CAPSULES
notes and applications from Bioanalytical Systems, Inc.

Study of Ferricyanide in Cyclic Voltammetry- BAS 100B

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 BAS 100B Electrochemical Analyzer, because of its simplicity of use, is ideal for teaching purposes, and can be mastered by learning a few basic commands.

The experiment outlined below demonstrates the determination of the following important information: the formal reduction potential ($E^{0'}$); 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).

Concentration Effects

To study the effect of varying concentration, CV's are obtained for each of the 2,4,6,8,and 10mM $K_3Fe(CN)_6$ using a scan rate of 20mV/s. An unknown (concentration) $K_3Fe(CN)_6$ solution can also be run.

1. Assemble the cell by placing the platinum working electrode, platinum wire auxiliary electrode, and Ag/AgCl reference electrode in the 2mM $K_3Fe(CN)_6$ solution. Degassing is not necessary because the sample is scanned only at potentials positive of O_2 reduction.

2. A cyclic voltammogram as shown in Fig. 1 can be obtained easily using the BAS 100B Electrochemical Analyzer by using a few simple commands as outlined below.

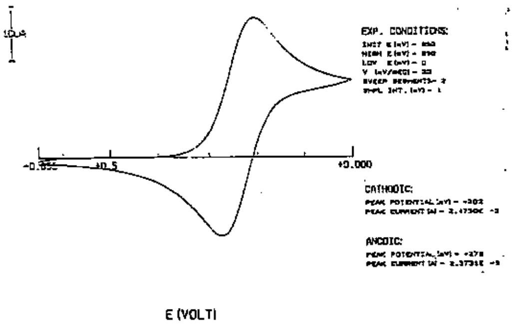

Figure 1. Cyclic voltammogram of 10mM $K_3Fe(CN)_6$ in 1M KNO_3. Scan rate = 20mV/s. Pt electrode.

Step	**Prompt**	**Response**
1	[POWER ON]	↵
2	DATE=##-##-##	↵
3	TIME=##-##-##	↵
4	OPERATING MODE=	CV↵
5	INIT E(MV)=#	650↵
6	HIGH E(MV)=#	650↵
7	LOW E(MV)=#	0↵
8	V(MV/SEC)=#	20↵
9	SWEEP SEGMENTS=	2↵
10	SENSITIVITY(A/V)=1.0E-#	5↵
11	*	LABEL↵
12	LABEL:	(Type in Title)↵
(e.g., 2MM $K_3FE(CN)_6$/1M KNO_3/H_2O/PTE)		
13	*	R↵
	RUN IN PROGRESS	
14	*	B↵
	(Data is scaled to screen)	
15	*	PB↵
	(Data is sent to plotter)	
	*	

3. The subsequent solutions can be analyzed by changing the solution and repeating steps 11-15 after the star prompt (*) appears. Be sure to polish the working (Pt) electrode and change the plotter paper after each run. If one wishes to overlay plots as in Fig. 2A, the scale factor must be frozen by typing **FRZ↵** after the star prompt. In order to overlay plots without plotting the experimental conditions or results, type **N↵**, **NAX↵**, then **PB↵** after each solution is scanned. The experimental results can be obtained by typing **X↵**.

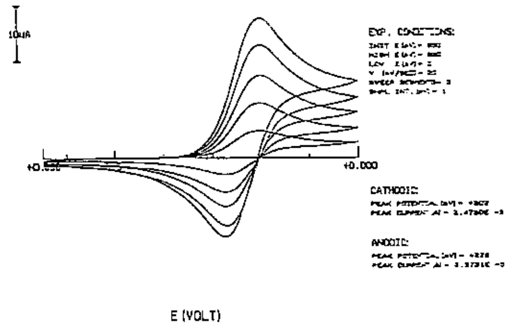

Figure 2(A). Cyclic voltammograms of $K_3Fe(CN)_6$ in 1M KNO_3. Scan rate = 20mV/s. Pt electrode. Concentration = 2,4,6,8,10 mM.

A plot of current vs. concentration (see Fig. 2B) can be done and the unknown concentration determined by extrapolation.

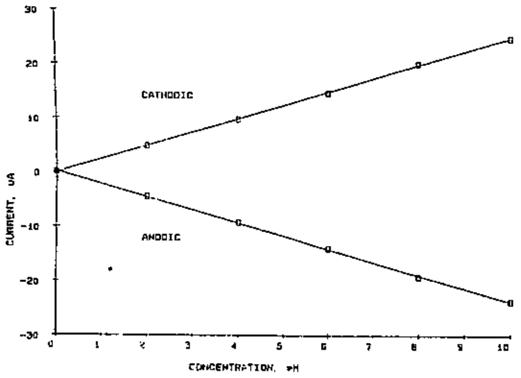

Figure 2(B). Plot of ip(cathodic and anodic) vs. concentration from voltammograms in (A).

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: 20,50,75,100,125,175,and 200 mV/s. This can be done by making a simple modification to the procedure above.

After the star prompt appears, type **CG↵**. Proceed from step 5 to step 8 to change the scan rate [V(MV/SEC)=#] to the desired value (e.g., 50). Continue with steps 9-15 to generate a voltammogram. Repeat this for each subsequent scan rate.

A plot of current vs. (scan rate)$^{1/2}$ (see Fig. 3B) can be done in order to determine the diffusion coefficient (D).

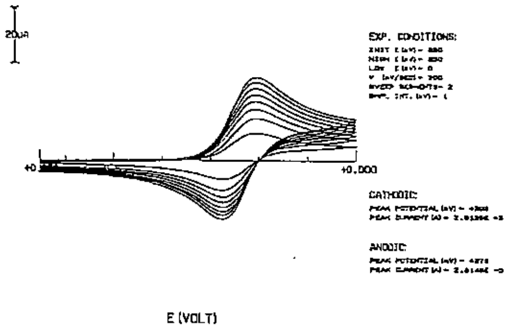

Figure 3(A). Cyclic voltammograms of 4mM K3Fe(CN)6 in 1M KNO3. Pt electrode. Scan rate = 20,50,75, 100, 125, 150, 175, and 200 mV/s.

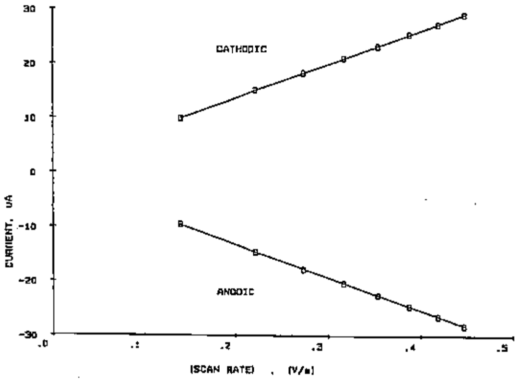

Figure 3(B). Plot of i_p(cathodic and anodic) vs $v^{1/2}$ from voltammograms in (A).

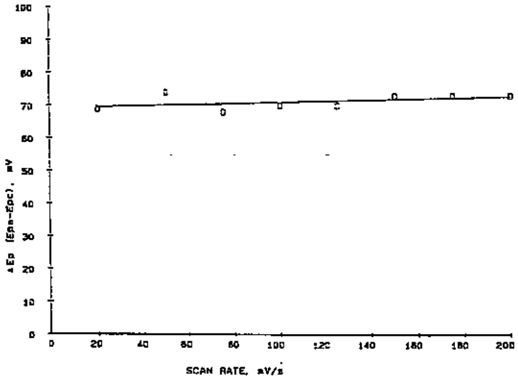

Figure 3(C). Plot of ΔE_p vs. scan rate(v) from voltammograms in (A).

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 are conveniently recorded on the voltammogram obtained using the BAS 100B as shown in Fig. 1. The peak current for an electrochemically reversible system (rapid electron transfer at the electrode surface) is described by the Randles-Sevcik equation:

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

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 i_p is proportional to $v^{1/2}$ for a reversible system. A plot of i_p vs. C should give a straight line with an intercept of zero. A large deviation from zero could indicate adsorption. A plot of i_p vs. $v^{1/2}$ gives a straight line, the slope of which can be used to determine the diffusion coefficient (slope $= 2.69\times10^5n^{3/2}AD^{1/2}C$) 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 ion (cathodic current) was 8.12×10^{-6} cm^2/s, with $n = 1$, $A = 0.02$ cm^2, and $C = 4.0 \times 10^{-6}$ mol/ cm^3, which is in agreement with published values ($D=7.63 \times 10^{-6}$ cm^2/s).

The formal reduction potential ($E^{0'}$) for a reversible system is centered between E_{pa} and E_{pc}:

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

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. 3C). 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).