

Cyclic Voltammetry of Ferrocene, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Co}(\text{bpy})_3]^{2+}$ and Iodide

Introduction

Cyclic voltammetry (CV) is a very useful electroanalytical technique. Many inorganic compounds contain transition metal centres that may take on several different oxidation states. The CV experiment can provide important information about the oxidation state of an element in a compound as well as the compound's stability under the experimental conditions employed. When conditions provide stable oxidized and reduced forms during the time period required to obtain a voltammogram (current-potential curve) CV is a simple and direct method for measuring the *standard reduction potential* (E°) of a complex. The $\text{Fe}^{\text{III/II}}$ redox couple of ferrocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, is an example of a well-behaved electrochemically reversible system in acetonitrile solution and is often used as an internal or *pseudo reference* when reporting standard reduction potentials of a redox active species (note: ferrocene is only partially or *quasi-reversible* in chlorinated electrolytes). The standard reduction potentials of the first oxidation and first reduction of a complex can be correlated to the energies of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. As a consequence the same HOMO–LUMO energy difference can sometimes determine the lowest energy electronic transition in the UV-vis spectrum of the same species (note: exceptions to this observation are common due to spectroscopic selection rules, and even if the HOMO–LUMO transition is spin-allowed it is also possible that the most intense low-energy maximum in the UV-vis spectrum can originate from a higher energy electronic transition; in other words, while it is always possible never assume that the lowest energy electronic transition is assigned to HOMO–LUMO without sufficient theoretical confirmation). For a compound whose lowest energy electronic transition is assigned to the HOMO–LUMO transition, the potential difference between the first oxidation and first reduction is often referred to as the *band-gap* (E_{BG}) of the system. This experiment will demonstrate the general CV method by showing how to obtain E° for a variety of redox couples accessible in the ferrocene, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Co}(\text{bpy})_3]^{2+}$ and iodide systems. The ferrocenium/ferrocene redox couple will be initially studied due to its established application as an in-situ *pseudo reference* in organic phase voltammetry. The redox active ruthenium, cobalt and iodide systems are pertinent in materials chemistry applications, e.g. in the following lab we will fabricate and characterize a dye-sensitized solar cell device using the ruthenium polypyridyl based N3 dye with $\text{Co}(\text{III/II})$ and I_3^-/I^- redox mediators. The CV apparatus used in this laboratory is a computer controlled CH 620 instrument. The hardware consists of a potentiostat with a rate determined scan capability. The software allows us to display a current (Amperes, A) versus potential (voltage, V) response for the analyte solution. A three electrode system is used to generate the current-potential response. These electrodes consist of a platinum disk working electrode (2 mm diameter), a platinum wire auxiliary (aka counter) electrode, and a Ag/AgCl reference electrode. The Ag/AgCl reference electrode will be initially calibrated using the

ferrocenium/ferrocene pseudo reference, previously prepared in Lab 4 (Figure 1). The electrochemical cell-top contains four holes; one for each of the electrodes and an additional opening to allow introduction of an inert gas atmosphere (typically used for deoxygenation by passing a stream of nitrogen prior to measurement). The surface of the Pt working electrode must be polished with powdered α -alumina (0.3 μm particle size) and rinsed with distilled water as a pretreatment. The instrument response is highly dependent upon the surface morphology of the working electrode. Polishing in this manner prior to each scan ensures reproducibility. Nitrogen should be passed through the solution for 10 minutes before any measurement is made - this is critical when applying a negative potential scan as dissolved O_2 may be reduced at the working electrode thus interfering with the substrate response. After passing nitrogen through the solution the tip of the deoxygenation tube should be raised above the surface of the liquid and a gentle flow of nitrogen continued throughout the experiment. *During the course of the CV the solution should remain quiescent and be oxygen free.* The use of a supporting electrolyte in CV experiments is to suppress migration of charged reactants and products - migration or *mass transfer* of the analyte should be completely diffusion controlled. There are some other sources of current in addition to the *Faradaic current* due to the analyte; these are collectively referred to as the background or *Ohmic current*. This principally involves capacitive (or charging) current due to build up of the *Helmholtz double layer*. At extreme potentials the background current may also include additional Faradaic current due to the electrolysis of electrolyte, impurities and even the electrode material itself.

A typical CV for the electrochemically reversible $\text{Fe}^{\text{III/II}}$, or more specifically the ferrocenium/ferrocene, redox couple is shown in Figure 1. The following is a complete step by step description of the observed current vs. potential response.

The initial potential (point *a*) at +0.10 V shows no current and therefore no electrolysis occurs in this potential region. The electrode is scanned toward a more positive potential (forward scan) toward point *b*. As the potential is made more positive between points *b* and *c* the electrode is now a sufficiently strong oxidant to oxidize the ferrocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$, to ferrocenium, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$. The concentration of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$ decreases rapidly at the electrode surface as the anodic current increases. At point *d* the concentration of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$ is substantially diminished causing the current to peak. From point *d* to *e* the current decays as $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$ becomes more depleted and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$ dominates the double-layer at the electrode surface. The scan is then reversed at +0.75 V indicated by point *f* (the switching potential, E_{sp}). Between points *f* and *g* the electrode potential is still sufficiently positive to oxidize $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$. A slope is still observed however due to the Ohmic current. At point *h* the electrode is a sufficiently strong reductant to begin reducing $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$, which has accumulated in the double layer at the electrode surface, and the reverse reaction $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+ + e^- \rightarrow (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$ occurs. Thus, the cathodic current rapidly increases to point *i* until the surface concentration of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$ is diminished causing the current to peak. From point *i* to *j*

the current decays as the double-layer is depleted of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$. One CV cycle has now been completed. The quantities E_{pa} (anodic peak), E_{pc} (cathodic peak), i_{pa} (anodic current) and i_{pc} (cathodic current) may be obtained directly from the CV plot. Note that the peak separation $\Delta E_{\text{p}} = 59 \text{ mV}/n$ for a n -electron couple.

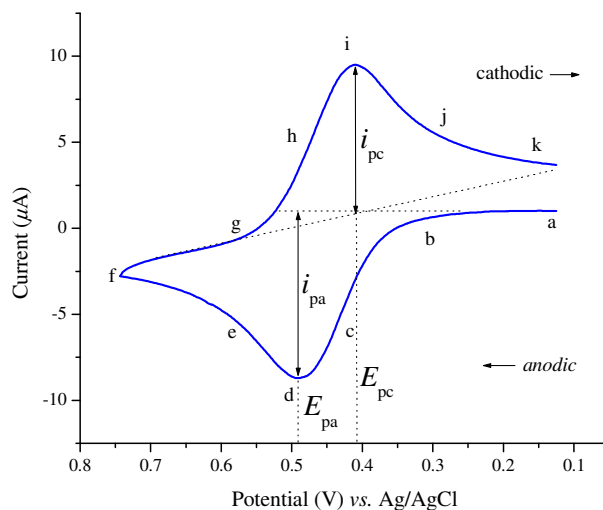


Figure 1: Cyclic voltammogram of ferrocene in 0.1 M Bu_4NPF_6 acetonitrile electrolyte ($E^\circ = +0.45 \text{ V}$; Pt working electrode, Pt-wire counter, aqueous Ag/AgCl reference, scan rate = 0.10 V s^{-1})

A redox couple in which both species rapidly exchange electrons with the working electrode is called an electrochemically reversible couple. The *formal potential* ($E^{\circ'}$) can be expressed in terms of the *standard reduction potential* (E°) using the Nernst equation where α_{red} and α_{ox} are the activity constants for both the reduced and oxidized species, respectively

$$E^{\circ'} = E^\circ - \frac{RT}{nF} \ln \frac{\alpha_{\text{red}}}{\alpha_{\text{ox}}} \quad \text{equation (i)}$$

The activity constants may be replaced with analyte concentration to yield equation (ii)

$$E^{\circ'} = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]} \quad \text{equation (ii)}$$

At the point in a cyclic voltammogram when $[\text{Red}] = [\text{Ox}]$ the expression $E^{\circ'} = E^\circ$ holds true for a reversible process. For a reversible redox couple, equimolar concentrations of reduced and oxidized species occur at the midpoint between the anodic and cathodic waves, therefore we can easily determine E° using the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials according to equation (iii).

$$E^\circ = \frac{E_{\text{pa}} + E_{\text{pc}}}{2} \quad \text{equation (iii)}$$

Procedure

For this experiment you will need to prepare 5 solutions. The class should separate into 5 independent groups each to prepare a single solution. Soln#1 is used as stock to prepare the remaining Soln#2 – Soln#5.

Soln#1	25 mL of 0.1 M Bu ₄ NPF ₆ in acetonitrile solution (this is our electrolyte solution)
Soln#2	5 mL of 1.0 mM ferrocene in 0.1 M Bu ₄ NPF ₆ acetonitrile electrolyte
Soln#3	5 mL of 1.0 mM [Ru(bpy) ₃][PF ₆] ₂ in 0.1 M Bu ₄ NPF ₆ acetonitrile electrolyte
Soln#4	5 mL of 1.0 mM [Co(bpy) ₃][ClO ₄] ₂ in 0.1 M Bu ₄ NPF ₆ acetonitrile electrolyte
Soln#5	5 mL of 1.0 mM KI in 0.1 M Bu ₄ NPF ₆ acetonitrile electrolyte.

Apart from the background, **for each scan you will need to make note of the E_{pc} , E_{pa} , ΔE_p , i_{pc} and i_{pa} .** Care should be taken that no bubbles remain on the electrodes prior to scan after degassing. The cell and electrodes are cleaned with acetone between each sample and air dried.

Expt. (i) Background

Use the 0.1 M Bu₄NPF₆ acetonitrile electrolyte Son#1. This is simply the neat electrolyte solution and will be used to record a background signal. Fill the cell with roughly 2 – 3 ml of the 0.1 M Bu₄NPF₆ acetonitrile supporting electrolyte only. While the system is being deoxygenated prepare the working electrode by polishing on an alumina pad. The instructor will familiarize the students with the operation of the computer program interfaced to the CV and the proper procedure for introducing and removing solutions from the cell. Set the initial potential to 0.00 V, the scan limits to +1.60 V and –2.00 V, sensitivity to 10⁻⁵ Amps and the number of sweeps to 3. The scan should be initiated in a positive direction with a scan rate of 0.10 V/s. After the deoxygenation is complete initiate the potential scan and a background CV of the supporting electrolyte is obtained. This scan with a wide potential range provides the operational limits of the experimental conditions throughout which the analyte can be investigated, i.e. the *potential window* of the electrolyte. For example in 0.1 M Bu₄NPF₆ acetonitrile supporting electrolyte at one extreme of potential the solvent (acetonitrile) will be oxidized and at the other extreme the solvent will be reduced. Save as “bkg” and proceed to scan sample (ii).

Expt. (ii) Calibration

Use 1.0 mM ferrocene in 0.1 M Bu₄NPF₆ acetonitrile electrolyte Soln#2. Follow the same procedure as above to obtain a CV of the Fe^{III/II} couple using the potential limits of +0 V and +0.60 V. Ferrocene typically does not display an observable reduction potential so scanning in the negative direction is unnecessary. A single redox wave should be observed with ΔE_p close to 59 mV. If satisfactory, save the file as “Fc” and proceed to sample (iii).

Expt. (iii) [Ru(bpy)₃]²⁺

Use 1.0 mM [Ru(bpy)₃][PF₆]₂ in 0.1 M Bu₄NPF₆ acetonitrile electrolyte Soln#3. Following deoxygenation, with the help of the instructor, record the *open circuit potential* (V_{OC}). This value will be used as the initial potential. Now successively scan in the positive and negative directions to estimate suitable values for E_{sp} . A single scan may then be set up starting from V_{OC} , scanning positive to the first E_{sp} , scanning negative to the second E_{sp} and setting the final potential also to V_{OC} . You should observe a total one oxidation and 3 successive reductions. Save as “Rubpy3”

Expt. (iv) [Co(bpy)₃]²⁺

Use 1.0 mM [Co(bpy)₃][ClO₄]₂ in 0.1 M Bu₄NPF₆ acetonitrile electrolyte Soln#4. Repeat as for the [Ru(bpy)₃][PF₆]₂ sample. Save as “Cobpy3”. Using the same sample proceed to the next step to determine the Co^{III/II} diffusion coefficient (there is no need to clean the cell at this stage).

Expt. (v) Diffusion Coefficient

The same Soln#4 is used to determine the diffusion coefficient (D) of [Co(bpy)₃]²⁺ by recording the effect of scan rate (v) on the potential-current response. Simply clean and polish the working electrode to rejuvenate the sample. Using the previous CV scan determine a suitable potential range to monitor only the Co^{III/II} couple (± 0.3 V of its standard reduction potential). Record multiple CVs at the following scan rates: 0.01, 0.02, 0.05, 0.10, 0.20, 0.50 and 1.00 V s⁻¹ (purging with nitrogen gas between scans). Save each scan as Co001, Co002...Co1.

Expt. (vi) KI

Use 1.0 mM KI₂ in 0.1 M Bu₄NPF₆ acetonitrile electrolyte Soln#5. Repeat as for the [Ru(bpy)₃][PF₆]₂ sample and save as “Iodide”.

Laboratory Report

[Note: the software will automatically duplicate all data as .txt files. This data will be uploaded on the course website for download]

- 1) Plot cyclic voltammograms as shown in Figure 1 (units should be **V** vs **μ A**) for Expt. (i), Expt. (ii), Expt. (iii), Expt. (iv) Expt. (v) and Expt. (vi). The scan rate dependent plots from Expt. (v) should be overlaid in a single plot. It is important to correct all data such that it is reported with respect to the ferrocenium/ferrocene standard reduction potential, i.e. the standard reduction potential of ferrocene should read 0.00 V.
- 2) In table format, report the values of E_{pa} , E_{pc} , ΔE_p , i_a and E° for each redox couple from Expt. (iii), Expt. (iv) and Expt. (vi). Report analogous data for Expt. (v) in a separate table. Each table caption should state very concisely experimental conditions and the reference system to which all data is reported.

- 3) If reversible Nernstian behavior is observed the electron stoichiometry can be easily estimated from the peak separation ΔE_p by the following relationship

$$\Delta E_p = E_{pa} - E_{pc} \cong 0.059/n$$

Using the determined values of ΔE_p for the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{bpy})_3]^{2+}$ systems determine n and add this data to the table.

- 4) For your discussion explain in detail your reasoning for any difference in standard reduction potentials of the $\text{Fe}^{\text{III/II}}$, $\text{Ru}^{\text{III/II}}$ and $\text{Co}^{\text{III/II}}$ redox couples. Please consider all variables which may influence E° , i.e. metal center, and ligand set.
- 5) The bpy based redox couples for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{bpy})_3]^{2+}$ should be discussed thereafter with similar detail. Comment on the value of n for the three bpy ligands. Which bpy ligand is reduced first?
- 6) Evidence of electrochemical reversibility can be ascertained if a linear plot is obtained by plotting the square-root of scan rate ($v^{1/2}$) versus current (i_p ; where $i_p = \text{total current} = i_{pa} + i_{pc}$). Using the variable scan rate experiments show that the $\text{Co}^{\text{III/II}}$ couple is electrochemically reversible.
- 7) From the same plot determine the diffusion coefficient D of the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ redox active species using the Randle-Sevcik equation

$$i_p = k n^{3/2} A D^{1/2} C v^{1/2}$$

where

i_p is the total current (Amp)

k is a constant = $2.69 \times 10^5 \text{ C mol}^{-1} \text{ V}^{-1/2}$

n is the electron stoichiometry

A is the electrode area (cm^2 ; the Pt disc is spherical and has a diameter of 2 mm)

D is the diffusion coefficient

C is the concentration (mol cm^{-3})

v is the scan rate (V s^{-1})

you must show calculations including units to determine units for D (note: $1 \text{ C} = 1 \text{ Amp s}$)

Further reading on applications of voltammetry is available at the following link
<http://www.currentseparations.com/issues/>

Any modern instrumental analysis or analytical text book will also provide sufficient background information on electrochemistry.