Electrochemical reaction kinetics measurement:
The Levich and Koutecký-Levich analysis tools

I – INTRODUCTION
Since EC-Lab v11.00, the Levich and Koutecký-Levich analysis tools are available. This note will aim at describing what is performed during this analysis and which information can be obtained.
The Rotating Disk Electrode (RDE) allows the user to control the velocity of the fluid. The steady-state mass transport conditions of the species involved in the redox reactions are then known [1,2].
The renewal of the solution at a disk electrode occurs thanks to an ascending movement of the solution perpendicularly to the electrode. The fluid is then ejected on the outside of the disk electrode (Fig. 1).

II – ROTATING DISK ELECTRODE EXPERIMENT: LEVICH CRITERION
II - 1 AIM AND PRINCIPLES
The aim of this experiment is to determine the diffusion coefficient of the concentration of the redox species. Whatever the value of the rate constant of the electronic transfer of the studied reaction $k^e$, there is always an overpotential for which the reaction rate will be limited by mass transfer, whether it is diffusion, as it is the case at an Ultra Micro Electrode (UME) or diffusion and convection, as it is the case for an RDE.

At an RDE submitted to a large overpotential, the current density $i = i/A$ where $A$ is the area of the electrode, is expressed as

$$i_{dR} = 0.620 n F R_{bulk} D_{R}^{2/3} \nu^{-1/6} \omega^{1/2}$$  \hspace{1cm} (1)$$

in the case of the oxidation of the species R and

$$i_{dO} = -0.620 n F O_{bulk} D_{O}^{2/3} \nu^{-1/6} \omega^{1/2}$$  \hspace{1cm} (2)$$

in the case of the oxidation of the species O, where $i_{dR}$ and $i_{dO}$ are the mass transport-limited current densities for an oxidation reaction and a reduction reaction, respectively; $n$ the number of electrons involved in the reaction, $F$ the Faraday constant (96500 C/mol), $R_{bulk}$ and $O_{bulk}$ the bulkl concentration of the species R and O, respectively in mol/cm$^3$, $D_R$ and $D_O$ the diffusion coefficients of R and O, respectively in cm$^2$/s and $\omega$ the rotation rate in rad/s.

Plotting the value of the mass transport limitation current as a function of the square root of the rotation speed, the graph should
be a straight line (the Levich plot), with a slope that can be named the Levich slope.

The values of this slope is, for the oxidation:

$$p_{La} = 0.620nF \cdot R_p^{bulk} D_e^{2/3} V^{-1/6}$$  \hspace{1cm} (3)

And for the reduction:

$$p_{Le} = -0.620nF \cdot O^{bulk} D_o^{2/3} V^{-1/6}$$  \hspace{1cm} (4)

Knowing the concentration of the species and the viscosity of the electrolyte, the diffusion constants of the redox species can be obtained.

II - 2 EXPERIMENT

The used electrolyte contains $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in an equimolar concentration of 0.005 mol/L of and KCl at a concentration of 0.1 mol/L of KCl. Let us consider that the temperature of the electrolyte is 20°C and that its kinematic viscosity is $10^{-2}$ cm²/s. The RDE is made of Pt and has a dimeter of 2 mm. The reaction occurring at the disk is:

$$Fe^{III} + e^- \leftrightarrow Fe^{II}$$  \hspace{1cm} (5)

The BluRev RDE was used for this experiment (Fig. 1).

Connect only one channel of the potentiostat to the cell using standard connection. The “Levich plot” experiment will load a series of techniques necessary to perform the Levich experiment (Fig. 2).

**Figure 3: The “Levich plot” experiment.**

The following parameters should be entered in the CV technique (Fig. 3).

**Figure 4: Settings to be entered in the CV technique.**

The OCV should be around 0.1-0.3 V/Ag/AgCl. The results are shown in Fig. 4 (they are also available C:\Users\...\Documents\EC-Lab\Data).
A hysteresis can be seen at the lower rotation rates, which shows that the experiment is not in the steady-state conditions, probably due to a scanning rate that is too fast. As the rotation speed increases, the conditions tend to be steady-state.

**Figure 5**: Results of the Levich plot experiment for FeII/FeIII oxidation/reduction. The current plateaus occur because the reaction is limited by mass transfer.

### II - 2 ANALYSIS

Open the Levich Analysis window (Fig. 6):

![Figure 6: The Levich Analysis window.](image1)

Enter the parameters shown in Fig. 6 for the viscosity, the surface of the electrode and the concentration of FeIII (the diffusion coefficient will be calculated by the analysis). The equation of the Levich current shown in Fig. 7 is the same as the Eqs. (1) and (2) apart from the coefficient, which is different because the equation above is written for a rotation speed in rotation per minute (rpm) as is used in EC-Lab. The diffusion coefficient is the sought after value so it must be selected. Click on “Calculate”, the Levich plot should appear: the experimental points and the least square regression plot (Fig. 8).

**Figure 7**: The Levich analysis window a) for the cathodic part and b) the anodic part of the curves shown in Fig. 5.
The calculated value of $D_{[Fe(CN)_6]^{3-}}$ is $6.8 \times 10^{-6}$ cm$^2$/s. The same analysis can be performed on the anodic part of the curves, for example by choosing a plateau potential of 0.595 V. The calculated value of $D_{[Fe(CN)_6]^{4-}}$ is $5.9 \times 10^{-6}$ cm$^2$/s. The same results can be used to determine the concentration of the species in solution knowing its diffusion coefficient. Then in the analysis window (Fig. 7) the concentration must be selected as the parameter to be calculated.

The same results can be analysed using the Koutecký-Levich extrapolation to determine the reaction standard constant as well as the symmetry factor.

III – ROTATING DISK ELECTRODE EXPERIMENT: KOUTECKÝ-LEVICH EXTRAPOLATION

III - 1 AIM AND METHOD

The aim of the Koutecký-Levich extrapolation is to determine for various potentials $E_n$ the electron transfer current $i_t$. It can also be used to determine the symmetry factor $\alpha$ (for a reduction reaction and $\alpha_o$ for an oxidation reaction) as well as the standard constant of the reaction $k^*$, knowing the standard potential $E^*$ of the reaction (5).

The method consists in:

1. Plotting the inverse of the current or current density as a function of the inverse square root of the rotation rate for various potentials $E_n$.
2. Extrapolating the obtained line to 0 ($\Omega^{-1/2} \rightarrow 0, \Omega \rightarrow \infty$), which gives the electron transfer current $i_t$ for various potentials $E_n$.
3. Plotting $\log |i_t|$ as a function of $E_n$ (Tafel representation) to obtain the symmetry factor $\alpha$ and the standard constant of the reaction (when the standard potential is known).

III - 2 ANALYSIS

Using the same data as for the Levich analysis, open the Koutecký-Levich analysis tool (Fig. 10). In the analysis parameters window in Fig. 9 enter the Parameters as shown and click on “Calculate”.

Two windows will then open:

- For each chosen potential, $1/i$ vs. $\omega^{-1/2}$ (Fig. 10).
- The Tafel plot $\log |i_t|$ vs. $E$, the values $i_t$ having been obtained by extrapolating the $1/i$ vs. $\omega^{-1/2} \rightarrow 0$ for each potential step (Fig. 11).
Figure 1: The Koutecký-Levich reconstructed Tafel plot.

The Koutecký-Levich analysis window will show the results of the analysis. Figure 12a and 12b shows the results for the cathodic and anodic part, respectively, of the curve shown in Fig. 5. Both calculated standard constants of the reaction are similar. The calculation will be more accurate if the selected potentials lead to a straight Tafel plot (in log representation).

With these potential boundaries, the determined values for $k^*$ and $\alpha$ changed and are now $6.10^{-2}$ cm²/s and 0.526, respectively. Larger values of $k^*$ could be obtained by better cleaning the RDE for instance.

It must be noted that the determination of the electronic transfer kinetic parameters using the Koutecký-Levich method is practically possible for values of $k^* \leq$ several $10^{-2}$ cm.s⁻¹, i.e. sluggish kinetics.

For higher values, the extrapolated values of $I_t^{-1}$ are too close to 0 and the uncertainties on their inverse values are too large to allow for a good $k^*$ determination.

It can be seen in Fig. 10: all lines should be parallel. In this intermediate case, all the lines are secant but $I_t^{-1}$ are not too close to 0.

Figure 12: The Koutecký-Levich analysis window for a) the cathodic part and b) the anodic part of the curves shown in Fig. 5.
For more information please see references [1,2,4,5].

III - 3 DETERMINATION OF THE NUMBER OF ELECTRONS BY THE KOUTECKÝ-LEVICH METHOD

In the case of a “quasi-reversible” (or neither reversible nor irreversible) reaction, the slope of the Koutecký-Levich extrapolation plot shown in Fig. 10 is expressed as [5]:

\[ p_{KL} = \frac{1.611 v^{1/6} (D_R^{-2/3} \exp \xi + D_O^{-2/3})}{(nF(R_{bulk} \exp \xi - O_{bulk})} \]  

(6)

With \( \xi = nf(E - E_{O/R}) \) and \( f = F/(RT) \).

The slope depends on the electrode potential.

In the case of an irreversible reaction, the slope of Koutecký-Levich extrapolation plots is expressed as:

\[ p_{KL} = \frac{1.611 v^{1/6}}{(nFD_O^{2/3} O_{bulk})} \]  

(7)

In this case, the slope does not depend on the electrode potential. Figure 11 for an irreversible reaction would show several parallel plots. Equation (7) could be used to determine the number of electrons involved in the reaction.

IV – CONCLUSION

The “LeVich plot” technique as well as the Levich and Koutecký-Levich analyses were presented. The Levich analysis allows the user to determine the diffusion constant of a reactive species and the diffusion constant of a reactive species and the Koutecký-Levich extrapolation method allows for sluggish kinetics to determine the kinetic parameters of the electronic transfer for the considered reaction.

Data files can be found in:

C:\Users\xxx\Documents\EC-Lab\Data\Samples\Fundamental Electrochemistry\ANS6 CV

REFERENCES

3) Technical Note#21 “External device control and recording”