DETERMINATION OF THE DIFFUSION COEFFICIENT VIA FOUR METHODS

General Schedule and Comments (this text is the same text that was present in Lab 2)

In general, the format for this class 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 Bio-Logic potentiostat using the EC-Lab software on a PC laptop
3. Perform experimental procedure(s), while being assisted by the TA and the Professor
4. As a class, discuss the activity, provide feedback, and recommend other activities
5. Clean-up work space, return items, and store electrodes for subsequent weeks. (You are not dismissed from the discussion section until this is complete.)

Since your discussion section is short (110 minutes) and we want to cover as much as possible, please use your time wisely. NOTE: You will need to save or print procedures and reference publications/files before you attend the hands-on discussion sections. This will help you to become acquainted with the experiments and more importantly, will allow you to stay connected to the potentiostat as you run the experiments, because there are sometimes issues with using the Internet and the potentiostat simultaneously.

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. This week, you will perform experiments where the observed behavior is almost exclusively dictated by diffusion. This condition is more ideal, because as we’ve seen in class, useful information can be obtained easily from experiments that are dominated by diffusive behavior.

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. You will determine the diffusion coefficient four ways: using cyclic voltammetry and linear diffusion from your carbon button electrode, using cyclic voltammetry and radial diffusion from a true ultramicroelectrode, and using a potential-step experiment with linear diffusion and chronoamperometry data that is analyzed using the Cottrell equation and an Anson plot. This activity will provide you with a better understanding of how to determine the diffusion coefficient by various electrochemical techniques for the oxidized and reduced halves of a redox couple.
Safety
You must bring personal protective equipment to the lab (i.e. lab coat and safety glasses/goggles). You must wear closed-toe shoes, pants, and a tee-shirt that covers your entire torso to be allowed to work in the hands-on discussion sections. These sections are mandatory so please do not get a zero due to improper lab attire. While in lab you will need to wear gloves, which we will supply (nitrile gloves). To reduce the possibility of electric shock to you and lab mates be sure you are working on the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment. Moreover, do not touch the electrodes while a potential bias is being applied between them.

Procedures
Part A: Determination of two diffusion coefficients via “typical” cyclic voltammetry

Tools/materials needed: 50 mL beaker, rubber bands, carbon button working electrode, platinum quasi-reference microelectrode, carbon cloth counter electrode, aqueous electrolyte solution of 1 mM \([\text{Fe}^{III/II}(\text{CN}_6)]^{3-/4-} + 100 \text{mM K}_2\text{SO}_4\)

(1) Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the redox couple solution.
(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 in 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

Part B: Determination of two diffusion coefficients with a commercial ultramicroelectrode (UME)

Tools/materials needed: 50 mL beaker, rubber bands, commercial platinum working ultramicroelectrode, carbon cloth counter electrode / quasi-reference electrode, aqueous electrolyte solution of 1 mM \([\text{Fe}^{III/II}(\text{CN}_6)]^{3-/4-} + 100 \text{mM K}_2\text{SO}_4\)

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 \(\langle I \rangle\) averaged over several potential steps, \(N\), where \(N\)
> 10 in order to obtain a sufficient signal-to-noise ratio. Otherwise, your data will be too noisy to interpret, because we are not using a Faraday cage.

Part C: Determination of two diffusion coefficients via potential-step experiments

**Tools/materials needed:** 50 mL beaker, rubber bands, carbon button working electrode, platinum quasi-reference microelectrode, carbon cloth counter electrode, aqueous electrolyte solution of 1 mM \([\text{Fe}^{III/II}(\text{CN}_6)]^{3-/4-}\) + 100 mM \(\text{K}_2\text{SO}_4\)

1. Set-up a three-electrode electrochemical cell in a clean beaker and then fill the beaker with ~25 mL of the redox couple solution.
2. Using the data from Part B, identify two potentials for each direction of bias polarization in the following areas (four potentials in total) and marked in blue on the sample graph:
   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. *If time permits, plot the data as though you were conducting a Cottrell analysis and Anson analysis and verify that they have the correct functional form.*

**Assignment** *(combined between this and the prior week’s activity; due Tuesday, February 28, 2017 at 8am PST)* Problems will be assigned this week. (You must show your work for credit on all problems.)