Cyclic Voltammetry of Hexachloroiridate(IV): An Alternative to the Electrochemical Study of the Ferricyanide Ion

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Abstract: An instrumental analysis experiment on the cyclic voltammetry of hexachloroiridate(IV) is described in this paper. The hexachloroiridate(IV)/hexachloroiridate(III) redox couple allows the analytical chemistry student to study the behavior of electrochemically reversible electron transfer with no complications. The cyclic voltammetric response of hexachloroiridate(IV)/hexachloroiridate(III) is compared with the ferricyanide/ferrocyanide redox couple, which has been known to exhibit quasireversible electron transfer as a result of film formation on the electrode surface. Considerations regarding the stability of the hexachloroiridate(IV) ion in 0.1 M KNO_3 are also addressed.

Introduction

One of the first electroanalytical techniques a student is likely to encounter in the undergraduate curriculum is cyclic voltammetry. Utilized by analytical and synthetic chemists alike, cyclic voltammetry is important in investigating the kinetics and mechanisms of redox reactions [1, 2]. Such experiments have been designed for the undergraduate laboratory [3, 4].

In cyclic voltammetry, the potential applied to an electrode, designated as the working electrode, is scanned in a linear fashion between two potential values. The working electrode serves as the surface where the electron transfer of the redox reaction occurs. The redox reaction occurs within the potential range defined by the two chosen potential values, and the potential at which the reduction or oxidation takes place provides qualitative information about the analyte of interest. The application of an electrical potential to a working electrode makes the surface an electrochemical reductant or oxidant, depending on the applied potential. As the applied potential becomes more negative, the electrode becomes a better reducing agent. Conversely, as the applied potential becomes more positive, the electrode becomes a better oxidizing agent.

In most analytical chemistry or electrochemistry courses, the theoretical treatment of the cyclic voltammetric response typically starts with the description of a kinetically rapid oxidation–reduction reaction at an electrode surface under mass-transfer-limited conditions. Therefore, the first introduction to cyclic voltammetry that chemistry students usually have is the study of a *reversible* redox reaction. When students successfully duplicate these conditions in the laboratory, the "duck-shaped" current–potential plot is obtained. One of the most common redox reactions used to illustrate a reversible cyclic voltammetric response is the reduction of the ferricyanide ion to ferrocyanide:

$$Fe(CN)_6{}^{3-} + e^- \rightarrow Fe(CN)_6{}^{4-} \tag{1}$$
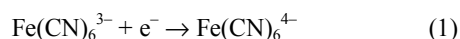
Unfortunately, it has been noted in the chemical literature that the ferricyanide/ferrocyanide redox reaction at an electrode surface may not the best choice to demonstrate such

reversible behavior [5, 6]. A passivating layer of Prussian blue $(KFe^{II}[Fe^{III}(CN)_6])$ may deposit on the electrode surface during the cyclic voltammetry experiment. The existence of this layer decreases the rate of electron transfer to the extent that the electrochemical behavior of ferricyanide becomes quasireversible. This deviation from reversibility can bewilder the analytical chemistry student, who depends upon systems free of complication in order to be properly introduced to theoretical cyclic voltammetric responses.

An alternative redox reaction which appears to be free from such experimental complications is the hexachloroiridate(IV)/hexachloroiridate(III) redox system. The hexachloroiridate(IV) ion can be reduced to hexachloroiridate(III) according to the following electron transfer reaction:

$$IrCl_6{}^{2-} + e^- \rightarrow IrCl_6{}^{3-} \tag{2}$$
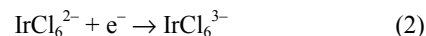
One of the purposes of this manuscript is to describe our study of the hexachloroiridate redox reaction, which can easily be completed in a three-hour laboratory period. This manuscript also seeks to compare the reversible behavior of the hexachloroiridate(IV)/hexachloroiridate(III) redox couple with the quasireversible response of ferricyanide/ferrocyanide obtained under identical laboratory conditions. Potential problems in the preparation of solutions for this experiment will also be addressed.

Experimental

Materials and Reagents. The two reagents needed in this experiment are potassium hexachloroiridate(IV) (K_2IrCl_6, Aesar) and reagent grade potassium nitrate (Fisher). Class A volumetric pipets and flasks as well as house distilled water were used to prepare solutions. Reagent grade potassium ferricyanide (Fisher) was used in the comparison study with potassium hexachloroiridate(IV).

Instrumentation. The electrochemical experiments were controlled with an IBM EC-225 Voltammetric Analyzer. Voltammograms were collected on a Data Translation DT-2805/5716 A/D board (Data Translation, Marlboro, MA), which was controlled using WinView software (Superlogics, Inc., Newton, MA) on a 486DX/66 interfaced to the EC-225. The data acquisition rate, controlled by Winview, was 20 Hz. The voltammetric current–
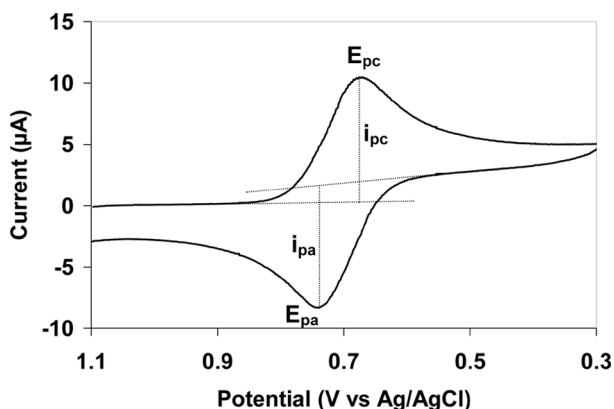
Figure 1. Cyclic voltammogram of 2.0 mM $IrCl_6^{2-}$. Sweep rate: 40 mV s^{-1}.

potential data were saved as ASCII files and plotted using a spreadsheet such as Excel.

Solution Preparation. An 0.1 M electrolyte solution was prepared by dissolving 2.53 g of potassium nitrate in enough distilled water to make 250 mL of solution. Approximately 50 mg of K_2IrCl_6 was handed to the student. The students emptied the K_2IrCl_6 into a 50-mL volumetric flask and dissolved the K_2IrCl_6 in the electrolyte solution. The sample vial was reweighed and the exact mass of the K_2IrCl_6 was determined by difference. The concentration of this K_2IrCl_6 stock solution is approximately 2.0 mM. Calibration standards in the range of 0.2 to 2.0 mM K_2IrCl_6 were prepared in 25-mL volumetric flasks by pipetting an appropriate aliquot of the K_2IrCl_6 stock solution and diluting to the mark with the potassium nitrate electrolyte solution. A previously prepared K_2IrCl_6 unknown was provided to the students.

Electrochemical Cell. A three electrode system consisting of a 2.0-mm-diameter platinum disk working electrode (CH Instruments), a Ag/AgCl reference electrode (CH Instruments), and a platinum-wire counter electrode was immersed in a small glass vial through holes drilled into a threaded plastic cap. Prior to the experiment, the working electrode was polished with a small amount of 0.05-micron alumina powder on a felt polishing pad (CH Instruments) and rinsed thoroughly with distilled water to remove alumina adhered to the electrode surface. A magnetic stir bar was placed in the solution whenever repeated voltammograms of a particular solution were required.

Procedure. The glass vial was filled approximately halfway with the solution to be measured and the three electrodes were immersed in the cell. The electrodes were connected to the potentiostat and a calibration curve was constructed by acquiring a cyclic voltammogram for each K_2IrCl_6 calibration standard at a sweep rate of 40 mV s^{-1}. The stock solution was placed in the electrochemical cell and a cyclic voltammogram was obtained at each sweep rate between 20 and 100 mV s^{-1}, with each subsequent sweep rate being increased by 20 mV s^{-1}.

Results and Discussion

Cyclic Voltammetry Experiment. Cyclic voltammograms of hexachloroiridate(IV) were acquired by scanning in a negative direction from +1.1 V to +0.3 V and back to +1.1 V. A representative voltammogram is shown in Figure 1. As the potential is scanned in a negative direction, the potential becomes sufficiently negative enough to force a one-electron reduction of hexachloroiridate(IV) to hexachloroiridate(III). During the second half of the potential cycle, the reoxidation of hexachloroiridate(III) to hexachloroiridate(IV) occurs as the electrode surface becomes a better oxidant.

The parameters of greatest interest for a reversible cyclic voltammogram are the peak cathodic potential (E_{pc}), the peak anodic potential (E_{pa}), the peak cathodic current (i_{pc}), and the peak anodic current (i_{pa}). Qualitative information about the redox couple can be obtained by calculating the formal redox potential of the voltammetric response:

$$E^{\circ\prime} = (E_{pa} + E_{pc})/2 \qquad (3)$$

The peak separation in a reversible cyclic voltammogram provides information about *n*, the number of electrons transferred:

$$\Delta E = (E_{pa} - E_{pc}) = 0.0592/n \qquad (4)$$

Quantitative information regarding the hexachloroiridate(IV) concentration is obtained from the peak heights according to the Randles–Sevcik equation:

$$i_p = (2.69\times10^5)n^{3/2}AD^{1/2}Cv^{1/2} \qquad (5)$$

where i_p is the peak current in amperes, *A* is the electrode area in cm^2, *D* is the diffusion coefficient in cm^2 s^{-1}, *C* is the concentration in mol cm^{-3}, and *v* is the sweep rate in V s^{-1}. It is apparent from this equation that the peak current is proportional to concentration, and a linear calibration curve may be constructed from voltammograms at different concentrations. A representative calibration curve constructed from this experiment is shown in Figure 2.

If the hexachloroiridate(IV) concentration is known, its diffusion coefficient may be calculated from Equation 5. Using the *CV* from Figure 1, the diffusion coefficient of hexachloroiridate(IV) in 0.1 M KNO$_3$ was determined to be 8.93×10^{-6} cm^2 s^{-1}. This compares favorably to the literature value of $(8.2 \pm 0.4) \times 10^{-6}$ cm^2 s^{-1} in 1 M HCl [7]. The effect of migration in increasing the magnitude of the diffusion coefficient should be negligible, based on practically identical diffusion coefficients for 1.0 mM ferricyanide of 7.2×10^{-6} and 7.26×10^{-6} cm^2 s^{-1} in 0.1 M and 1.0 M KCl, respectively [8]. In addition, the diffusion coefficient for 2.0 mM ferricyanide in 0.1 M KNO$_3$, calculated from the first ferricyanide cyclic voltammogram (see Figure 6), was determined to be 7.01×10^{-6} cm^2 s^{-1}. This is almost identical to the literature value of 7.09×10^{-6} cm^2 s^{-1} under the same conditions, suggesting little difference between KCl and KNO$_3$ as supporting electrolytes [8].

Eq 5 also predicts that the peak current of a reversible redox process plotted against the square root of the sweep rate must vary in a linear fashion. Figure 3 indicates to the students that the voltammetric response of hexachloroiridate(IV) is indeed linearly dependent on the square root of the sweep rate between 20 and 100 mV s^{-1}. This dependence was determined to be linear with sweep rates of at least 500 mV s^{-1} but was not plotted because higher sweep rates necessitate a change in the data acquisition rate. Because this software-controlled parameter remained constant at 20 Hz throughout the experiment, a maximum sweep rate of 100 mV s^{-1} was chosen so that a data point spacing of no greater than 5 mV would be obtained.
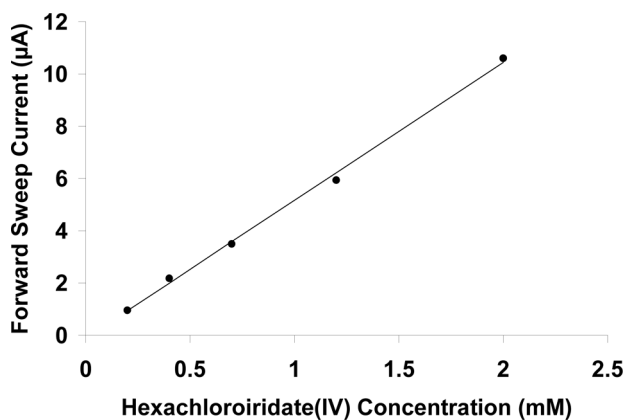
Figure 2. Hexachloroiridate(IV) calibration curve. The best-fit line was determined by linear regression analysis.
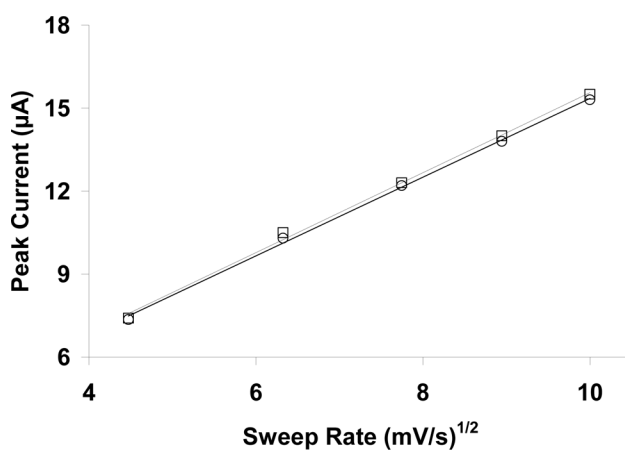

Figure 3. Voltammetric peak current dependence on sweep rate. Cathodic peak current is represented by square data markers and anodic peak current is represented by circular data markers. The best-fit line for each data set was determined by linear regression analysis.

The ratio of cathodic and anodic peak currents may also be used to determine reversibility of a redox reaction. For a reversible redox process

$$i_{pc}/i_{pa} = 1 \qquad (6)$$

The nearly identical slopes from the linear regression analysis of the cathodic and anodic peak currents in Figure 3 indicate that the peak current ratio is approximately one.

Comparison of Hexachloroiridate(IV) with Ferricyanide. There are two advantages to developing a cyclic voltammetric experiment which uses hexachloroiridate(IV) instead of ferricyanide. The first advantage is that deoxygenation of the sample solution by sparging with nitrogen or argon gas is not necessary with the hexachloroiridate(IV) ion. A comparison of cyclic voltammograms with and without deoxygenation for both ions is illustrated in Figure 4. The switching potential for hexachloroiridate(IV) occurs at 0.3 V, which is too oxidative of an environment for any appreciable reduction of dissolved oxygen;. However, the cathodic peak of ferricyanide, a poorer oxidizing agent than hexachloroiridate(IV), merges with a second voltammetric wave, which corresponds to the reduction of dissolved oxygen.
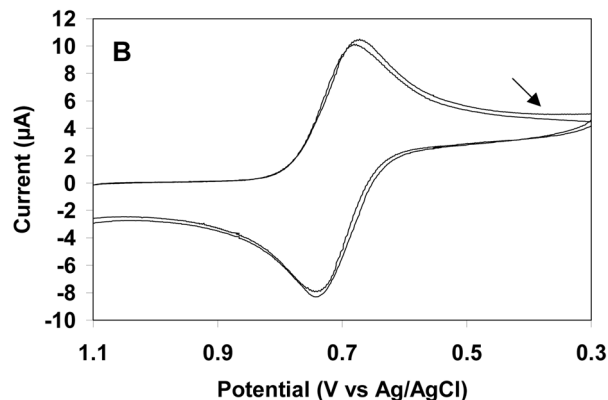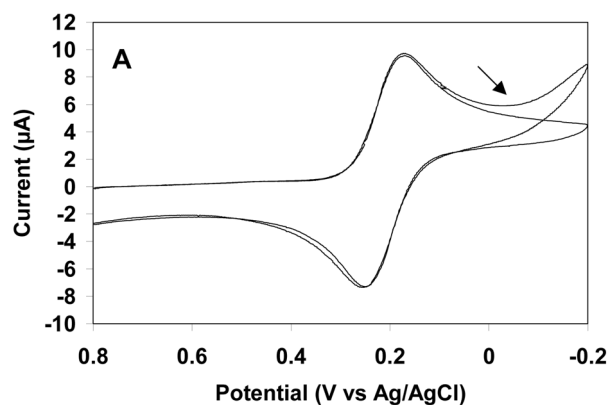

Figure 4. Comparison of cyclic voltammetric responses with and without deoxygenation for ferricyanide (**A**) and hexachloroiridate(IV) (**B**). Voltammograms obtained without deoxygenation are designated with an arrow.

The second advantage in incorporating hexachloroiridate(IV) instead of ferricyanide into an undergraduate cyclic voltammetry experiment is that one can avoid the formation of a passivating film on the electrode surface, which would decrease the reversible nature of the electron transfer reaction. In order to decide whether the cyclic voltammetric response of hexachloroiridate(IV) remained unchanged over the course of an experiment, a freshly polished platinum working electrode was immersed in a 2.0 mM hexachloroiridate(IV) solution and 12 consecutive voltammograms, each spaced five minutes apart, were obtained. The working electrode was repolished and an identical experiment was performed using 2.0 mM ferricyanide. The ferricyanide solution was deoxygenated to avoid the oxygen reduction wave. The first, sixth, and twelfth voltammograms obtained in 2.0 mM hexachloroiridate(IV) are plotted in Figure 5. Note that there is no significant change in the peak separation or peak height during the acquisition of these voltammograms. The peak separation is 69, 64, and 63 mV for the first, sixth and twelfth voltammograms respectively. This agrees well with the expected peak separation of 59 mV for a reversible redox reaction.

The cyclic voltammetric response for 2.0 mM ferricyanide is shown in Figure 6. The increasing peak separation and decreasing peak height during the course of the experiment indicates passivation of the platinum electrode surface after a
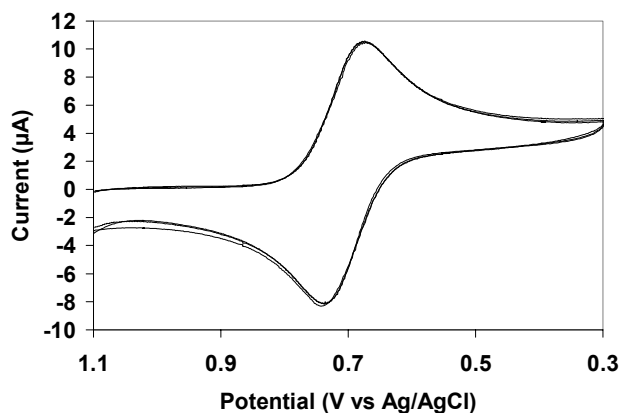
Figure 5. The first, sixth, and twelfth cyclic voltammograms of 2.0 mM hexachloroiridate(IV) in 0.1 M KNO$_3$. Sweep rate: 40 mV s^{-1}.
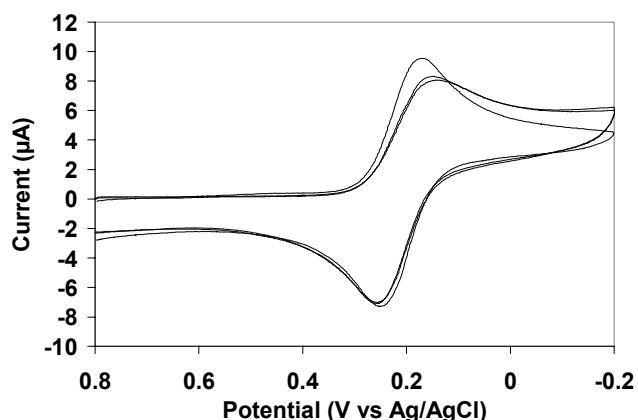

Figure 6. The first, sixth, and twelfth cyclic voltammograms of 2.0 mM ferricyanide in deoxygenated 0.1 M KNO$_3$. Sweep rate: 40 mV s^{-1}.
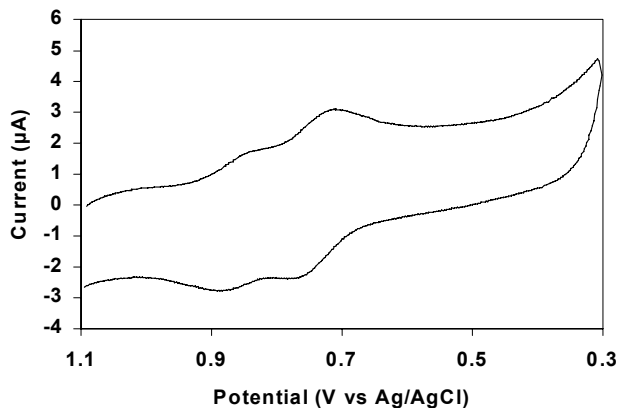

Figure 7. A cyclic voltammogram of 0.8 mM hexachloroiridate(IV) after six-weeks storage under ambient conditions. Sweep rate: 40 mV s^{-1}.

few voltammograms have been acquired. Peak separations of 80, 108, and 111 mV for the first, sixth, and twelfth runs indicate increasingly quasireversible behavior.
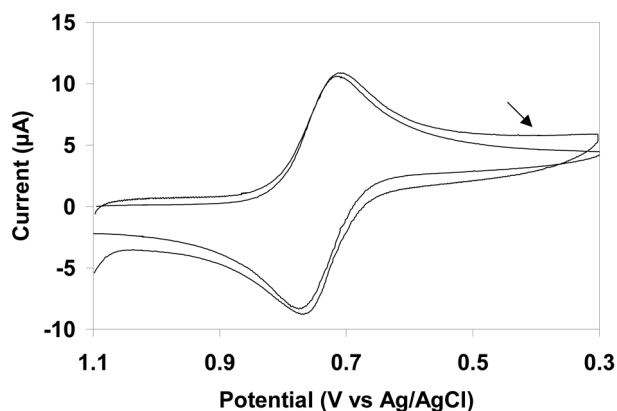

Figure 8. Cyclic voltammograms of freshly prepared 2.0 mM hexachloroiridate(IV) and 2.0 mM hexachloroiridate(IV) stored in a refrigerator for six weeks. The arrow is pointing to the voltammogram from the refrigerated solution.

Hexachloroiridate(IV) Stability. It is desirable to have the flexibility to prepare laboratory unknowns some time prior to the scheduled laboratory. In our hands, it has been noted that storage of hexachloroiridate(IV) solutions for a few weeks under ambient light and temperature results in partial decomposition of the complex. A cyclic voltammogram of a 0.8 mM hexachloroiridate(IV) solution in 0.1 M KNO$_3$ is shown in Figure 7. Although the hexachloroiridate(IV) ion is a relatively stable complex, it has a formal potential of 0.71 V versus Ag/AgCl and is therefore an effective oxidizing agent. Reduction of hexachloroiridate(IV) has been reported to proceed quite rapidly in basic solution and more slowly in neutral and weakly acidic aqueous solutions [9]. Once reduction to the hexachloroiridate(III) ion occurs, aquation occurs more readily than with the oxidized complex [10]. Based on the potential difference of approximately 0.14 V between the two redox responses, it is likely that the second reversible redox couple is the aquopentachloroiridate(III) complex [7]. However, cyclic voltammograms of hexachloroiridate(IV) in 0.1 M KNO$_3$ stored in the refrigerator over the same six-week interval exhibit no indication of a substitution reaction. A comparison of a freshly prepared hexachloroiridate(IV) solution with a six-week-old refrigerated solution is shown in Figure 8. It is possible that increasing the acidity of the supporting electrolyte might increase the longevity of prepared hexachloroiridate(IV) solutions.

Conclusion

Cyclic voltammetry of hexachloroiridate(IV) enables the instrumental analysis student to study the behavior of a reversible redox reaction without the complication of deoxygenation or a passivating film. Although potassium hexachloroiridate(IV) is more expensive than potassium ferricyanide ($54 per gram for potassium hexachloroiridate(IV) versus $40 per 500 grams for potassium ferricyanide), this experiment can easily be performed with 50 milligrams of material. Under these circumstances, one gram of potassium hexachloroiridate(IV) could last 2 to 3 years for an instrumental class containing six pairs of students.

Safety and Disposal Information. The Material Safety Data Sheet (MSDS) for potassium hexachloroiridate(IV) indicates that this compound, a black powder, is an eye and skin irritant. It may be harmful if inhaled, ingested or absorbed through the skin. Although only milligram-sized quantities are used in this experiment, latex gloves should be used to prevent skin contact.

Iridium is one of the elements in the platinum group. Iridium and its compounds are therefore relatively expensive. Solutions containing iridium used in this experiment should not be discarded down the drain and should be saved for reclamation of the iridium if possible.

Supporting Material

The laboratory handout (550231sps1.pdf) is included in the supporting documentation. The efforts of P.T. Kissinger and W.R. Heineman have been instrumental in establishing cyclic voltammetry experiments such as this one as part of the undergraduate laboratory curriculum. The theoretical description of this technique in the laboratory handout was based on their well-written account of cyclic voltammetry for the undergraduate laboratory [1].

References and Notes

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