DETERMINATION OF DIFFUSION COEFFICIENTS USING FIVE METHODS

General Schedule and Comments *(this text is the same that was presented for Lab 2)*

In general, the format for this "discussion" session will be the same every week and is as follows:

1. Present brief outline of experiments, goals, and updates
2. Break into groups of two or three, set-up work space, and connect to the BioLogic potentiostat using the EC-Lab software on a PC laptop
3. Perform experimental procedure(s), while being assisted by the Instructor
4. If time permits, as a class provide feedback on the activity and recommend other activities
5. Clean-up work space, return items, and store electrodes for subsequent weeks. *(You are not dismissed from the discussion session until this is complete.)*

It is recommended that you read through the procedures and reference publications/files <u>*before*</u> *you watch the experiment video and attend the hands-on discussion sessions. This will help you to become acquainted with the experiment and formulate questions to ask during the discussion session. Being interactive with the videos (i.e. by actively asking yourself questions as to why the experiment is set up in a certain way and why data looks the way it does, etc.) will increase your knowledge and comfort with the techniques shown. This will help with completion of homework assignments and allow you to implement techniques in your own research.*

Introduction

Last week you performed experiments in which effects due to migration played a dominant role, i.e. iR drop, limiting current, and slow RC charging of the double layer, as well as effects on $E^{o'}$ due to non-ideality. This week, you will perform experiments where the observed behavior is predominantly dictated by diffusion. This condition is often desired, because as we saw in class, many equations derived to allow us to interpret electrochemical data assume that the only means of mass transfer is by diffusion.

Purpose

The purpose of this hands-on discussion activity is to become more familiar with techniques used to measure the useful parameter of diffusion coefficient of a redox-active molecule. For this, you will determine the diffusion coefficient five ways: based on data obtained from cyclic voltammetry and electrochemical impedance spectroscopy measurements using a carbon button electrode so that linear diffusion dominates, based on data obtained from cyclic voltammetry and electrochemical impedance spectroscopy measurements using a microelectrode so that radial diffusion dominates, and based on data obtained from potential-step potentiostatic chronoamperometry measurements using a carbon button electrode so that linear diffusion dominates and analysis occurs using the Cottrell equation and an Anson plot. This activity will provide you with a better understanding of how to determine diffusion coefficients for the oxidized and reduced halves of a redox couple using various electrochemical techniques.

Safety

For each hands-on discussion session you must bring and wear personal protective equipment consisting of a lab coat and safety glasses/goggles. In addition, at a minimum you must wear closed-toe shoes, pants, and a tee-shirt that covers your entire torso. While in lab you will also need to wear gloves, which we will supply as nitrile gloves. In addition, to reduce the possibility of electric shock to you and your labmates be sure to control the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment. Moreover, you would not touch the electrodes while a potential bias is being applied between them, especially the counter electrode.

Procedures

Part A: Determining diffusion coefficients by "typical" cyclic voltammetry and by electrochemical impedance spectroscopy

Tools/materials needed: ~50 mL beaker, **carbon button working electrode**, platinum quasi-reference microelectrode (QRE), carbon cloth counter electrode, aqueous electrolyte solution of 0.5 mM $[Fe^{III/II}(CN_6)]^{3-/4-}$ containing 100 mM K_2SO_4

(1) Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the aqueous electrolyte solution of redox couple. *Note: Only submerge the cloth portion of your counter electrode in the electrolyte.*

(2) Set-up EC-Lab to perform a two-step experiment consisting of an OCV followed by a CV. Determine the parameters and potential range necessary to observe the complete redox behavior for the redox couple during the CV. You can do so via a "quick and dirty" run where you can change the potential window in real time to capture its complete behavior. *Don't forget to click the key image to edit the options in real-time.*

(3) Based on the potential range determined from step 2, perform the following electrochemical measurements *without stirring*:
   a. OCV: for 30 seconds, recording the potential every second
   b. CV: 500 mV/s scan rate for several reproducible sweeps
   c. CV: 250 mV/s scan rate for several reproducible sweeps
   d. CV: 100 mV/s scan rate for several reproducible sweeps
   e. CV: 20 mV/s scan rate for several reproducible sweeps
   f. PEIS: $E_{DC} = E_{oc}$, E_{AC} = 10 mV, 1 MHz – 0.1 Hz, 10 pt/decade

Part B: Determining diffusion coefficients using a microelectrode

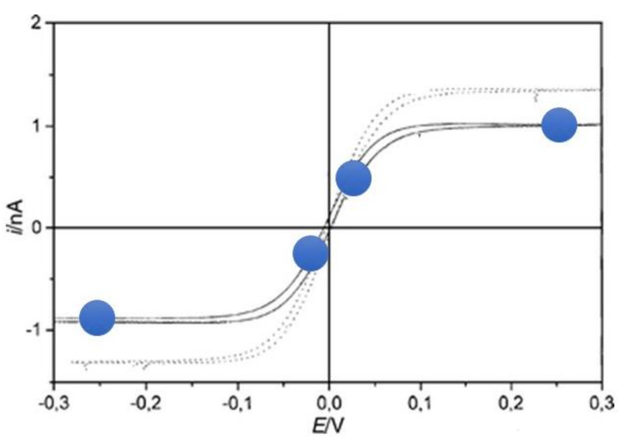
Tools/materials needed: ~50 mL beaker, **platinum working microelectrode**, carbon cloth (or Ag/AgCl) counter electrode / quasi-reference electrode (QRE), aqueous electrolyte solution of 0.5 mM $[Fe^{III/II}(CN_6)]^{3-/4-}$ containing 100 mM K_2SO_4

Set-up a *two-electrode* electrochemical cell and perform the same electrochemical measurements as in Part A, step 3, again *without stirring. For your own edification, feel free to compare these results with data obtained using a three-electrode configuration. For either of these configurations plot <I> averaged over several potential steps, N, where N >> 10 in order to obtain a sufficient signal-to-noise ratio. Otherwise, your data may be too noisy to interpret, because we are not using a Faraday cage.*

Part C: Determining diffusion coefficients by potential-step experiments

Tools/materials needed: ~50 mL beaker, **carbon button working electrode**, platinum quasi-reference microelectrode (QRE), carbon cloth counter electrode, aqueous electrolyte solution of 0.5 mM $[Fe^{III/II}(CN_6)]^{3-/4-}$ containing 100 mM K_2SO_4

(1) Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the aqueous electrolyte solution of redox couple.
(2) Using the data from Part B, identify two potentials for each direction of polarization bias in the following areas marked in blue on the example graph (four potentials in total):
    a. Diffusion-limited regime
    b. Electron-transfer-limited regime



(3) For each of the four potentials perform a chronoamperometry experiment *without stirring* for enough time and at a small enough resolution so that Cottrell and Anson analyses can be conducted. *Plot the data as though you were conducting a Cottrell analysis and Anson analysis and verify that they have the correct functional form.*

Assignment 3 – Lab 5 *(combined with last week's activity; due on Monday, November 6, 2023 at noon)* (You must show your work for credit on all problems.)

1. Using the data provided to you for Lab 5, or your own data if your laboratory experiments were successful, do the following. *Assume that the carbon button electrode had a diameter of 3 mm, the platinum microelectrode had a diameter of 100 µm, and each half of the redox couple was present at 0.5 mM.*
   - **a.** Explain what a quasi-reference electrode is *and* why were you able to use one for most of these experiments.
   - **b.** For the data obtained using the largest CA potential steps, indicate which type of plot would show the most linear trend in the data, e.g. log(y) *vs.* x.
   - **c.** For the data obtained using the smallest CA potential steps, explain whether diffusion coefficients can be obtained in a straightforward manner.
   - **d.** The Purpose section of this lab activity mentioned that there are five ways to calculate diffusion coefficients using data from CV, EIS (Warburg equation *(Google it)*), Cottrell analysis, and an Anson plot, each under conditions of linear diffusion, and then using data from CV under radial diffusion. Using *each way*, calculate D for at least one of the redox-active species *and* include plots to support your conclusions.