CAPSULES
notes and applications from Bioanalytical Systems, Inc.
July 1997

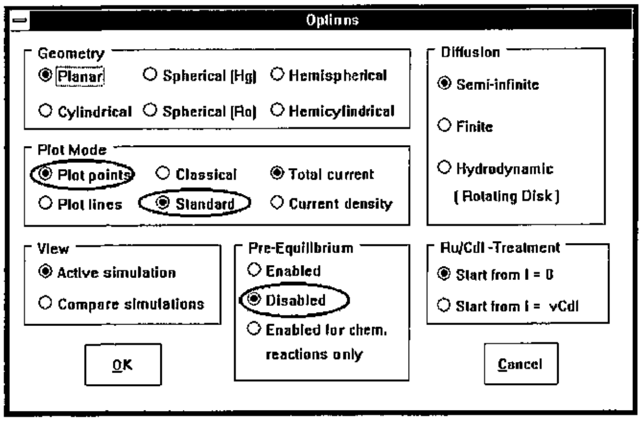
Using DigiSim® to Simulate Single-Step Chronoamperometry

Purpose

Although cyclic voltammetry is widely used in teaching labs for characterization of redox systems, the principles of this technique are often poorly understood. One of the purposes of the BAS cyclic voltammetry (CV) simulator DigiSim® has been to help students understand the factors that control the current response obtained in a CV experiment. However, the presence of many factors (e.g., diffusion, electron transfer kinetics, homogeneous chemical reactions) can cause considerable confusion. The effects of electron transfer kinetics can be eliminated using chronoamperometry (or other potential step techniques) by careful selection of the step potential. If the electron transfer reaction under investigation does not undergo any coupled chemical reactions, the current response of a chronoamperometry experiment is controlled completely by the rate of diffusion; that is, this experiment provides a good illustration of the effects of diffusion. Although it is strictly a CV simulator, DigiSim can be "tricked" into performing a chronoamperometry simulation

Method

In order to simulate single-step-chronoamperometry using DigiSim, we take advantage of the feature which allows us to disable the pre-equilibrium computation. This computation (which is normally activated during CV experiments) ensures that the concentrations of all species initially present in the solution are at the concentrations defined by the starting electrode potential (**E$_{start}$**) and all the thermodynamic parameters (**E$^{o\prime}$**s and **K$_{eq}$**'s) defined in the **CV/Chemical Parameters** dialog box. If this calculation is disabled, it is then possible to select values of **E$_{start}$**, **E$_{rev}$** and **E$_{end}$** which are virtually identical and whose values, relative to the **E^{o}**(s) operative in the system, will effect a faradaic process. As an example let us consider the following system:



Options

Geometry: ● Planar ○ Spherical (Hg) ○ Hemispherical ○ Cylindrical ○ Spherical (Ro) ○ Hemicylindrical

Diffusion: ● Semi-infinite ○ Finite ○ Hydrodynamic (Rotating Disk)

Plot Mode: ● Plot points ○ Classical ● Total current ○ Plot lines ● Standard ○ Current density

View: ● Active simulation ○ Compare simulations

Pre-Equilibrium: ○ Enabled ● Disabled ○ Enabled for chem. reactions only

Ru/Cdl-Treatment: ● Start from t = 0 ○ Start from t = vCdl

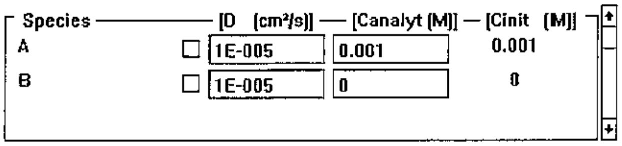
Figure 1. **Options** dialog box for chronoamperometry simulation.

A + e = B (E^{o} = 0.5 V; **k$_s$** = 10^4 cm/s; $\alpha = 0.5$)

The mechanism is entered into the **Mechanism** dialog box in the usual way. In the following section, the adjustments that must be made when setting up the simulation are described, and the accuracy of this simulation is evaluated.

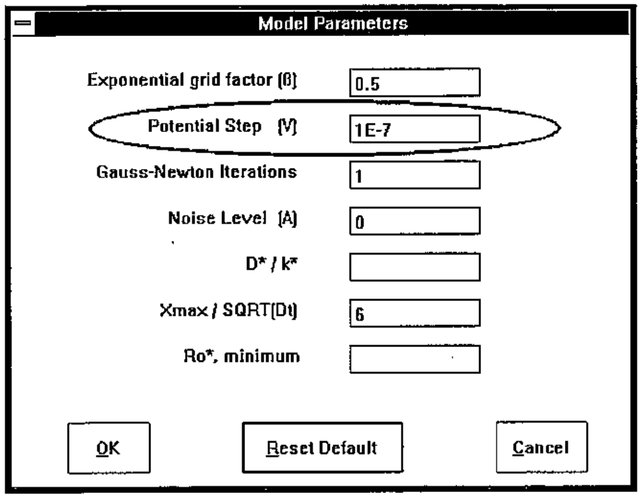
1.Open the **Options** dialog box, **Disable** the **Pre-Equilibrium** and, for the purposes of this example, activate **Plot points** and the **Standard** plot:

2.In the **CV/Chemical Parameters** dialog box:
a.Set **E$_{start}$** = 0 V and **E$_{rev}$** = **E$_{end}$** = +0.0001 V (thereby effecting a single scan from 0 to +0.0001V). While other values might be selected (e.g., **E$_{start}$** = -0.5 V and **E$_{rev}$** = **E$_{end}$** = -0.4999 V) the abscissa tick mark labels will become crowded, difficult to read, and in, some cases, rounded off).
b.Set **v** = 1.0 x 10-4 V/s (thereby effecting, for this example, a chronoamperogram lasting 1.0 s).



Species		[D (cm²/s)]	[Canalyt (M)]	[Cinit (M)]
A	☐	1E-005	0.001	0.001
B	☐	1E-005	0	0

Figure 2. Comparison of **C$_{analyt}$** and **C$_{init}$**.



Exponential grid factor (β) 0.5

Potential Step (V) 1E-7

Gauss-Newton Iterations 1

Noise Level (A) 0

D* / k*

Xmax / SQRT(Dt) 6

Ro*, minimum

Figure 3. Model Parameters for chronoamperometry simulation.

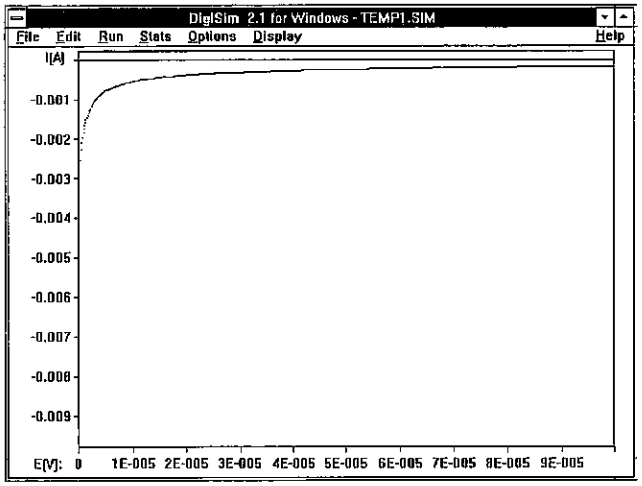


Figure 4. Chronoamperometry simulation in **Standard** mode.

c.Set $\mathbf{E^o}$ = +0.5 V (thereby ensuring that the concentration of species A will be virtually zero at the electrode surface; in principle, however, any value greater than about +0.2 V may be selected for $\mathbf{E^o}$).

d.Set $\mathbf{C_{analyt}}$ for species **A** = 0.001 M. Note that the initial and analytical concentrations are identical, since the pre-equilibrium calculation has been disabled.

3. Open the **Model Parameters** dialog box and set the **Potential Step** = 1.0×10^{-7} V.

The size of the potential step, ΔE, is chosen to effect the desired number of time-steps, *N*, in the simulation:

$$N = \frac{|E_{end} - E_{start}|}{\Delta E}$$

4.**Run** the simulation. The resulting simulation is shown in F4.

The dependence of the current (i) as a function of time (t) is given by the Cottrell equation:

$$i = \frac{nFAD^{1/2}C}{(\pi t)^{1/2}}$$

where:

n = number of electron transferred

F = Faraday's constant (C/mol)

A = electrode surface area (cm^2)

D = diffusion coefficient (cm^2/s)

C = concentration (mol/cm^3)

It should be noted that this equation assumes a planar surface, stable reactant and product, a uniform initial concentration, and a homogeneous medium. Modifications of this equation for spherical diffusion, microelectrodes and other geometries have been derived.

Results

To evaluate the chronoamperometric response, we have to convert the voltages on the: abscissa to time, t:

$$\Delta t = \left|\frac{\Delta E}{v}\right|$$

We can confirm the accuracy of the simulations by computing the value of the Cottrell parameter:

$$P_{cottrell} = \frac{|i|(\pi t)^{1/2}}{nFAD^{1/2}C}$$

Values of $\mathbf{P_{Cottrell}}$ are given in T1.

To read current values from the simulated graph, first expand the area of interest.

{Display}⇒{Zoom}

After defining the area of interest (e.g., between 0 and 1×10^{-6} V - equivalent to 0 to 0.01 s) individual data points can be seen (as the **Plot Points** option was selected). The current-voltage coordinates of

n	t/s	$P_{Cottrell}$
1	1.0E-3	1.759100
2	2.0E-3	0.844487
3	3.0E-3	1.149767
4	4.0E-3	1.104282
5	5.0E-3	1.039122
6	6.0E-3	1.019522
7	7.0E-3	1.012763
8	8.0E-3	1.009436
9	9.0E-3	1.007850
10	1.0E-2	1.006606
15	1.5E-2	1.002346
20	2.0E-2	1.001336
25	2.5E-2	1.001054
30	3.0E-2	1.000723
35	3.5E-2	1.000383
40	4.0E-2	1.000217
45	4.5E-2	1.000145
50	5.0E-2	1.000085

Table 1. Values of $\mathbf{P_{Cottrell}}$ for selected points.

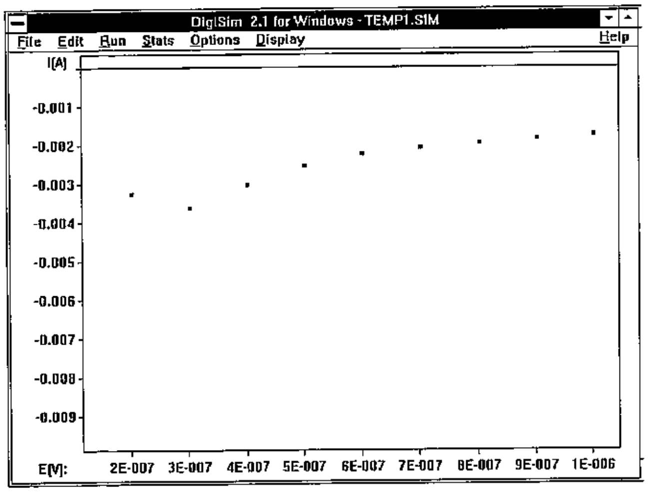


Figure 5. Expanded plot of chronoamperometry simulation at early time points.

any given point are obtained by placing the cursor close to the point and clicking the mouse (the coordinates are shown in the upper left corner of the display). The values of $\mathbf{P_{Cottrell}}$ for selected points are presented in the table above. There is oscillation in the first few points, followed by rapid convergence to better than 0.1% error for n>20. The oscillation results from the response of the simulation to a large instantaneous perturbation by an implicit finite difference formalism which is designed to respond to a series of small potential steps (the default value for the potential step is 0.005 V; this value is defined in the **Model Parameters** dialog box). The formalism which generated the data in T1 used a value of $D^* = 10$, where $D^* = D\Delta t/\Delta x^2$ (D is the largest diffusion coefficient used in the calculation, Δt is the time increment, and Δx is the thickness of the volume element closest to the electrode surface). More complicated systems involving species with different diffusion coefficients and/or homogeneous chemical kinetics will utilize values of $D^* > 10$. Then, if Cottrellian behavior is followed, the errors may differ slightly from those reported in T1. In general, however, the accuracy of any chronoamperometric simulation will be within 0.1% when n > 20.

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Authors

Stephen W. Feldberg, Brookhaven National Laboratory, Upton, NY.
Manfred Rudolph, Friedrich-Schiller Universitat, Jena, Germany.