

Supplementary File

Critical Aspects in Exploring Time Analysis for the Voltammetric Estimation of Kinetic Parameters of Surface Electrode Mechanisms Coupled with Chemical Reactions

Rubin Gulaboski^{1*}, Valentin Mirceski^{2,3}, Milivoj Lovric⁴

¹Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

²Institute of Chemistry, Faculty of Natural Sciences and Mathematics, University "Ss Cyril and Methodius", Arhimedova 5, 1000, Skopje, Macedonia

³Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, University of Lodz, Tamka 12, 91-403 Lodz, Poland

⁴Divkovićeva 13, Zagreb 10090, Croatia

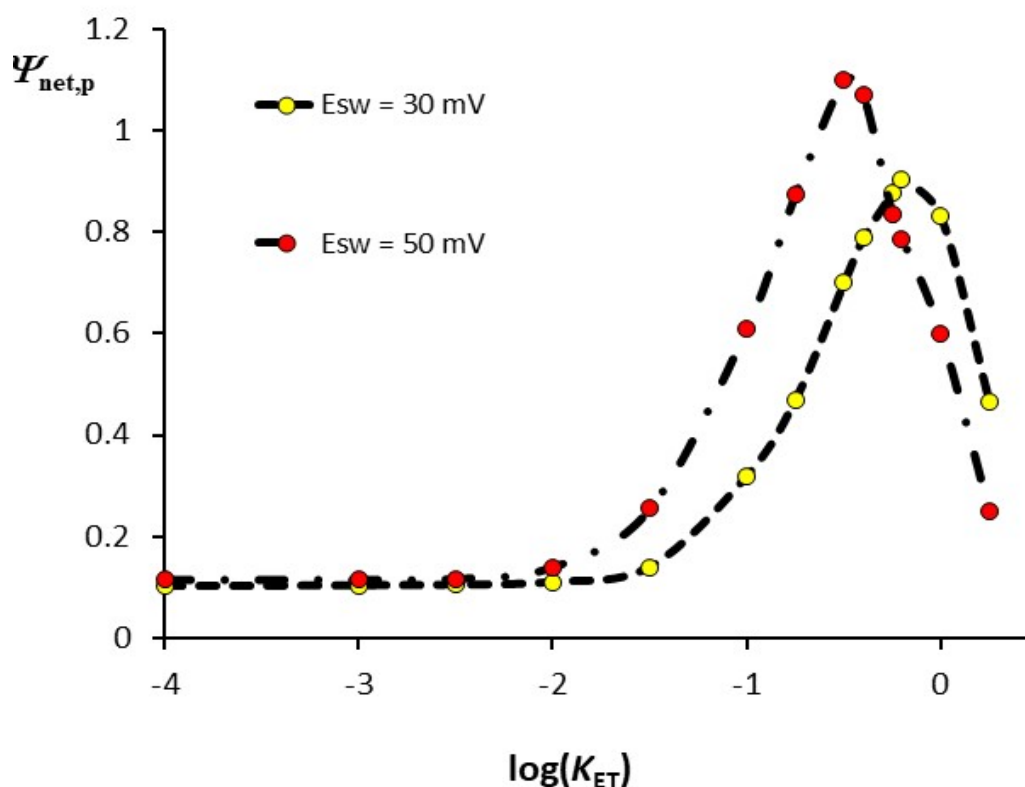


Fig. S1. Simple surface electrode reaction: Dependence of the net-peak current $\Psi_{\text{net,p}}$ on the logarithm of the dimensionless electrode kinetic parameter K_{ET} (quasireversible maximum) simulated for two values of the SW amplitude (the values are given in the plot). The simulation conditions are: electron transfer coefficient $\alpha = 0.5$, the stoichiometric number of electrons $n = 2$, temperature $T = 298$ K, and step potential $dE = 4$ mV.

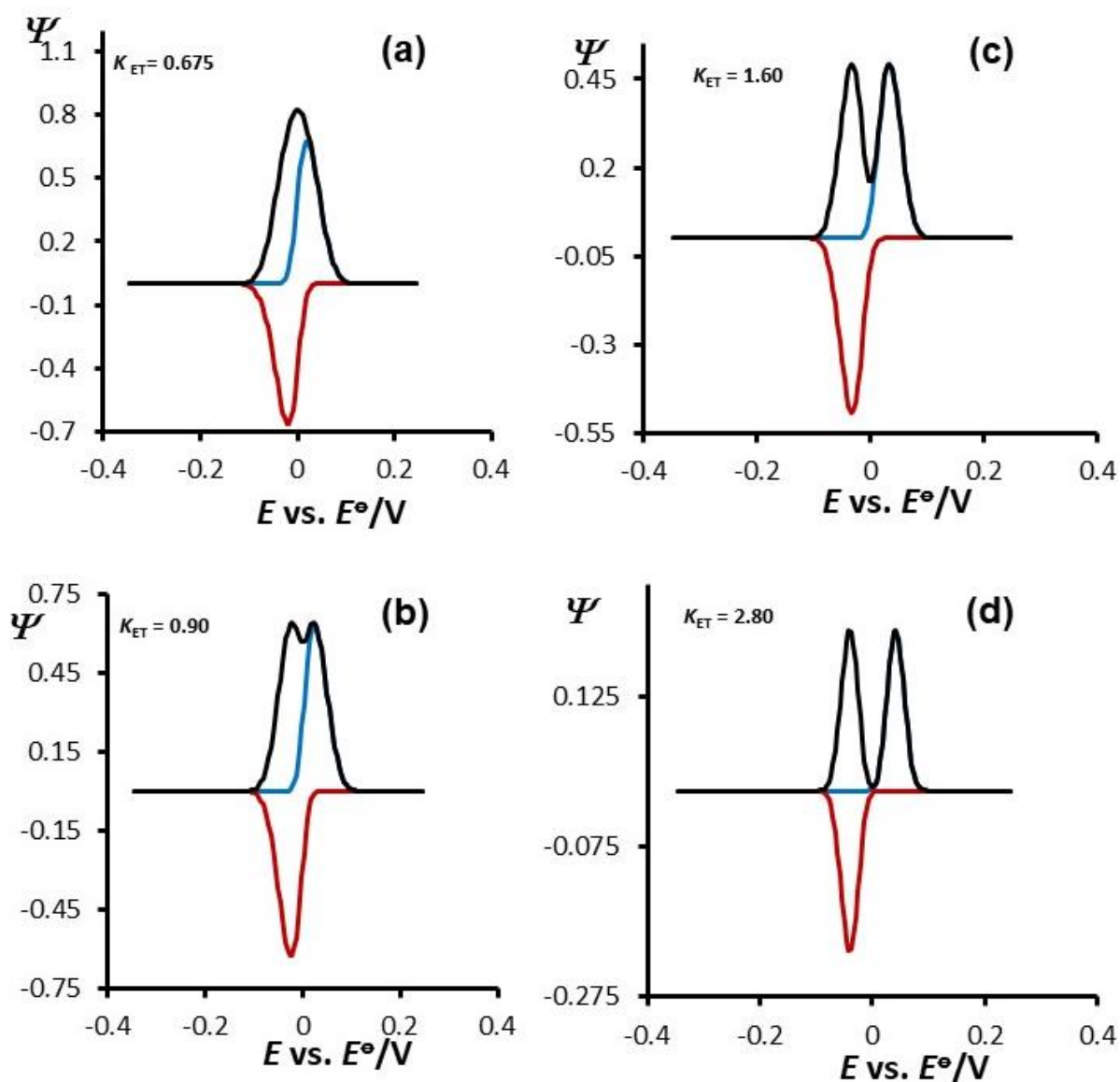


Fig. S2. Simple surface electrode reaction: The phenomenon of the net-peak splitting as a function of dimensionless electrode kinetic parameter K_{ET} (the values are given in the plot), for the SW amplitude of $E_{sw} = 50$ mV. Other conditions of the simulations are identical as for Fig. S1.

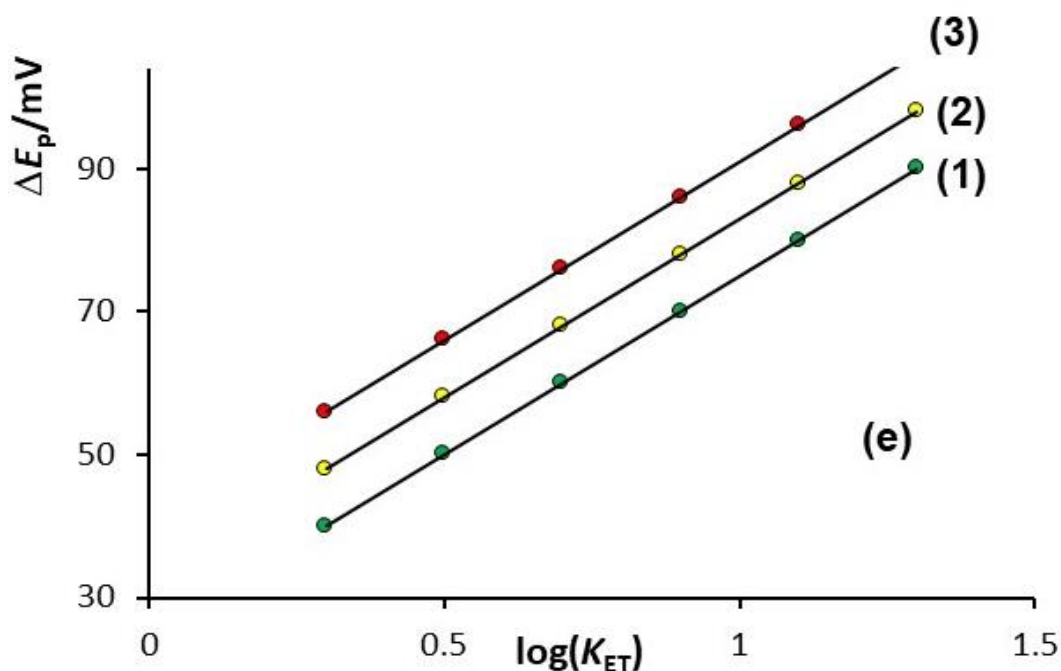


Fig. S3. Simple surface electrode reaction: The potential separation ΔE_p of the split net-peaks as a function of the logarithm of the dimensionless electrode kinetic parameter K_{ET} for the SW amplitudes of $E_{sw} = 30$ mV (1), 40 mV (2) and 50 mV (3). Other conditions of the simulations are identical as for Fig. S1

Literature

1. J. M. Saveant, *Elements of molecular and biomolecular electrochemistry: An electrochemical approach to electron transfer chemistry*, John Wiley & Sons, (2006) DOI:10.1002/0471758078
2. R. G. Compton, C. E. Banks, *Understanding voltammetry*, 2nd Edition, Imperial College Press, London, UK (2011).
3. A. J. Bard, L. R. Faulkner, *Electrochemical methods. Fundamentals and applications*, 3rd edition, John Wiley & Sons, Inc. (2004).
4. A. Molina, J. Gonzales, *Pulse voltammetry in physical electrochemistry and electroanalysis*, in *Monographs in electrochemistry* (F. Scholz, ed.), Berlin Heidelberg, Springer (2016).

5. J. G. Osteryoung, J. J. O'Dea, *Square-Wave Voltammetry*, *Electroanalytical chemistry: a series of advances*, Marcel Dekker, Inc: New York (1986).
6. V. Mirceski, R. Gulaboski, Recent achievements in square-wave voltammetry (a review), *Maced. J. Chem. Chem. Eng.*, **33**, 1-12 (2014).
7. V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl, M. Hoth, Square-wave voltammetry-a review on the recent progress, *Electroanal.*, **25**, 2411-2422 (2013) <https://doi.org/10.1007/s10008-011-1397-5>
8. F. A. Armstrong, *Electrifying metalloenzymes in: Metalloproteins: Theory, calculations and experiments* (A. E. Cho, W.A Goddar, eds), CRC Press, Taylor&Francis Group, London, New York (2015).
9. F. A. Armstrong, *Applications of voltammetric methods for probing the chemistry of redox proteins*, In: *Bioelectrochemistry: Principles and practice* (G. Lenaz, G. Milazzo, eds), vol. 5, Birkhauser Verlag AG, Basel (1997).
10. F. A. Armstrong, H. A. Heering, J. Hirst, Reactions of complex metalloproteins studied by protein-film voltammetry, *Chem. Soc. Rev.*, **26**, 169-179 (1997).
11. C. Leger, P. Bertrand, Direct electrochemistry of redox enzymes as a tool for mechanistic studies, *Chem. Rev.*, **108**, 2379-2438 (2008) DOI: doi.org/10.1021/cr0680742
12. R. Gulaboski, V. Mirceski, Application of voltammetry in biomedicine-recent achievements in enzymatic voltammetry, *Maced. J. Chem. Chem. Eng.*, **39**, 153-166 (2020) DOI: [10.20450/mjce.2020.2152](https://doi.org/10.20450/mjce.2020.2152)
13. R. Gulaboski, V. Mirceski, I. Bogeski, M. Hoth, Protein-film voltammetry: electrochemical enzymatic spectroscopy. A review on recent progress. *J. Solid State Electrochem.*, **16**, 2315-2328 (2012) <https://doi.org/10.1007/s10008-011-1397-5>
14. R. Gulaboski, V. Mirceski, M. Lovric, Square-wave protein-film voltammetry: new insights in the enzymatic electrode processes coupled with chemical reactions, *J. Solid State Electrochem.*, **23**, 2493-2506 (2019) <https://doi.org/10.1007/s10008-019-04320-7>
15. R. S. Nicholson, Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics, *Anal. Chem.*, **37**, 1351-1355 (1965)
16. E. Gileadi, Charge and mass transfer across the metal/solution interface, *Israel J. Chem.*, **48**, 121-131 (2008) <https://doi.org/10.1560/IJC.48.3-4.121>
17. R. J. Klinger, J. K. Kochi, Electron transfer kinetics from cyclic voltammetry. Quantitative description of electrochemical reversibility, *J. Phys. Chem.*, **85**, 1731-1741 (1981)
18. E. Laviron, General expressions of the linear potential sweep voltammogram in case of diffusionless electrochemical systems. *J. Electroanal. Chem.*, **101**, 19-28 (1979)
19. R. Gulaboski, M. Lovric, V. Mirceski, I. Bogeski, 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**, 130-137 (2008) doi: 10.1016/j.bpc.2008.09.015

20. R. Gulaboski, V. Mirceski, I. Bogeski, M. Hoth, Protein-film voltammetry: electrochemical enzymatic spectroscopy. A review on recent progress, *J. Solid State Electrochem.*, **16**, 2315-2328 (2012) <https://doi.org/10.1007/s10008-011-1397-5>
21. V. Mirceski, R. Gulaboski, Surface catalytic mechanism in square-wave voltammetry. *Electroanal.*, **13**, 1326-1334 (2001).
22. **R. Gulaboski**, V. Mirceski, M. Lovric, I. Bogeski, Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry. *Electrochem. Commun.*, **7**, 515-522 (2005).
23. V. Mirceski, R. Gulaboski, The surface catalytic mechanism: a comparative study with square-wave and cyclic staircase voltammetry, *J. Solid State Electrochem.*, **7**, 157-165 (2003).
24. V. Mirceski, M. Lovric, Split square-wave voltammograms of surface redox reactions. *Electroanal.*, **9**, 1283-1287 (1997).
25. R. Gulaboski, M. Janeva, V. Maksimova, New aspects of protein-film voltammetry of redoxenzymes coupled to follow-up reversible chemical reaction in square-wave voltammetry, *Electroanal.*, **31**, 946-956 (2019) <https://doi.org/10.1002/elan.201900028>
26. V. Mirceski, E. Laborda, D. Guziejewski, R. Compton, New approach to electrode kinetic measurements in square-wave voltammetry: amplitude-based quasireversible maximum. *Anal. Chem.*, **85**, 5586-5594 (2013) DOI:10.1021/ac40008573
27. V. Mirceski, D. Guziejewski, K. Lisichkov, Electrode kinetics measurements with square-wave voltammetry at a constant scan rate. *Electrochim. Acta* **114**, 667-673 (2013) <https://doi.org/10.1016/j.electacta.2013.10.046>
28. R. Gulaboski, Theoretical contribution towards understanding specific behaviour of “simple” protein-film reactions in square-wave voltammetry. *Electroanal.*, **31**, 545-553 (2019) <https://onlinelibrary.wiley.com/doi/10.1002/elan.201800739>
29. R. Gulaboski, V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, *Electrochim. Acta* **167**, 219-225 (2015) <https://doi.org/10.1016/j.electacta.2015.03.175>