ANALYSIS OF REDOX PROTEINS DIMERIZATION MECHANISM IN CYCLIC VOLTAMMETRY

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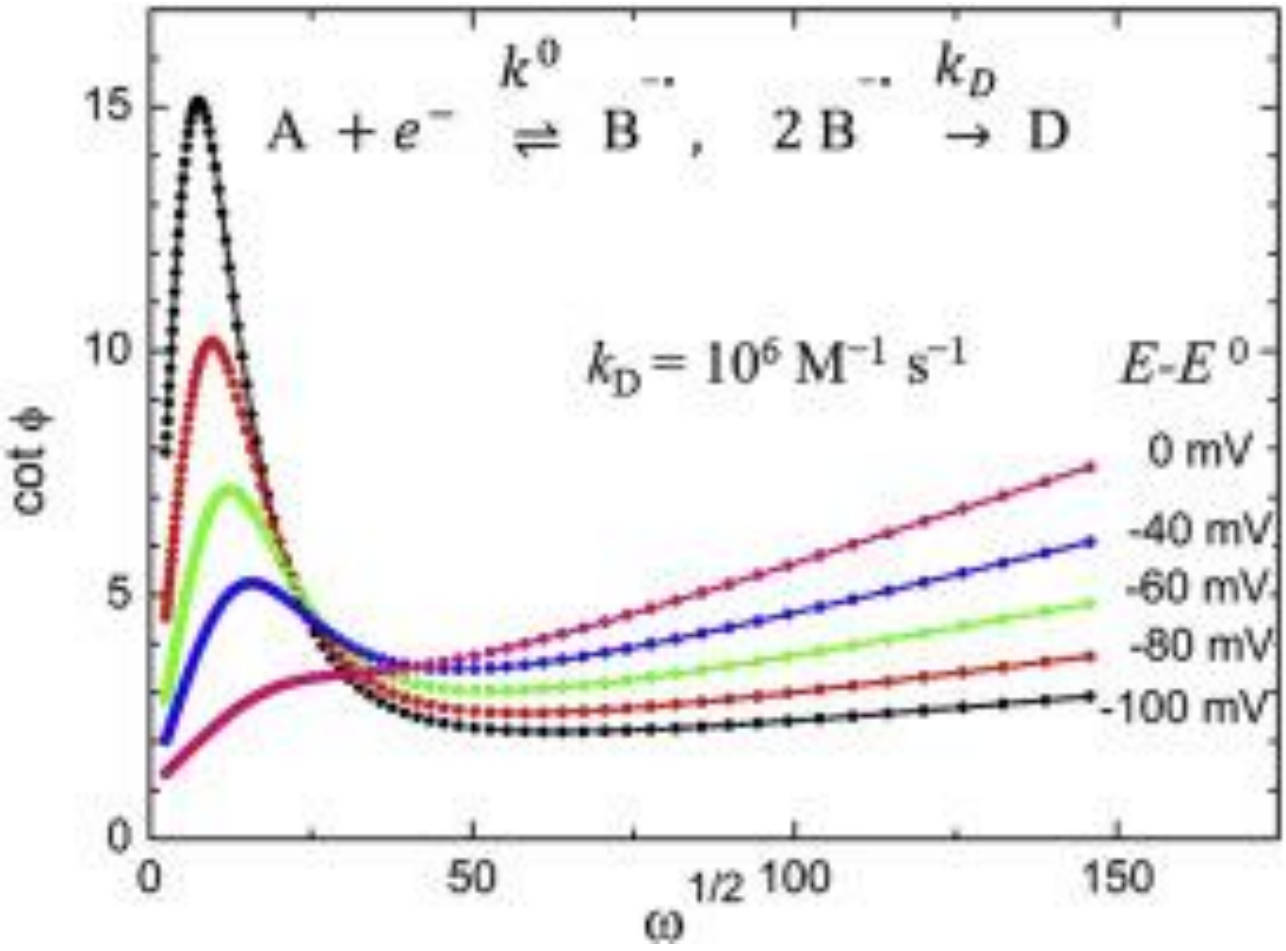
Abstract

Redox proteins play a crucial role in electron transfer processes in biological systems. Cyclic voltammetry (CV) is a widely used electrochemical technique to investigate the redox properties of these proteins. Dimerization reactions of redox proteins can significantly impact their electrochemical behavior in cyclic voltammetry. Here are some major features of redox protein dimerization reactions in cyclic voltammetry:

1. Peak shape and position: Dimerization of redox proteins can lead to changes in the peak shape and position in cyclic voltammograms. In some cases, dimerization may result in the appearance of additional peaks corresponding to dimeric species or altered peak positions compared to monomeric forms. The presence of dimeric species can give rise to complex voltammetric behavior.
2. Peak currents: Dimerization reactions can affect the peak currents observed in cyclic voltammetry. The formation of dimers may lead to changes in the rate of electron transfer or alter the accessibility of redox-active sites, resulting in variations in the magnitude of the peak currents. This can provide insights into the kinetics and mechanism of dimerization processes.
3. Electron transfer kinetics: Dimerization of redox proteins can influence the electron transfer kinetics observed in cyclic voltammetry. The formation of dimers may lead to changes in the rate constants associated with electron transfer processes, affecting the shape and magnitude of the voltammetric peaks. Analysis of the peak shapes and current densities can provide information about the kinetics of dimerization reactions.
4. Redox potential shifts: Dimerization reactions can induce shifts in the redox potentials of the redox-active sites within the protein. The formation of dimers may result in changes in the local environment, altering the electrostatic and steric effects on the redox centers. These potential shifts can be observed as changes in the peak potentials in cyclic voltammetry, providing insights into the thermodynamics and structural aspects of dimerization.
5. Stability and reversibility: Dimerization reactions can influence the stability and reversibility of redox processes in cyclic voltammetry. The presence of dimeric species may affect the stability of the redox-active sites or alter the ability of the protein to undergo reversible electron transfer. Analysis of the peak shapes, peak currents, and peak separations can provide information about the stability and reversibility of the dimeric forms.

It is important to note that the specific features observed in cyclic voltammetry experiments depend on the nature of the redox protein, the specific dimerization reaction, and the experimental conditions employed. The interpretation of CV data in the context of redox protein dimerization requires careful analysis and comparison with appropriate control experiments and theoretical models. In this work we present a set of simulated voltammograms that can give hints about complexity of dimerization of redox proteins.


k^0
k_D
A + e^- ⇌ B , 2 B → D
$k_D = 10^6\ M^{-1}\ s^{-1}$
E-E^0
0 mV
-40 mV
-60 mV
-80 mV
-100 mV
cot ϕ
15
10
5
0
0
50
100
150
$\omega^{1/2}$

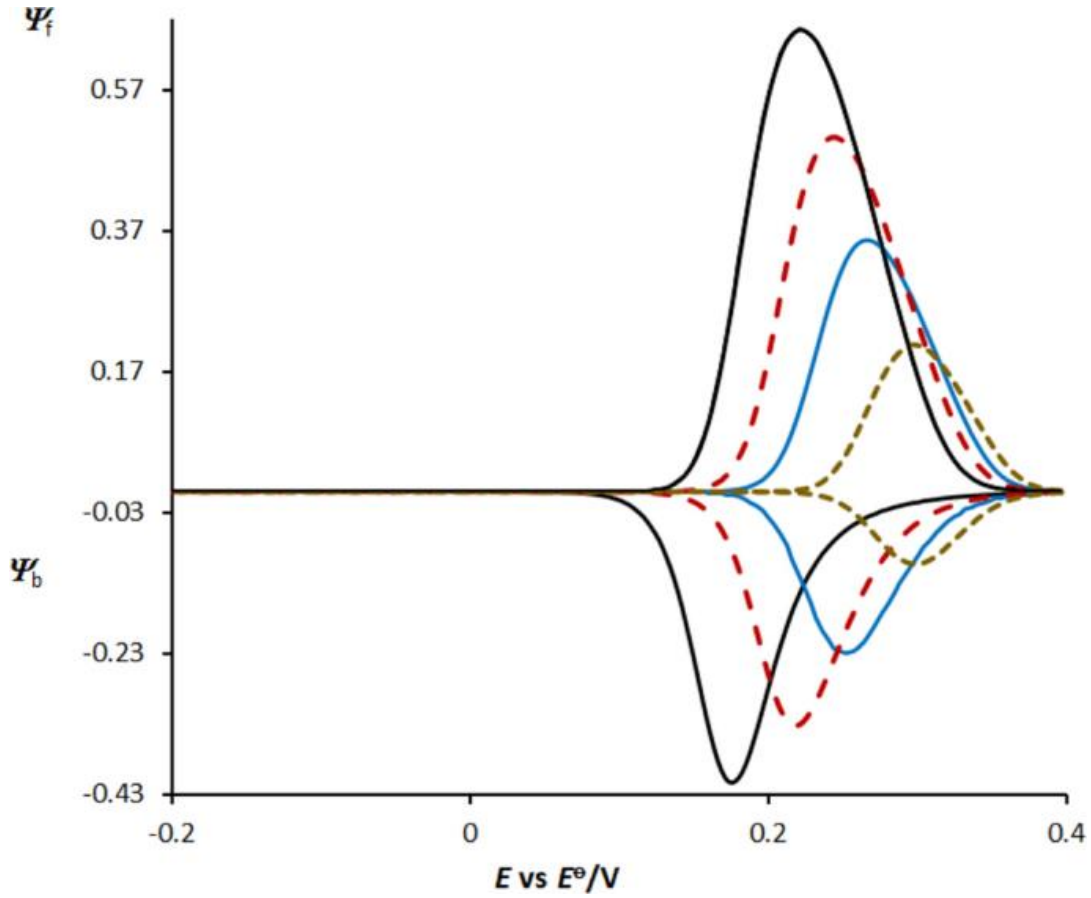

Ψ_f
Ψ_b
0.57
0.37
0.17
-0.03
-0.23
-0.43
-0.2
0
0.2
0.4
E vs E^e/V

Figure 1. Cyclic voltammograms showing the effect of initial redox protein concentration. Curves are simulated at moderate concentrations of initial form of lipophilic redox protein

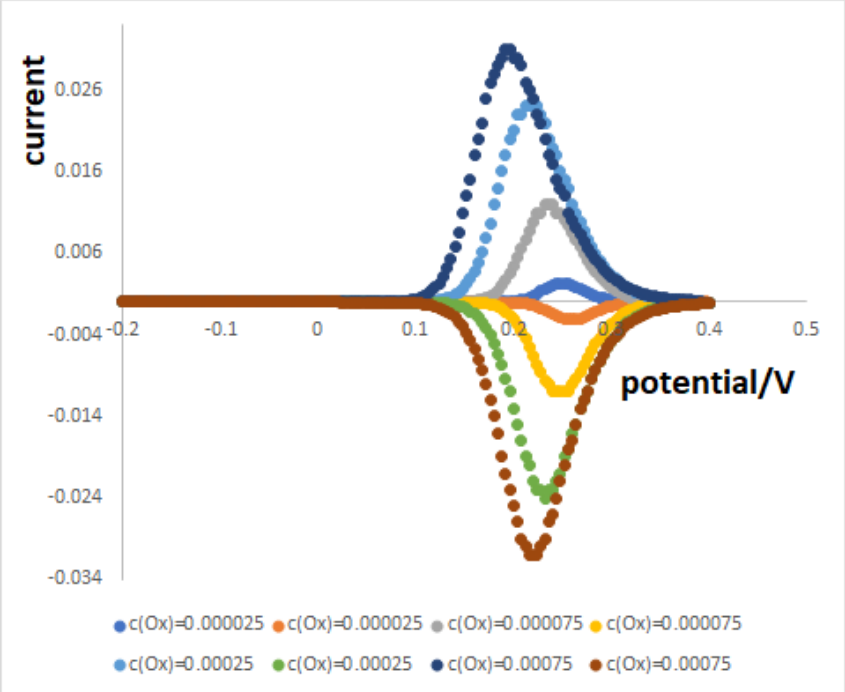


Figure 2. Cyclic voltammograms showing the effect of initial redox protein concentration. Curves are simulated at large concentrations of initial form of lipophilic redox protein

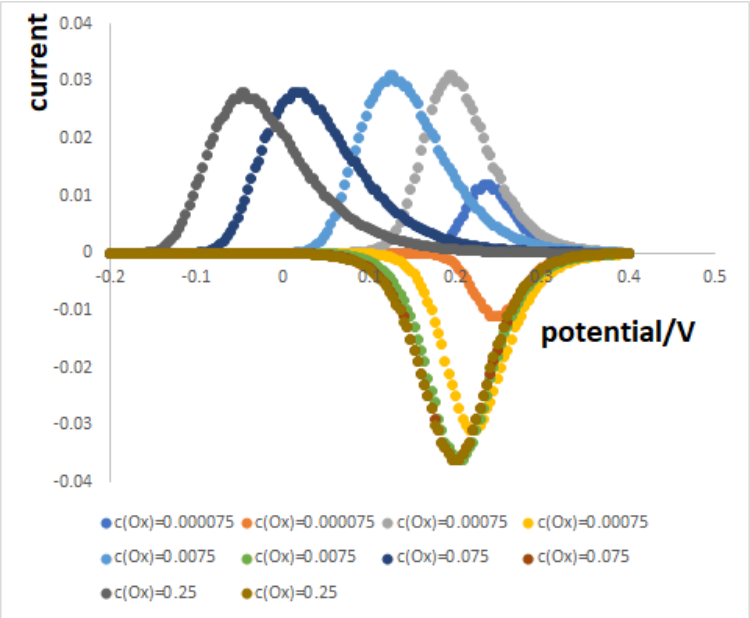


Figure 3. Influence of chemical rate parameter to the features of cyclic voltammograms of lipophilic redox protein involved in electrochemical dimerization reaction

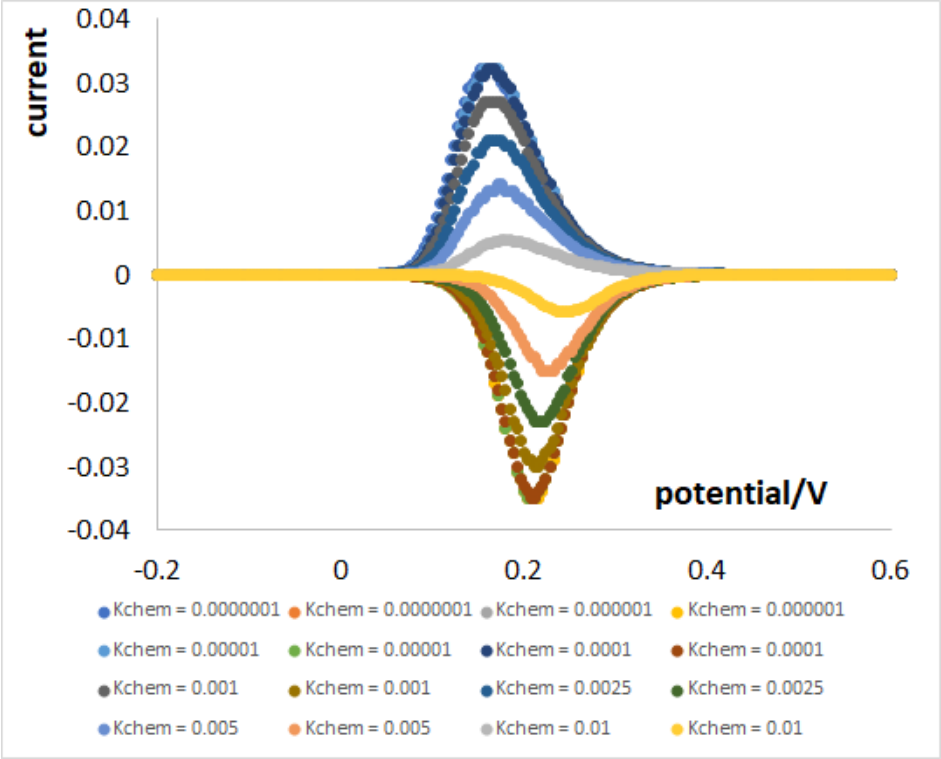
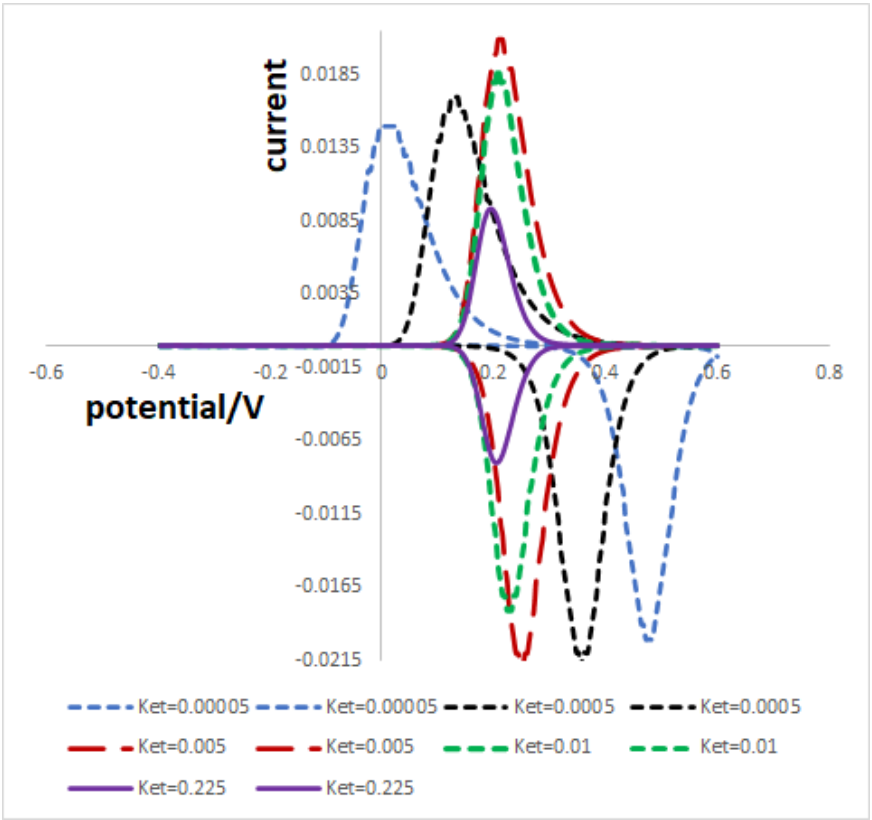


Figure 4. Influence of electron transfer rate parameter to the features of cyclic voltammograms of lipophilic redox protein involved in electrochemical dimerization reaction



REFERENCES

1. S. Lazarova, P. Apostoloski, R. Gulaboski, Electrochemically induced dimerization of lipophilic redox proteins: Theoretical insights in protein-film square-wave voltammetry, ***Monatshefte für Chemie-Chemical Monthly*** *154* (2023), 595-603
2. R. Gulaboski, E. S. Fereira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garau, V. Lippolis, A. F. Silva, ***Journal of Physical Chemistry C***, ***112*** (2008) 153-161
3. V. Mirceski, R. Gulaboski, ***Journal of Physical Chemistry B***, ***110*** (2006) 2812-2820
4. V. Mirceski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (2002) 813-818
5. R. Gulaboski, V. Mirceski, S. Mitrev, ***Food Chemistry*** 138 (2013) 116-121
6. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435
7. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842
8. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, ***Cell Calcium*** 43 (2008) 615-621
9. B. Sefer, R. Gulaboski, V. Mirceski, ***Journal of Solid State Electrochemistry*** 16 (2012) 2373-2381.
10. V. Mirceski, R. Gulaboski, ***Bulletin of the Chemists and Technologists of Macedonia*** 18 (1999) 57-64.
11. R. Gulaboski, C. M. Pereira, ***Electroanalytical Techniques and Instrumentation in Food Analysis***; in Handbook of Food Analysis Instruments (2008) 379-402.
12. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, ***Journal of Physical Chemistry B*** 110 (2006) 12530-12538.
13. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, ***Analytical Chemistry*** 91 (2019) 14904-14910.

14. V. Mirceski, R. Gulaboski, F. Scholz, ***Journal of Electroanalytical Chemistry*** 566 (2004) 351-360.

15. R. Gulaboski, V. Mirceski, S. Mitrev, ***Food Chemistry*** 138 (2013) 116-121

16. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435

17. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842

18. R. Gulaboski, V. Mirceski, F. Scholz, ***Amino Acids*** 24 (2003) 149-154

19. V. Mirceski, R. Gulaboski, ***Croatica Chemica Acta*** 76 (2003) 37-48.

20. F. Scholz, R. Gulaboski, ***Faraday Discussions*** 129 (2005) 169-177.

21. V. Mirceski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (2002) 814-819.

22. R. Gulaboski, K. Caban. Z. Stojek, F. Scholz, ***Electrochemistry Communications*** 6 (2004) 215-218.

23. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, ***Electroanalysis*** 31 (2019) 2488-2506