Cyclic Voltammetry of $[Ru(bipy)_3]^{2+}$

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 a half-reaction. The $Fe^{III/II}$ couple of ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, 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. 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. This experiment will demonstrate the general CV method by showing how to obtain the formal reduction potentials ($E^{o\prime}$) for the $Ru^{III/II}$ and $bpy/bpy^{\bullet-}$ redox couples of the previously prepared $[Ru(bipy)_3]^{2+}$ complex (expt.7). In addition, electrochemical reversibility will be investigated by a variable scan rate experiment.

The CV apparatus is computer controlled. It consists of a potentiostat with scan capability and contains a display of current versus potential (voltage). A three electrode system is used. The electrodes in this experiment consist of a working electrode (glassy carbon), a platinum 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 ($E^{o\prime} = +0.450$ V vs. Ag/AgCl in 0.1 M Bu_4NPF_6 acetonitrile electrolyte; with peak separation $\Delta E^{o\prime} \approx 60$ mV). Subsequent $E^{o\prime}$ measurements will be recorded using the Ag/AgCl reference electrode and later referenced versus the $Fc^{+/0}$ redox couple (Fc = ferrocene). The electrochemical cell 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 α-alumina (0.3 μm) 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.*

A typical CV for the electrochemically reversible $Fc^{+/0}$ redox reaction 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, $(\eta^5\text{-}C_5H_5)_2Fe^{II}$, to ferrocenium, $[(\eta^5\text{-}C_5H_5)_2Fe^{III}]^+$. The concentration of $(\eta^5\text{-}C_5H_5)_2Fe^{II}$ decreases rapidly at the electrode surface as the anodic current increases. At point *d* the concentration of $(\eta^5\text{-}C_5H_5)_2Fe^{II}$

is substantially diminished causing the current to peak. From point *d* to *e* the current decays as $(\eta^5\text{-}C_5H_5)_2Fe^{II}$ becomes more depleted and $[(\eta^5\text{-}C_5H_5)_2Fe^{III}]^+$ 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 $(\eta^5\text{-}C_5H_5)_2Fe^{II}$. At point *h* the electrode is a sufficiently strong reductant to reduce $[(\eta^5\text{-}C_5H_5)_2Fe^{III}]^+$, which has accumulated adjacent to the electrode surface and the reaction:$[(\eta^5\text{-}C_5H_5)_2Fe^{III}]^+ + e^- \rightarrow (\eta^5\text{-}C_5H_5)_2Fe^{II}$ occurs at the electrode surface. Thus, the anodic current rapidly increases to point *i* until the surface concentration of $[(\eta^5\text{-}C_5H_5)_2Fe^{III}]^+$ is diminished causing the current to peak. From point *i* to *j* the current decays as solution surrounding the electrode is depleted of $[(\eta^5\text{-}C_5H_5)_2Fe^{III}]^+$. One CV cycle has now been completed. The quantities E_{pa}, E_{pc}, i_{pa}, and i_{pc} may be obtained directly from CV diagrams similar to that shown here or computed using specific modeling software. 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. This interface behaves like an electrical capacitor in that it can store charge.

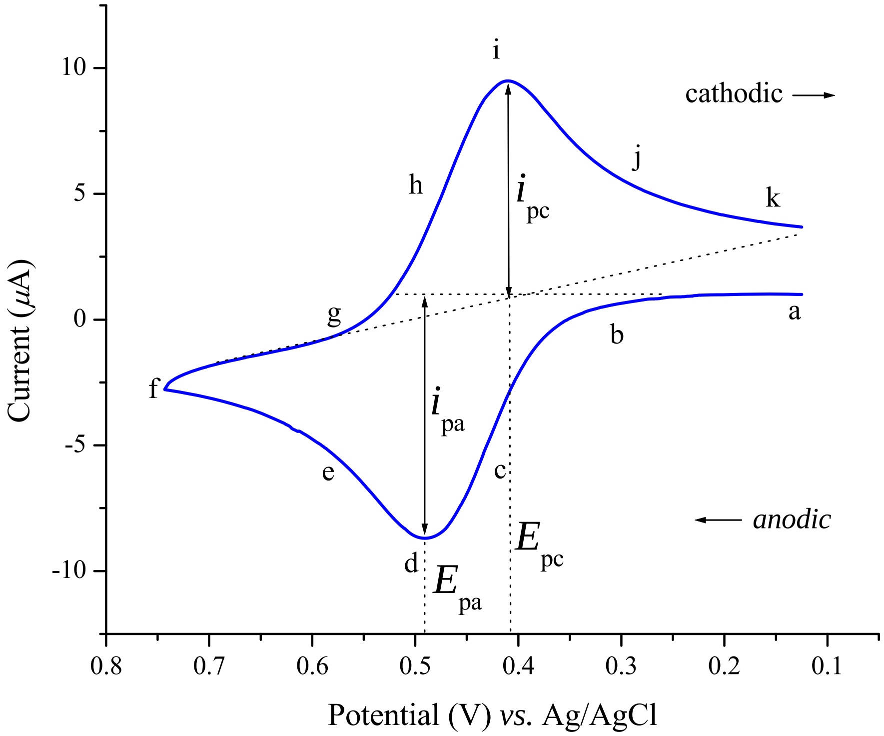

Fig. 1: Cyclic voltammogram of ferrocene reported vs. Ag/AgCl in 0.1 M Bu_4NPF_6 acetonitrile electrolyte ($E^{o'}$ = 0.45 V).

A redox couple in which both species rapidly exchange electrons with the working electrode is called an electrochemically reversible couple. The formal reduction potential ($E^{o\prime}$) for a reversible couple is centered between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials.

$$E^{o\prime} = (E_{pa} + E_{pc})/2$$

Procedure

From a stock 0.1 M Bu_4NPF_6 acetonitrile solution available in the lab, prepare:

1) a 5 mL stock solution of approximately 0.2 mM ferrocene.

2) a 5 mL stock solution of approximately 1.0 mM $[Ru(bpy)_3]^{2+}$

Note that both solutions are 0.1 M in the Bu_4NPF_6 supporting electrolyte. Fill the cell with 5 ml of 0.1 M Bu_4NPF_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 –1.80 V. The scan should be initiated in a positive direction with a scan rate of 50 mV/s. After the deoxygenation is complete switch on the working electrode and wait for approximately 10 s until the current has reached a constant value. Initiate the potential scan and a background CV of the supporting electrolyte is obtained. Similar scans with such long ranges are carried out prior to any CV experiment because they provide 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 Bu_4NPF_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.

After turning off the working electrode, wash the cell with several small volumes of acetone, air dry and refill with the 5 mL stock solution of 0.2 mM ferrocene in 0.1 M in Bu_4NPF_6 supporting electrolyte. Follow the same procedure as above to obtain a CV of the $Fe^{III/II}$ couple within the potential limits of 0 V to +0.80 V. Measure and record i_{pc} and i_{pa} using the computer software. Make a hard copy of the CV with the E_{pc} and E_{pa} clearly indicated. The same solution is used to observe the effect of sweep rate (ν). Gently move the working electrode up and down in the solution being careful not to introduce oxygen to the system. This process restores the electrode surface to the initial conditions. Repeat CVs at the following rates: 20, 50, 75, 100, 150 and 250 mV/s performing the restorative process between scans. Measure and record i_{pc} and i_{pa} for every scan as well as E_{pc} and E_{pa}. Care should be taken that no bubbles remain on the electrodes. Make a hard copy of each CV which includes values of E_{pc} and E_{pa}. Again rinse the cell with acetone and air dry. To the cell add the 5 mL stock solution of 1.0 mM $[Ru(bpy)_3]^{2+}$. Follow the same procedure as above to obtain a CV of the $Ru^{III/II}$ couple and the bpy based reductions *(determine your own potential limits!)*. Measure and record i_{pc} and i_{pa} using the computer software for each redox couple. Make a hard copy of the CV with the E_{pc} and E_{pa} clearly indicated for each redox couple.

Laboratory Report

1. Using the data generated from the CV scans of ferrocene and $[Ru(bpy)_3]^{2+}$ report the values of E_{pa}, E_{pc}, i_{pa}, i_{pc}, and $E^{o\prime}$ for each redox couple observed at a scan rate of 50 mVs^{-1}.

2. The effect of scan rate (ν) on the CV can be described by the Randle-Sevcik equation

$$i_p = (2.69 \text{ x } 10^5)n^{3/2} A\, D^{1/2}\, C\, \nu^{1/2}$$

where
i_p is the peak current (i_{pa} anodic and i_{pc} cathodic)
n is the electron stoichiometry
A is the electrode area (cm^2)
D is the diffusion coefficient
C is the concentration (mol/cm^3)
ν is the scan rate (V/s)

A plot of i_{pc} and i_{pa} versus $\nu^{1/2}$ can generate the diffusion coefficient for the system. Evidence of electrochemical reversibility can be ascertained by the independence of ΔE_p on ν. From the experiment using variable scan rate, show that the ferrocene system is electrochemically reversible (hint:make a plot of *scan rate vs. peak separation*). Also report the diffusion coefficient for ferrocene (the diameter of the glassy carbon electrode is 0.3 mm).

3. Report $E^{o\prime}$ of each $[Ru(bpy)_3]^{2+}$ couple versus the *calibrated* Ag/AgCl reference electrode and the $Fc^{+/0}$ redox couple.

4. Normalized absorption and emission spectra were used to calculate the band gap of the $[Ru(bpy)_3]^{2+}$ complex (lecture). Compare this to the electrochemically determined band gap.

5. The number of electrons (n) transferred to the electrode for a reversible couple is given by

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

Calculate the values of ΔE_p and n for the $[Ru(bpy)_3]^{2+}$ complex. Comment on the value of n for the three bpy ligands?

References

1. Kissinger, P. T., Heineman, W. R., *J. Chem. Educ*., **1983**, *60*, 702.
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3. Evans, D. H., O'Connell, K. M., Petersen, R. A., Kelly, M. J., *J. Chem. Educ*., **1983**, *60*, 290.

Some good WEB sites describe some of the fundamentals:
http:/www.epsilon-web.net/Ec/manual/Techniques/CycVolt/cv_analysis.html
http://www.bath.ac.uk/~chsact/solartron/electro/html/cv.htm
http://soulcatcher.chem.umass.edu/web/downloads/cyclicv.html (a very nice simulation package from U.Mass Amherst)
http://poohbah.cem.msu.edu/courses/cem419/cem372cyclicvoltammetry.pdf
http://www.biol.paisley.ac.uk/macro/Enzyme_Electrode/Chapter1/Cyclic_Voltammetry1.htm