

Fitting Experimental Cyclic Voltammetry Data with Theoretical Simulations Using DigiSim[®] 2.1

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Digital simulation software, such as the BAS cyclic voltammetry simulator DigiSim, can be used to extract quantitative mechanistic data from experimental data. However, such data should be examined critically to prevent misinterpretation. This article outlines how DigiSim can be used for fitting simulated and experimental data, and discusses the various pitfalls that can arise.

The ultimate purpose for a cyclic voltammetry simulator is to match simulated and experimental data, thereby confirming the mechanism proposed by the user for the redox chemistry of the system under investigation, as well as providing values for the associated thermodynamic and kinetic parameters. Although the introduction of DigiSim has facilitated the computational aspects of such studies, much expertise is required from the user both in terms of selecting the mechanism and analyzing the parameter values generated by DigiSim. The aim of this article is to show how DigiSim can be used for fitting experimental data and to illustrate some of the potential problems that can arise.

The fitting protocol in DigiSim can be divided into four stages:

- Select experimental data files for fitting
- Enter a mechanism
- Enter estimated values of the chemical and electrochemical

parameters, and select those to be fitted

- Run the DigiSim fitting routine

It is important to realize that, for a given CV, there may be several mechanisms and parameter value sets that provide a good match between the experimental and simulated data. Therefore, effective parameter optimization requires data from CV experiments run under a wide range of different experimental conditions. These include varying parameters, such as the scan rate and the reactant concentration, as well as the electrode geometry and dimensions (although temperature is also used as an experimental variable, all the experimental data files used in a given fitting run should have been recorded at the same temperature, since many of the thermodynamic and kinetic parameters optimized by DigiSim are temperature dependent).

A number of different text file formats are recognized by DigiSim and can be used for loading experimental files into DigiSim (data files

from BAS, PAR, and CYPRESS instruments, as well as a generic USER format for data from home-built data acquisition systems). However, the data files generated using commercial equipment typically do not contain all the data for the experimental conditions. For example, text files generated using the BAS 100B/W and the CV-50W systems do not contain values for the temperature, the reactant concentrations, and the electrode parameters. Although this information can be added manually using any word processing program (note that the modified data files must be saved in a text (ASCII) format), it can also be added using the **Export Data** command in DigiSim 2.1. This function converts any recognized experimental data file into the DigiSim USER format, and it will also add specified parameter values to the file header (these values are automatically read by DigiSim when the data file is selected for fitting). A BAS .TXT file and the corresponding DigiSim .MOD file (this is the extension given to files

F1

Comparison of the
formats of a BAS .txt
file (A) and a DigiSim
.mod file (B).

Date: 13-NOV-89
Time: 08:59:41
Label:
Cyclic Voltammetry

Exp. Conditions:
Init E (mV) = 0
High E (mV) = 750
Low E (mV) = 0
Init P/N = P
V (mV/sec) = 100
Number of Segments = 2
Sample Interval (mV) = 1
Quiet Time (sec) = 2
Sensitivity (A/V) = 1E-5

2 Sets of Data
Total Number of Data Points = 1500

Potential (mV), Current (A)

Segment = 1
Positive
Number of Data Points = 750

1.0, +1.160e-007
2.0, +1.129e-007
3.0, +1.099e-007
4.0, +1.068e-007
5.0, +1.038e-007
6.0, +1.007e-007
7.0, +9.768e-008
8.0, +9.463e-008
9.0, +9.158e-008
10.0, +8.852e-008
11.0, +8.852e-008
12.0, +8.547e-008
13.0, +8.242e-008
14.0, +7.937e-008
15.0, +7.631e-008
16.0, +7.326e-008
17.0, +7.326e-008
18.0, +7.021e-008
19.0, +7.021e-008
20.0, +6.716e-008
21.0, +6.410e-008
22.0, +6.105e-008
23.0, +5.495e-008
24.0, +5.189e-008
25.0, +4.884e-008
26.0, +4.884e-008
27.0, +4.579e-008
28.0, +4.579e-008
29.0, +4.579e-008

(A)

source program: DIGISIM WINDOWS
program version: 2.1
file type: CV

experimental parameters:
Estart (V): 0
Eswitch (V): 0.75
Eend (V): 0
v (V/s): 0.1
temperature (K): 298
cycles: 1
electrode geometry: planar
area (cm²): 0.08
diffusion: semi-infinite

species parameters:
Canal[A] (M/l): 0.001

data statistics:
Imin: -1.631E-005
Imax: 1.083E-005

experimental CV curve:
number of E(V), I(A) couples: 1500

0.001 , 1.16E-007
0.002 , 1.129E-007
0.003 , 1.099E-007
0.004 , 1.068E-007
0.005 , 1.038E-007
0.006 , 1.007E-007
0.007 , 9.768E-008
0.008 , 9.463E-008
0.009 , 9.158E-008
0.01 , 8.852E-008
0.011 , 8.852E-008
0.012 , 8.547E-008
0.013 , 8.242E-008
0.014 , 7.937E-008
0.015 , 7.631E-008
0.016 , 7.326E-008
0.017 , 7.326E-008
0.018 , 7.021E-008
0.019 , 7.021E-008
0.02 , 6.716E-008
0.021 , 6.41E-008
0.022 , 6.105E-008
0.023 , 5.495E-008
0.024 , 5.189E-008
0.025 , 4.884E-008
0.026 , 4.884E-008
0.027 , 4.579E-008
0.028 , 4.579E-008
0.029 , 4.579E-008
0.03 , 4.274E-008

(B)

processed using **Export Data**) are compared in **F1**, and there are a number of important points to note:

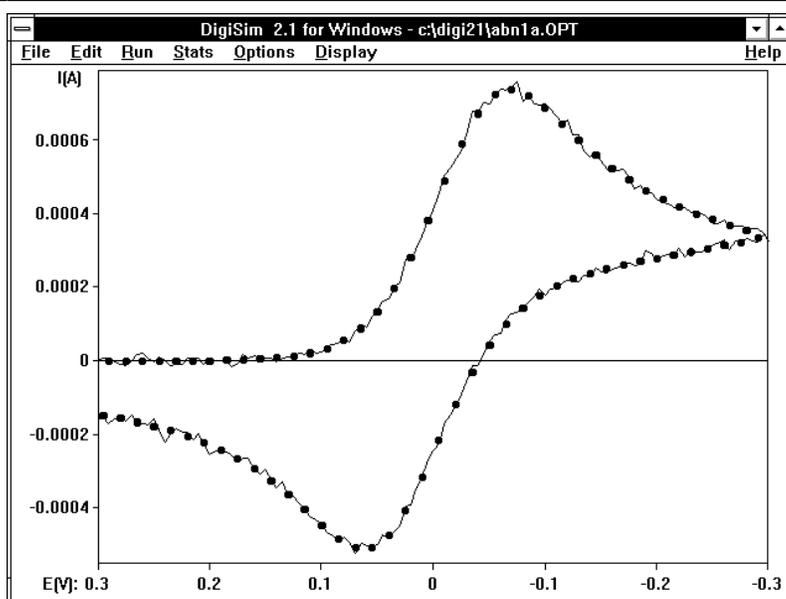
- The data must be arranged as potential-current couples
- The number of data couples must be given in the header
- The potential and current values within a data couple must be separated using a comma
- The current values must obey the **Classical** convention; that is, cathodic currents are positive (**Imin** and **Imax** values must be adjusted accordingly)
- The potential of the first data point must lie at $E_{\text{start}} \pm x V$, where x is the size of potential step.

A simplified USER format, in which the experimental parameters, species parameters, and data statistics have been omitted, is also acceptable.

The next two steps (choosing the redox mechanism and estimating parameter values) depend significantly on the expertise and intuition of the user. Although DigiSim cannot automatically suggest a mechanism, it can assist indirectly in these steps by developing the user's intuition. Since most DigiSim simulations require only a few seconds to run, the user can efficiently explore the differences between the cyclic voltammetric responses of different mechanisms and the effects of varying the associated parameter values. A few preliminary simulations can provide considerable insight into a given mechanism and can suggest appropriate values for the parameters to be optimized.

Once a mechanism has been entered and the appropriate parameter values are selected, the parameters to be optimized can be specified. Although there are a number of parameters that can be optimized (redox potentials, electron transfer kinetic parameters, equilibrium constants, chemical reaction rate constants, and diffusion coefficients), the choice of parameters should be made judiciously. In or-

Comparison of "experimental" (line) and simulated data (circles) for the quasi-reversible electron transfer reaction $A + e = B$.



der to better appreciate the problems that can arise with parameter selection, we must first discuss how DigiSim performs the fitting operation.

DigiSim uses an iterative Gauss-Newton method for the fitting routine, which seeks to optimize the parameter values in order to minimize the standard deviation, σ :

$$\sigma = \sqrt{\frac{\sum_{l=1}^n (i_{sim} - i_{expt})^2}{n}}$$

where n is the number of data points being compared, i_{sim} and i_{expt} are corresponding simulated and experimental data points (n is an adequate approximation of $n-1$ because there are a large number of data points). If only one parameter was being varied, then the fitting routine would search for the minimum in a 2-D plot of the standard deviation vs. the parameter value. However, if the number of parameters was increased, the dimensionality of the error plot (or the error hypersurface) would increase; if there were k selected parameters, the error hypersurface would be a $k+1$ dimensional plot. As the number of parameters is increased, the computational time is increased and the possibility of locating a local minimum in

the error hypersurface, rather than the global minimum, also increases. Therefore, it is unreasonable to program DigiSim to optimize all possible parameters and then expect DigiSim to generate the correct value for each of them. In addition, there are parameters that are known to be coupled (i.e., there is an infinite number of combinations of the parameter values that generate identical cyclic voltammograms); these generate a trough in the error hypersurface rather than a minimum. There are a number of well-known examples of coupled parameters (A is the sole initial species in all of these examples):

- The parameters D_B and E^0 for the reversible electron transfer reaction $A + e = B$.
- The parameters k_s and E^0 for the completely irreversible (i.e., no reverse wave is evident) electron transfer reaction $A + e = B$.
- The parameters k_f and E^0 for the completely reversible electron transfer reaction $A + e = B$, followed by the chemical reaction $B = C$ ($K_{eq} \gg 1$, $RTk_f/Fv \gg 1$; i.e., no reverse wave is evident).

Other parameters may be similarly coupled under the particular conditions being used in a given fitting operation.

Even if a fitting operation does detect a minimum in the error hypersurface, this still does not guarantee that the optimized values are correct, and these values must be examined critically. It is important to check that a true minimum has been found, rather than a local minimum; in addition, the sensitivity of the quality of the fit (the confidence limits) should be investigated for each parameter.

The simplest way to check whether the true minimum has been found is to run the fitting routine again using different initial values for the selected parameters. If the minimum found is indeed the true minimum, then the optimized values should be independent of the initial values. Several different sets of initial values should therefore be tried whenever the fitting operation is used.

There are two ways to access the confidence limits. DigiSim automatically calculates the limits from the covariance matrix during the fitting operation, and these values are displayed in **Confidence Limits** under the **Stats** menu. The confidence limits can also be calculated using **Chi²-Test** (under the **Run** menu). In this analysis, one of the selected parameters (the target parameter) is held at a fixed value, and the remaining parameters are again varied in order to find the new minimum in the error hypersurface. This process is repeated for a number of different values of the target parameter (the range of values should bracket the previously optimized value), and the value of X^2 (relative to the minimum value) is plotted as a function of the log of the target value (or as a function of the E^0 value, if this is the target parameter). This plot shows the sensitivity of the fit to variations in the value of the target parameter.

The calculation of the confidence limits and the operation of the Chi^2 analysis is best illustrated by an example. This example uses "experimental" data synthesized using DigiSim. The mechanism is A

F3

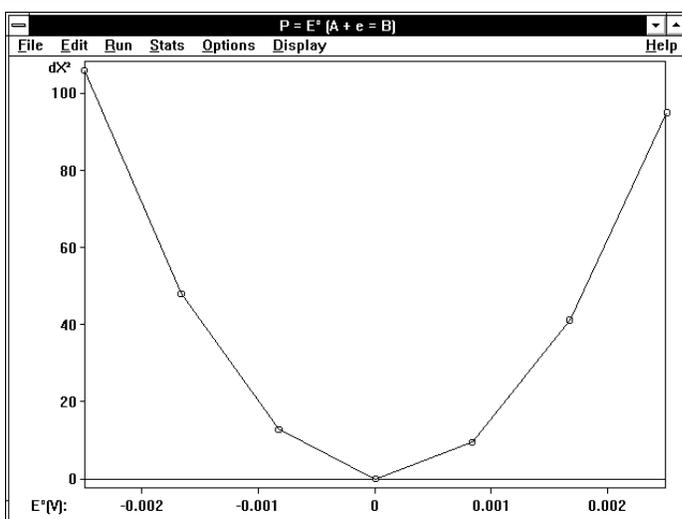
Dialog box for χ^2 -Test of the simulated data shown in **F2**.

F4

Confidence Limits dialog box showing the upper and lower limits of the target parameter derived from both the covariance matrix and the χ^2 test of the simulated data shown in **F2**.

F5

Plot of dX^2 vs. E^0 showing the results of the χ^2 test of the simulated data shown in **F2**.



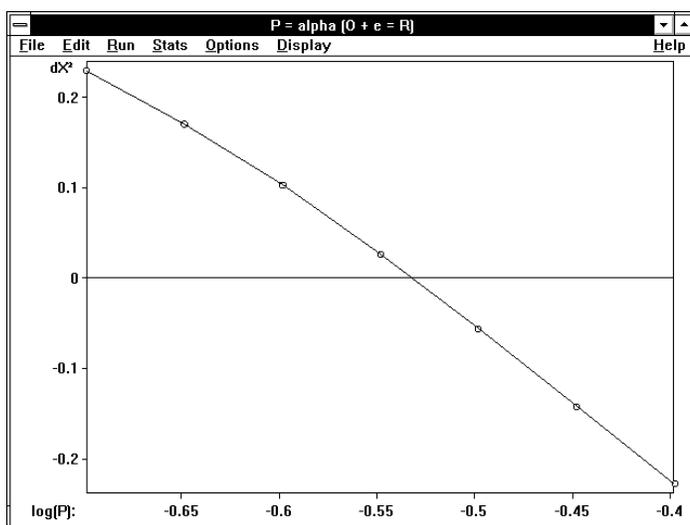
+ $e = B$, with $E^0 = 0$ V, $k_s = 0.01$ cm/s, $C_{\text{analyt}} A = 0.001$ M, and $\text{Noise} = 1E-5$ A (default values were used for all other parameters). This simulation was saved as **abn1.sim**. The “simulated” file for fitting used the identical mechanism (note that the syntax for entering mechanisms is case sensitive), with the initial guesses for E^0 and k_s of 0.1 V and 0.1 cm/s, respectively. The best fit simulated data and the original “experimental” data are shown in **F2**.

Once the fitting operation is complete, the χ^2 analysis can be run. Select **χ^2 -Test** from the **Run** menu to generate the dialog box shown in **F3**. Once the target parameter (E^0) and the upper and lower limits have been entered, click **Ok** to start the test. The E^0 value is set at 7 different values equally spaced in the specified range (± 0.0025 V), and k_s is optimized for each of these values. At the end of the test, a dialog box containing the optimized value and the upper and lower limits for the target parameter at the 68% confidence level from both the covariance matrix and the χ^2 test are displayed (**F4**) (the limits for the 95% or 99.7% confidence levels are also available). This provides a quantitative measure of the sensitivity of the fit to the value of the target parameter; the same information is also shown graphically (**F5**) by the plot of dX^2 (the change in X^2 from its minimum value) as a function of E^0 . It should also be noted that the confidence limits calculated using the two methods are almost equal; however, if there was a trough in the error hypersurface, there might have been significant differences in the confidence limits and the possibility of parametric coupling would have to be considered.

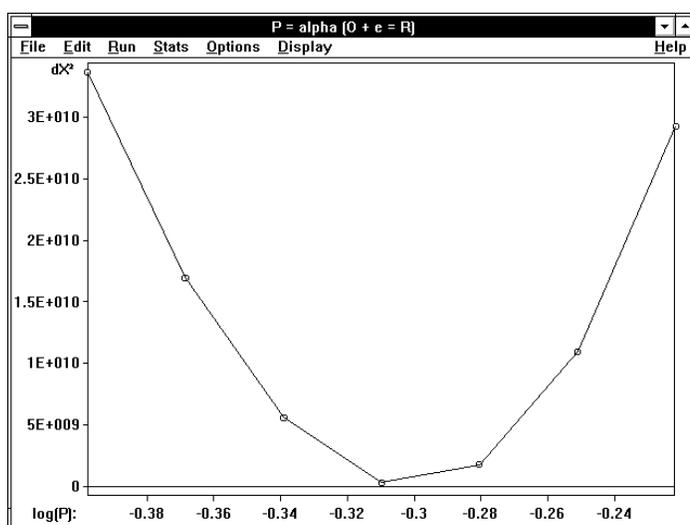
The confidence limits calculated in this example give a value of about 2.5×10^{-4} V for the standard deviation of E^0 ; that is, the fit is sensitive to small variations in the value of E^0 , and hence the opti-

F6

Plot of dX^2 vs. $\log \alpha$ for the electron transfer reaction $A + e = B$ ($E^0 = 0$ V, $\alpha = 0.5$, and $v = 1$ V/s) under A) reversible ($k_s = 1e^4$ cm/s, E^0 and α optimized) and B) quasi-reversible conditions ($k_s = 0.001$ cm/s, E^0 , k_s and α optimized).



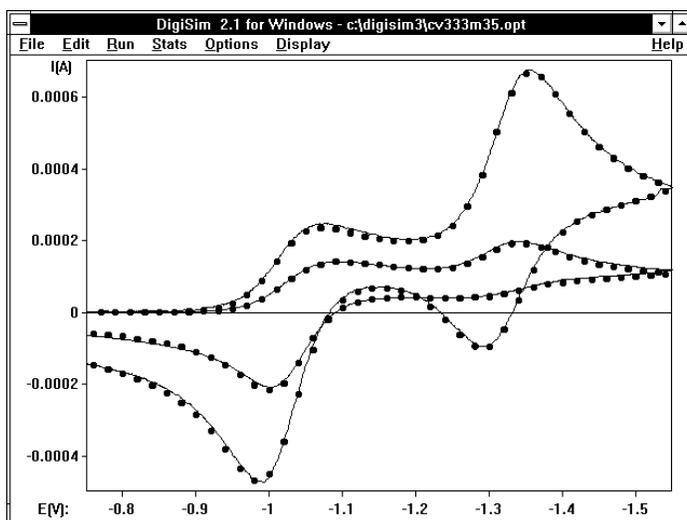
A



B

F7

Comparison of experimental (lines) and simulated (circles) data for a nickel(II) complex in the presence of bipyridine at scan rates of 40 and 333 V/s (1).



mized value generated by the fitting routine is valid. However, there are cases where the quality of the fit is not significantly affected by variations in the values of a given parameter. Consider the effect of varying α for the electron transfer reaction $A + e = B$ ($E^0 = 0$ V, $\alpha = 0.5$, and $v = 1$ V/s) under reversible ($k_s = 1e^4$ cm/s, E^0 and α optimized) and quasi-reversible conditions ($k_s = 0.001$ cm/s, E^0 , k_s and α optimized). The value of α has little effect on the quality of the fit for the reversible process, and this is reflected in the plot of dX^2 versus $\log \alpha$ (F6A) (α varied over the range ± 0.1 from the optimized value). In contrast, varying α over the equivalent range for the quasi-reversible process has a dramatic effect on the quality of the fit (F6B). The invariant behavior shown in F6A can also be observed when the target parameter is coupled to another parameter.

One factor that has not yet been discussed is the quality of the experimental data. In addition to subtraction of the background current and compensation of the solution resistance, the experimentalist should ensure that the experimental conditions (particularly the temperature) are carefully controlled. If adequate care is taken, it is possible to obtain very good agreement between the experimental and simulated data over a wide range of conditions. This is illustrated in F7, which shows the experimental (line) and simulated (circles) data for a nickel(II) complex in the presence of bipyridine at scan rates of 40 and 333 V/s (1).

Reference

1. E-G. Jaeger and M. Rudolph, *J. Electroanal. Chem.*, in press

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