

## Cyclic Voltammetry of $[\text{Ru}(\text{bpy})_3]^{2+}$

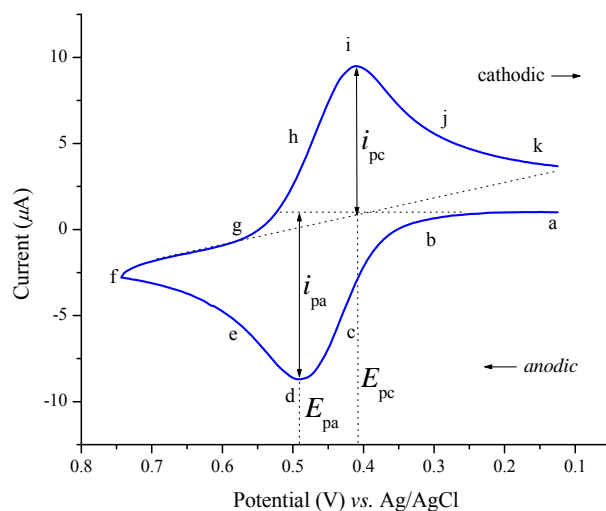
### Introduction

Cyclic voltammetry (CV) is a very useful electroanalytical technique. Many inorganic compounds contain elements 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 in the solvent system in which it is studied. When conditions provide stable oxidized and reduced forms during the time required to obtain a voltammogram (current-potential curve) CV is a simple and direct method for measuring the *formal potential* of an electrochemical half-reaction. 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 formal potentials of inorganic/organometallic complexes (note: even though we start with Fe(II) we always report the redox couple from a reduction perspective as standard). The formal potentials of the first oxidation and first reduction of a complex can often be correlated to the energies of its highest-occupied-molecular-orbital (HOMO) and lowest-unoccupied-molecular-orbital (LUMO). Similarly, this HOMO-LUMO energy difference, i.e. the *band-gap* of the system, typically determines the lowest energy electronic transition in the UV-Vis spectrum (exceptions to this arise due to spectroscopic selection rules). This experiment will demonstrate the general CV method by showing how to obtain the formal reduction potentials ( $E^{\text{o}}$ ) for the  $\text{Ru}^{\text{III/II}}$  and  $\text{bpy/bpy}^{\cdot-}$  redox couples of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex chemistry.

The CV apparatus is computer controlled. It consists of a *potentiostat* with scan capability and contains a display of current (amps) versus potential (voltage). A three electrode system is used. The electrodes in this experiment consist of a platinum disk working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. The Ag/AgCl reference electrode will be initially calibrated using the previously prepared ferrocene internal standard in experiment 6 ( $E^{\text{o}} = +0.450$  V vs. Ag/AgCl in 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile electrolyte; with peak separation  $\Delta E^{\text{o}} \approx 60$  mV). The electrochemical cell-top contains four holes. One for each of the electrodes and one for introducing an atmosphere of gas (typically used for deoxygenation by bubbling a stream of nitrogen prior to measurement). The surface of the working glassy carbon electrode should be polished with powdered  $\alpha$ -alumina (0.3  $\mu\text{m}$ ) and rinsed with distilled water as a pretreatment. Nitrogen should be passed through the solution for 10 minutes before any measurement is made. After bubbling nitrogen through the solution the tip of the deoxygenation tube should be raised above the surface of the liquid and a 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. 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 current*. They include the

electrolysis of impurities, the electrolysis of the electrolyte, the electrolysis of the electrode material, and capacitive (or charging) current. The first three are faradaic currents, whereas the last one is a property of the interface between the electrode and the solution known as the *ohmic current*. This interface behaves like an electrical capacitor in that it can store charge.

A typical CV for the electrochemically reversible  $\text{Fe}^{\text{III/II}}$  redox reaction of ferrocene is shown in Figure 1. The initial potential (point *a*) at 0.10 V shows no current and therefore no electrolysis when the electrode is switched on. 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 ferricenium,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$ . 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  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$  surrounds the electrode. The scan is then reversed at 0.75 V indicated by point *f* (the switching potential). Between points *f* and *g* the anodic current continues because the potential is still sufficiently positive to oxidize  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{II}}$ . At point *h* the electrode is a sufficiently strong reductant to reduce  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^{\text{III}}]^+$ , which has accumulated adjacent to the electrode surface and the 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 solution surrounding the electrode 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  $E_{\text{pa}}$  (anodic peak),  $E_{\text{pc}}$  (cathodic peak),  $i_{\text{pa}}$  (anodic current) and  $i_{\text{pc}}$  (cathodic current) may be obtained directly from CV diagrams similar to that shown here or computed using specific modeling software.



**Fig. 1:** Cyclic voltammogram of ferrocene in 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile electrolyte ( $E^{\circ} = 0.45$  V).

A redox couple in which both species rapidly exchange electrons with the working electrode is called an electrochemically reversible couple. The *half-wave potential* ( $E_{1/2}$ ) can be expressed in terms of the *standard reduction potential* ( $E^\circ$ ) by using the Nernst equation where  $\alpha_{\text{red}}$  and  $\alpha_{\text{ox}}$  are the activity constants for both the reduced and oxidized species, respectively.

$$E_{1/2} = E^\circ - \frac{RT}{nF} \ln \frac{\alpha_{\text{red}}}{\alpha_{\text{ox}}}$$

Assuming identical values for  $\alpha_{\text{red}}$  and  $\alpha_{\text{ox}}$ , the expression  $E_{1/2} = E^\circ$  holds true for a reversible process and we can determine the standard reduction potential from cyclic voltammetry using the anodic ( $E_{\text{pa}}$ ) and cathodic ( $E_{\text{pc}}$ ) peak potentials with the relationship

$$E^\circ = \frac{E_{\text{pa}} + E_{\text{pc}}}{2}$$

## Procedure

For this experiment you will need to prepare three solutions for measurement:

- 15 mL of 0.1 M  $\text{Bu}_4\text{NPF}_6$  in acetonitrile solution.
- 5 mL of 1.0 mM ferrocene in 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile electrolyte.
- 5 mL of 1.0 mM  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  in 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile electrolyte.

Apart from the background, **for each scan you will need to make note of the  $E_{\text{pc}}$ ,  $E_{\text{pa}}$ ,  $i_{\text{pc}}$  and  $i_{\text{pa}}$** . 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 both samples and air dried.

### (i) Background

Use the 0.1 M  $\text{Bu}_4\text{NPF}_6$  acetonitrile electrolyte solution. This is simply the neat electrolyte solution and will be used to record background signal as for preparation of solutions (ii) and (iii). Fill the cell with 5 ml of 0.1 M  $\text{Bu}_4\text{NPF}_6$  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 and the scan limits to +1.60 V and -2.00 V. The scan should be initiated in a positive direction with a scan rate of 50 mV/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 potential at which the experiment can be run, i.e. the *potential window* of the electrolyte. For example in 0.1 M  $\text{Bu}_4\text{NPF}_6$  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).

*(ii) Calibration.*

Use the 1.0 mM ferrocene solution in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile electrolyte. Follow the same procedure as above to obtain a CV of the Fe<sup>III/II</sup> 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  $\Delta E_p = 60$  mV. If satisfactory, save the file as “calibration” and proceed to sample (iii).

*(iii) [Ru(bpy)<sub>3</sub>]<sup>2+</sup>*

Use the 1.0 mM [Ru(bpy)<sub>3</sub>]<sup>2+</sup> solution in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile electrolyte. 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 scan in the positive direction to observe the Ru<sup>III/II</sup> couple, switch the bias to continue scanning in the negative direction. You should observe a total of 3 successive reductions and again switch the potential to check reversibility setting  $V_{OC}$  as the final potential. Save as “ru(bpy)3”

*(iv) Diffusion Coefficient*

The same [Ru(bpy)<sub>3</sub>]<sup>2+</sup> solution is used to observe the effect of scan rate (v). Simply clean and polish the working electrode to rejuvenate the sample. Using the previous CV scan determine a suitable potential range to monitor the Ru<sup>III/II</sup> couple only ( $\pm 0.3$  V of the formal potential). Repeat CVs at the following rates: 10, 20, 50, 75, 100, 150 and 250 mV/s (purging with nitrogen gas between scans). Save each scan as Ru20, Ru50...etc.

**Laboratory Report**

- 1) Report the values of  $E_{pa}$ ,  $E_{pc}$ ,  $i_{pa}$ ,  $i_{pc}$ , and  $E^\circ$  from the CV scan of ferrocene versus the Ag/AgCl reference electrode.
- 2) Report the values of  $E_{pa}$ ,  $E_{pc}$ ,  $i_{pa}$ ,  $i_{pc}$ , and  $E^\circ$  from the CV scan of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> versus the ferrocene pseudo-reference electrode.
- 3) 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 peak current ( $i_p$ ). Using the variable scan rate experiments show that the Ru<sup>III/II</sup> couple is electrochemically.
- 4) From the same plot determine the diffusion coefficient of the Ru<sup>III/II</sup> couple using the Randle-Sevcik equation

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2}$$

where

$i_p$  is the peak current (Amps ;  $i_{pa}$  anodic +  $i_{pc}$  cathodic)

$n$  is the electron stoichiometry

$A$  is the electrode area ( $\text{cm}^2$ ; the Pt disc has a diameter of 2 mm)

$D$  is the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )

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

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

- 5) Normalized absorption and emission spectra were used to calculate the band gap of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex in the previous experiment. Compare this value to the electrochemically determined band gap.
- 6) The number of electrons ( $n$ ) transferred to the electrode for a reversible couple can be determined from the slope of the Randle-Sevcik plot. Similarly, if Nernstian behavior is observed the redox stoichiometry can be easily estimated from the peak separation  $\Delta E_p$  by the following relationship

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

Using the determined values of  $\Delta E_p$  for the three  $[\text{Ru}(\text{bpy})_3]^{2+}$  reductions comment on the value of  $n$  for the three bpy ligands. Which bpy ligand is reduced first?

For a primer study check the following link

[www.currentseparations.com/issues/20-2/20-2d.pdf](http://www.currentseparations.com/issues/20-2/20-2d.pdf)

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