REDOX CHEMISTRY WITH A PORPHYRIN MOLECULE

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 before 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

Thus far in the hands-on discussion sessions you have performed measurements that have resulted in cyclic voltammograms with diffusion-limited hysteretic behavior due to interfacial electron-transfer reactions with simple one-electron-transfer molecules in water, i.e. aqueous ferricyanide/ferrocyanide. This week you will perform experiments using non-aqueous electrolyte solutions containing hemin, a ferric (Fe^{III}) porphyrin, to observe diffusion-limited, non-diffusion-limited, and irreversible electron-transfer behavior.

Purpose

The purpose of this hands-on discussion activity is to become more familiar with simple phenomena that occur during hysteretic cyclic voltammetry measurements and analyses of the underlying electron-transfer behavior. You will perform three "coulombo-chemical" measurements involving hemin and non-aqueous electrolytes, and you will evaluate how the scan rate affects the data. The conditions evaluated include hemin dissolved in solution and with bound solvent ligands, hemin dissolved in solution and with bound amine ligands, and hemin bound to an electrode surface and with bound solvent ligands. This activity will provide you with a better understanding of how cyclic voltammetric behavior is dictated by experimental parameters and

how to correct the data for effects due to uncompensated resistance that are often significant in non-aqueous electrolytes.

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, do not touch the electrodes while a potential bias and/or an electronic current is being applied between them, especially the counter electrode. Caution: The non-aqueous solvents and methylimidazole ligand used in this activity can be adsorbed through skin and sinuses and therefore, you should use caution when handling them, making sure to rigorously use a gloved hand and pour and cap solutions in a fume hood. If skin or eye contact occurs, you should immediately flush them with copious amounts of water for at least 15 minutes and notify someone. If inhalation occurs, you should have someone escort you out of the room to inhale fresh air.

Procedures

Part A: Analysis of hemin redox processes in solution

Tools/materials needed: vial, septum, stir bar, needles, silica glass with a thin layer of conductive fluorine-doped tin oxide (FTO) working electrode (~1 cm x ~5 cm), Ag/AgCl (KCl sat'd) reference electrode, carbon cloth or carbon rod counter electrode, methylimidazole, dimethylsulfoxide (DMSO) electrolyte solution containing 100 mM $LiClO_4$ and 1 mM hemin

(1) In a fume hood, set-up a **gas-tight** three-electrode electrochemical cell using a septum in a vial half-filled with the DMSO electrolyte/hemin solution and including a stir bar.
(2) In a fume hood, degas the solution using an input needle immersed into the solution to bubble for ~5 min with an inert gas (Ar or N_2) and an output needle to allow the purge gases to exit the cell.
(3) Perform the following electrochemical measurements, **without stirring**.
    a. OCV: for 30 seconds, recording the potential every second
    b. CV: sweep between **-0.2 V** and **-1.5 V** *vs* RE (so that two iron-based redox events can be observed, i.e. $Fe^{III/II}$ and $Fe^{II/I}$) at a scan rate of 25 mV/s for several reproducible sweeps, *and then increase the scan rate to 100 mV/s, followed by 500 mV/s and finally 2 V/s, each measuring several reproducible sweeps with obvious peaks for the cathodic and anodic processes*.
    c. PEIS: $E_{DC} = E_{oc}$, E_{AC} = 10 mV, 1 MHz – 1 Hz, 10 pt/decade

(4) Inject 1 drop of pure methylimidazole into the electrolyte solution, stir the solution for several seconds, and then repeat the electrochemical procedure above **at 100 mV/s only, again, without stirring**.

Part B: Analysis of hemin redox processes on an electrode surface

Tools/materials needed: vial, septum, needles, silica glass with a thin layer of conductive fluorine-doped tin oxide (FTO) working electrode (~1 cm x ~5 cm), Ag/AgCl (KCl sat'd) reference electrode, carbon cloth or carbon rod counter electrode, neat acetonitrile, DMSO solution containing concentrated hemin and no supporting electrolyte, acetonitrile electrolyte solution containing 100 mM $LiClO_4$

(1) In a fume hood, apply several drops of the concentrated DMSO solution containing hemin onto an FTO electrode, angled to concentrate the solution at one end, and allow it to dry.
(2) Dunk the electrode in neat acetonitrile to remove loosely bound hemin molecules.
(3) In a fume hood, set-up a **gas-tight** three-electrode electrochemical cell using a septum in a vial half-filled with the *hemin-free* acetonitrile electrolyte solution.
(4) In a fume hood, degas the solution using an input needle immersed into the solution to bubble for ~5 min with an inert gas (Ar or N_2) and an output needle to allow the purge gases to exit the cell.
(5) Perform the following electrochemical measurements, **without stirring**.
    a. OCV: for 30 seconds, recording the potential every second
    b. CV: sweep between **0 V** and **-1.1 V** *vs* RE at a scan rate of 25 mV/s for several reproducible sweeps, *and then increase the scan rate to 100 mV/s, followed by 500 mV/s and finally 2 V/s, each measuring several reproducible sweeps with obvious peaks for the cathodic and anodic processes*
    c. PEIS: $E_{DC} = E_{oc}$, E_{AC} = 10 mV, 1 MHz – 1 Hz, 10 pt/decade

Assignment 5 – Lab 8 *(not combined with any other activities; now due Friday, December 8, 2023 at noon)* (You must show your work for credit on all problems.)

1. Complete a short survey via the link that will be emailed to you *and* end-of-quarter course evaluations. *(We are able to tell who completed each, but we cannot associate answers with individual students.)*

2. Using the data provided to you for Lab 8, or your own data if your laboratory experiments were successful, do the following.
    a. Part A: CV Data for Hemin Dissolved in Solution
        i. In the absence of methylimidazole, determine the anodic and cathodic peak currents for each scan rate. Submit a plot of these values as a function of the scan rate *and* a plot of these values as a function of the square root of the scan rate. Determine which dataset exhibits the most linear trend. *Also* explain whether this was the expected outcome *and* indicate possible causes of any unexpected non-linearity.

ii. In the absence of methylimidazole, determine the anodic and cathodic peak potentials *and* peak splitting for each scan rate, first correcting each of these values for the iR_u drop obtained using the EIS data. *Also* explain whether these values were expected.

iii. Based on the data, and not necessarily data from the literature, speculate as to what methylimidazole did in your system *and* support your hypothesis by explaining your observations.

b. Part B: CV Data for hemin bound to the FTO surface

i. Assume that we obtained nice data (like in **Part A**) and report which scan-rate dependence you expected to be linear for your data *and* explain why.

ii. Assume that we obtained nice data (like in **Part A**) and report the expected value of the peak splitting for your data *and* why.

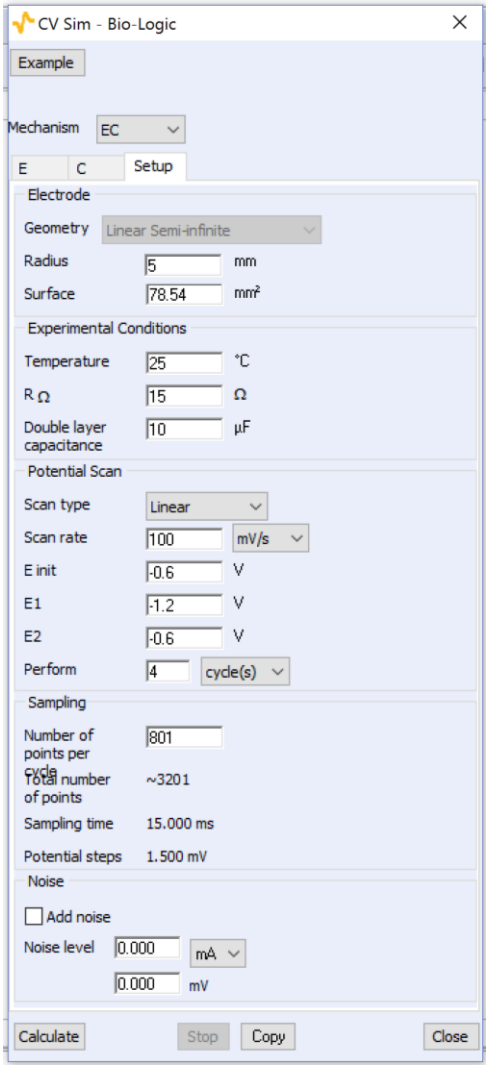
3. Using the EC-Lab software, simulate cyclic voltammograms for a non-catalytic EC reaction, i.e. electron transfer followed by a chemical step.

a. Go to "Analysis", "General Electrochemistry", and "CV Sim…" menu.

b. Simulate CVs and copy data for the following parameters:

i. E only mechanism

1. Mechanism: *EC*
2. E tab: *Reduction*; $z = 1$; $E^o = -0.9$ V; $k^o = 1$ cm/s; $\alpha_f = 0.5$; $C_A^* = 1E\text{-}3$ mol/L; $C_B^* = 0$ mM; $D_A = 1E\text{-}5$ cm^2/s; $D_B = 1E\text{-}5$ cm^2/s
3. C tab: $k_f = 0$ s^{-1}; $k_b = 1$ s^{-1}
4. Setup: Use the rather precise values *and units* from the screenshot shown here.
5. Click the "Calculate" button.
6. Only show the 1st cycle on the plot and then right click on the graph and choose "Copy" and then "Copy Data" (Alt D).
7. Copy and paste the data into a blank Excel table.



ii. EC mechanism: Repeat the above steps varying k_f as 1, 10, 100, and 1000 s^{-1} by simulating each CV and copying and pasting the data for the 1st cycle of each to the same Excel table.

iii. Mostly E mechanism: Repeat the above steps with $k_f = 100$ s^{-1} and scan rate = 100,000 mV/s and copy and paste the data for the *2nd cycle* to the same Excel table. Then, using these same values simulate the case when $R_\Omega = 500\ \Omega$, a reasonable value for non-aqueous electrochemical

measurements in the presence of 100 mM electrolyte, and copy and paste the data for the *2nd cycle* to the same Excel table.

c. Submit *one plot* containing your first *five* simulated CVs, of the *1st scan only* from each CV in **Parts i and ii**, and not the sixth and seventh simulated CVs in **Part iii**. *Also*, explain the processes that dictate the observed changes in behavior.

d. Submit *one plot* containing your last *two* simulated CVs, of the *2nd scan only* from each CV in **Part iii**. *Also*, explain the processes that dictate the observed behaviors.