

CV Sim: Simulation of the simple redox reaction (E), Part I: The effect of scan rate

I – INTRODUCTION

CV Sim is a powerful tool implemented in EC-Lab® that allows the user to simulate current vs. potential curves resulting from a voltammetry experiment. A vast array of parameters can be modified, making CV Sim a very accessible tool to understand what kind of information can be obtained by voltammetry on the electrochemical systems being studied. In this application note, the simplest conditions are used:

The reaction is a simple redox reaction:



where A is the oxidizing species, B the reducing species, z the number of electrons, only the oxidizing species is present in the solution. Only linear voltammetry is performed.

In this note, the effect of the voltage scan on the shapes of the *I* vs. *E* curves is described for a reversible and an irreversible reaction. There is no ohmic drop and no double layer capacitance. The effect of these two factors will be described in part II of this note.

II – DEFINITIONS

We define the linear voltammetry as a forward potential scan performed from the initial potential E_{init} to the first vertex potential (either higher or lower than the standard potential). The cyclic voltammetry is a potential scan starting at E_{init} , going forward to the first vertex potential and backward to a second vertex potential. A cycle is defined as a potential scan from the first vertex potential to the second and back to the first (Figs. 1a and 1b).

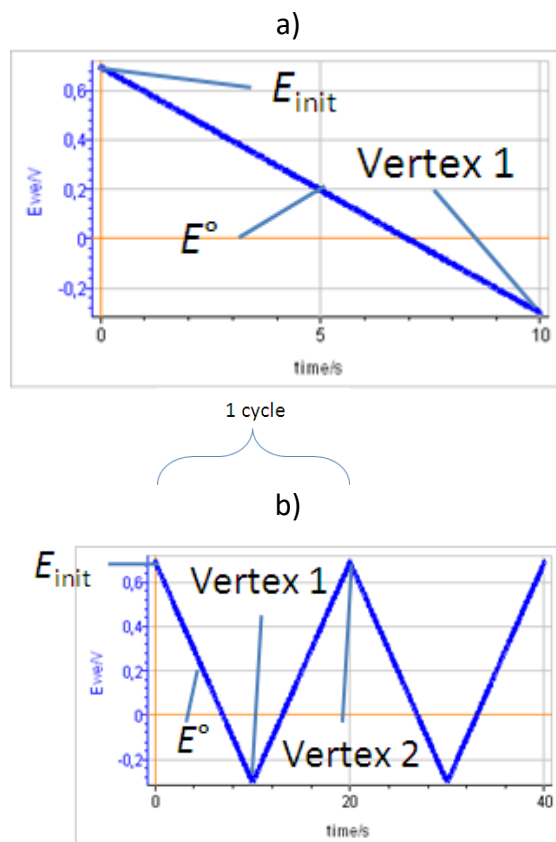


Figure 1: Potential vs time during a) linear voltammetry and b) cyclic voltammetry ($E_{init} = 0.7$ V, $E^\circ = 0.2$ V, Vertex 1 = -0.3 V, Vertex 2 = 0.7 V).

The peak current I_p is defined as the maximum current obtained during the forward linear potential scan. The corresponding potential is named the peak potential E_p (Fig. 2). It is worth noting that the oxidizing species' concentration C_A at the electrode interface tends toward 0 at a potential lower than E_p . At E_p the interfacial concentration is around 20% of the initial concentration.

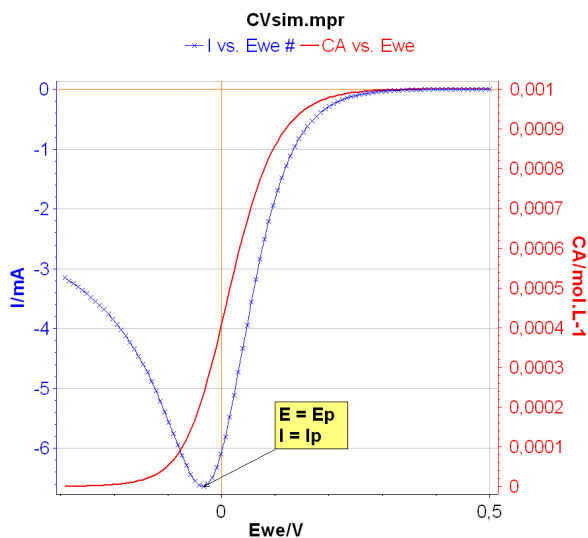


Figure 2: The peak current I_p and peak potential E_p .

III – DESCRIPTION OF CV SIM

The CV Sim tool is available in the Analysis tab of the main menu of EC-Lab® (or EC-Lab Express®) (Fig. 3).

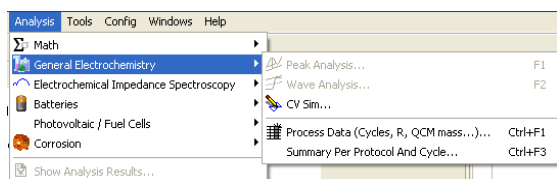
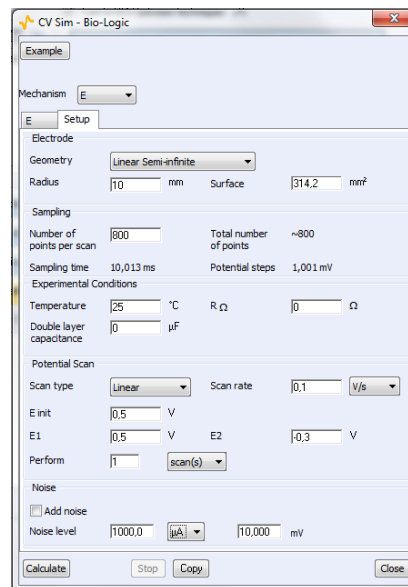


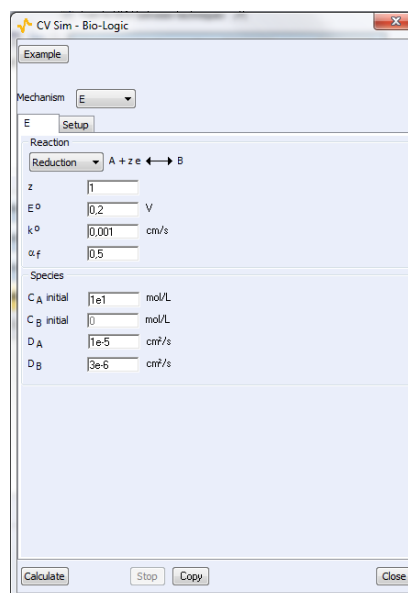
Figure 3: Where to find the CV Sim tool in EC-Lab®.

Once CV Sim is open, it is possible to choose which reaction is simulated: from one to five step redox reaction (E to EEEEE), involving from one to 6 species (Fig. 4a). EC, CE reactions are also available (not shown in Fig. 4a). E stands for electron transfer and C for chemical reaction. It is also possible to choose an example from a selection of preset parameters, often referring to conditions used in publications.

Two parameters windows are available: the first one is related to the reaction itself (Fig. 4a) and the second window is related to the experimental parameters (Fig. 4b). For a classic CV from E_{init} to Vertex 1 (E_1) and then Vertex 2 (E_2), the number of scans is 2. For a linear scan, the number of scans is 1.



a)



b)

Figure 4: The parameters windows related to b) the reaction and a) the experimental setup.

By clicking Calculate, the simulated $I-E$ curve corresponding to the parameters set in the two former windows can be obtained (Fig. 5). The corresponding data file named CVsim.mpr is located in EC-Labvxx.xx\Data. Each time a new simulation is performed the "CVsim.mpr" file is replaced. In order to keep the data, the user must change the name of this file.

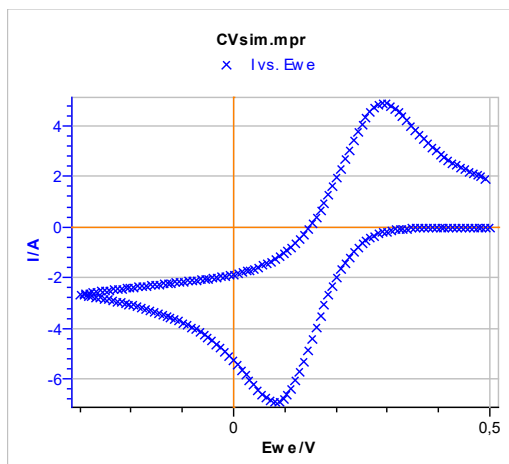


Figure 5: Cyclic voltammety corresponding to the default parameters set in Figs. 2a) and 2b).

IV – THE EFFECT OF THE SCAN RATE

IV - 1 THE REVERSIBLE REACTION

The parameters are the following:

- $k^\circ = 10 \text{ cm}\cdot\text{s}^{-1}$
- Initial C_A : $10^{-5} \text{ mol}\cdot\text{cm}^{-3}$ ($10^{-2} \text{ mol}\cdot\text{L}^{-1}$) and initial C_B : 0
- $D_A = D_B = 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$
- $A = 0.03142 \text{ cm}^2$ (linear semi-infinite electrode)
- $E_{\text{init}} = E^\circ + 0.3 \text{ V}$
- $E_1 = -0.3 \text{ V}$

Note that k° has been chosen high enough to ensure that the reaction can be considered reversible. In a real experiment, the standard constant value of a reaction is not known.

A reaction can be considered reversible if I_p increases with the scan rate and E_p stays constant as is shown in Fig. 6.

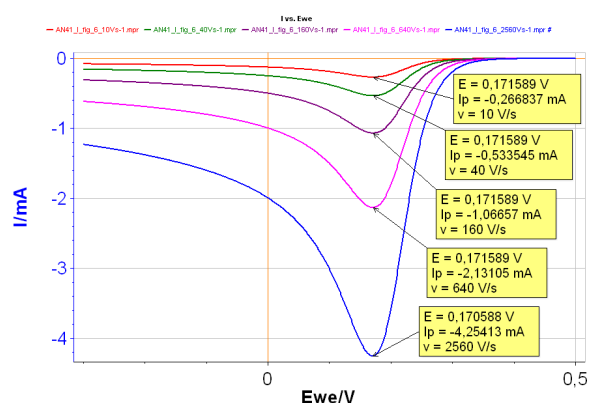


Figure 6 : Current vs. potential response with increasing scan rates: Red curve: 10 V s^{-1} ; Green curve: 40 V s^{-1} ; Purple curve: 160 V s^{-1} ; Pink curve: 640 V s^{-1} ; Blue curve: 2560 V s^{-1} with $k^\circ = 10 \text{ cm s}^{-1}$.

From the curves in Fig. 6, it can be seen that I_p is proportional to $v^{1/2}$, with v the scan rate: as v is multiplied by 4, I_p is multiplied by 2. Plotting I_p as a function of $v^{1/2}$ gives the following curve (Fig. 7):

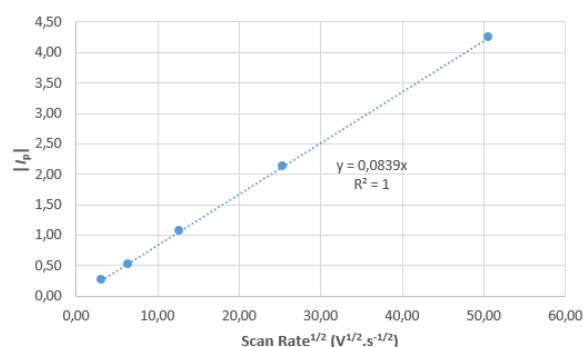


Figure 7 : $|I_p|/A$ vs. $v^{1/2} / (\text{V}\cdot\text{s}^{-1})^{1/2}$.

Using this curve and knowing all the other parameters, we can calculate the factor M :

$$M = \frac{I_p}{AnFC_A * \sqrt{nf v D_A}} \quad (2)$$

with $f = F/RT$.

The results are the following:

Table I : M values as a function of the scan rate v.

v / V.s ⁻¹	M
10	0.4460
40	0.4459
160	0.4457
640	0.4453
2560	0.4444

As the scan rate increases, the factor *M* decreases further away from 0.446, which is the theoretical value given by Bard *et al.* [1, p. 231].

$$I_p = -0.446 AnFC_A * \sqrt{nf v D_A}; f = \frac{F}{RT} \quad (3)$$

From the results shown in Tab. I, it is clear that as the scan rate increases the reaction becomes less reversible.

The peak potential *E_p* can help in determining the standard potential *E°* of the reaction:

$$E_p = E^\circ - \frac{1}{2nf} \ln \frac{D_A}{D_B} \frac{1.109}{nf} \quad (4)$$

$$E_p = E^\circ - \frac{1.109}{nf} \text{ if } D_A = D_B \quad (5)$$

IV - 2 THE IRREVERSIBLE REACTION

The parameters are the following:

- *k°* = 0.001 cm s⁻¹
- Initial *C_A*: 10⁻⁵ mol cm⁻³ (10⁻² mol.L⁻¹) and initial *C_B*: 0
- *D_A* = *D_B* = 10⁻⁶
- *A* = 0.03142 cm² (linear semi-infinite electrode)
- *E_{init}* = *E°* + 0.3 V
- *E₁* = - 0.3 V

In the case of an irreversible reaction both *I_p* and *E_p* change when the scan rate changes (Fig. 8): the higher the scan rate, the higher *|I_p|* and the lower *E_p* in the case of a reduction

reaction. *I_p* is again proportional to *v*^{1/2} following this relation [1, p. 236]:

$$I_p = -0.496 AnFC_A * \sqrt{\alpha_r nf v D_A}; f = \frac{F}{RT} \quad (6)$$

Similarly to the reversible reaction, it is possible to recalculate the factor and find a value of -0.496.

The slope of the *|I_p|* vs. *v*^{1/2} curve (Fig. 9) can be used to determine, using relation (6), the diffusion coefficient *D_A* or the symmetry factor *α_r*.

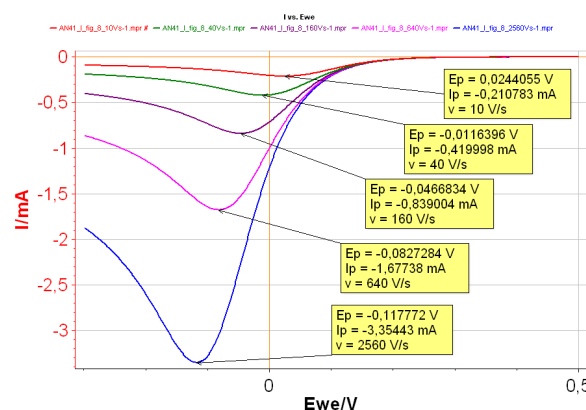


Figure 8 : I vs. E with increasing scan rates: Red curve: 10 V s⁻¹ ; Green curve: 40 V s⁻¹ ; Purple curve: 160 V s⁻¹ ; Pink curve: 640 V s⁻¹ ; Blue curve: 2 560 V s⁻¹ with *k°* = 0.001 cm² s⁻¹.

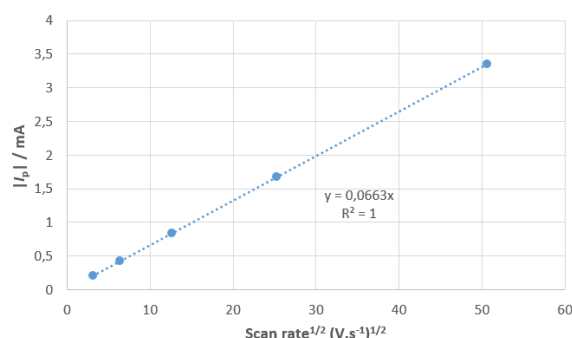


Figure 9 : *|I_p|* / *A* vs. *v*^{1/2} / (V s⁻¹).

If *E_p* is plotted as a function of log(*v*), it can be seen that there is a linear relationship (Fig. 10).

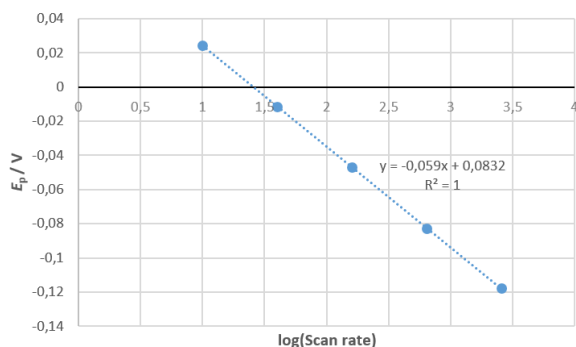


Figure 10 : E_p/V vs. $\log(v)$.

The relationship between E_p and the scan rate is also given by Bard *et al.* [1, p. 236]:

$$E_p = E^\circ + \frac{1}{\alpha_r n f} - \left(0,78 + \ln \frac{k^\circ}{\sqrt{\alpha_r n f v D_A}} \right) \quad (7)$$

In this case, the standard reaction constant k° can be determined as well as the symmetry factor α_r .

V – CONCLUSION

CV Sim is a powerful tool that can be used to discover information obtained by voltammetry on a redox reaction.

To summarize, to investigate a redox system in the standard condition, one needs to make several CVs with different scan rates and analyse the evolution of I_p and E_p with the scan rate:

- If E_p is invariant and $|I_p|$ is proportional to $v^{1/2}$, it means the reaction is reversible (high k°). What can be measured are the diffusion coefficient D_A and the standard potential E° of the reaction.

- If E_p varies with $\log(v)$ and $|I_p|$ is proportional to $v^{1/2}$, this means that the reaction is irreversible (low k°). The symmetry factor α_r and the standard constant k° of the reaction can be measured.

Whatever the value of k° , it is possible to shift from a reversible to an irreversible behavior by increasing the potential scan rate.

In a real experiment, there is an ohmic drop and the double layer capacitance current is not negligible. They must be taken into account, which is possible with CV Sim and is the subject of the second part of this application note.

Data files can be found in :

C:\Users\xxx\Documents\EC-Lab\Data\Samples\Fundamental Electrochemistry\AN41_

REFERENCES

1) A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, Hoboken, (2001).

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