

Cyclic Voltammetry of Hexachloroiridate(IV)
CH 426 Laboratory Experiment
Winter 2000

In cyclic voltammetry (CV), the potential is scanned linearly from an initial value, E_{initial} , to a second value and then back to E_{initial} (or some other final potential). This potential excitation signal is illustrated in Figure 1 for a scan from 1.0 to 0.4 V versus the reference electrode, which in this case is a silver-silver chloride electrode (SSCE). At a potential of 0.4 V vs SSCE, the potential scan direction is reversed, returning back to the original potential of 1.0 V. One or more potential cycles can be performed, hence the term “cyclic” voltammetry.

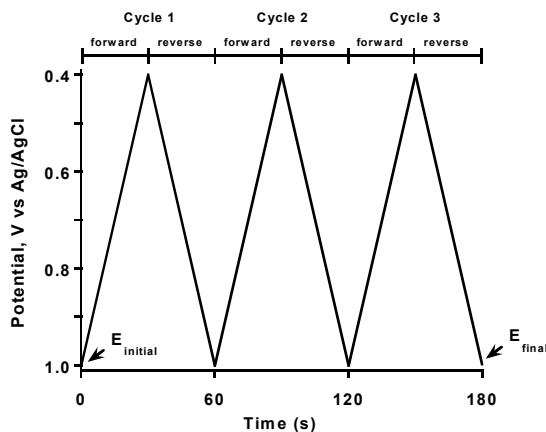


Figure 1. A cyclic voltammetry potential waveform with switching potentials at 1.0 and 0.4 V vs. SSCE.

Figure 2 illustrates the current response signal obtained when the potential excitation signal in Figure 1 is applied to a platinum electrode immersed in 2.0 mM K_2IrCl_6 as the electroactive species in aqueous 0.1 M KNO_3 as the supporting electrolyte.

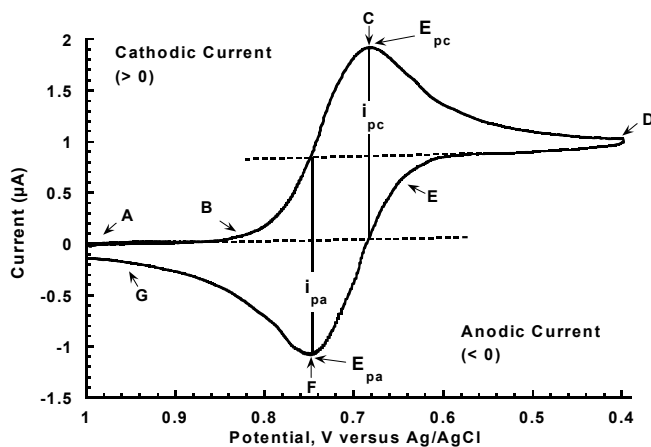
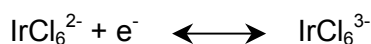


Figure 2. Cyclic voltammogram of 2 mM K_2IrCl_6 in 0.1 M KNO_3 using the potential waveform in Figure 1. The surface area of the platinum electrode is 0.79 mm^2 .

As the potential is scanned in a negative direction (**A**), the electron supplied by the electrode becomes an increasingly stronger reducing agent. A cathodic current (**B**) occurs when an electron supplied by the electrode is energetic enough to reduce hexachloroiridate(IV) to hexachloroiridate(III) because of the following electrode process:



The cathodic current increases rapidly until the concentration of hexachloroiridate(IV) approaches zero **at the electrode surface**. At this point, the current reaches a maximum value (**C**). The current then decays at a rate of $t^{-1/2}$ as the solution adjacent to the electrode surface is depleted of hexachloroiridate(IV), having been electrochemically reduced to hexachloroiridate(III).

The scan direction is switched in the positive direction at 0.4 V (**D**) for the reverse scan. As the applied potential becomes more positive versus the reference electrode, the electrode becomes an increasingly powerful oxidizing agent. Hexachloroiridate(III), which has been generated at the electrode surface by the preceding reduction reaction, can now be oxidized back to hexachloroiridate(IV) (**E**). This generates anodic current, which rapidly increases until the surface concentration of hexachloroiridate(III) approaches zero. The current then peaks (**F**) and decays as the solution adjacent to the electrode is depleted of hexachloroiridate(III). The first cycle is completed when the potential reaches 1.0 V. Any potential more positive than 0.9 V would be suitable as an initial potential in that the reduction of hexachloroiridate(IV) would not occur when the initial potential is applied.

In summary, hexachloroiridate(III) is electrogenerated from hexachloroiridate(IV) in the forward scan as the electrode becomes an increasingly powerful reducing agent. This results in a cathodic current. In the reverse scan, the electrode becomes an increasingly powerful oxidizing agent. Any hexachloroiridate(III) electrogenerated from the forward half of the waveform then is reoxidized back to hexachloroiridate(IV). This results in an anodic current. The generation of oxidized and reduced chemical species at an electrode surface provides information about the stability of these electrogenerated species and the kinetics regarding their formation.

The parameters of greatest interest for a cyclic voltammogram, such as the one shown in Figure 2, are:

1. The cathodic peak current (i_{pc})
2. The cathodic peak potential (E_{pc}).
3. The anodic peak current (i_{pa})
4. The anodic peak potential (E_{pa})

The peak potentials supply information about the identity of the analyte and the kinetics of the oxidation/reduction process. The peak currents supply information about analyte concentration and the stability of the electrogenerated species.

The most convenient method for measuring peak currents involves extrapolation of the baseline current. This is shown in Figure 2. The baseline used in estimating the cathodic peak current is extrapolated from the potential range prior to reduction of hexachloroiridate(IV) (before point **B**). The baseline used in estimating the anodic peak current is extrapolated from the potential range prior to reoxidation of hexachloroiridate(III) (before point **E**).

An electrochemically reversible redox couple is defined as a pair of stable chemical compounds which undergo kinetically fast electron exchange when forced to do so by a change in the

applied potential at the electrode surface. The formal reduction potential (E°) for a reversible couple is the average of the anodic and cathodic peak potentials shown in the following equation:

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

The magnitude of separation between the anodic and cathodic peak potentials in an electrochemically reversible reaction defines the number of electrons, n , transferred in that electrode reaction:

$$\Delta E_p = E_{pa} - E_{pc} = 0.0592/n$$

The reduction of hexachloroiridate(IV) to hexachloroiridate(III) is a one-electron process. The cyclic voltammogram for this redox couple should *ideally* exhibit a peak separation of 0.0592 V. Slow electron transfer at the electrode surface, referred to as an irreversible process, causes this peak separation to increase.

The magnitude of the peak current in the cyclic voltammogram provides information regarding the concentration of the analyte according to the Randles-Sevcik equation for the forward sweep of the first cycle:

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

where i_p = peak current, A
 n = electron stoichiometry, eq/mol
 A = electrode area, cm^2
 D = diffusion coefficient, cm^2/s
 C = concentration, mol/cm^3
 v = scan rate, V/s

Accordingly, the peak current increases with the square root of the scan rate and is directly proportional to concentration.

The values of i_{pa} and i_{pc} should be close for a simple reversible couple. That is:

$$i_{pa} / i_{pc} = 1$$

If additional chemical processes occur as a result of generating a species electrochemically, this peak current ratio may deviate significantly from one.

References

1. Kissinger, P.T.; Heineman, W.R., "Laboratory Techniques in Electroanalytical Chemistry," Marcel Dekker, NY, NY, 1984, Chapter 3.
2. Kissinger, P.T.; Heineman, W.R. *J. Chem. Educ.* **1983**, *60*, 702-706.

Apparatus

Instrument: IBM EC-225 Voltammetric Analyzer

Recorder: Winview data acquisition software on an IBM 486DX-66 MHz.

Electrochemical Cell:

Working Electrode:

2.0 mm diameter Pt disk electrode.

Reference Electrode: Ag/AgCl

Auxiliary Electrode: Pt wire

Magnetic stirrer and stirbar

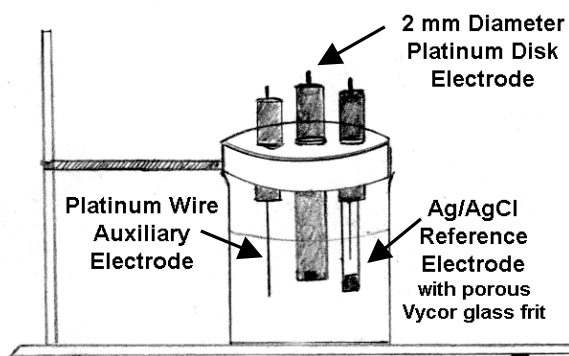


Figure 3. Voltammetric Cell for CV Experiment

Chemicals

KNO_3 : Prepare 250 mL of 0.1 M KNO_3

Stock K_2IrCl_6 : Obtain a vial from the stockroom that contains approximately 50 mg K_2IrCl_6 , weigh the vial, empty the contents into a 50 mL volumetric flask, and accurately weigh **by difference** the mass of K_2IrCl_6 added to the flask. Dissolve the K_2IrCl_6 in 0.1 M KNO_3 . Calculate the concentration of this stock solution in mM.

Dilute K_2IrCl_6 : Make three additional K_2IrCl_6 solutions by adding 3.00, 5.00, and 10.00 mL to separate 25 mL volumetric flasks with volumetric pipets. Dilute to the mark with 0.1 M KNO_3 . Calculate the concentration of each solution in mM.

K_2IrCl_6 unknown: Obtain 20 mL of a hexachloroiridate(IV) solution from the stockroom

Procedure

A) Experimental Setup

- 1) Turn on the computer and the voltammetric analyzer. The Winview data acquisition software should boot up automatically.
- 2) While the computer is booting, prepare the platinum disk electrode. Take the felt polishing pad and sprinkle a **small** amount of 0.05 micron alumina powder on a small area of the pad. Add a few drops of distilled water to the alumina and polish the platinum surface on the pad for 30 seconds with a moderately light circular motion. Rinse the surface thoroughly with distilled water and wipe dry with a clean tissue.
- 3) The electrochemical cell is assembled as shown in Figure 3 and filled with 0.1 M KNO_3 so that the ends of the electrodes are immersed. No deoxygenation is necessary because the applied potential is not negative enough to generate a current from the reduction of dissolved oxygen.

- 4) The voltammetric analyzer can be set up with the following parameters:
 - a) Initial Potential = 1.100 V
 - b) Final Potential = 0.300 V
 - c) Current Range = 5 μ A
 - d) Cell = 3el (which stands for three-electrode cell)
 - e) Sweep rate = 40 mV/s
 - f) Sweep Waveform = \wedge (looks like an upside down V)

- 5) Setup the data acquisition software in the following manner:
 - a) Put a 3.5" floppy in the disk drive
 - b) Click on the Load Previous Settings button
 - c) In the Load Settings Window click on the File button and select CV.SET
 - d) Click on the Load button to load the cyclic voltammetry settings file. When the Confirm File Overwrite window pops up, click on the No button so that no file overwrite occurs. The Single Graph Acquisition window should now appear.
 - e) Click on Settings Menu button and then click on the File button on the bottom right hand part of the screen. Choose a filename to save your first CV, which will be of your solvent, 0.1 M KNO_3 .
 - f) Click on the Settings OK button and click on the Yes button when Confirm File Overwrite window appears.

- 6) Click on the Start button to initiate data acquisition. When the white graph window appears, press the Start button on the voltammetric analyzer. When the scan is finished, press the Enter key or click the Stop button to stop data acquisition. Repeat steps 5e, 5f, and 6 each time a new cyclic voltammogram is to be acquired.

Note: Whenever the electrodes are removed from solution, make sure you switch the cell OFF prior to removing the electrodes from solution. Don't forget to turn the cell on after immersing the electrodes in a new solution.

B) Experiment

1) Background

- a) The working electrode is switched on (cell is switched from OFF to 3el). After allowing the current to attain a constant value (about 10 seconds), the potential scan is initiated (i.e. Step 6 above) and a background CV of the supporting electrolyte solution is obtained.

2) Effect of Concentration on the Cyclic Voltammetry of Hexachloroiridate(IV)/(III)

- a) The effect of concentration on peak current is observed by obtaining CV's on each of the dilute K_2IrCl_6 solutions as well as the stock K_2IrCl_6 solution. A CV of the unknown K_2IrCl_6 solution should be obtained.

3) Effect of Sweep Rate on the Cyclic Voltammetry of Hexachloroiridate(IV)/(III)

- a) The effect of scan rate on the voltammograms is observed by using the stock K_2IrCl_6 solution and recording CV's at the following sweep rates: 20, 40, 60, 80, and 100 mV/s. Between each scan, initial conditions at the electrode surface are restored by stirring the solution for 30 s. Allow 60 s after stirring for the solution to come to rest before obtaining a CV.

Data Treatment

- 1) Determine $E^{\circ'}$ and n for the hexachloroiridate(IV)/(III) couple in 0.1 M KNO_3 from the stock solution CV in part 2 of the experiment. Compare your $E^{\circ'}$ value with the one reported in the literature (+0.93V vs NHE).
- 2) Determine the effect of sweep rate, v , on peak height by calculating i_{pc} and i_{pa} for the five scan rates used. Plot i_{pc} and i_{pa} versus $v^{1/2}$. Is the plot linear?
- 3) Construct a calibration curve from the data in part 2, report the linear regression parameters, and determine the concentration of the unknown from the peak current of the unknown CV.
- 4) Determine the diffusion coefficient of hexachloroiridate(IV) in 0.1 M KNO_3 using the Randles-Sevcik equation.