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Physical Chemistry Laboratory
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# Determination of Electron Transfer in Ferrocene Mixed-Valent Compounds

## Introduction

Electron Transfer (ET) reactions are fundamentally important in chemistry. In ET reactions, no bond breakage or bond formation takes place during formation of products from reactants. However, this simple act of transferring an electron from one molecule to another is crucial in nature, and critical to many current chemical processes in industry. For instance, ET reactions are used in the human body to carry out respiration. The electron transport chain in mitochondria, the center of respiration, rely on ET reactions. In plants, ET reactions are key in photosynthesis when transforming solar energy to chemical energy. In industry, the Haber-Bosch process transforms the inert nitrogen gas from the atmosphere to ammonia, a more reactive nitrogen compound used as a precursor for fertilizers.

The objective of this experiment is to investigate ET in mixed-valent (MV) compounds utilizing electrochemical methods. We will utilize covalently bonded ferrocene dimer molecules as models for these studies.

## Electron Transfer

In order for Electron Transfer to take place you need a center of oxidation (electron donor) and a center of reduction (electron acceptor). Oxidation is a process that involves the loss of an electron, and reduction involves the gain of an electron. You cannot have an oxidation take place without a reduction because that lost electron has to go somewhere. Therefore, these processes are commonly known as oxidation-reduction reactions or redox events.

There are two types of electron transfer: inner sphere, outer sphere. In outer-sphere electron transfer, the center of reduction (the 'electron donor') and the center of oxidation (the electron acceptor") are not bonded to each other, and the electron transfer occurs through the space between the two. Outer-sphere electron transfer is very common in typical redox reaction in the synthetic laboratory. On the other hand, in inner-sphere electron transfer the ET event occurs through a covalent bond formed between the donor and acceptor and a linker ligand. The discovery of inner-sphere electron transfer mechanism was worthy of a Nobel Prize.

## Mixed-valent

Mixed-Valent compounds serve as good models for the study of the inner-sphere ET mechanism using electrochemical methods and spectroscopy techniques. Mixed-valent compounds are molecules where the center of oxidation and the center of reduction are similar chemical species but they have different oxidation states.

Mixed-valent compounds are widely used because they are great models for investigating electron transfer. Most mixed-valent complexes are composed of two metallic (M) redox centers bridged by a linker molecule (L). A simple example of this set-up can be found in below in Figure 1.

**Figure 1.**

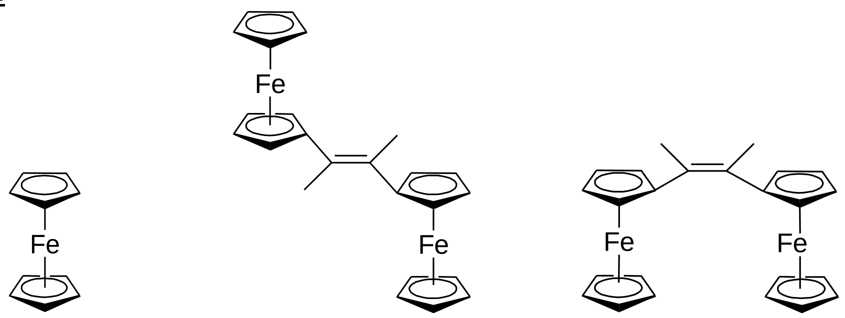
In this laboratory practice we will be studying the electron transfer in mixed-valent complexes in which the electron donor and acceptor moieties are ferrocene complexes. We will use cyclic voltammetry in order to measure the thermodynamic equilibrium of the comproportionation reaction depicted in equation 1 (*Fc* = ferrocene).

Eq (1) $$[Fc\qquad\qquad] \quad [Fc\qquad\qquad] \rightleftharpoons 2[Fc\qquad\qquad]$$

A large equilibrium constant means that the concentration of the products will be favored. In contrast, a small value for $K_c$ means that the equilibrium lies to the left (reactants). The degree of electron transfer in the mixed-valent complex can be inferred by measuring $K_c$, and we will use electrochemical methods to do so.

The first compound that you will be analyzing in this experiment is ferrocene. Ferrocene is composed of a single iron ion sandwiched between two cyclopentadienyl ligands (Figure 2a). The other two compounds are ferrocene dimers covalently linked by a methylated alkene. The linker ligand yields two possible diastereoisomers (E-dimethyldiferrocenylethylene and Z-dimethyldiferrocenylethylene), and we will be using both (Figure 2b and 2c respectively).

**Figure 2.**



**(a)** **(b) E** **(c) Z**

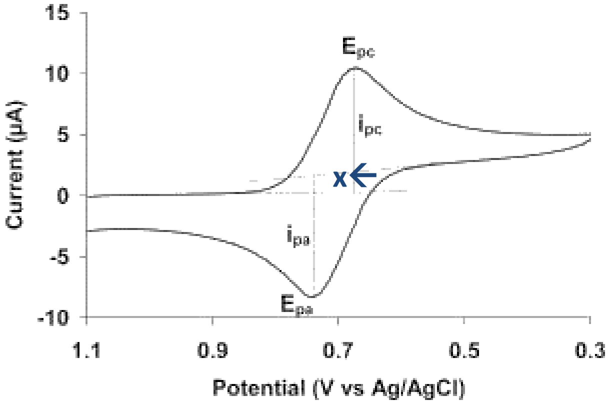
**Electrochemistry**

The electrochemical method we will use is called cyclic voltammetry (CV). In cyclic voltammetry, a potential is applied to the molecule as the potential is increased linearly over time. This applied potential occurs at the working electrode, which may be a cathode or anode depending on the direction of the scan. When performing an electrochemical reduction, the potential is scanned to negative values. When an electron is removed from the electrode and given to the molecule a current is observed in the voltammogram (CV). This bump describes a reduction event of the sample.

When the same process is performed in the reverse direction the sample may be oxidized. When the potential is scanned toward positive values, an electron may be removed from the molecule towards the anode oxidizing the sample. This oxidation event creates a current that is shown as a bump in the anodic direction.

An example of a CV can be found below in Figure 3.

**Figure 3**.



The peak reduction potential is labeled $E_{pc}$ (Fig. 3) and the peak oxidation potential is labeled $E_{pa}$ (Fig. 3). The difference between the peak reduction potential and the peak oxidation potential gives us the half-wave potential, $E_{1/2}$. This half-way potential $E_{1/2}$ is the redox potential of the electrochemical event, and can be quantitatively measured by (equation 2).

Eq (2)

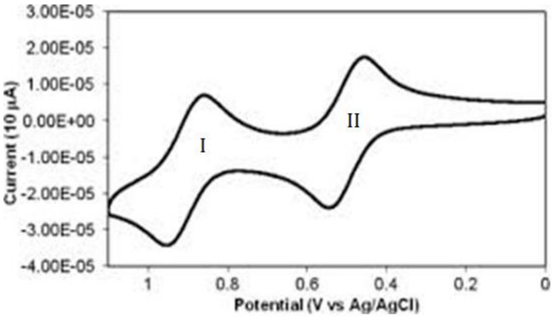
We can utilize cyclic voltammetry to measure the degree of electronic communication between to redox centers by measuring the difference in $E_{1/2}$ between two redox events. Electronic communication can be loosely defined by "how much" do two redox centers "see" or "feel" each other. In other words, if you take an electron from a redox center, does the other one feel it? And if so, by how much? Figure 4 shows the cyclic voltammogram of a sample with two redox events belonging to a system of the M-L-M type. Each bump represents a redox event belonging to one of the two metal centers.

To find the half-wave potential in the CV (Figure 4), we need to find the half-wave potential of the first (I) and the second (II) redox event using equation 2. Next, use equation 3 to find the difference between the half-wave potentials of both redox events.

Eq(3)

A molecule capable of strong electron transfer will have good electronic communication between the redox centers. In this case, the CV will show a two different redox events separated by a "long" distance. A molecule with poor electron transfer will have less electronic communication and will be one where the two redox events are "very close" to each other. The terms "long" and "very close" are very loosely defined here. Later on we will quantitatively delineate what are “long” or “short” or “somewhere in between” differences in $E_{1/2}$ between redox events.[1]

**Figure 4.**



### Equilibrium Constant

With the half-wave potential ($\Delta E_{1/2}$) from the cyclic voltammetry experiments the equilibrium can be calculated by using the Nernst equation (equation 4).

Eq(4)

$$K_c = \exp(\frac{F\Delta E_{1/2}}{RT})$$

Temperature is represented by T in the Nernst equation. R and F each represent the gas constant and the Faraday constant, respectively.

### ET classification

To evaluate mixed-valent complexes according to their equilibrium constants, we use the Robin-Day classification scheme. The Robin-Day classification scheme divides molecules into three different classes (Class I, Class II, Class III).

A Class I molecule has the least amount of electronic communication with a value of $K_c < 10^2$. Class III molecules have a value of $K_c < 10^6$, and these Class III molecules have the best electron communication. Class II molecules have intermediate electronic communication and $K_c$ lies between $10^2$ and $10^6$.

The difference in degree of electronic communication of molecules can be explained by looking at how the redox centers of molecules are linked. In a molecule with two redox centers linked covalently (Figure 5a), one redox center gains an electron for the first redox event. If the second redox center can feel the presence of the extra electron then there is good electronic communication. When there is good electronic communication between the redox centers then it would be harder to carry out a second redox event and add an electron to the second redox center (for a total of two added electrons to the molecule). To overcome the good electronic communication and carry out a second redox event the potential applied to the molecule would have to be great, so the difference in potential between the first redox event

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[1] The degree of electronic communication is directly related to the rate of the electron transfer in mixed-valent samples. Large electronic communication means fast ET rates, while small electronic communication means slow ET rates. In this practice we will focus only on the thermodynamic aspect of ET.

and the second would be large. This can be observed in a cyclic voltammogram where the two redox events are well defined. The $\Delta E_{1/2}$ will be larger.

A molecule (Figure 5b) not linked to the second redox center would have worse electronic communication and it is easier to add a second electron. The molecule with worse electronic communication will have a CV where the redox events are not well defined and the potential difference is less. The $\Delta E_{1/2}$ will be smaller.

**Figure 5.**

## Procedure

Our electrochemical set-up requires a three-electrode system which includes a working electrode (Pt or graphite disk), an auxiliary electrode (a Pt wire) and a reference electrode (Ag/AgCl in an aqueous NaCl solution). The working and the auxiliary electrodes serve as the cathode or anode depending on the direction of the scan. When scanning in the direction of a reduction (to the right) the working electrode is the cathode (were the reduction takes place) and the auxiliary electrode is the anode, and the when scanning in the direction of an oxidation (to the left) the working electrode is the anode (where the oxidation takes place) and the auxiliary electrode is the cathode. The concentrations of your substrate should be 2mM, and each solution must contain 0.1 M of an electrolyte.

Turn on the CH Instruments Electrochemical Workstation. Wait about twenty seconds for the instrument to boot up. Go to “Start” and “Run” and type: “C:\CHI”. Choose “CHI760D (Electrochemical Software)”. If a dialog boxes appear, press “OK” until you see the software open. With the software open, choose "Setup"→"Hardware Test." You should hear a clicking sound and a dialog box should appear. At the end of each of the six tests, you should see "OK" If you see something other than "OK" after any of those tests, wait a minute and run the Hardware Test again. If the Hardware test fails go to "Setup"→"System," and make sure COM 3 is selected. Press “OK,” and repeat.

1) You will need to make about 20-30 mL of three solutions of each ferrocene derivatives (Figure 2). These solutions must have a 2 mM concentration of ferrocene (or the derivatives) and 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in the 50 mL beaker provided.
2) Bubble the solution with nitrogen for about 15 minutes.
3) Next, gently feed the platinum wire through the smallest hole on the plastic cap provided.
4) Place the cap on the beaker such that the platinum mesh rests on the bottom of the beaker.

5) Take the yellow cap off of the platinum working electrode. Place the platinum working electrode in the larger plus-shaped hole, and place the white non-aqueous $Ag^+$/AgCl reference electrode in the smaller circular hole.
6) Attach the green alligator clip to the working electrode, the white alligator clip to the reference electrode, and the red alligator clip to the flat end of the platinum counter electrode.
7) These wires may be stiff and may move the electrodes around. Make sure none of the electrodes touch one another, which would cause a short circuit. Furthermore, shake off any bubbles that may have collected on your electrodes.
8) To check if you have properly set up your electrochemical cell, choose "Control"→"Open Circuit Potential."
9) Open the "CV Par.bin" file with the CH Instruments software. This will load the experimental parameters.
10) Choose "Control"→"Run Experiment."
11) When the run is over, choose "Graphics"→"Present Data Plot." Make sure to "Save As" and save your file to your U: drive as "your initials_ferrocene CV."
12) Run the experiment two more times (steps 1 -10) for E-dimethyldiferrocenylethylene and Z-dimethyldiferrocenylethylene.
13) Record the half-wave potential and calculate for each compound.
14) Report your data and calculations in a lab report with an ACS style format. Turn in the lab report in one week.

## Report

Your report should at least include the following information:

1) An introduction (in your own words!) of what electronic communication is and how have physical chemists measured it (other than electrochemistry!).
2) A well written account of the procedures that you performed in this laboratory
3) A results section that describes what you observed. Including your calculated $K_c$, .
4) A discussion section describing the significance of your results. What systems show strong, weak, or no electronic communication?
5) A conclusion summarizing the key take home points of this laboratory practice.

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