

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).

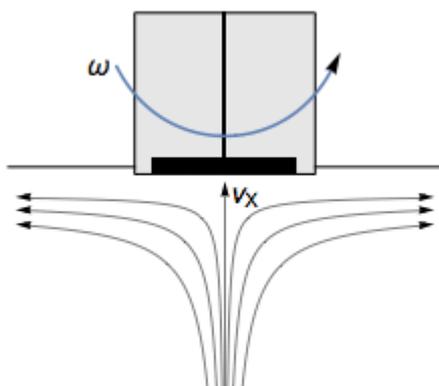


Figure 1: Fluid movement at a uniformly rotating disk electrode. v_x is the axial velocity of the fluid.

The control of the steady-state hydrodynamics of the fluids results in solving the kinetic reactions of the redox reactions. Several relationships can also be deduced that lead to the determination of kinetic factors of the considered species and redox reactions: the Levich relationship can be used to determine the diffusion coefficient of the electroactive species and the Koutecký-Levich analysis can lead to the standard constant of the reaction as well as the symmetry factor.

II – ROTATING DISK ELECTRODE EXPERIMENT: LEVICH CRITERION

II – 1 AIM AND PRINCIPLES

The aim of this experiment is to determine the diffusion coefficient or the concentration of the redox species. Whatever the value of the rate constant of the electronic transfer of the studied reaction k° , 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

$$i_{dR} = 0.620nFR^{\text{bulk}}D_R^{2/3}\nu^{-1/6}\omega^{1/2} \quad (1)$$

in the case of the oxidation of the species R and

$$i_{dO} = -0.620nFO^{\text{bulk}}D_O^{2/3}\nu^{-1/6}\omega^{1/2} \quad (2)$$

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 bulk concentration of the species R and O, respectively in mol/cm³, D_R and D_O the diffusion coefficients of R and O, respectively in cm²/s, ν the cinematic viscosity of the electrolyte in cm²/s and ω the rotation rate in rad/s.

Plotting the value of the mass transport limited 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

$$p_{La} = 0.620nFR^{\text{bulk}}D_R^{2/3}\nu^{-1/6} \quad (3)$$

for the oxidation,

$$p_{Lc} = -0.620nFO^{\text{bulk}}D_O^{2/3}\nu^{-1/6} \quad (4)$$

for the reduction.

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 0.01 mol/L of $K_3[Fe(CN)_6]$ and 0.25 mol/L of KCl. Let us consider that the temperature of the electrolyte is 20 °C and that its kinematic viscosity is $10^{-6} \text{ cm}^2/\text{s}$. The RDE is made of Pt.

The reaction occurring at the disk is:



If using the ALS RRDE-3A, use a DB-9 to RRDE connector (P/N#: 092-22/11) to connect the RRDE to the auxiliary I/O of the potentiostat/galvanostat.

On the RRDE do not use the Motor port, only Purge, In and Ground. Set the rotation switch to “Remote”.

Setup your cell with reference and counter electrodes. Additional info is provided in the Technical Note #21 [3].

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).

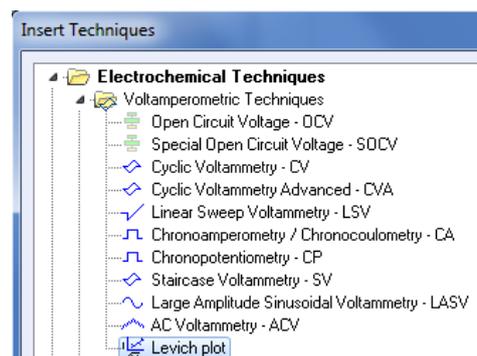


Figure 2: The “Levich plot” experiment.

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

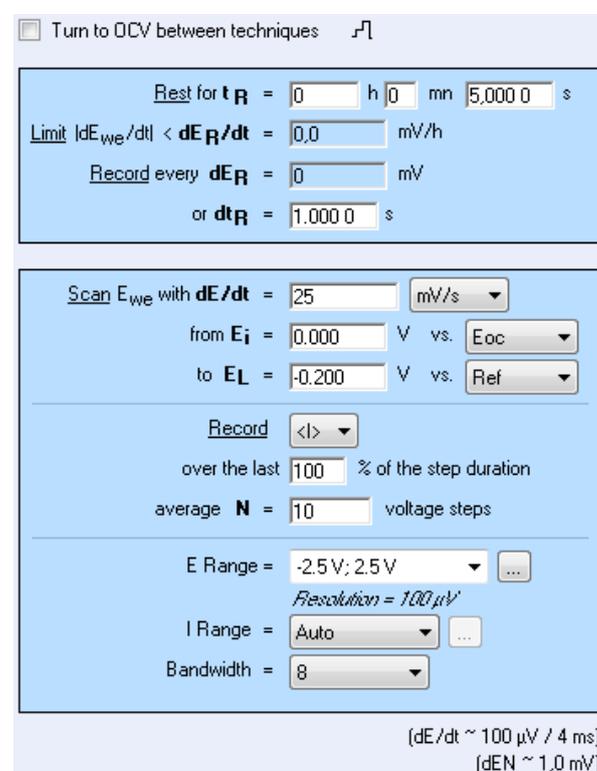


Figure 3: Settings to be entered in the LSV technique.

The OCV should be around 0.3-0.5 V/SCE.

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.

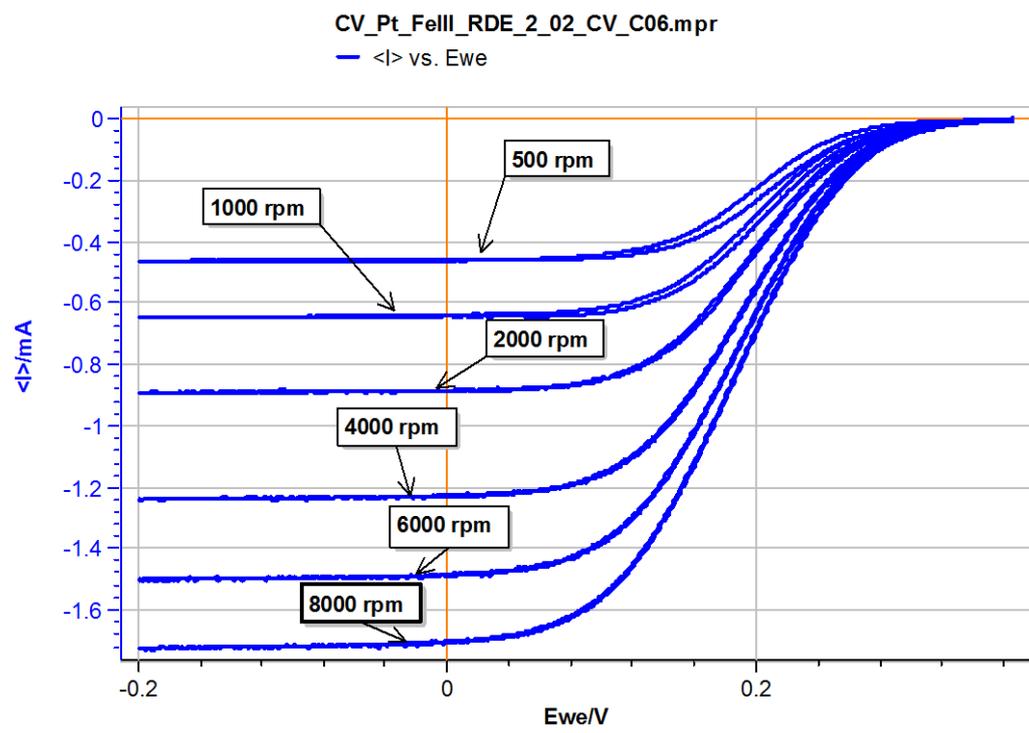


Figure 4: Results of the Levich plot experiment for Fe^{III} reduction. The current plateaus occur because the reaction is limited by mass transfer.

II – 3 ANALYSIS

Open the Levich Analysis window (Fig. 5):

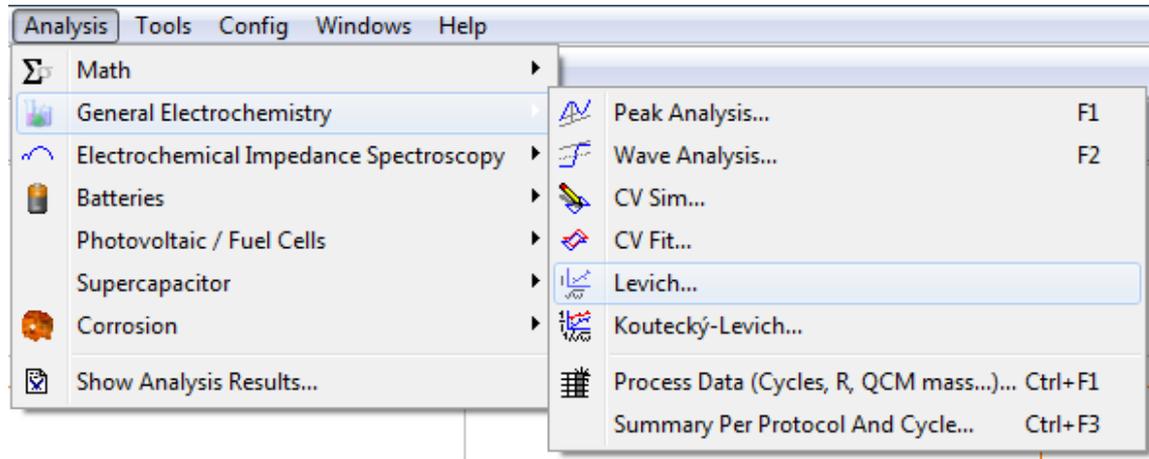


Figure 5: The Levich Analysis window.

Enter the parameters shown in Fig. 6 for the viscosity, the surface of the electrode and the concentration of Fe^{III} (the diffusion coefficient will be calculated by the analysis). The equation of the Levich current shown in Fig. 6 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 value searched for so it must be selected. Click on "Calculate", the Levich plot should appear: the experimental points and the least square regression plot (Fig. 7).

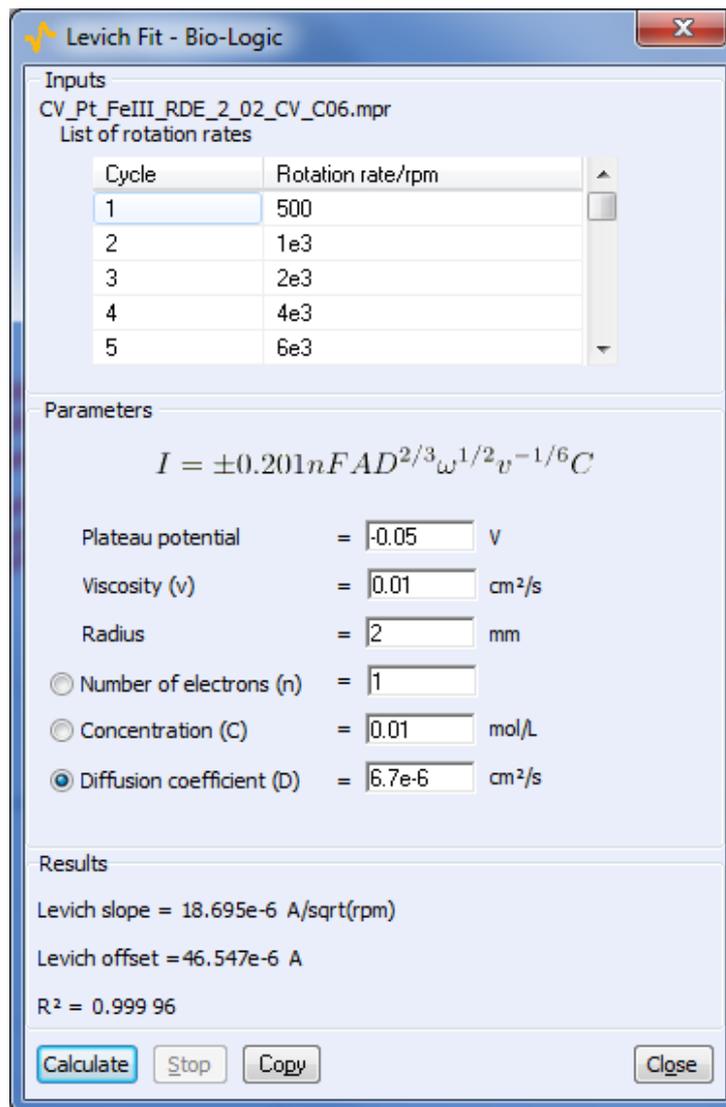


Figure 6: The Levich analysis parameters window.

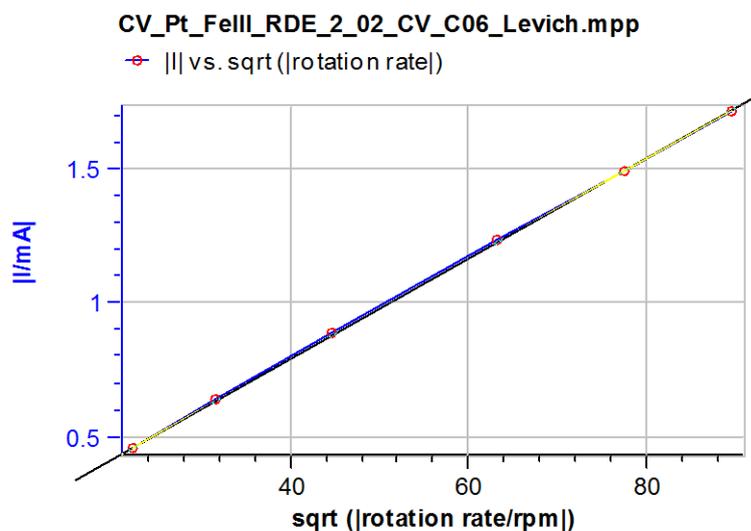


Figure 7: The Levich plot showing the mass transfer limited current at a potential of -0.05 V for all the rotations vs. the square root of the rotation rate.

The calculated value of $D_{\text{Fe}^{\text{III}}}$ is $6.7 \times 10^{-6} \text{ cm}^2/\text{s}$. 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. 6) the concentration must be selected as the parameter to be calculated.

The same results can be analyzed 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 α , (α_r for a reduction reaction and α_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 expressed in rpm 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 α 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. 8). In the analysis parameters window in Fig. 9 enter the Parameters as shown and click on “Calculate”.

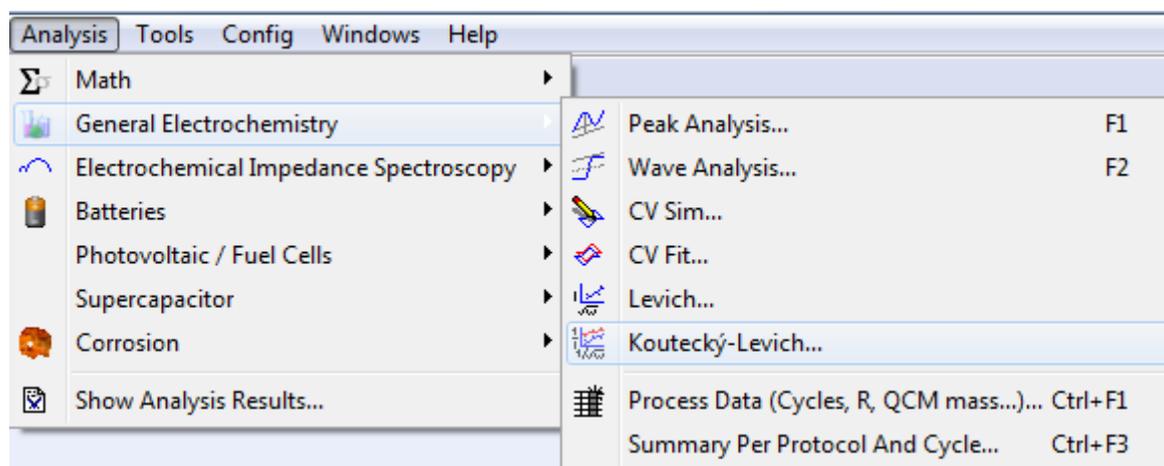


Figure 8: The Koutecký-Levich analysis window.

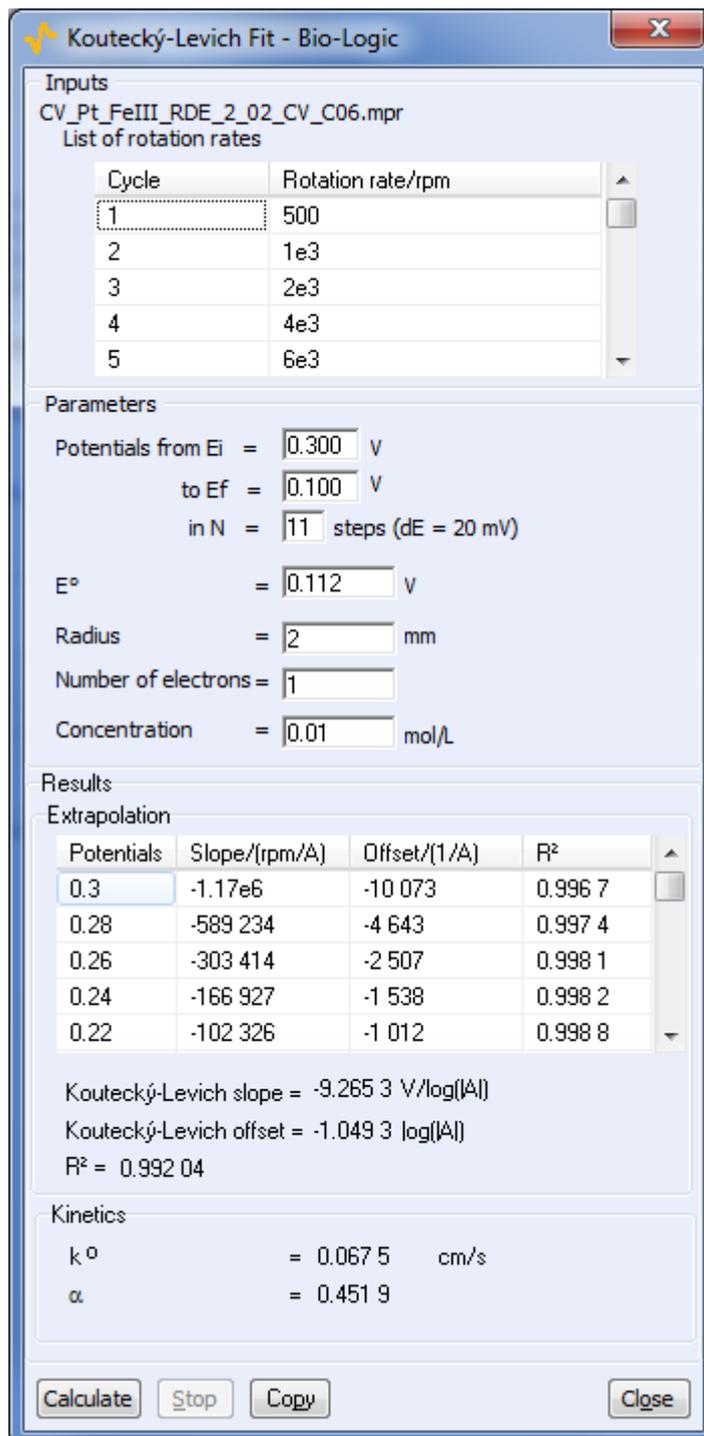


Figure 9: The Koutecký-Levich parameters.

Two new windows will then open:

. for each chosen potential, $1/I$ vs. $\omega^{-1/2}$

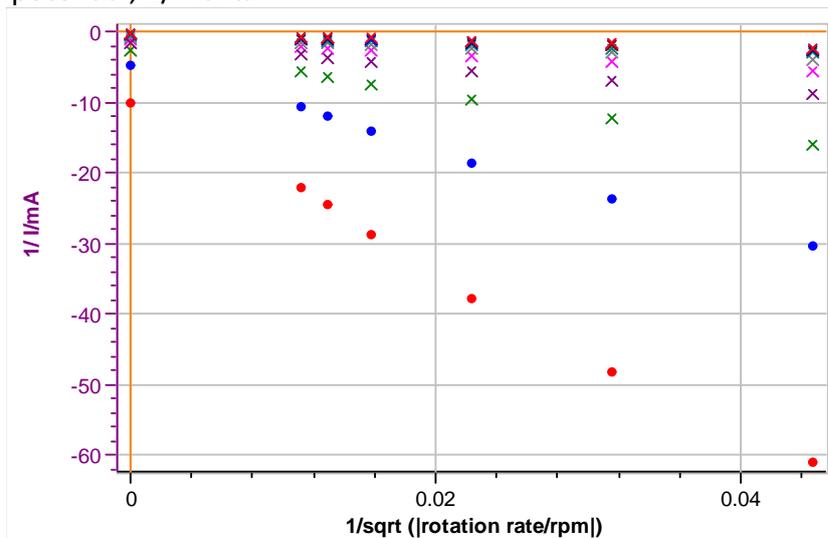


Figure 10: The Koutecký-Levich extrapolation plot.

. the Tafel plot $\log |I_t|$ vs. E , the values I_t having been obtained by extrapolating the $1/I$ vs. $\omega^{-1/2}$ curves above, at $\omega^{-1/2} \rightarrow 0$ for each potential step.

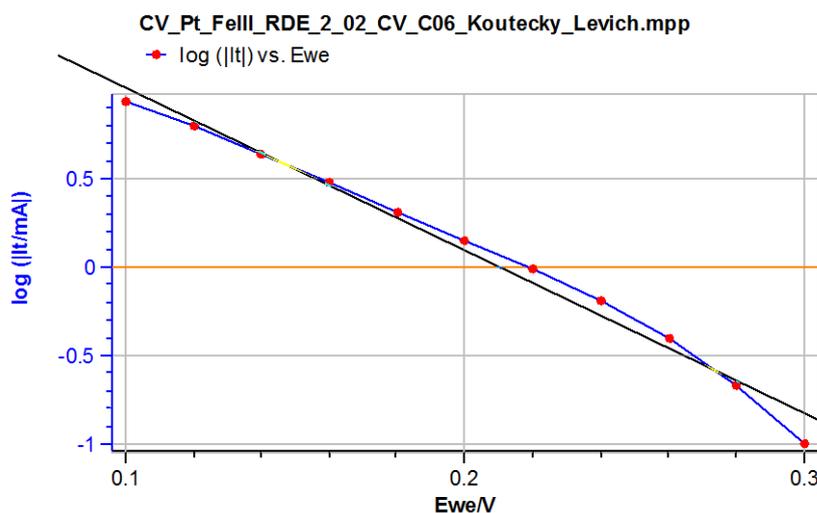


Figure 11: The Koutecký-Levich reconstructed Tafel plot.

The calculation will be more accurate if the selected potentials lead to a straight Tafel plot (in log representation). In Fig. 8, 0.3 to

0.1V/SCE might be too large, choosing 0.2 to 0.1 V/SCE leads to a straight Tafel plot as can be seen in Fig. 12.

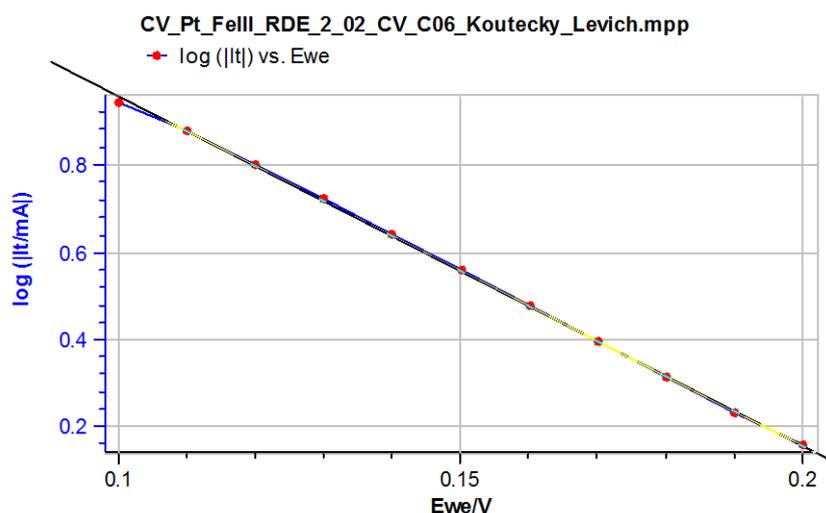


Figure 12: The Koutecký-Levich reconstructed Tafel plot with adjusted potential boundaries.

With these potential boundaries, the determined values for k^0 and α changed and are now $6 \times 10^{-2} \text{ cm}^2/\text{s}$ and 0.526, respectively. Larger values of k^0 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 $k^0 \leq$ several $10^{-2} \text{ cm}\cdot\text{s}^{-1}$, ie 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 a good k^0 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.

For more information please see references [1,2,4,5].

IV– CONCLUSIONS

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 Koutecký-Levich extrapolation method allows for sluggish kinetics to determine the kinetic parameters of the electronic transfer for the considered reaction.

REFERENCES

- 1) J.-P. Diard, B. Le Gorrec, C. Montella, *Cinétique électrochimique*, Hermann, Paris, (1996) 120, 129.
- 2) A. J. Bard, L. R. Faulkner, *Electrochemical methods, Fundamentals and Applications*, 2nd ed., Wiley, New York, (2001), 335
- 3) [Technical Note#21](#) “External device control and recording”
- 4) F. J. Vidal-Iglesias, J. Solla-Gullón, V. Montiel, A. Aldaz, *Electrochem. Com.* 15 (2012) 42.
- 5) J. Koutecký, B.G. Levich, *Zhurnal Fizicheskoi Khimii USSR* 32 (1958) 1565.