11

ROTATED DISK ELECTRODE

Purpose
The aim of this experiment is to use one method of cyclic voltammetry, the
rotated disk voltammetry, to determine the diffusion coefficient of the analyte.

Experimental Apparatus
  Potentiostat
  Pine Instrument Company AFMSRX Analytical Rotator
  Platinum rotated disk electrode (mounted on arbor)
  Three electrode cell (with large opening for rotated disk electrode)
  Platinum auxiliary electrode
    SCE (saturated calomel electrode) reference electrode
    Alumina polishing solution

Reagents and Chemicals

<table>
<thead>
<tr>
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<th>per expt</th>
<th>per 20 expts</th>
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</thead>
<tbody>
<tr>
<td>potassium ferricyanide, K$_3$Fe(CN)$_6$ (329.26 g/mol)</td>
<td>250 mg</td>
<td>5 g</td>
</tr>
<tr>
<td>potassium nitrate, KNO$_3$ (101.11 g/mol)</td>
<td>30 g</td>
<td>600 g</td>
</tr>
<tr>
<td>ultrapure water</td>
<td>300 ml</td>
<td>6 l</td>
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Description

A general definition for the term voltammetry (recall exp. 10) is any
electrochemical technique that involves controlling the potential of an electrode
while simultaneously measuring the current flowing through that electrode. The
electrode in question is usually called the working electrode in order to
distinguish it from other electrodes that are present in the electrochemical cell.
Voltammetry is usually performed by connecting an electrochemical potentiostat
to an electrochemical cell. The cell contains a test solution and three electrodes:
working, reference, and auxiliary (also known as counter). Special electronic
circuitry within the potentiostat permits the working electrode potential to be
controlled with respect to the reference electrode without any appreciable current
flowing through the reference electrode. Rather, the current is forced to flow
between the working electrode and the auxiliary electrode at such a magnitude,
that the desired potential is maintained between the working and the reference
electrodes. This unusual arrangement has two principle benefits. First, the
reference electrode is protected from internal electrochemical changes caused
by current flow. Second, measurement errors related to the resistance of the test
solution are kept to a minimum.
There are quite a number of voltammetric techniques. Each differs in the precise manner that the working electrode potential is changed during the experiment. In some techniques, a potential sweep is applied to the working electrode, in others; a sudden potential step or complex pulse sequence is used. Another distinguishing feature is whether or not the solution is moving with respect to the surface of the working electrode. In most cases, the solution is motionless, but there exist many hydrodynamic methods in which solution moves toward the electrode along a well-defined flow pattern. The rotated disk electrode is an example of a hydrodynamic method.

The analyte used in this experiment is the ferricyanide anion, Fe(CN)$_6^{3-}$, which contains an iron atom in the +3 oxidation state. At the surface of a working electrode, a single electron can be added to the ferricyanide anion. This causes it to be reduced to the ferrocyanide anion, Fe(CN)$_6^{4-}$, which contains an iron atom in the +2 oxidation state. This simple one electron exchange between the analyte and the electrode is very well behaved, and it is reversible. This means that the analyte can be easily reduced to Fe(CN)$_6^{4-}$ and then easily oxidized back to Fe(CN)$_6^{3-}$ again.

A pair of analytes differing only in oxidation state is known as a redox couple. The electrochemical half-reaction for the Fe(CN)$_6^{3-}$ / Fe(CN)$_6^{4-}$ redox couple can be written as follows:

$$\text{Fe(CN)}_6^{3-} + e^- \leftrightarrow \text{Fe(CN)}_6^{4-}$$  \hspace{1cm} (1)

The formal potential associated with this half-reaction is near +400 mV vs. the normal hydrogen electrode (NHE). If the working electrode is held at a potential more positive than +400 mV, then the analyte tends to be oxidized to the Fe(CN)$_6^{3-}$ form. This oxidation at the working electrode causes an anodic current to flow (i.e., electrons go into the electrode from the solution). At potentials more negative than +400 mV, the analyte will be reduced to Fe(CN)$_6^{4-}$. This reduction at the working electrode causes a cathodic current to flow (i.e., electrons flow out of the electrode into the solution).

**Rotated Disk Voltammetry**

The working electrode potential is slowly swept back and forth across the formal potential of analyte. The working electrode itself is rotated at a very high speed. This rotational motion sets up a well-defined flow of solution towards the surface of the rotating disk electrode. The flow pattern is akin to a vortex that literally sucks the solution (and the analyte) towards the electrode.

Experimental results are generally plotted as a graph of current vs. potential, and a typical rotated disk voltammogram is shown in Figure 1. The voltammogram exhibits a sigmoidal shaped wave, and the height of this wave provides the analytical signal.
It is important to note that the layer of solution immediately adjacent to the surface of the electrode behaves as if it were stuck to the electrode. While the bulk of the solution is being stirred vigorously by the rotating electrode, this thin layer of solution manages to cling to the surface of the electrode and appears (from the perspective of the rotating electrode) to be motionless. This layer is called the \textit{stagnant layer} in order to distinguish it from the remaining bulk of the solution.

Analyte is conveyed to the electrode surface by a combination of two types of transport. First, the vortex flow in the bulk solution continuously brings via convection fresh analyte to the outer edge of the stagnant layer. Then, the analyte moves across the stagnant layer via simple molecular diffusion. The thinner the stagnant layer, the sooner the analyte can diffuse across it and reach the electrode surface. Faster electrode rotation makes the stagnant layer thinner. Thus, faster rotation rates allow the analyte to reach the electrode faster, resulting in a higher current being measured at the electrode.

The \textit{Levič} equation predicts the current observed at a rotating disk electrode. This equation takes into account both the rate of diffusion across the stagnant layer and the complex solution flow pattern. In particular, the \textit{Levič} equation gives the height of the sigmoidal wave observed in rotated disk voltammetry. The sigmoid wave height is often called the \textit{Levič} current, \(i_L\), and it is directly proportional to the analyte concentration, \(c\). The \textit{Levič} equation is written as

\[
 i_L = (0.620) n F A D^{2/3} \omega^{1/2} \nu^{-1/6} c \tag{2}
\]

where \(\omega\) is the angular rotation rate of the electrode (rad/s) and \(\nu\) is the kinematic viscosity of the solution (cm\(^2\)/s). The kinematic viscosity is the ratio of the solution viscosity to its density. For pure water, \(\nu = 0.0100\) cm\(^2\)/s, and for the solvent used in this experiment (1.0 mol/l KNO\(_3\)), \(\nu = 0.00916\) cm\(^2\)/s. The electrochemically usual parameters are \(n\), the number of electrons exchanged in the redox process, \(A\), the electrode area given in cm\(^2\), \(D\), diffusion coefficient in cm\(^2\) s\(^{-1}\), \(F\) the Faraday constant and \(c\) is the bulk concentration, but given in mol/cm\(^3\).

\textbf{Procedure}

All glassware used for electrochemistry should be as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. A supply of ultrapure water is required for proper solution preparation. The ultrapure water can be either deionized, ultrafiltered (DIUF) water or "conductivity water" or "HPLC grade" water.

It is absolutely essential that proper care be taken of the electrodes. The working rotated electrode should not be left in any solution for prolonged period of time and NEVER OVERNIGHT when not used. Also, the level of the solution
should not reach above the upper Teflon sleeve under which are located the mounting screws. When the electrode is rotating, the level of the solution will decrease. Once the rotation stops, the level might rise above the safe limit. Hence the argument for not leaving the electrode that is not used in the solution. Additionally, there might be slight seepage between the electrode and the sleeve, eventually corroding the inside connections.

A. Solution preparation

The two solutions required for this experiment should be prepared by the student. The electrolyte solution is 1.0 mol/l potassium nitrate in water. This solution provides an electrically conductive solvent suitable for use with voltammetry. The analyte solution is a 6.4 mmol/l solution of potassium ferricyanide made using the electrolyte solution as the solvent.

1) Electrolyte solution (250 ml)

Prepare a very clean 250 ml volumetric flask being sure that the last three rinsings of this flask are done with ultrapure water. Weigh exactly approximately 25.30 g of KNO₃ and transfer it quantitatively to the flask. Fill the flask with about 200 ml of ultrapure water and allow the potassium nitrate to dissolve. Once dissolution is complete, fill the flask "to the line" using ultrapure water and mix well. The resulting solution is about 1.0 mol/l KNO₃.

2) Analyte solution (100 ml)

Prepare a very clean 100 ml volumetric flask being sure that at least the last rinsing of this flask is done with ultrapure water. Using a sensitive microbalance, weigh as exactly as possible 210.7 mg of potassium ferricyanide, K₃Fe(CN)₆, and transfer it into the flask. Fill the flask with about 75 ml of electrolyte solution and allow the K₃Fe(CN)₆ to dissolve. Once dissolution is complete, fill the flask "to the line" using electrolyte solution and mix well. The resulting solution should have an analyte concentration of 6.4 mmol/l, however a more accurate concentration can be computed, based on the actual mass of K₃Fe(CN)₆ that was used to prepare the solution.

B. Background scan

A simple background voltammogram of the pure electrolyte solution is a good way to confirm the purity of the solution, the cleanliness of the glassware, and the preparation of the polished working electrode all in a single step. Any
electroactive impurities from the solvent or dirty glassware will show up as unexplained peaks in the background scan. In addition, a fouled or improperly polished electrode surface usually causes a larger background current.

3) Obtain a platinum disk working electrode suitable for mounting in the electrode rotator apparatus. Be sure to note the surface area of the disk in square centimeters in your lab notebook. Polish the electrode as needed using an alumina slurry on a polishing cloth. After polishing, wash the electrode with ultrapure water and wipe clean. The electrode surface should be mirror bright and free of defects.

4) Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode. Carefully mount the platinum disk working electrode in the rotator and then lower it into the cell. Note that the electrode should not be rotating during the background scan.

5) Fill the electrochemical cell with pure electrolyte solution. If desired, the oxygen in the cell may be purged by first bubbling nitrogen through the solution and then continuously blanketing the solution with a steady flow of nitrogen for the duration of the experiment. Oxygen is unlikely to interfere with this experiment, however.

6) When using the Pine potentiostat, set the Pine potentiostat program as follows: Segments 10, Initial 0.2 V, rise up to 0.4 V, low –0.3, final 0.2 V, sweep 0.05 V/s, current – auto.

7) Once the experiment settings have been adjusted to match those in part 6) start the scan by clicking the “Perform” soft button. The resulting cyclic voltammogram should be relatively featureless and without significant peaks. At negative potentials, the voltammogram should exhibit some cathodic current due to the reduction of hydronium ion. If the background current is excessive, the electrode should be polished. It is also possible that the electrolyte solution is contaminated, which would require preparing a new solution.

8) After acquiring a satisfactory background voltammogram, label the axes appropriately and save the graph.

Next, several rotated disk voltammograms are obtained using various rotation rates.

9) (Switch to the yellow solution.) Turn on the electrode rotator and adjust the rotational speed of the electrode to 4000 rpm. Make certain that the flow of solution in the cell is non-chaotic and that
the surface of the rotating electrode remains immersed in the solution.

10) Turn the scan on (“Perform”) to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +400 mV to −300 mV when using a calomel electrode as the reference. The wave should have a sigmoidal appearance rather than the asymmetric peak shape typically observed during cyclic voltammetry. On the return sweep, the current signal should retrace the path followed during forward sweep. Fig. 1 shows a typical rotated disk voltammogram for potassium ferricyanide. Note that the positive orientations for both the potential and current may be different on the actual plot.

![Rotated Disk Voltammogram](image)

**Figure 1: A Rotated Disk Voltammogram for Ferricyanide**

11) After acquiring a satisfactory voltammogram, save the data for further processing and graphing. Note the units, in particular those for current, as the saved numbers are stripped of any units. Save the data for further evaluation or more conveniently, create a spreadsheet to use the same sheet for the additional experiments (12).

12) In addition to the voltammogram just acquired at 4000 rpm, repeat step 10 and acquire voltammograms at these other seven rotation rates: 3200, 2500, 1800, 1300, 900, 600 and 400 rpm. In each case, be sure to note the rotation rate and the Levič current in your laboratory notebook.

**Data Analysis**

a) Using the Levič currents (sigmoid heights) from the series of rotated disk voltammograms acquired at various rotation rates,
prepare a plot of the Levič current versus the square root of the angular rotation rate. Note that the rotation rates may have to be converted from units of rpm to radians per second using the relationship \( \omega = \frac{2 \pi}{60} \).

b) Perform a linear least squares analysis on the data to find the equation of the best straight line that fits the data.

c) Use the slope of the line together with the Levič equation to estimate the diffusion coefficient for the ferricyanide anion. Pay close attention to proper units and report your answer in cm\(^2\)/s. Note that the kinematic viscosity for 1.0 mol/l KNO\(_3\) is 0.00916 cm\(^2\)/s.

Report Questions

1) List the diffusion coefficient result that you obtained with appropriate unit and error.

2) Compare the result with that in available literature. If a voltammetry laboratory was performed prior to this one during the course, compare the values from RDE and cyclic voltammetry. Which of the two appears more reliable?