CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Study of Ferricyanide in Cyclic Voltammetry- CV-27

Cyclic voltammetry (CV) is the most versatile electroanalytical technique for the study of electroactive species, widely used in industrial applications and academic research laboratories. Despite this, there are few CV experiments designed for students to teach them this invaluable technique. This capsule gives one such application. The $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ couple is studied because it is known to be a well behaved electrochemically reversible system, making it suitable for teaching purposes(1). The CV-27 Voltammograph is a general purpose voltammetric and amperometric controller, well suited for a wide variety of teaching purposes.

The experiment outlined below demonstrates determination of the following important information: the formal reduction potential ($E^{0\prime}$); the number of electrons transferred in the redox process (n); the diffusion coefficent (D); electrochemical reversibility; and the effects of varying concentration and scan rate.

Experimental

A 100ml stock solution of 10mM $K_3Fe(CN)_6$ in 1M KNO_3 is prepared and serial dilutions of this solution are performed to give 25ml solutions of 2,4,6,8 mM $K_3Fe(CN)_6$ in 1M KNO_3(1).

Setup - Before turning on the CV-27 Voltammogram, check the rear panel and X-Y Recorder to see if the following settings and connections are made (see Fig. 1):

I Polarity = + rdn.
Filter = 0.001
E Polarity = -

For Y-axis: Clear wire- plug in **I OUT** of CV-27 and **H** (red cap) of **Y1** of X-Y Recorder.
Black wire- plug in **Common** of CV-27 and **L** (black cap) of **Y1** of X-Y Recorder.
For X-axis: Clear wire- plug in **Appl. E** of CV-27 and **H** (red cap) of **X** of X-Y Recorder.
Black wire- plug in **Common** of CV-27, then **L** (black cap) and **G** (blue cap) of **X** of X-Y Recorder.

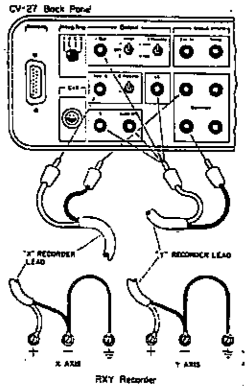

Figure 1. Illustration of CV-27 connections to RXY Recorder.

Assemble Cell - Plug the cell lead cable in the **Cell** socket on the CV-27 rear panel. Add the solution to be analyzed (2mM $K_3Fe(CN)_6$ in 1M KNO_3), place the cap on and lower the electrodes into solution. Finally, attach the wires to the electrodes (red = auxiliary(Pt wire), black = working(Pt), white = reference(Ag/AgCl)). Degassing is not necessary because the sample is scanned only at potentials positive of O_2 interference.

Set Parameters - On the front panel, set **CELL MODE** to standby **(STBY)**, turn **Power** on, and set **GAIN** = 0.005 mA/V. Turn the **DISPLAY** knob to **App. E.** Set **FUNCTION = E2**, then **INITIAL E** = 0.0 by turning the **E2** inner (large) knob. Next, set **FUNCTION** = **E1**, then **INITIAL E** = 0.65V by turning the **E1** outer (small) knob.

To enter the upper limit of the scan, change the **DISPLAY** to **+ Lim**, then set **E LIMIT** = 0.65V by turning the + outer (small) knob.

To enter the lower limit of the scan, change the **DISPLAY** to **- Lim**, then set **E LIMIT** = 0.0 by turning the - outer (small) knob.

To set the scan rate, change the **DISPLAY** to **Scan Rate.** Set **SCAN** = 0.1 V/s, then turn the **SCAN RATE** knob until 20 mV/s is on the display.

The parameters of the voltammograph are now set so that the potential is scanned negatively (forward scan) from 0.65 V to 0.0 V, at which point the scan direction is reversed, causing a positive scan back to the original potential of 0.65 V (a cycle is completed; hence, the name " cyclic" voltammetry).

Recorder -

Step 1- Turn the X-Y Recorder Power on.

Step 2- Insert graph paper and align with lower left corner.

Step 3- Turn **CHART** toggle to **HOLD**, and **X SERVO** to **ON**.

Step 4- Set **X RANGE** = 50mV/cm, and **Y-RANGE** =0.5V/cm. These settings translate into 50 mV/cm for the **X** or potential(E) axis and 2.5uA (0.5 V/cm x 0.005 mA/V or **Y-RANGE** x **GAIN**) for the **Y** or current(i) axis of the voltammogram.

Step 5- Set **PEN** to **DOWN**, then adjust the position of the pen using the **X** and **Y POSITION** controls.

Step 6- When the voltammogram is complete, it can be removed by flipping the **CHART** toggle to **RELEASE** and removing the paper.

Run Voltammogram - If not done already, a 2 mM solution of $K_3Fe(CN)_6$ in 1 M KNO_3 should be added to the cell.

Step 1- Change the **DISPLAY** to **App E** in order to view the applied potential.

Step 2- Run the voltammogram by turning **CELL MODE** to **CELL**, then **FUNCTION** to **SCAN.** The voltammogram will sweep through a cycle and continue to cycle until stopped.

Step 3- In order to stop the scan, put **PEN UP** and turn **FUNCTION** to **HOLD.**

Step 4- Change graph paper.

Step 5- Finally, set **FUNCTION** back to **E1**, and **CELL MODE** to **STBY** in order to disconnect the cell from the CV-27 electronics. A cyclic voltammogram as shown in Fig. 2 is obtained using the CV-27 with an XY Recorder.

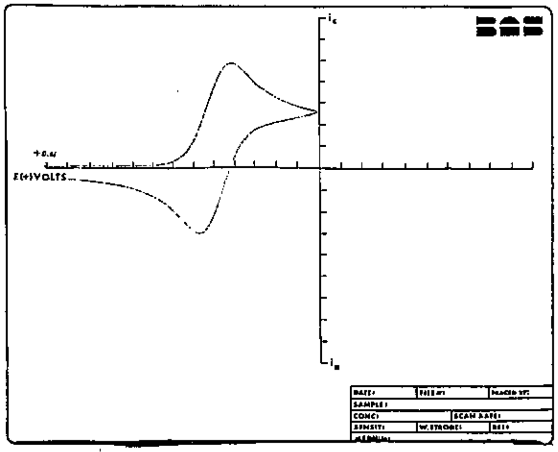

Figure 2. Cyclic voltammogram of 10μM $K_3Fe(CN)_6$ in 1M KNO_3. Scan rate = 20 mV/s. Pt electrode.

Concentration Effects - To study the effect of varying concentration, CV's are obtained for each of the 2,4,6,8,10mM $K_3Fe(CN)_6$ solutions using a scan rate of 20 mV/s. To do this, repeat the procedure outlined above in "Run Voltammogram" using the 4,6,8,10 mM solutions of $K_3Fe(CN)_6$ in 1M KNO_3. After each scan polish the working electrode with alumina.

A plot of current vs. concentration (see Fig. 3B) can be done and the unknown concentration determined by extrapolation.

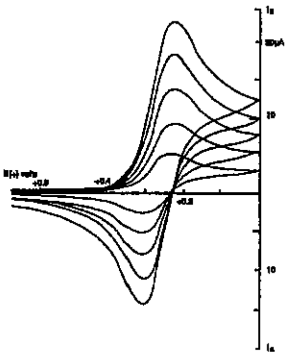

Figure 3(A). Cyclic voltammograms of $K_3Fe(CN)_6$ in 1M KNO_3. Scan rate = 20mV/s. Pt electrode. Concentration = 2,4,6,8,10 mM.

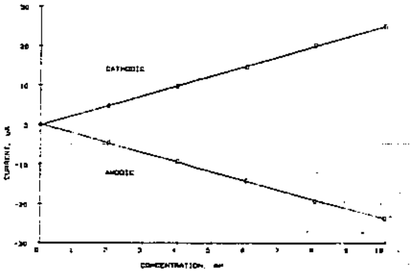

Figure 3(B). Plot of i_p(cathodic and anodic) vs. $v^{1/2}$ from voltammograms in (A).

Scan Rate Effects - The effect of the scan rate(v) on the voltammograms is observed by using the 4mM $K_3Fe(CN)_6$ in 1M KNO_3 solution and recording CV's at the following rates: 20,50,75,100,125,150,175,and 200 mV/s. The scan rate can be changed by using the **SCAN** knob to change the placing of the decimal point (look at the display to determine if V/s or mV/s), then fine tune using the **SCAN RATE** knob. After the scan rate is changed, the procedure outlined in "Run Voltammogram" is followed to obtain a voltammogram. Repeat this for each subsequent scan rate.

A plot of current vs. (scan rate)$^{1/2}$ (see Fig. 4B) can be done in order to determine the diffusion coefficient (D). Note: In order to maximize or minimize the size (height) of the plot, adjust the **Y RANGE** on the recorder; higher values decrease the size of the plot, lower values increase the size of the plot. If this is not done, the voltammogram may be too large or small for the paper. A "dry" run may be performed with the **PEN UP** to avoid this. For the scan rates (v) = 20,50,75,100,125,150,175, and 200 mV/s, the respective settings of 0.25,0.5,0.5,0.5,0.5,1,1,and 1 for **Y RANGE** gave the best results. The Y or current(i) axis values can be determined by multiplying Y-RANGE by gain (**Y-RANGE x GAIN**) to obtain current per cm. The X or potential(E) axis remains unchanged at 50 mV/cm.

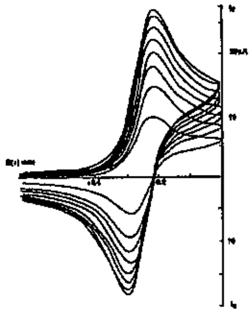

Figure 4(A). Cyclic voltammograms of 4mM $K_3Fe(CN)_6$ in 1M KNO_3. Pt electrode. Scan rate = 20,50,75,100,125,150,175,and 200 mV/s.

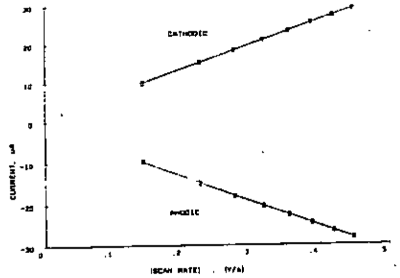

Figure 4(B). Plot of i_p(cathodic and anodic) vs. $v^{1/2}$ from voltammograms in (A).

Discussion

The important parameters obtained from a cyclic voltammogram are the anodic peak current(i_{pa}), cathodic peak current(i_{pc}), anodic peak potential(E_{pa}), and cathodic peak potential(E_{pc}); all of which can be determined from the voltammogram as illustrated in Fig. 5. The peak current for an electrochemically reversible system (rapid electron transfer at the electrode surface) is described by the Randles-Sevcik equation:

$$i_p=(2.69x10^5)n^{3/2}AD^{1/2}Cv^{1/2}$$

where i_p is peak current(A), n is electron stoichiometry, A is electrode area (cm^2), D is diffusion coefficient (cm^2/s), C is concentration (mol/cm^3), and v is scan rate (V/s)(2). Thus, i_p is proportional to C and ip is proportional to $v^{1/2}$ for a reversible system.

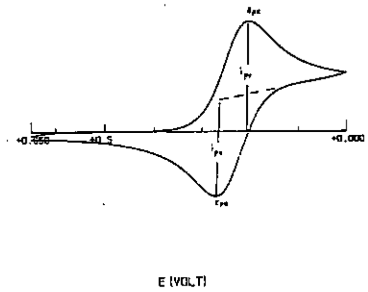

Figure 5. Cyclic voltammogram of 8 mM $K_3Fe(CN)_6$ in 1M KNO_3 illustrating determination of E_{pa}, E_{pc}, i_{pa}, and i_{pc}.

A plot of i_p vs. C (Fig. 3B) should give a straight line with an intercept of zero. A large deviation from zero could indicate adsorption. A plot of i_p vs. $v^{1/2}$ (Fig. 4B) gives a straight line, the slope of which can be used to determine the diffusion coefficient (slope = $2.69x10^5n^{3/2}AD^{1/2}C$) if n, A, and C are known. The area of the electrode(A) can be determined by geometric measurement ($A=3.1416r^2$). In this case, the diffusion coefficient for ferricyanide (cathodic current) was 7.96 x 10^{-6} cm^2/s, with n = 1, A = 0.02 cm^2, and C = 4.0 x 10^{-6} mol/cm^3, which is in agreement with published values (D = 7.63 x 10^{-6} cm^2/s). The formal reduction potential ($E^{0\prime}$) for a reversible system is centered between E_{pa} and E_{pc}:

$$E^{0\prime} = \frac{E_{pa} + E_{pc}}{2}$$

The number of electrons transferred (n) in a reversible system can be determined from the anodic and cathodic peak potential separation:

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

A plot of ΔE_p vs. scan rate(v) should, according to the Randles-Sevcik equation, ideally give a slope of zero with $\Delta E_p = 0.059/n$ independent of scan rate. However, at higher scan rates, ΔE_p starts to increase (see Fig. 4C). This may be due to slow electron transfer kinetics, or ohmic potential (iR) drop. Also, the ΔE_p observed experimentally may be slightly greater than the 0.059V value expected for a one electron transfer. This may be due to filtering (of the background signal) effects of the output current (discussed in detail in an earlier Capsule), to "edge" effects of convergent diffusion, or due to nonideality of the electrode surface in combination with solvent and salt effects.

(1) Kissinger,P.T., Heineman,W.R., J. CHEM. ED., 60, 702 (1983).

(2) Kissinger,P.T., Roston,D.A., Van Benschoten,J.J., Lewis,J.Y., Heineman,W.R., J. CHEM. ED., 60, 772 (1983).