := 0.004$ $Esw := 0.06$ $EsII := 0.35$

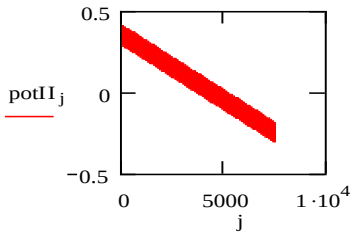
$n := 2$ $F := 96500$ $R := 8.314$ $T := 298.15$ $\alpha := 0.5$

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

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

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





$ks1 := 1$ $ks2 := 1$ $f := 10$ $kf := 0.00001$ kf is a chemical rate constant of pseudo-first order

$K1 := \frac{ks1}{f}$ $K2 := \frac{ks2}{f}$ $\lambda := \frac{kf}{f}$ λ is a dimensionless chemical parameter

$$M_j := e^{-\lambda \cdot \frac{j}{50}} - e^{-\lambda \cdot \frac{j+1}{50}}$$

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

$$\Psi I_1 := \frac{K1 \cdot e^{-\alpha \cdot \Phi I_1}}{1 + \frac{K1}{50} \cdot e^{-\alpha \cdot \Phi I_1} + K1 \lambda^{-1} \cdot e^{\Phi I_1 \cdot (1-\alpha)} \cdot M_1}$$

$$\Psi II_1 := \frac{\left(\Psi I_1 \cdot \frac{K2}{50} \cdot e^{-\alpha \cdot \Phi II_1} \right) - K2 \cdot \lambda^{-1} \cdot e^{-\alpha \cdot \Phi II_1} \cdot \Psi I_1 \cdot M_1}{1 + \frac{K2 \cdot e^{-\alpha \cdot \Phi II_1}}{50} \cdot \left(1 + e^{\Phi II_1} \right)}$$

The equations (1) and (2) are recursive formulas for the SURFACE ECE MECHANISM

$$\Psi I_j := \frac{K1 \cdot e^{-\alpha \cdot \Phi I_j} - \frac{K1}{50} \cdot e^{-\alpha \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \Psi I_i - K1 \lambda^{-1} \cdot e^{\Phi I_j \cdot (1-\alpha)} \cdot \sum_{i=1}^{j-1} \Psi I_i \cdot M_j}{1 + \frac{K1}{50} \cdot e^{-\alpha \cdot \Phi I_j} + K1 \lambda^{-1} \cdot e^{\Phi I_j \cdot (1-\alpha)} \cdot M_1} \qquad (1)$$

$$\Psi II_j := \frac{\frac{K2}{50} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \sum_{i=1}^{j-1} \Psi I_i - K2 \lambda^{-1} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \sum_{i=1}^{j-1} \Psi I_i \cdot M_j - \frac{K2}{50} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j} \right) \cdot \sum_{i=1}^{j-1} \Psi II_i}{1 + \frac{K2}{50} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j} \right)}$$

(2)

By Ψj is assigned current for the SURFACE ECE Mechanism

SIMPLE SURFACE REDOX REACTION

$z := 2$

$$\phi I_j := z \cdot \frac{F}{R \cdot T} \cdot potI_j$$

$$II_1 := \frac{K1 \cdot e^{-\alpha \cdot \phi I_1}}{1 + \frac{K1 \cdot e^{-\alpha \cdot \phi I_1} \cdot \left(1 + e^{\phi I_1}\right)}{50}}$$

$$II_j := \frac{K1 \cdot e^{-\alpha \cdot \phi I_j} - K1 \cdot e^{-\alpha \cdot \phi I_j} \cdot \frac{\left(1 + e^{\phi I_j}\right)}{50} \cdot \sum_{i=1}^{j-1} II_i}{1 + \frac{K1 \cdot e^{-\alpha \cdot \phi I_j} \cdot \left(1 + e^{\phi I_j}\right)}{50}}$$

$\Psi_j := \Psi I_j + \Psi II_j$

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

$\Psi If_p := \Psi I_{(p+1)\cdot 50}$ $\Psi Ib_p := \Psi I_{50\cdot p+25}$ $\Psi Inet_p := \Psi If_p - \Psi Ib_p$

$\Psi IIb_p := \Psi II_{50\cdot p+25}$ $\Psi IIf_p := \Psi II_{(p+1)\cdot 50}$ $\Psi IInet_p := \Psi IIf_p - \Psi IIb_p$

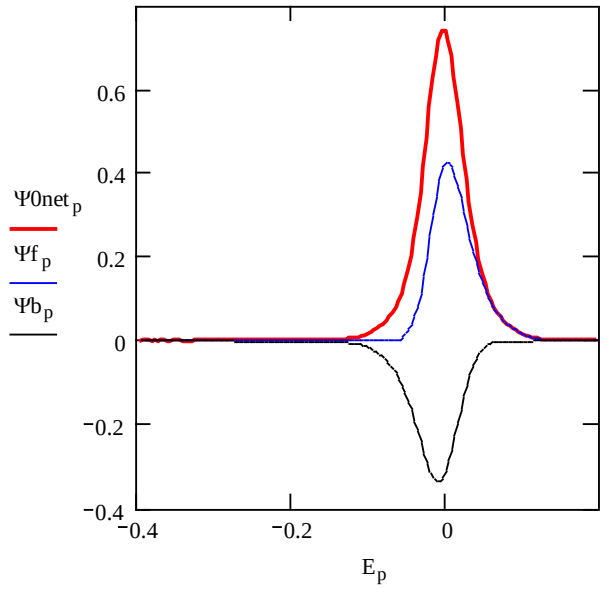
$\Psi b_p := \Psi_{50\cdot p+25}$ $\Psi f_p := \Psi_{(p+1)\cdot 50}$ $\Psi net_p := \Psi f_p - \Psi b_p$

$E_p := EsI - p \cdot dE$ $\Psi 0net_p := \Psi Inet_p + \Psi IInet_p$ FOR ECE MECHANISM

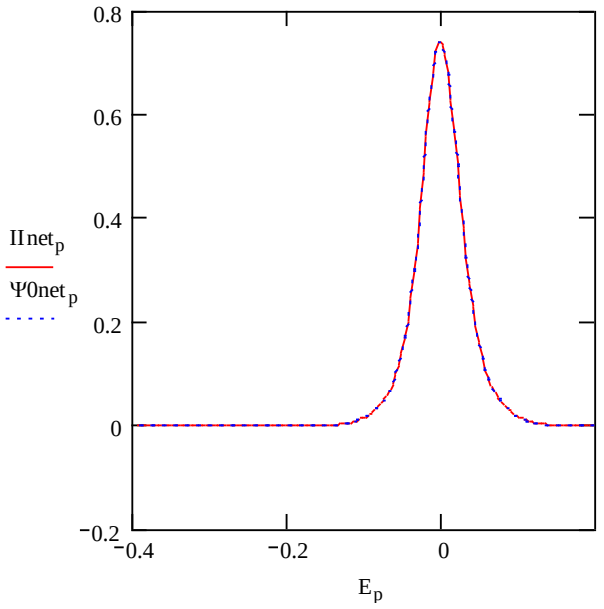
$IIf_p := II_{(p+1)\cdot 50}$

$IIb_p := II_{50\cdot p+25}$

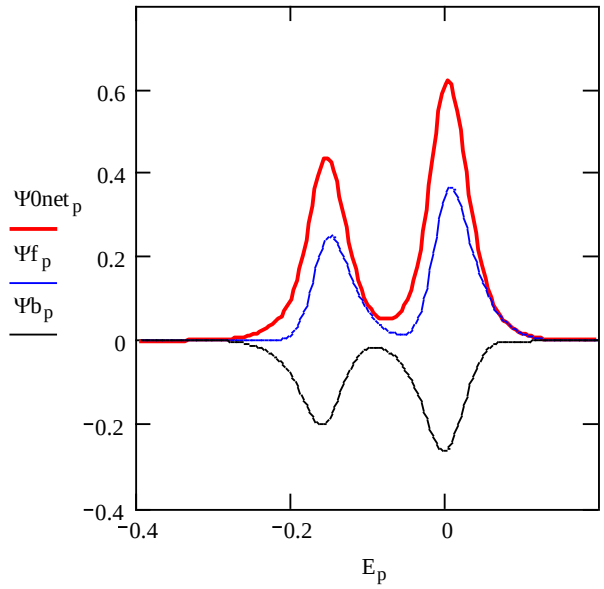
$IInet_p := IIf_p - IIb_p$ FOR SIMPLE SURFACE REDOX REACTION



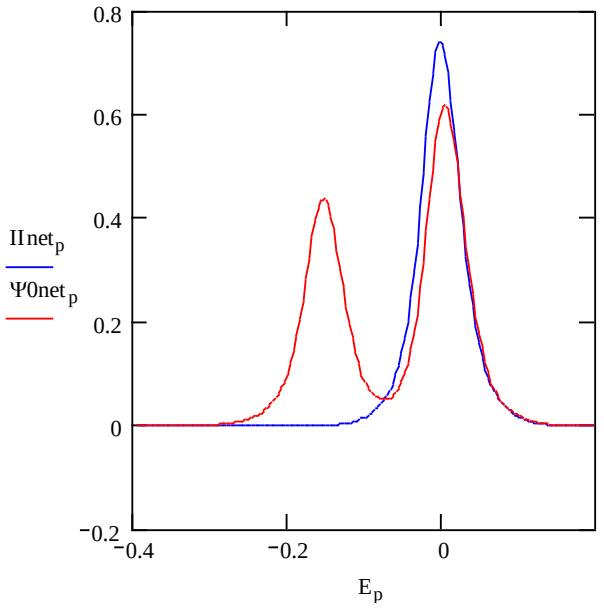
Voltammogram of surface ECE mechanism
Est(II) - Est(I) = -150 mV
K1 = K2 = 0.1
This voltammogram is simulated for small value of the chemical rate constant
λ = 0.000001.



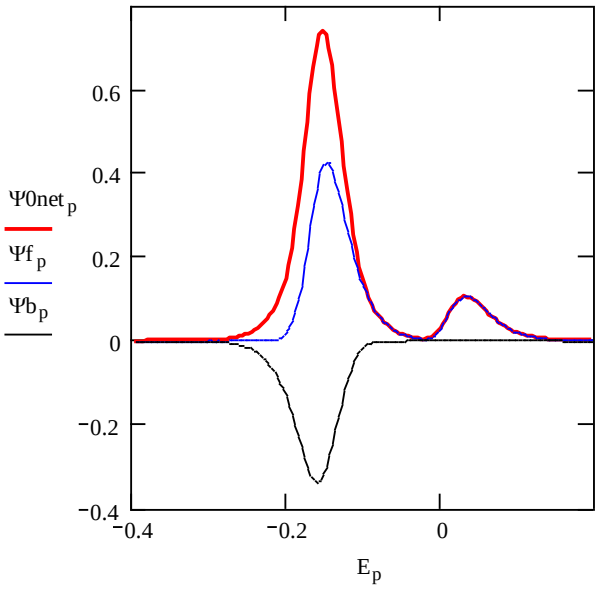
Voltammograms of surface ECE mechanism from previous case (blue line) and that of simple surface reaction (red line). The simple surface reaction is simulated for the value of the kinetic parameter
K = 0.1



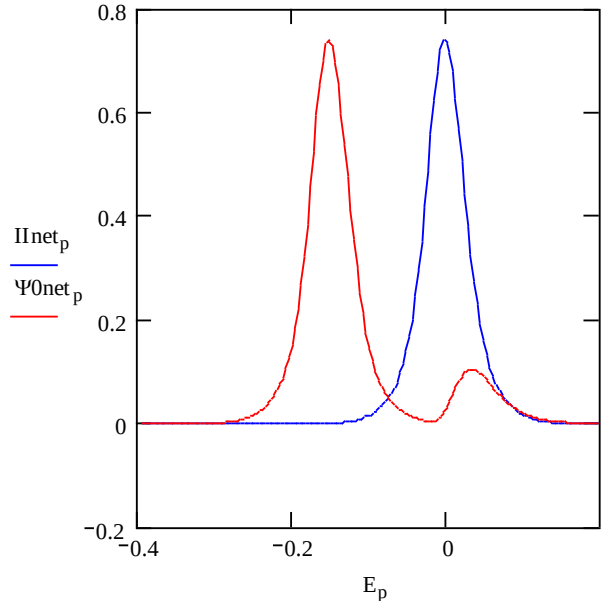
Voltammogram of surface ECE mechanism
Est(II) - Est(I) = -150 mV
K1 = K2 = 0.1
This voltammogram is simulated for moderate value of the chemical rate constant
λ = 0.01.



Voltammograms of surface ECE mechanism from the case above (red line) and that of simple surface reaction (blue line). The simple surface reaction is simulated for the value of the kinetic parameter
K = 0.1



Voltammogram of surface ECE mechanism
Est(II) - Est(I) = -150 mV
K1 = K2 = 0.1
This voltammogram is simulated for big value of the chemical rate constant
λ = 1



Voltammograms of surface ECE mechanism from the case above (red line) and that of simple surface reaction (blue line). The simple surface reaction is simulated for the value of the kinetic parameter
K = 0.1

REFERENCES

1. A. J. Bard, L. R. Faulkner, *Electrochemical methods. Fundamentals and applications*, 3rd edition, John Wiley & Sons, Inc. 2004.
2. V. Mirceski, S. Komorsky-Lovric, M. Lovric, *Square-wave voltammetry, Theory and application*, Springer, Berlin, Germany, 2007.
3. M. Lovric, "Square-wave voltammetry," in *Electroanalytical Methods*, F. Scholz, Ed. Springer, Berlin, Germany, 2nd edition, 2010.
4. J. G. Osteryoung, J. J. O'Dea, *Square-Wave Voltammetry, Electroanalytical chemistry: a series of advances*. Marcel Dekker, Inc: New York, 1986.
5. M. Lovric, J. Osteryoung, *Electrochim. Acta* **1982**, *27*, 963.
6. M. Lovric, J. J. O'Dea, J. Osteryoung, *Anal. Chem*. **1983**, *55*, 704.
7. C. Serna, A. Molina, *J. Electroanal. Chem*. **1999**, *466*, 8.
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. F. Garay, C. A. Barbero, *Anal. Chem*. **2006**, *78*, 6740.
10. V. Mirceski, M. Lovric, *Electroanal*ysis **1997**, *9*, 1283.
11. M. Lovric, *J. Electroanal. Chem.* **1983**, *153*, 1.
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. 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.
14. 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.
15. 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.
16. 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.
17. 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.
18. 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.
19. 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.

20. 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.

21. 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.

22. 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.

23. 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.

24. 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.

25. 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.

26. 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.

27. 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.

28. 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.

29. 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.

30. 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.

31. 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.

32. 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.

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

34. 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.

35. 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.

36. 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.

37. 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.

38. 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.

39. 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.

40. 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.

41. 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.

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

43. 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.

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

45. 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.

46. 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

47. 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.

48. 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.

49. 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.

50. 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.

51. 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.