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Kinetic Parameter Extraction of Square Wave Voltammograms from DNA-Modified Gold Electrodes MARC MCWILLIAMS, CHRIS WOHLGAMUTH, JASON SLINKER, University of Texas at Dallas — The field of surface bound electrochemistry is important in a variety of applications specifically sensing. A fundamental understanding of the processes involved could help to improve detection limits, optimize rates of detection and direct changes in device design. Accurate extraction of electrochemical kinetic parameters such as the rate constant k and charge transfer coefficient α from cyclic voltammograms can be challenging when confronted with large background currents and relatively weak signals. The commonly used technique of Laviron analysis is both time consuming and somewhat subjective. Square wave voltammetry (SWV) is therefore an ideal alternative method given that it maximizes signal while minimizing capacitive effects. In this experiment kinetic parameters of DNA-modified gold electrodes are obtained from SWV curves through background subtraction followed by nonlinear least squares fitting using a first order quasi-reversible surface process model. The fitting is accomplished using the Nelder-Mead simplex algorithm with standard parameters and a convergence condition of less than 0.0001%. General agreement with experimental data is shown with varying levels of confidence. Difficulties specific to this experiment are discussed as well as the possible benefits of utilizing the Bayesian statistical approach of nested sampling when confronted with multiple peaks of interest and the background source is well defined.

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