Laboratory session 2:

Potentiometric and Voltammetric Study of the Ferricyanide/Ferrocyanide Redox Couple in Aqueous Solution of Potassium Chloride

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Objectives. The objective of this lab session is the potentiometric and voltammetric study of the $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ redox couple. The potentiometric study allows us to determine the formal potential of this redox couple in equilibrium conditions. Conversely, the voltammetric study allows this same variable to be measured dynamically. Furthermore, it also allows the diffusion coefficient of $Fe(CN)_6^{3-}$ ions to be calculated, since the reduction and oxidation rates are controlled by diffusion. Finally, it allows the system to be evaluated in terms of electrochemical reversibility.

Key concepts: Potentiometry, cyclic voltammetry, diffusion, reversibility, formal potential

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1. Introduction

In the lab session, the electrochemical behavior of potassium ferrocyanide in chloride solution is studied by cyclic voltammetry and potentiometry. The objective of this practical is to obtain kinetic and thermodynamic information from the equilibrium:

$$Fe(CN)_6^{3-} + 1e^- \longleftrightarrow Fe(CN)_6^{4-} \qquad (1a)$$

$$K_3\left[Fe(CN)_6\right] + K^+ + 1e^- \longleftrightarrow K_4\left[Fe(CN)_6\right] \qquad (1b)$$

Potentiometry is a static, or equilibrium, technique that gives information about an electrochemical system without passing an electric charge through the electrochemical cell (i = 0). There are no redox reactions that change the system's composition (equilibrium). This technique allows the formal potential of a redox couple to be estimated by measuring the electromotive force (e.m.f, ε) of a cell comprised of two electrodes: a working electrode (where the reaction of interest is occurring) and a reference electrode which has a stable and wellknown potential. The e.m.f. is the difference in electric potential of the cell measured when the electron flow from the anode to the cathode is zero.

In the lab session, the following electrochemical cell will be used:

$$|Ag|AgCl(s)|KCl(3M)||Fe(CN)_6^{3-}(aM),\ Fe(CN)_6^{4-}(bM)|Pt$$

The electromotive force of reversible systems, such as the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple, is described by the empirical Nernst equation:

$$\varepsilon_{medido} = E^{o'} - E_{AgCl/Ag} - \frac{RT}{nF}\ln\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]} \qquad (2)$$

where $E^{o'}$ is the formal potential of the ferricyanide/ferrocyanide redox couple, $E_{AgCl/Ag}$ the potential of the AgCl/Ag electrode with respect to the normal hydrogen electrode (reference electrode), R the gas constant, T the absolute temperature, F the Faraday constant and n the number of exchanged electrons. Thus, $E^{o'}$ is determined by plotting e.m.f. versus ln([ferrocyanide]/[ferricyanide]).

Voltammetry is a dynamic technique that gives kinetic and thermodynamic information from intensity-potential curves, i-E. To plot these curves, the IUPAC sets the criteria that cathodic currents (reduction) are negative and anodic currents (oxidation) positive. In many books, especially American ones, the opposite criterion is followed.

The technique directly determines the rate at which a reaction occurs on an electrode (electron transfer reactions), given that it measures the current i at any given time, which is directly proportional to the reaction rate:

$$|i| = \left|\frac{dq}{dt}\right| = |z|F\,\frac{dn}{dt} \qquad (3)$$

where q is the circulating charge, z the charge of the ion undergoing the charge/discharge process on the electrode, and n is the number of moles of exchanged ions.

There are three electrodes in most cyclic voltammetry experiments: the working electrode (W), at which the reaction happens; the reference electrode (R), the electrode to which the potential of the working electrode is referenced (the current that passes between the working and reference electrodes is nearly zero); and the auxiliary electrode (A) that ensures that no current runs through the non-polarizable reference electrode. Normally, cyclic voltammetry is applied so that the electric potential difference between the working electrode (W) and the reference electrode (R) varies linearly with time between the initial value (E_i, starting potential) and the final value of the forward scan (E_{v1}, first switching potential). At this point, the scan direction is then reversed, and the potential is swept back to the initial potential, or to a different one (second switching potential, Figure 1). During the potential scan, the current at the working electrode is plotted versus the applied potential difference to give the cyclic voltammogram trace. This trace depends on both faradaic and nonfaradaic processes, as well as the nature and shape of the electrode. Therefore, it is not possible to obtain an analytical expression for the dependence of the current intensity with respect to the potential applied. Only mathematical expressions for the peak intensity and the corresponding potential can be obtained, based on variables such as the scan rate, the concentration of electroactive species and their respective diffusion coefficients.

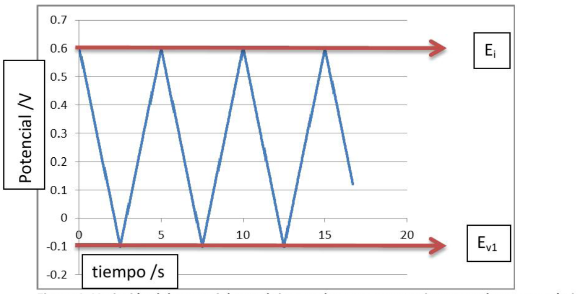

Figure 1. Variation of potential with time during a voltammetric experiment.

The important parameters of a cyclic voltammogram are: the potential of the cathodic (**E_{pc}**) and anodic (**E_{pa}**) peaks, the intensity of the cathodic (**i_{pc}**) and anodic (**i_{pa}**) peak, the starting potential and the switching potential. The half-peak potential ($E_{p/2}$) may also be of interest to study electrochemical systems. $E_{p/2}$ is the potential corresponding to half the peak current. Figure 2 shows how to determine the peak and half-peak potentials and currents.

In our case, we will study the process of reducing ferricyanide to ferrocyanide on the working electrode. In a simplified scheme, the ferricyanide in the bulk solution will approach the working electrode where the reduction takes place, then ferrocyanide ions will also diffuse into the bulk solution. Thus, the electrical current is an appropriate measure of this overall reaction rate, given that this is directly proportional to the amount of substance produced at each electrode, according to Faraday's law of electrolysis.

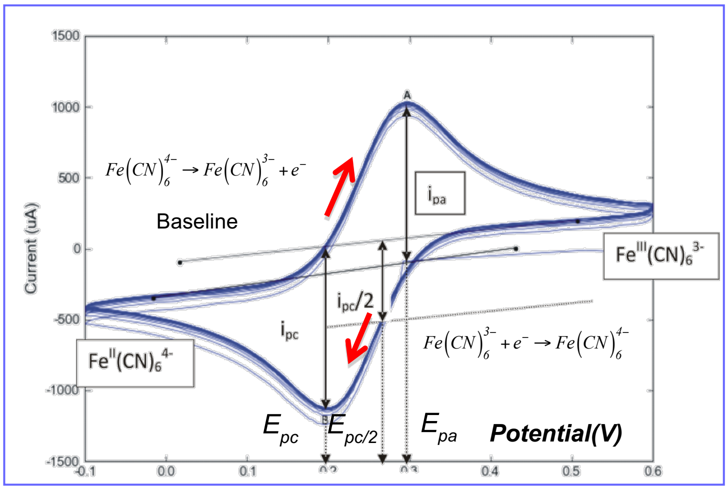

Figure 2: Obtained voltammetric curves. Voltammetric criteria for determining peak intensities and potentials and half-peak potentials.

In a first approach, it is assumed that the system is reversible, i.e. the reaction is reasonably fast in both directions. Consequently, the surface concentration of reactants and products are maintained close to their equilibrium values, which can be calculated using the Nernst equation. Furthermore, it is also assumed that the bulk concentrations are constant and that electron transfer is a diffusion-controlled reaction. In these conditions, the ***Randles–Sevcik*** equation describes the effect of scan rate and diffusion coefficient on the peak current:

$$i_p = 0.4463 nFA\,c\left(vD\frac{nF}{RT}\right)^{1/2} \qquad (4)$$

where i_p is the peak intensity (mA), v the scan rate (V/s), n the number of electrons transferred in the surface reaction, A the electrode area (cm^2), D the diffusion coefficient of ferricyanide ions (cm^2/s), and c its concentration in the bulk solution (mol/L). At room temperature (25 ºC), it becomes:

$$i_p\,(mA) = (2.6865\times10^5)\,A\,D^{1/2}\,c\,v^{1/2} \qquad (5)$$

Using the relationships defined by this equation, the diffusion coefficient of electroactive species (ferricyanide) can be determined with a plot of i_p vs. $v^{1/2}$, which should be linear when the system is reversible. Thus, the gradient of this plot provides information about the diffusion coefficient of ferricyanide ions. The formal potential can be estimated from the equation:

$$E^{o'} = \frac{1}{2}(E_{pc} + E_{pa}) \qquad (6)$$

In a reversible voltammogram, both oxidation and reduction waves appear in a symmetric form with respect to the potential axis at a similar peak potential. If the reduction process is chemically and electrochemically reversible, the difference between the anodic and cathodic peak potentials, called the peak-to-peak separation (ΔEp), is 56.5/n mV at 25°C (2.22RT/nF), and the width at half max on the forward scan of the peak is 59 mV. Regarding the current, reversible couples are characterized by $i_{pa}/\,i_{pc} \approx 1$. Finally, this current ratio and the peak potentials of reversible waves are independent of the scan rate.

In contrast, many redox processes observed by cyclic voltammetry are quasi-reversible or non-reversible. This irreversibility is indicated by $i_{pa}/\,i_{pc} \neq 1$. ΔEp also increases with an increase in the scan rate. The individual peaks are reduced in size and widely separated. Generally, the peak-height decreases as the electron transfer becomes slower. The peak also becomes less sharp than in the reversible case. Furthermore, totally irreversible systems are characterized by a shift of the peak potential with the scan rate. This is because the rates of interfacial electron transfer are slower than the rates of mass transport to and away from the electrode.

Note: electrochemically reversible processes in which the electron transfers are fast, and the processes follow the Nernst equation, are often referred to as *Nernstian*.

2. Experimental Procedure

2.1 Solutions

- *1 M KCl solution*
- 0.17 M $K_3[Fe(CN)_6]$ *solution*
- 0.25 M $K_4[Fe(CN)_6]$ *solution*
- *10% NH_3 solution (electrode cleaning solution)*

2.2 Potentiometric determination of the formal potential, E°'

Potentiometric measurements are carried out using a four-neck round-bottom flask. To run the assay, insert the working Pt electrode (1cm in diameter) and the reference Ag/AgCl electrode, and fill the flask with 25mL of 1M KCl and 5mL of 0.17M $K_3[Fe(CN)_6]$ until the ends of the electrodes are submerged. The glass stirring rod is inserted into the third neck, and the fourth is reserved for successive additions of 1 mL of 0.25M $K_4[Fe(CN)_6]$.

When the first addition of potassium ferrocyanide is made, add the stirring rod and stir the solution to homogenize the concentration between the electrode surface and the bulk solution. Then, the e.f.m. is measured in triplicate. The potentiometer is prepared for this purpose by pressing the mV button three times (without stirring the solution) and taking the measurement once the reading has stabilized. The operation is complete after the addition of 8 mL of potassium ferrocyanide.

The formal potential, E°', is then determined from Nernst's empirical law, plotting e.m.f. vs. ln([ferrocyanide]/[ferricyanide]). Note: it is necessary to previously measure the solution temperature.

2.3 Voltammetric determination of the diffusion coefficient, D.

***a*) Cell preparation**

- Clean the working electrode (Pt disk electrode): place the electrode in a beaker and fill the beaker with 10% ammonia solution until the electrode is covered. Soak the electrode for a few minutes and rinse the electrode thoroughly with distilled water to remove all traces of the cleaning solution.
- Add 25mL of 1M KCL and 0.5mL of 0.17M ferricyanide into the four-neck round-bottom flask. Homogenize the solution.
- Introduce the reference electrode, the Pt disk working electrode, and the Pt wire auxiliary electrode into the four-neck round-bottom flask

***b*) Connection of the three-electrode cell to the potentiostat**

The connection cables and the electrodes are labeled. Connect the Ag/AgCl (3M KCl) reference electrode to the blue cable, the Pt disk working electrode to the red cable and the Pt wire auxiliary electrode to the white cable.

***c)* Performing voltammetric assays**

We will register voltammograms at a range of scan rates

a) Connect the portable potentiostat µStat 400, Metrohm-DropSens, pressing the blue button. A green pilot light will turn on
b) Turn on the computer
c) Run *Dropview*

d) Connect the software to the device by clicking on

e) Click *New Method*

f) Select *Cyclic Voltametry*

Introduce the following parameters:
Ebegin (V): 0.6 (starting potential)
Evtx1 (V): -0.1 (switching potential)
Evtx2 (V): 0.6 (second switching potential, if it does not exist then it is equal to the starting potential)
Estep: 0.002 (potential step, 2 mV)
Srate (V/s): 0.5 (scan rate)
Nscans:10

g) The voltammogram can be started, paused or stopped with

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h) If necessary, select automatic or manual scale by pressing

i) The plots are saved in the *File* menu, using *Save visible curves*

j) Repeat for cyclic voltammogram experiments at the following scan rates: *0.4 V* s^{-1}, *0.3 V* s^{-1}, *0.25 V* s^{-1}, *0.2 V* s^{-1}, *0.15 V* s^{-1}, *0.1 V* s^{-1}, 0.06 *V* s^{-1}

k) Copy all files to a Pen Drive or External Hard Drive for later use

l) Select the *Curves* tab. The performed scans will be shown

m) Select the *Measurements* tab. Quantitative electrochemical analysis can be carried out by clicking on

***d*) Cleaning of electrodes**

At the end of the practical, put the Pt disk electrodes into a beaker with the 10% ammonia solution.

3. Results

3.1 Potentiometric determination of formal potential, Eº'

Derive the formal redox potential of the ferricyanide/ferrocyanide couple from the potentiometric data.

3.2 Voltammetric determination of the diffusion coefficient, D

1- Measure the peak potential and intensities of the anodic and cathodic peaks and their respective half-peak potentials at the different scan rates. Derive the formal potential from E_{pc} and E_{pa}

2- Calculate the value of the formal potential, Eº', from the values of Epc and Epa.

3- Evaluate the reversibility of the system

4- Plot the dependence of the peak intensity (i_p) with the scan rate ($v^{1/2}$) and estimate the diffusion coefficient of ferricyanide ions in aqueous potassium chloride solution (*Randles-Sevcik* equation, eq.(4))

4. Questions

4.1 Preliminary Questions

1. Find information on cyclic voltammetry.

2. Find information on the $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ redox couple.
   What is the diffusion coefficient of ferricyanide ions in aqueous potassium chloride solution? What is the normal redox potential of this couple? Provide the values found with their bibliographic reference.

3. Before starting the practice, carefully read the article cited in reference [8]. In particular, pay attention to the subsections: "Cyclic Voltammetry", "Cyclic Voltammetry Profile", "Understanding the "Duck" Shape: Introduction to the Nernst Equation" and "Importance of the Scan Rate".

4.2 Post-laboratory Questions

1. Explain the electrochemical structure and behavior of the AgCl/Ag/xM KCl reference electrode. Why is it considered a reference electrode?

2. What does the slope and y-intercept of the potentiometric straight line depend on?

3. Why is KCl added to the ferricyanide/ferrocyanide solutions?

4. Would it be possible to derive the formal potential of the ferri/ferrocyanide couple from voltammetry data?

5. Assess the possibilities that cyclic voltammetry and potentiometry offer as quantitative and qualitative analysis techniques. Which parameters would be of interest in each case?

6. Why is it necessary to subtract the baseline before the voltammetric peak-analysis is executed?

7. Why are there peaks in a cyclic voltammogram?

8. In cyclic voltammetry, can reversibility be lost as the scan rate increases?

9. Ohmic drop is a drop in potential due to resistance of the solution; that is, the difference in potential required to move ions through the solution. Using Ohm's law, this drop can be calculated to be equal to the product of the current and the uncompensated resistance. Taking this into account, does the ohmic drop influence the shape of voltammograms?

Appendix A. Material

Shared material on each table:
- One thermometer
- Two portable potentiostats µStat 400, Metrohm-DropSens
- Two potentiometers (milli-voltmeter)
- Two personal computers connected to the network

Material for each pair:
- One four-neck round-bottom flask
- One glass rod
- One 1-mL graduated pipette, one 5-mL volumetric pipette and one 25-mL volumetric pipette
- One Ag/AgCl (3M KCl) reference electrode
- One Pt disk electrode (1cm in diameter).
- One Pt wire auxiliary electrode

Products (previously prepared):
- 1M KCl
- 0.17 M $K_3[Fe(CN)_6]$
- 0.25 M $K_4[Fe(CN)_6]$
- 10 % NH_3 (electrode cleaning solution)

References

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