

THE OXIDATION OF FERROCENE; A CYCLIC VOLTAMMETRY EXPERIMENT

1. Purpose

In this experiment the redox couple ferrocene/ferrocenium will be studied in an aprotic solvent using the technique of cyclic voltammetry. In particular, the experimental variables affecting the cyclic voltammetry data and their interpretation will be investigated.

2. Introduction

Cyclic voltammetry is a very versatile electrochemical technique which allows to probe the mechanics of redox and transport properties of a system in solution. This is accomplished with a three electrode arrangement whereby the potential relative to some *reference* electrode is scanned at a *working* electrode while the resulting current flowing through a *counter* (or *auxiliary*) electrode is monitored in a quiescent solution. The technique is ideally suited for a quick search of redox couples present in a system; once located, a couple may be characterized by more careful analysis of the cyclic voltammogram.

More precisely, the controlling electronic is designed such that the potential between the reference and the working electrodes can be adjusted but the big impedance between these two components effectively forces any resulting current to flow through the auxiliary electrode. Usually the potential is scanned back and forth linearly with time between two extreme values – the switching potentials. When the potential of the working electrode is more positive than that of a redox couple present in the solution, the corresponding species may be oxidized (*i.e.* electrons going from the solution to the electrode) and produce an *anodic* current. Similarly, on the return scan, as the working electrode potential becomes more negative than the reduction potential of a redox couple, reduction (*i.e.* electrons flowing away from the electrode) may occur to cause a *cathodic* current. By convention, anodic currents are negative and cathodic currents positive.

The magnitude of the observed *faradaic* current can provide information on the overall rate of the many processes occurring at the working electrode surface. As is the case for any multi-step process, the overall rate is determined by the slowest step. For an redox reaction induced at a working electrode, the rate determining step may be any one of the following individual step depending on the system: rate of *mass transport* of the electro-active species, rate of adsorption or de-sorption at the electrode surface, rate of the electron transfer between the electro-active species and the electrode,

or rates of the individual chemical reactions which are part of the overall reaction scheme.

For the oxidation reaction involving n electrons



the *Nernst Equation* gives the relationship between the potential and the concentrations of the oxidized and reduced form of the redox couple *at equilibrium* (at 298 K):

$$E = E^{0'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]_{d=0}}{[\text{Red}]_{d=0}} \quad (2)$$

where E is the applied potential and $E^{0'}$ the formal potential; the subscript $d=0$ is meant to emphasize that $[\text{Ox}]$ and $[\text{Red}]$ represent surface concentrations at the electrode/solution interface, *not* bulk solution concentrations. Note that the Nernst equation may or may not be obeyed depending on the system or on the experimental conditions.

A typical voltammogram is shown in Fig. 1. The scan shown starts at a slightly negative potential, E_i , up to some positive switching value, E_{switch} , at which the scan is reversed back to the starting potential. The current is first observed to peak at E_{pa} (with value i_{pa}) indicating that an oxidation is taking place and then drops due to depletion of the reducing species from the diffusion layer. During the return scan the processes are reversed (reduction is now occurring) and a peak current is observed at E_{pc} (corresponding value, i_{pc}). Providing that the charge-transfer reaction is reversible, that there is no surface interaction between the electrode and the reagents, and that the redox products are stable (at least in the time frame of the experiment), the ratio of the reverse and the forward current $i_{pr}/i_{pf} = 1.0$ (in Fig. 1 $i_{pa} = i_{pf}$ and $i_{pc} = i_{pr}$). In addition, for such a system it can be shown that 1) the corresponding peak potentials E_{pa} and E_{pc} are independent of scan rate and concentration, 2) that $(E_{pa} + E_{pc})/2$ is a good approximation of $E^{0'}$ the formal potential for the redox reaction and 3) that $E_p = E_{pa} - E_{pc}$ should be close to $59/n$ mV (for a n electron transfer reaction) at all scan rates. These features are very convenient diagnostic tools to test for reversibility of a redox process and stability of the products; if any of these features is not satisfied, it is an indication that the system is not fully reversible.

In simple terms, the working electrode may be regarded as a "reagent" of adjustable oxidizing or reducing strength. However, this is a purely conceptual image. In actual fact, the electrochemical processes are occurring at the interface of two different phases, the electrode and the electro-active species in solution. In other words, the processes under studies are heterogeneous in nature.

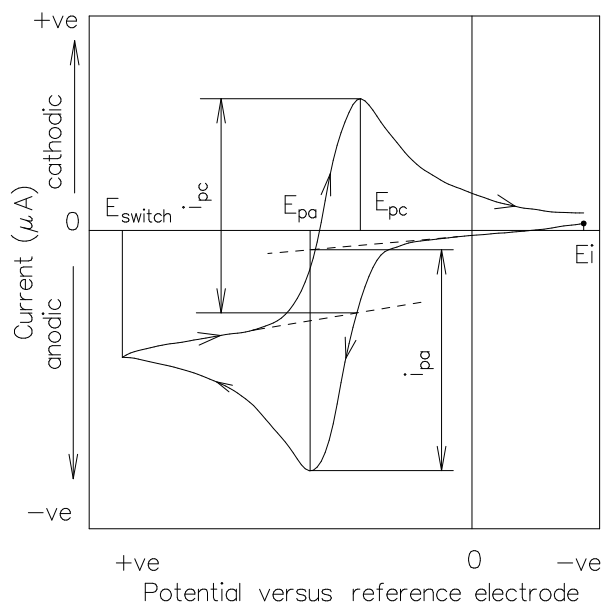


Figure 1. Typical cyclic voltammogram; the quantities of interest and how to obtain them from the scan are shown.

For the electron transfer to occur, the molecules in solution have to approach the electrode. In a cyclic voltammetry experiment, the solution is kept unstirred; in this situation, mass transport can occur only by diffusion due to concentration gradients created around the electrode surface. Such concentration–distance profiles at different steps of a cyclic voltammogram scan are illustrated in Fig. 2.

The magnitude of the observed signal will be very much a function of these diffusional properties of the system. Intuitively, the current intensity (*i.e.* the flow of electrons) is expected to depend on the surface area of the working electrode and the concentration of the electro-active species. Also, one can expect the voltage scanning rate to affect the concentration profile around the electrode which itself directly affects the rate of charge transport, and for this matter the diffusion coefficient appears explicitly. The expression of the peak current (A) for the forward sweep in a reversible system at 298 K is given by the Randles–Sevcik equation,

$$i_{pf} = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C^* \quad (3)$$

where n is the number of electron equivalent exchanged during the redox process, A (cm^2) the active area of the working electrode, D ($\text{cm}^2 \text{s}^{-1}$) and C^* (mol cm^{-3}) the diffusion coefficient and the bulk concentration of the electro-active species; ν is the voltage scan rate (V s^{-1}). In the present experiment, the dependence of i_{pf} on scan rate and concentration will be examined.

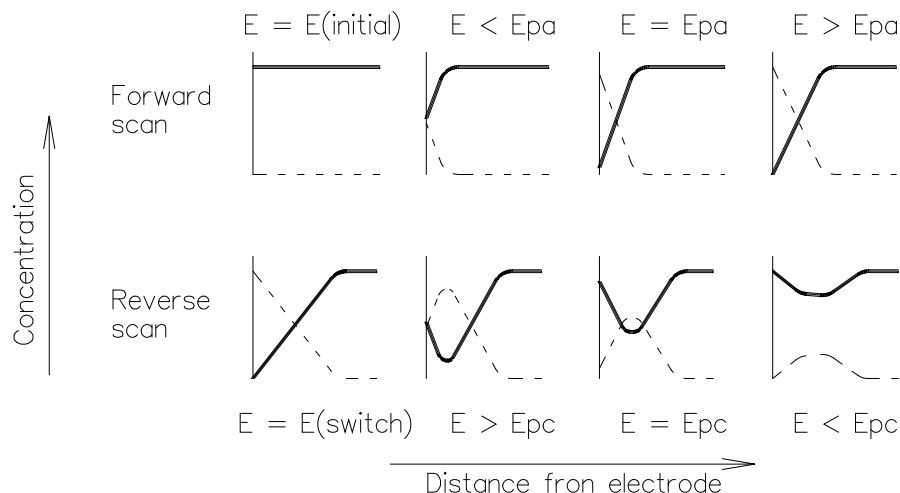


Figure 2. Qualitative diagrams showing concentration--distance profile at various stage of the cyclic voltammogram shown in Fig. 1; the solid lines correspond to the reducing species and the dotted lines to the oxidizing species (adapted from reference 1).

3. Experimental.

3.1 EQUIPMENT.

- EGG Instrument, model *VersaStat II*, computer controlled via *Power Suite*TM software.
- Electrodes.
 - *Silver wire reference electrode.* At the beginning of the session, the silver wire reference electrode must be cleaned by dipping it in *conc* HNO_3 for 30 s followed immediately with rinsing with distilled water then acetone.
 - *Counter electrode.* A platinum wire is used as counter electrode; it should be rinsed with acetone and thoroughly dried before use.
 - *Working electrode.* The working electrode consists of a thin platinum rod (2.0 mm diameter) imbedded in an epoxy sheath, such that only a 2 mm disc is exposed to the solution. The disc surface should be gently polished before each new scan by rubbing it for a few seconds on a piece of tissue paper. Usually this is sufficient to provide a “clean” surface for the run. However if the performance of the electrode appears to deteriorate (distorted voltammograms) the electrode should be

scrubbed with *wet* fine emery paper (600 grade), polished with wet “crocus” paper, rinsed abundantly with water then dried.

- All the glassware needed is kept in the drying oven in a crystallization dish; at the end the experiment, return all the glassware to the drying oven for storage. Please, mention any breakage to the instructor. As the presence of water degrades the quality of the data, all rinsing should be done with acetone and/or acetonitrile.
- Ferrocene ($\text{Fe}(\text{Cp})_2$), tetraethyl ammonium perchlorate (TEAP) kept in a desiccator, dry acetonitrile (HPLC grade) kept over molecular sieves (avoid agitating the acetonitrile bottle to prevent the drying agent dust from lifting).

3.2 SAMPLE PREPARATION.

- Prepare 50 ml of a 0.1 M TEAP/ CH_3CN solution which will serve as background electrolyte for all the $\text{Fe}(\text{Cp})_2$ solutions.
- Using the special glass weighing boat provided, weigh out the required amount of $\text{Fe}(\text{Cp})_2$ to prepare 10 ml of a 10 mM stock solution. Transfer quantitatively this amount to a 10 ml volumetric flask and fill it up to the mark with the 0.1 M TEAP solution prepared above.
- Prepare from the 10 mM $\text{Fe}(\text{Cp})_2$ three 10 ml samples with concentrations 1 mM, 2 mM and 4 mM by proper dilution of the stock – again use the 0.1 M TEAP solution to fill to the mark the 10 ml volumetric flasks.

3.3 SCANNING PROCEDURES.

In all the following, glassware and anything entering in contact with the solution should be dry. All runs take place in the housing “BAS cell stand”, which integrates a stirrer and a bubbler.

- Transfer the first ferrocene solution to the cell container (start with the lowest concentration), add a micro stirring bar, snap on the plastic cap, insert the electrodes and the nitrogen line. Position the assembly inside the housing, just under the cell clamp (this is where the stirring motor is located). Turn the “STIR” switch *On*. Leave the “PURGE” knob in the *Off* position; the gas flow can be controlled with the rotating knob “Test sample”. Adjust the nitrogen to a gentle flow (1 to 5 bubbles a second).
- Let stir and bubble for 2 – 3 minutes before the scan, but the solution *must* be still during the CV scan (*i.e.*, turn stirring *Off* and pull the nitrogen tubing just out of the solution while keeping the nitrogen flowing above the solution surface to prevent O_2 from reaching the solution).
- On the computer screen, activate Experiment properties.
 - Click on the Cell definition tab. Enter your Comments, choose Silver wire in the Reference Electrode window, choose Solid

Electrode as working electrode and enter the surface area as 0.0314 cm^2 . Do not touch the other options.

- Click on the Scan Definition tab. Set the Initial Potential to 0.0, Vertex to 1.0, Final potential to 0.0, and enter the Scan rate you are about to use.
- Click on the Prescan Definition tab. Set Equilibration to 10 s (stirrer off) and leave the rest alone.
- To start the scan, click on the RUN button; the voltammogram is displayed as it builds up.
- To save the data, move the mouse cursor on the plot area, click the right button of the mouse to get the Export data file option; the data are saved as text files and can be easily imported into a spreadsheet program.

3.4 DATA COLLECTION.

For each of the three ferrocene solution record a series of voltammogram at different scan rates; use 300, 200, 100, 50, 20, 10 mV s^{-1} . When changing scan rate, stir the solution for 30 s with the magnetic stirrer then let the solution rest for ~ 10 s before starting a new scan. Clean the working electrode between each scan; just pull out the electrode from the solution and rub its face firmly on a piece of tissue paper. If the aspect of the voltammogram seems to get worse (noisy signal or distorted curves), the platinum disk electrode may have to be re-polished (see above).

3.5 DETERMINATION OF THE SILVER WIRE ELECTRODE POTENTIAL

(This step may be omitted)

All the potentials recorded so far in the experiment are relative to the reference electrode used, namely the silver wire electrode. These values can be converted to potentials with respect to the normal hydrogen electrode (NHE). The potential of the silver wire *versus* the Ag/AgCl (3M NaCl) electrode (itself +0.197 V vs NHE) can be obtained simply by measuring the difference of potential developed (with a digital voltmeter for instance) between the two electrodes immersed in the background electrolyte used for the experiment. Then, all the measured potentials can be shifted appropriately.

4. Data Analysis/Discussion

The values of i_{pa} , i_{pc} , E_{pa} and E_{pc} must be obtained from each voltammogram; Fig. 1 shows the meaning and how to measure these quantities on a typical voltammogram.

Import your each of your data file into a spreadsheet and generate a graph of the particular run. The simplest way to obtain the desired quantities is to get a printout of the graph and with a ruler measure on the paper the relevant distances in mm; it is then a simple matter to turn the measured distances into Volts or Amperes using the proper scaling factor obtained from the axis of the plot. Organize tables to show all the measured values as a function of scan rate and concentration.

- Plot i_{pf} versus $\nu^{1/2}$ (where ν is in V s^{-1}) for each ferrocene concentration. Comment on the linearity (or lack of) of the plots and what can be inferred from this result; do your data behave according to Eqn. 3 (which implies in particular, that the fitted line should go through the origin)?
- From each of the above plots obtain a value of the diffusion coefficient of ferrocene in acetonitrile (the diameter of the Pt disk is 2 mm). Eventually report one value for this parameter. For comparison purpose, the diffusion coefficient of naphthalene in the same solvent, is $2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 298 K.
- How do the values of $\Delta E_p = E_{pa} - E_{pc}$ vary with scan rate and ferrocene concentration? How do they compare with the value expected for a reversible system? What about the value of ΔE_p extrapolated at zero scan rate (or high scan rate) and zero concentration? From these considerations, what can you say about the reversibility of the present system?
- For each voltammogram measure the ratio i_{pr} / i_{pf} ; comment on its value and any dependence on experimental variables.
- Based on your results, what would be the best conditions to study the present system and why?
- Using Eqn. 2 and taking your value of $E_{1/2}$ as an approximation of E^0 , estimate the ratio [ferrocenium]/[ferrocene] at 0 V versus the silver wire electrode and then at 0.6 V; at $E_{1/2}$ (assume that all activity coefficients are unity)?
- Obtain the thermodynamic quantities ΔG^0 , ΔS^0 , ΔH^0 and K_{eq} from your electrochemical measurements and compare with accepted values.

5. REFERENCES

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