An Introduction to Cyclic Voltammetry

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Cyclic voltammetry has become a popular tool in the last fifteen years for studying electrochemical reactions. Organic chemists have applied the technique to the study of biosynthetic reaction pathways (1) and to studies of electrochemically generated free radicals (2). An increasing number of inorganic chemists have been using cyclic voltammetry to evaluate the effects of ligands on the oxidation/reduction potential of the central metal ion in complexes and multinuclear clusters (3). This type of information plays an integral part in many of the approaches directed toward solar energy conversion (4) and in model studies of enzymatic catalysis (5). Knowledge of the electrochemistry of a metal complex can be useful in the selection of the proper oxidizing agent to put the metal complex in an intermediate oxidation state (6). Electrochemical methodology has also been exploited as a novel means of introducing functional groups and removing blocking agents (7).

There are several good texts that deal with the theory and practice of modern voltammetry in depth (8–10). Also, many instrumental analysis textbooks give a very brief overview of the method. However, the needs of a researcher interested in applying the technique for the first time are somewhere between these two extremes. Instructors of instrumental analysis who want to teach modern electrochemistry are faced with a similar dilemma due to the lack of suitable background material for the students to read. This article is intended to help meet those needs.

The CV Experiment

The voltage applied to the “working” electrode is scanned linearly from an initial value, E1, to a predetermined limit, EM, (known as the switching potential) where the direction of the scan is reversed (see Fig. 1a). The operator can halt the scan anywhere or let the instrument cycle between EM and some other preselected value, E2. The current response is plotted as a function of the applied potential. Often there is very little difference between the first cycle and successive scans. However, the changes that do appear on repetitive cycles are important keys to unlocking information about reaction mechanisms (as will be shown later in this paper).

Figure 1b shows a current-voltage curve (or voltammogram) for Fe(CN)₆³⁻. As the potential is scanned in the negative direction the current rises to a peak and then decays in a regular manner. The current depends on two steps in the overall process, the movement of electroactive material to the surface and the electron transfer reaction. The electron transfer rate constant for a reduction process is a function of potential and can be described theoretically.

\[ k_t = k^0 \exp \left( \frac{-\alpha n F}{R T} (E - E^{\circ}) \right) \]  

(1)

where \( k^0 \) is the standard heterogeneous electron-transfer rate constant. (Its value is a property of the reaction between the particular compound and the electrode surface used.) The number of electrons transferred per molecule is \( n \); \( F \) is the Faraday; \( R \) is the universal gas constant; \( T \) is the Kelvin; and \( E^{\circ} \) is the formal reduction potential. (The prime signifies that the effect on the free energy of the reactants and products embodied in activity coefficients has been combined with the thermodynamic reduction potential to form a term that is directly measurable but subject to solution conditions.) The term \( \alpha \) is known as the transfer coefficient. It arises because only a fraction of the energy that is put into the system (in the form of the applied potential) lowers the activation energy barrier. Its value varies from zero to unity (often \( \sim 0.5 \)) depending on the shape of the free energy surfaces for the reactants and products.

The exponential dependence of \( k_t \) on the applied potential accounts for the steep rise in the current. However, the electrolysis of the reactant depletes its concentration near the surface. Since the experiment is performed at a stationary electrode in an unstirred solution, diffusion is the principal means of moving the reactant to the surface. This relatively slow mode of mass transport cannot maintain a steady-state concentration profile in the region close to the electrode. Therefore, the depletion zone grows. In a sense, the average distance that the reactant molecules must travel to reach the surface increases. Consequently, the rate of mass transport decreases. The dependence on mass transport, and the fact that a finite rate for the reverse electron transfer process is possible, prevent the current from increasing exponentially

\[ E = \frac{E_p + E_a}{2} \]  

Figure 1. a) Applied potential program. \( E_{1a} \) and \( E_{2a} \) are switching potentials. b) Typical cyclic voltammogram of 1 mM K₃[Fe(CN)₆] at a platinum electrode in aqueous 0.1 M KCl solution. The scan rate was 100 mV/sec and the reference electrode was Ag/AgCl in 0.1 M KCl solution.

\[ E^{\circ} \]  

This is a simplification. For a well-written and much more detailed explanation of the significance of the transfer coefficient and symmetry factors see pp. 917–929 of ref.(27).
with potential. Eventually the mass transport step becomes rate determining and the current reaches a maximum. Since the concentration gradient continues to decrease, the rate of mass transport continues to decrease causing the current to decay. Beyond the peak the current is actually dependent on time and independent of the applied potential. In this diffusion-limited region the current is proportional to \( t^{-1/2} \).

An advantage of the cyclic voltammetry experiment is that a significant concentration of product (in this case, the reduced form) has been generated near the electrode on the forward scan. When the scan direction is reversed, the reduced form is oxidized back to the original starting material and the current for the reverse process is recorded (see Fig. 1b). The electron transfer rate constant for the reverse (or oxidation) process is similarly controlled by the applied potential.

\[
k_r = k^o \exp \left( \frac{(1 - \alpha) nF}{RT} \right) (E - E^{oc})
\]  

(4)

**Determination of the Formal Reduction Potential**

It is common practice to report the average of the forward and return peak potentials as the formal reduction potential for the redox couple. This is an approximation that is most accurate when the electron transfer process is reversible and the diffusion coefficients for the oxidized and reduced forms are the same. If the reaction is reversible, then the separation in the peak potentials, \( \Delta E_p \), will be close to 58/n mV (at 25°C). (This relationship can be used to evaluate \( n \).)

By reversible, electrochemists mean that the reaction is fast enough to maintain the concentrations of the oxidized and reduced forms in equilibrium with each other at the electrode surface. The proper equilibrium ratio at a given potential is determined by the Nernst Equation:

\[
E = E^{oc} - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right)
\]  

(5)

where \( O \) is the oxidized form and \( R \) is the reduced form.

**How fast is fast enough?** Many systems look reversible when the voltage is scanned slowly but at higher scan rates \( \Delta E_p \) appears greater than 58/n mV. Reversibility is, then, a matter of degree and depends on the stress that is applied to the system. Matsuda and Ayabe indicated that for scanning voltammetry any deviations from reversible behavior will be imperceptible if the value of \( k^o \) (in cm/sec) is greater than the numerical value of 0.30v/2 (where \( v \) is the scan rate in V/sec) (11). Voltamograms recorded at scan rates up to 10 V/sec are common. Some instruments are capable of scanning up to 1000 V/sec. Therefore, electron transfer reactions with rate constants greater than 10 cm/sec will be reversible even in the very fastest experiments.

Redox couples whose peaks shift farther apart with increasing scan rate are categorized as quasi-reversible. (Some authors merely say irreversible.) There are some cases in which the peaks are so widely separated (\( k^o \geq 2 \times 10^{-5} \) cm/sec) that no parts of the two peaks overlap on the potential axis at all. These are generally known as “totally irreversible” systems. A subset of this class are those reactions that yield products that cannot be recycled electrochemically to give back the original reactants (for example, those that involve extensive bond breaking and/or loss of substituents to solution). These are “chemically irreversible” reactions, and many yield no return peak at all.

Another characteristic of reversible systems is the dependence of the peak height on the square root of the scan rate. At 25°C the peak current is

\[
i_p = (2.69 \times 10^{-2}) (D_0 a)^{1/2} AD_{1/2} (C_o)^{1/2}
\]  

(6)

The current will be in amperes when \( A \) is in cm², \( D_0 \) is in cm²/sec, \( v \) is in volts/sec, and \( C_o \) is the bulk concentration in moles/cm³. The peak current for a quasi-reversible system is not proportional to \( v^{1/2} \) except when the peaks are so widely separated that the system is more appropriately described as totally irreversible.

Although the average of the peak potentials can be a good estimate of the \( E^{oc} \) for a reversible redox reaction, one must be careful not to attribute high accuracy to the determination.

In Nicholson and Shain’s classic paper on the theory of voltammetry at stationary electrodes (12), they point out that the position of the return peak, even for a reversible system can shift as much as 5 mV depending on the choice of the switching potential, \( E_s \). (The farther \( E_s \) is from \( E_p \), the more nearly symmetric about the reduction potential the peaks will be.) Also their work indicates that the midpoint between the peaks is really an estimate of \( E_{1/2} \) (\( E_{1/2} \) is a term from polarography that was given to the potential where the current is half the value of that on the current plateau.) Fortunately, the diffusion coefficients have a small effect. Even if \( D_0/D_R = 2 \), the error introduced by assuming \( E_{1/2} = E^{oc} \) would be only ~9mV for a single electron exchange process.

Some workers have found that the broad point at the top of the current peak makes it difficult to determine the true position of the peak precisely. They prefer to read the potential where the current is half the value of the peak current. This half-peak potential (for a reversible redox couple at 25°C) is related to the polarographic \( E_{1/2} \) value by the following equation:

\[
E_{1/2} = E^{oc} + \frac{28.0}{n} \text{mV}
\]  

(7)

(The sign is positive for a reduction process.)

Estimating formal reduction potentials from quasi-reversible voltammograms is less reliable the farther the peak separation deviates from the reversible case. Theoretical work shows that as the scan rate is increased, slow electron transfer kinetics can make the peak potentials shift in such a manner that they are no longer symmetric about the \( E_{1/2} \) for the redox couple. The problem is worse the farther the electron transfer coefficient, \( \alpha \), is from 0.5. A rough indication of the magnitude of the error that may be introduced by averaging the pair of cathodic and anodic peak potentials for a quasi-reversible voltammogram can be derived from graphical data prepared by Matsuda and Ayabe (11). For an \( \alpha \)-value of 0.3 and peak separations of 108, 312, and 592 mV, the midpoint between the peaks would be on the negative side of the actual \( E_{1/2} \) value by 2, 4.4, and 104 mV, respectively. (For an \( \alpha \)-value of 0.7 the error would have the same magnitude with the opposite sign.)

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² The mathematics that describe a scanning experiment are quite complicated. However, an application of Fick’s First Law of Diffusion tells us that the current at any time is proportional to the concentration gradient for the reactant:

\[
i = nFAD_0(x \partial C / \partial x)|_{x=0,1}
\]  

(2)

\( A \) is the electrode area; \( D_0 \) is the diffusion coefficient of the oxidized species; \( t \) is time; and \( x \) is the distance from the electrode surface. An experiment in which the voltage is stepped instead of scanned out to a potential where the current is diffusion controlled is much easier to model mathematically. (This is chronoamperometry.) In that case

\[
(x \partial C / \partial x)|_{x=0,1} = C_o \sqrt{\pi D_0 t}
\]  

(3)

where \( C_o \) is the concentration of the oxidized material in the bulk solution (in moles/cm³). It seems reasonable, then, that scanning to the same voltage would also cause the current to fall off as \( t^{-1/2} \).

³ Rates of heterogeneous reactions are referenced to unit surface area and have units of mol sec⁻¹ cm⁻². Since the rate is expressed as the product of \( kC \), the rate constant, \( k \), must have units of cm sec⁻¹ when concentration is given in mol cm⁻³.

⁴ Equation (6) assumes a planar electrode. For a spherical electrode (such as a hanging mercury drop) \( i_p = (2 \pi a) (b_0 + 0.752) nFAD_0 C_o / \rho \).

⁵ \( E_{1/2} = E^{oc} - RT/nF \ln (D_0/D_R)^{1/2} \).
The point to remember is that one should use conditions that give the most reversible behavior possible. For quasi-reversible systems the scan rate should be slowed down to minimize $\Delta E_p$. There is a lower limit for the scan rate, however. This limit is set by our ability to maintain a convection-free solution. Convection often sets in after times as short as 30 seconds, unless special precautions against stray vibrations and other sources of convection are taken.

The type and condition of the working electrode surface can make a difference in the electron transfer kinetics. Often solid electrodes need to be polished and/or cleaned by exposing them to oxidizing agents. In some cases workers advocate "activating" the electrode surface (particularly carbon electrodes) by application of a sequence of extreme positive and negative potentials. (For more discussion about surface effects and pretreatment procedures see references (13–15).

**Peak Currents and Coupled Chemical Reactions**

The height of the current peak can be used to determine the concentration of the reactant in the bulk solution. However, other electrochemical methods (such as differential pulse voltammetry) are better suited for this task. The real forte of this technique is the analysis of homogeneous chemical reactions that are coupled to the electron transfer process. Diagnosis of coupled chemical reactions is often based on the relative heights of the anodic and cathodic peaks. For example, consider a reversible charge transfer followed by an irreversible chemical reaction (entry III in the table). If the conversion of $R$ to $Z$ is fast and the potential is scanned slowly, some of $R$ will be lost to $Z$. Less $R$ will be available for the oxidation back to 0 on the return scan and, therefore, the anodic peak will be smaller. In the extreme case, $k$ may be so fast relative to the scan rate, that all of $R$ will be converted to $Z$ and the return peak will be absent entirely. Figure 2 illustrates how the voltammograms change depending on the ratio of the chemical rate constant to the scan rate. (Note that the y-axis is the normalized current as given by the function: $i/(n^{3/2}FAD^{1/2}C_v^{1/2})$.)

Nicholson and Shain have demonstrated that the ratio of the anodic to cathodic peak currents can be predicted from the rate constant for the chemical step, $k$, and the time, $\tau$, spent between $E_{1/2}$ and the switching potential, $E_s$ (15). ($E_{1/2}$ will be the midpoint between the peaks at very high scan rates where the following chemical reaction does not have time to consume a significant amount of $R$.) The theoretical relationship is plotted in Figure 3. Experimentally we can use the graph to obtain an estimate of $k$ for the chemical step. (For experimental values of $i_{pa}/i_{pc}$, find the corresponding theoretical value of $\log (k\tau)$. Solve for $k\tau$ and divide by the experimental value of $\tau$.)

Other electrochemical mechanisms can be identified. A list of some of the more common ones is given in the table. Figure

![Figure 2: Cyclic voltammograms for a reversible electron transfer followed by an irreversible chemical step for various ratios of the chemical rate constant to scan rate, $k/\alpha$ where $\alpha = nF/RT$ and $\nu$ is volts/second. (Adapted with permission from Anal. Chem., 39, 706–723 (1984).)](image)

![Figure 3: Ratio of anodic to cathodic (or reverse to forward) peak current as a function of $k$ for a reversible electron transfer followed by a chemical step. (Adapted with permission from Anal. Chem., 39, 706-723 (1984))](image)

**Electrochemical Mechanisms Involving Coupled Chemical Reactions**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reaction</th>
<th>Current Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Reversible electron transfer, no chemical complications</td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s = 500$</td>
</tr>
<tr>
<td>II. Reversible electron transfer followed by a reversible chemical reaction—ECE mechanism</td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s$</td>
</tr>
<tr>
<td></td>
<td>$R \xrightarrow{k_1} Z$</td>
<td>$i_s$</td>
</tr>
<tr>
<td>III. Reversible electron transfer followed by an irreversible chemical reaction—CE mechanism</td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s$</td>
</tr>
<tr>
<td></td>
<td>$R \rightarrow Z$</td>
<td>$i_s$</td>
</tr>
<tr>
<td>IV. Reversible chemical reaction preceding a reversible electron transfer—CE mechanism</td>
<td>$Z \xrightarrow{k_1} O$</td>
<td>$i_s$</td>
</tr>
<tr>
<td></td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s$</td>
</tr>
<tr>
<td>V. Reversible chemical reaction preceding an irreversible electron transfer—CE mechanism</td>
<td>$Z \xrightarrow{k_1} O$</td>
<td>$i_s$</td>
</tr>
<tr>
<td></td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s$</td>
</tr>
<tr>
<td>VI. Reversible electron transfer followed by an irreversible regeneration of starting material—catalytic mechanism</td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s$</td>
</tr>
<tr>
<td></td>
<td>$R + Z \rightarrow O$</td>
<td>$i_s$</td>
</tr>
<tr>
<td>VII. Irreversible electron transfer followed by an irreversible regeneration of starting material</td>
<td>$O + ne \rightarrow R$</td>
<td>$i_s$</td>
</tr>
<tr>
<td></td>
<td>$R + Z \rightarrow O$</td>
<td>$i_s$</td>
</tr>
<tr>
<td>VIII. Multiple electron transfer with intervening chemical reaction—ECE mechanism</td>
<td>$O + n_e \rightarrow R$</td>
<td>$R \rightarrow Y$</td>
</tr>
<tr>
<td></td>
<td>$Y + n_e \rightarrow Z$</td>
<td>$i_s$</td>
</tr>
</tbody>
</table>
Figure 4. Ratio of anodic to cathodic (or reverse to forward) peak currents as a function of rate of voltage scan for various electrochemical mechanisms. (Adapted with permission from Anal. Chem., 36, 706-723 (1964).)

Figure 5. Rate of shift of potential as a function of scan rate for various electrode mechanisms. (Adapted with permission from Anal. Chem., 36, 706-723 (1964).)

Figure 6. Methods for determining the proper baseline for measurement of the peak current for the reverse scan. (a) Recording the signal versus time and stopping the first scan at $E_s$. (b) Using an X-Y recorder and stopping the scan at $E_s$ until $i$ approaches a steady state before scanning back. (c) Parameters used for calculation of the current ratio using Nicholson's method, eqn. (10).

There are occasions when neither of these two methods is convenient. Nicholson (19) has indicated that the proper current ratio can also be calculated using the following equation.

$$\frac{i_{pa}}{i_{pc}} = \frac{(i_{pa})_0}{i_{pc}} \frac{0.485(i_{pa})_0 + 0.086}{i_{pc} + 0.086} \quad (8)$$

In eqn. (8), $i_{pc}$ is the peak current for the forward process; $(i_{pa})_0$ is the absolute current at the switching potential; and $(i_{pa})_0$ is the uncorrected return peak current measured from the current axis. (See Fig. 6c.)

There are some systems in which a coupled chemical reaction yields electroactive by-products. In these cases multiple scans can be beneficial. For example, the product of electron transfer in the oxidation of aniline is thought to be a free radical that very rapidly dimerizes (13).

$\text{p-aminodiphenylamine (III)}$ that is formed is much more easily oxidized at the applied potential and a further two electron oxidation occurs.

Measurement of the peak current is fairly simple for the forward scan. The proper baseline can be obtained by recording the background current for a scan without the analyte under the same conditions (same electrolyte, surface pretreatment, etc.). The reverse scan is more complicated since the electrolysis for the forward process still contributes to the total current until the scan has passed the foot of the (forward) wave again. The generally accepted approach is to assume that the contribution of the forward process to the total current continues to decrease with the square root of the time during the reverse scan. The baseline curve for the return scan can be obtained by stopping the forward scan at the switching potential with the recorder sweeping along the $x$-axis as a function of time. This is shown in Figure 6a.

A second approach is to stop the scan at a convenient spot (at least $35 \text{ mV}$ past $E_s$ for the forward scan) and hold the potential until the current is relatively constant. The appropriate baseline is shown in Figure 6b (13).
needed at the working electrode no current flows through the reference electrode and its potential remains constant. (For discussion of reference electrode see references (25) and (26).) A three-electrode system also permits one to minimize voltage errors due to ohmic (or IR) loss through solution by placing the reference electrode close to the working electrode surface. The voltage represented by the product of the current and uncompensated resistance (mainly the solution resistance between the reference and working electrodes) is wasted and does not appear across the electrode/solution interface. Since the peak current increases with the square root of the scan rate, the voltage error increases at the same rate. In cases where the error is of the order of millivolts, the peaks from even a totally reversible redox couple will appear to separate as though the system were quasi-reversible. Therefore the experimenter should be cautious about drawing conclusions concerning electron transfer kinetics when either the current or uncompensated resistance is large. Some manufacturers incorporate a positive feedback circuit in their equipment to compensate for IR loss.

Another source of error in the applied voltage arises from the variation in the rates at which ions diffuse across the ion bridge separating the reference electrode from the sample solution. The net difference in the movement of cations compared to anions results in a charge separation and, therefore, an electrochemical potential difference. These junction potentials can be minimized by choosing supporting electrolyte ions with similar diffusion coefficients (such as K⁺ and Cl⁻).

Mercury working electrodes are limited to the negative potential range. Platinum and various carbon electrodes are popular for performing oxidations. However, solid electrodes are susceptible to adsorption, or surface fouling, and surface oxidation. For example, platinum forms an oxide film that shows a large reduction peak near +0.8 V in 0.5 M H₂SO₄ versus the normal hydrogen electrode. Fortunately, a surface current can be identified easily as such since the peak height is directly proportional to the scan rate. Often, judicious choice of solution conditions and electrode pretreatment can minimize this problem.

In summary, cyclic voltammetry is a convenient tool for obtaining qualitative information about electron transfer processes. It is also a rapid method for obtaining good estimates of formal reduction potentials, formation constants and, sometimes, the number of electrons transferred per reactant molecule and rate constants, if the user is aware of its limitations.

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**Literature Cited**


