Theoretical Concepts and Applications of a Rotating Disk Electrode

J. Nikolic, E. Expósito, J. Iniesta, J. González-García, and V. Montiel*
Departamento de Química Física, Universidad de Alicante, Ap. 99, 03080 Alicante, Spain; **vicente.montiel@ua.es*

Cathodic and anodic processes are made up of different kinds of heterogeneous chemical reactions that usually involve the transfer of electrons across the interface between a solid and an adjacent solution phase. Obviously, the continuous conversion of reactant to product requires the supply of reactant to the electrode surface and the removal of product. In addition, mass transport usually becomes the dominant consideration when dilute solutions are dealt with.

When emphasizing the importance of mass transport processes, the supply and removal of reactant and product contribute to three different processes. Three forms of mass transport can be important in electrochemistry: (i) diffusion, defined as the movement of a species due to a concentration gradient; (ii) convection, in which the movement is due to external mechanical energy—for example, electrode rotation; (iii) migration due to a potential gradient—that is, only the charged species is affected (*1*, *2*).

In laboratory experiments, it is very interesting to work under experimental conditions in which the mass transport regime is totally defined and well known, and describable by a set of solvable mathematical equations. A rotating disk electrode (RDE) is a device that creates a totally defined solution flow pattern in which the mass transport of the species is almost completely due to convection (*2–4*). This property allows the RDE to be used to calculate parameters related to mass transport, such as the diffusion coefficient of the various electroactive species (D_i). The calculated values were $D_{\mathrm{Fe(CN)_6}^{3-}} = 2.6 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$, $D_{\mathrm{Fe(CN)_6}^{4-}} = 2.7 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$. The forced convection causes an important diminution in the Nernst diffusion layer, which significantly increases the limiting current density.

In this paper, voltammograms related to the oxidation and reduction reactions associated with the redox couple $\mathrm{Fe(CN)_6}^{3-}/\mathrm{Fe(CN)_6}^{4-}$ were recorded by using an RDE of vitreous carbon. The objective is to demonstrate to students the equations that govern mass transport in an RDE and show them the influence of mass transport and charge transfer in electrochemical reactions. They will calculate the diffusion coefficient of $\mathrm{Fe(CN)_6}^{3-}$ and $\mathrm{Fe(CN)_6}^{4-}$. Finally, they will become familiar with very important techniques and tools in basic electrochemistry, such as linear sweep voltammetry applied to the RDE electrode.

The following laboratory experiment was developed for advanced students of chemistry or electrochemical engineering. It was designed to be performed in approximately four hours by groups of two or three people. The students must present a full report on the experiment at the end. The report consists of the experimental plan, a brief summary of the theory behind the experiment, presentation of data and data analysis, a discussion of the results, and finally, any suggestions that could improve the experiment.

Theoretical Concepts

An RDE is a polished disc surrounded by an insulating sheath of substantially larger diameter. The structure is rotated about an axis perpendicular to the surface of the disc electrode. This movement of rotation leads to a very well defined solution flow pattern, as can be seen in Figure 1. The rotating structure acts as a pump, pulling the solution upward and then throwing it outward.

According to the Nernst diffusion layer model, the electrolyte can be divided into two zones (Fig. 2):

1. A first region close to the surface of the electrode with thickness δ, where it is assumed that there is a totally stagnant layer and thereby diffusion is the only mode of mass transport.
2. A second zone outside the first region where a strong convection occurs, and all species concentrations are constant.

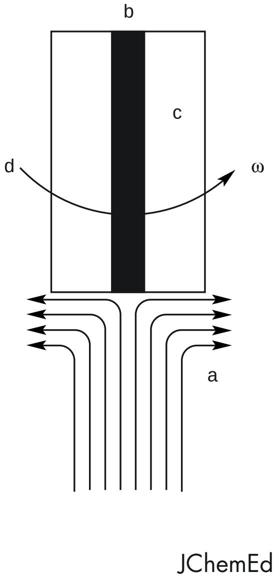

Figure 1. Solution movement caused by rotation of an RDE. a: flow of electrolyte solution; b: vitreous carbon electrode; c: RDE body; d: direction of electrode rotation.

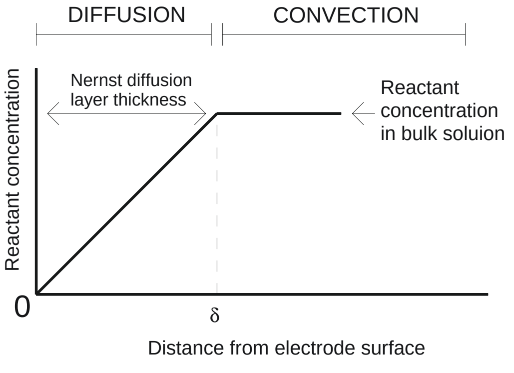

Figure 2. Representation of the Nernst diffusion layer profile model.

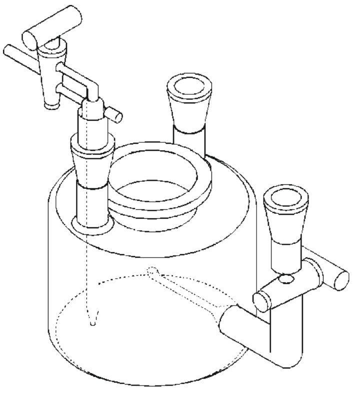

Figure 3. Scheme of the voltammetric cell.

In these experimental conditions Levich deduced an expression relating the thickness (δ) of the first region with experimental variables such as the diffusion coefficient (D) and the rotation speed of the electrode (ω):

$$\delta = 1.61 \times \nu^{0.166} \times D^{0.33} \times \omega^{-0.5} \tag{1}$$

The Nernst diffusion layer concept permits a trivial derivation of the current density at an RDE for potentials when the electrode reaction is mass-transport controlled. Since the surface concentration of the electroactive species is zero, the limiting current density (j_L) is given by

$$j_L = n \times F \times D \times \frac{c}{\delta} \tag{2}$$

Finally, eqs 1 and 2 lead to the Levich equation:

$$j_L\left(\mathrm{A\,m^{-2}}\right) = 0.62nFD^{0.67}\left(\mathrm{m^2\,s^{-1}}\right)\nu^{-0.166}\left(\mathrm{m^2\,s^{-1}}\right)c\left(\mathrm{mol\,m^{-3}}\right)\omega^{0.5}\left(\mathrm{rad\,s^{-1}}\right) \tag{3}$$

where n is the number of electrons involved in electrode reaction; F is the Faraday constant, 96,500 C $\mathrm{mol^{-1}}$; ν is the kinematic viscosity; c is the concentration of electroactive species in bulk solution; and ω is the rotation speed. Hence, the test for mass transport control is that the plot of j_L vs $\omega^{0.5}$ is linear and passes through the origin. It can also be seen that the limiting current density is proportional to the concentration and that the diffusion coefficient may be determined when the kinematic viscosity is given.

Experimental Details

Description of the Experimental Setup

Voltammetric curves were recorded using a potentiostat Radiometer Copenhagen, with an electrochemical analyzer DEA332 and an electrochemical interface IMT102. The RDE was an EDI10000 rotating disc electrode, Radiometer Copenhagen. The working electrode was an RDE of vitreous carbon, 2-mm diameter. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum wire. An all-glass voltammetric cell (volume 150 mL) was used (Fig. 3). All experiments were carried out at room temperature.

All solutions were prepared using superpure water (ρ = 18 MΩ cm). The reagents were $K_3Fe(CN)_6$ (Panreac PRS, 98% purity), $K_4Fe(CN)_6$ (Panreac PRS, 98% purity), and $Na_2SO_4 \cdot 10H_2O$ (Panreac PRS, 98% purity).

Table 1. Linear Sweep Voltammetry Parameters

Parameter	Value
Bulk solution	10 mM $K_3Fe(CN)_6$, 20 mM $K_4Fe(CN)_6$, 0.1 M Na_2SO_4
Volume	150 mL
Initial sweep direction	positive
Initial potential	−800 mV vs SCE
Final potential	1200 mV vs SCE
Scanning rate	5 mV s^{-1}
Rotation speed	210 rad s^{-1}, fixed or variable value

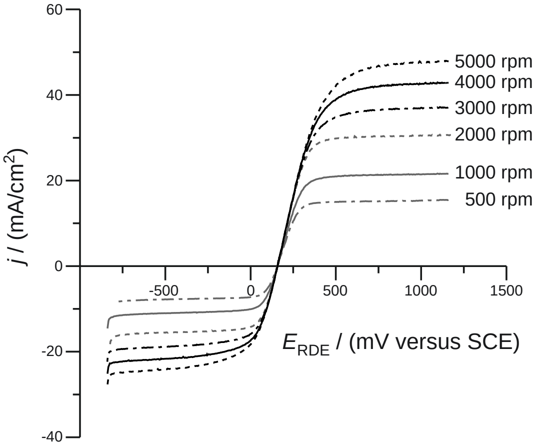

Figure 4. Current density vs potential curves as a function of rotation rate for a solution of $K_3Fe(CN)_6$ (10 mM) + $K_4Fe(CN)_6$ (20 mM) in Na_2SO_4 (0.1 M) at a vitreous carbon RDE. Sweep rate: 5 mV s^{-1}.

Experimental Procedure

The current is monitored with respect to the applied potential at a known sweep rate and the information is recorded on an *X–Y* plotter. Important parameters to consider when using linear sweep voltammetry are shown in Table 1, for our particular processes.

Before each laboratory session, to facilitate the students' work and shorten the duration of the experiments, instructors should polish the working electrode with α-alumina (0.05-μm diameter), to remove any impurity and obtain a reproducible surface. They should also prepare the bulk solution and bubble nitrogen inside it, to remove dissolved oxygen. This is important because O_2 can be reduced on the RDE, disturbing the voltammograms of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple. For 150 mL of solution, a bubble time of 1 h is sufficient.

It can be seen in eq 3 that the limiting current density (j_L) of an electrochemical process is proportional to the electroactive species concentration (c) and to the square root of the rotation speed (ω). To prove the validity of eq 3, students record a series of current density-vs-potential curves at various rotation speeds. Figure 4 shows the results obtained. It is interesting that all voltammetric curves in Figure 4 cross the *X*-axis at the same potential value. The redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is reversible and the electronic transfer is very fast. In reversible electronic transfer reactions, the electronic transfer process is not dependent on rotation speed.

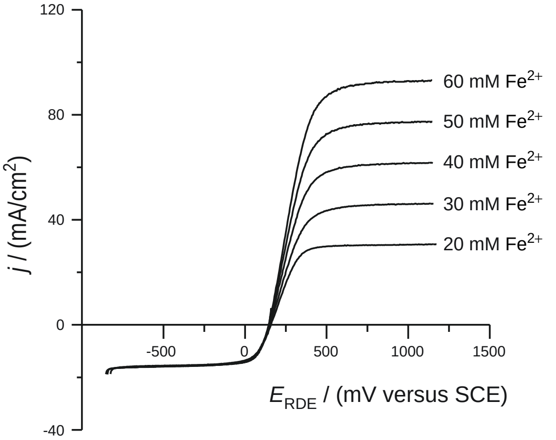

Figure 5. Current density vs potential curves as a function of $K_4Fe(CN)_6$ concentration at a vitreous carbon RDE. Solution composition: $K_3Fe(CN)_6$ (10 mM) + $K_4Fe(CN)_6$ (20–60 mM) in Na_2SO_4 (0.1 M). Rotation rate: 2000 rpm. Sweep rate: 5 mV s^{-1}.

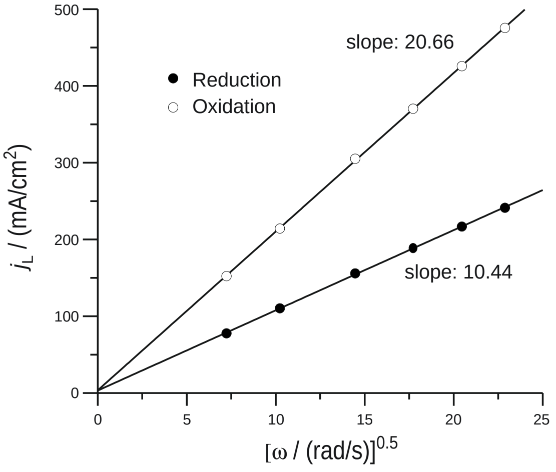

Figure 6. Plots of j_L vs $\omega^{0.5}$ from the curves in Fig. 4. Working solution: $K_3Fe(CN)_6$ (10 mM) + $K_4Fe(CN)_6$ (20 mM) in Na_2SO_4 (0.1 M) at a vitreous carbon RDE.

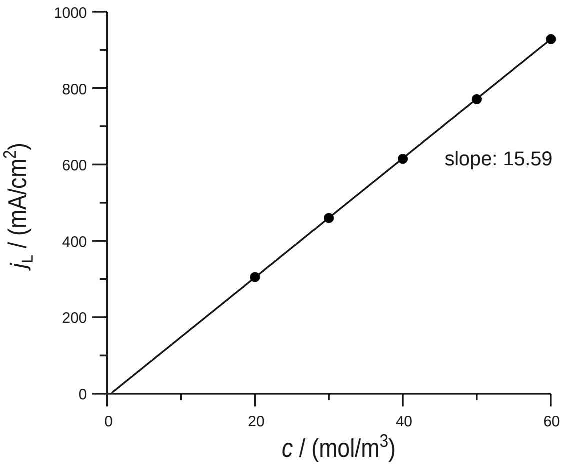

Figure 7. Plot of j_L vs c from the curves in Fig. 5. Working solution: $K_3Fe(CN)_6$ (10 mM) + $K_4Fe(CN)_6$ (variable) in Na_2SO_4 (0.1 M) at a vitreous carbon RDE. Rotation speed: 2000 rpm.

The next step is to study the influence of the concentration of $K_4Fe(CN)_6$ on the current density-vs-potential curves. In this phase of the practice session, students must add the necessary mass of $K_4Fe(CN)_6$ to the previous solution in the voltammetric cell to achieve a final $K_4Fe(CN)_6$ concentration of 30 mM as the bulk solution. After that, the salt must be dissolved and the current density–RDE potential plot is recorded at 2000 rpm. The same procedure is applied to increase the solution concentration to 40, 50, and 60 mM $K_4Fe(CN)_6$ and to record the corresponding current density–RDE potential plots. The results are shown in Figure 5.

Figures 6 and 7 show that an increase in RDE rotation speed and electroactive species concentration cause an increase in the limiting current density. This is the predicted behavior according to the Levich equation. Later on, these curves will be treated quantitatively.

Data Processing

Verification of Levich's Equation

It can be seen that the test for mass transport control in RDE experiments is that a plot of j_L vs $\omega^{0.5}$ plot will present a constant slope and pass through the origin. In the same way, a j_L vs c plot will also be linear and will pass through the origin. Figure 6 shows plots of j_L vs $\omega^{0.5}$ from the curves in Figure 4 in both oxidation and reduction processes. The j_L values corresponding to each rotation speed were measured at −500 mV for the reduction process and at 1000 mV for the oxidation reaction. At both potentials, the electrodic reactions show a clear plateau of current density. It can be seen that both plots are linear, confirming mass transport control in the plateau zone of the voltammograms. The straight lines have very different slopes because the $K_4Fe(CN)_6$ concentration is twice that of the $K_3Fe(CN)_6$ concentration.

To check the influence of $K_4Fe(CN)_6$ concentration, the plot of j_L vs c from the voltammograms in Figure 5 is shown in Figure 7. The j_L values were measured at 1000 mV. The plot is linear, according to Levich's equation, thus confirming mass transport control.

Distinction between Kinetics of Charge-Transfer, Mixed, and Mass-Transport Controlled Regions

It is seen in Figure 5 that near to the equilibrium potential (at ca. +160 mV vs SCE), the electrodic reactions are controlled by charge transfer and the current densities are independent of rotation speed. When the overpotentials are increased, the system enters the region of mixed control, and the current density becomes gradually more dependent on the rotation speed. Finally, at high enough overpotentials, the current density is totally independent of the RDE potential.

This illustrates well how the RDE may be used to rapidly distinguish between the kinetics of charge-transfer, mixed, and mass-transport controlled regions.

Calculation of Diffusion Coefficient

In the last part of the exercise, students calculate the diffusion coefficients of both electroactive species, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, in these experimental conditions. The diffusion coefficients can be calculated (eq 4) according to Levich's equation (eq 3) and using the slopes of the lines in Figure 6 (representation of j_L versus $\omega^{0.5}$) provided the kinematic viscosity of the bulk solution is known. The kinematic viscosity of the bulk solution was measured in our laboratory at 20 °C, its value being approximately 1.1×10^{-6} m^2 s^{-1} at this temperature. This value should be given to the students, although it is easy to measure during the class.

$$\text{slope} = 0.62 \times n \times F \times D^{0.67}\ (\text{m}^2\ \text{s}^{-1}) \times \nu^{-0.166}\ (\text{m}^2\ \text{s}^{-1}) \times c\ (\text{mol m}^{-3}) \quad (4)$$

1. The results obtained for $Fe(CN)_6^{4-}$ ion (oxidation process) were:

$$20.66 = 0.62 \times 1 \times 96{,}500 \times D_{Fe(CN)_6^{4-}}^{0.67} \times (1.1 \times 10^{-6})^{-0.166} \times 20$$

$$D_{Fe(CN)_6^{4-}}^{0.67} = 1.76 \times 10^{-6}$$

$$D_{Fe(CN)_6^{4-}} = 2.5 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$$

2. The results obtained for $Fe(CN)_6^{3-}$ ion (reduction process) were:

$$10.44 = 0.62 \times 1 \times 96{,}500 \times D_{Fe(CN)_6^{3-}}^{0.67} \times (1.1 \times 10^{-6})^{-0.166} \times 10$$

$$D_{Fe(CN)_6^{3-}}^{0.67} = 1.78 \times 10^{-6}$$

$$D_{Fe(CN)_6^{3-}} = 2.6 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$$

Finally, the diffusion coefficient of $Fe(CN)_6^{4-}$ from the data recorded in Figure 7 (representation of j_L vs c) was calculated. In this case, the slope of the straight line is given by

$$\text{slope} = 0.62 \times n \times F \times D^{0.67} (\text{m}^2\ \text{s}^{-1}) \times \nu^{-0.166} (\text{m}^2\ \text{s}^{-1}) \times \omega^{0.5} (\text{rad s}^{-1}) \quad (5)$$

$$15.59 = 0.62 \times 1 \times 96{,}500 \times D_{Fe(CN)_6^{4-}}^{0.67} \times (1.1 \times 10^{-6})^{-0.166} \times 14.47$$

$$D_{Fe(CN)_6^{4-}}^{0.67} = 1.83 \times 10^{-6}$$

$$D_{Fe(CN)_6^{4-}} = 2.7 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$$

As observed, the values of the $Fe(CN)_6^{4-}$ diffusion coefficient calculated from Levich's equation and the variation of the rotation speed or the concentration are very similar.

Conclusion

This exercise allows students to use very important techniques and tools in basic electrochemistry, such as linear sweep voltammetry applied to RDE. Students also apply theoretical models to calculate a basic hydrodynamic parameter, the diffusion coefficient.

During the exercise, students clearly observe the influence of mass transport on the kinetics of the electrochemical reactions of the redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and how the increase of rotation speed or concentration of electroactive species enhances the mass transport characteristics of the electrochemical reaction.

wSupplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

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