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Application of Convolutive Voltammetric Curve
Fitting Techniques to Non-Reversible Electrochemical Systems

by

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Abstract

Curve fitting based on the semiderivative is extended to non-reversible charge transfer kinetics and to homogeneous kinetics. Using data generated by digital simulation, the sech² waveform is shown to be an adequate description of systems with non-reversible charge transfer kinetics. Systems involving homogeneous kinetics are not well described by the sech² waveform, but may be accurately fitted with a convolution-based waveform. In both cases, physically significant parameters may be obtained from curve fitting the model to the electrochemical data.
Brief

Convolution potential voltammetry is applied to the curve-fitting of electrochemical systems involving homogeneous kinetics or non-reversible charge transfer kinetics. Physically significant parameters may be obtained.
Linear sweep voltammetry (l.s.v.) has found applications not only in electrochemical analysis but also in studies of bulk solution and interfacial thermodynamics and kinetics. Curve fitting of l.s.v. waves has been shown to be a valuable technique in some of these applications. Until recently curve fitting of linear sweep voltammograms has been done only with the assumption of empirical peak functions, in which many arbitrary parameters are used in order to achieve a good fit,\textsuperscript{1-3} or by the fitting of voltammograms with peak shapes assumed from single peak data,\textsuperscript{4,5} or both. In the last year a new technique based on semidifferential voltammetry, has been applied to curve fitting of reversible l.s.v. waves.\textsuperscript{6} This technique, called semidifferential voltammetric curve fitting (s.v.c.f.), numerically transforms a reversible l.s.v. wave into a hyperbolic secant squared waveform, and has been shown to enhance resolution of overlapping waves in both linear sweep and anodic stripping voltammetry. Advantages of this technique are that fitting parameters are directly related to physical parameters of the electrochemical system, and that no parameters need be assumed in fitting transformed l.s.v. waves.

Unfortunately, reversible electrochemical systems are rather rare. If one considers, as an example, the electrochemical system in which a metal complex dissociates to give free metal and ligand, followed by reduction of the free metal, one often finds non-reversible charge transfer kinetics, non-labile homogeneous kinetics, or both. For any of these cases the sech\textsuperscript{2} fitting function used in semidifferential voltammetric curve fitting is not the correct fitting function for the semiderivative of the l.s.v. wave.

Curve fitting of l.s.v. waves of systems with non-reversible kinetics with numerical techniques can still be useful, however. It has been shown that the semiderivative of an irreversible charge transfer is similar in
appearance to a $\text{sech}^2$ function; therefore, application of semidifferential voltammetric curve fitting to non-reversible charge transfer systems might be possible. For small perturbations from reversibility, semiderivatives of l.s.v. waves exhibiting non-labile homogeneous kinetics should be nearly $\text{sech}^2$ in form; application of semidifferential voltammetric curve fitting to such systems might be useful. Semidifferential voltammetry is only one of a number of numerical techniques, known collectively as convolutive potential sweep voltammetry, that relate current, a numerically transformed function of the current called the semiintegral, and applied potential in simple analytical expression for a number of electrochemical systems, especially in limiting cases of kinetic behavior. Convolutive voltammetric curve fitting (c.v.c.v.) should be possible in these limiting cases at least.

This paper will investigate the effectiveness of the semidifferential voltammetric curve fittings technique to l.s.v. waves exhibiting non-reversible charge transfer kinetics and will determine the effectiveness of both the semidifferential voltammetric and convolutive voltammetric curve fitting techniques for l.s.v. systems in which the kinetic mechanism is that of a non-labile chemical reaction preceding a reversible charge transfer.

THEORY

In order to prevent confusion, a brief discussion of the meaning of the term 'reversible' will be undertaken in the sense in which it is applied in this paper to both charge transfer kinetics and to the CE kinetic mechanism. Following Matsuda and Ayabe, a given charge transfer

$$A + ne^- \rightarrow B$$  \hspace{1cm} (eqn. 1)

is defined as reversible if the dimensionless heterogeneous rate constant

$$\Lambda = \frac{k^*}{\rho^{\text{RT}} nF}$$  \hspace{1cm} (eqn. 2)
(where \( D \) is the diffusion constant, assumed to be the same for oxidized and reduced species; \( \nu \) is the scan rate; \( k^0 \) is the heterogeneous rate constant, \( \alpha \) is the transfer coefficient, and other symbols have their usual meaning) is larger than 15; the charge transfer is defined as irreversible if \( \Lambda < 10^{-2(1+\alpha)} \), and is defined as quasi-reversible otherwise. Non-reversible charge transfers include both quasi-reversible and irreversible charge transfers.

The CE mechanism is defined by

\[
C \xrightarrow{\frac{k_f}{k_b}} A \\
A + ne \rightleftharpoons B
\]

(eqn. 3)

where \( k_f \) and \( k_b \) are the homogeneous first order rate constants and where \( K = \frac{k_f}{k_b} \) is the equilibrium constant. In this study the charge transfer step is understood to be reversible. Following Saveant and Vianello,\(^8\) if the dimensionless homogeneous rate constant is defined as

\[
\lambda = \frac{k_f + k_b \cdot RT}{\nu \cdot nF}
\]

(eqns. 4)

three limiting cases of kinetic behavior occur. For \( \lambda \gg 0 \), essentially no preceding reaction occurs, and the mechanism is the same as Eqn. 1 for a reversible charge transfer. This is commonly called pure diffusion-controlled behavior. The l.s.v. wave has the same shape and peak potential as the wave for the reversible charge transfer. For \( \lambda \gg \infty, K \gg 0 \) the homogeneous kinetics are much faster than the charge transfer, and in this case one may think of the system as being comprised of a species that is itself electroactive and undergoes a reversible charge transfer; i.e., the mechanism becomes

\[
C + ne^- \rightleftharpoons B
\]

(eqn. 5)

This is called modified diffusion kinetic behavior. This wave has the same shape as the wave for the reversible charge transfer, but the peak potential is shifted negatively relative to the peak potential for the reversible charge...
transfer. For $\lambda \to 0$, $K \to \infty$, a balance is achieved wherein a constant flux of $A$ is always maintained to the electrode as the applied potential is made very negative; this is called pure kinetic behavior. The resultant l.s.v. wave in this case looks like a polarographic wave, reaching limiting current at negative potentials.

According to Fig. 1 of Ref. 9, as $\lambda$ increases from 0 to $\infty$ the l.s.v. wave changes in character from pure diffusion-controlled to pure kinetic to modified diffusion-controlled. Systems with kinetic behavior between zones of limiting behavior have l.s.v. waves that have a shape between that of the shapes of the waves for pure kinetic behavior and that of either pure or modified diffusion-control. In this paper, a reversible homogeneous kinetic system will be defined as showing either pure diffusion-controlled or modified diffusion-controlled behavior; an irreversible homogeneous kinetic system will be defined as showing pure kinetic behavior; other systems will be designated as non-reversible homogeneous kinetic systems. The values of $\lambda$ for the boundaries of the different zones of kinetic behavior depend on the value of the equilibrium constant. For $K = 10^{-4}$, the equilibrium constant used for the systems studied in this work, the boundary of the pure diffusion zone is $\lambda < 0.03$; the boundaries of the pure kinetic zone are $0.4 < \lambda < 6 \times 10^2$; the boundary for the modified diffusion zone is $\lambda > 2 \times 10^4$.

The theory of semidifferential voltammetry for both a reversible charge transfer and for a labile CE mechanism (i.e., the modified diffusion system) has been described elsewhere.\textsuperscript{10-12} The semiderivative of an l.s.v. wave for a system with a reversible charge transfer without preceding homogeneous kinetics is\textsuperscript{11}

$$e(E) = \frac{nFm^*}{4RT} \text{sech}^2 \left[ \frac{nF}{2RT}(E - E_{1/2}) \right]$$

(eqn. 6)
where
\[ m^* = (D_u)^{1/2} n F A C_{ox}^* \]  
(eqnn. 7)

and where \( C_{ox}^* \) is the bulk concentration of the oxidized species and \( A \) is the surface area of the electrode. The potential at the peak maximum for this system is the reversible half-wave potential; i.e.,
\[ E_p = E^{R}_{1/2} \]  
(eqnn. 8)

For a reversible charge transfer preceded by labile kinetics (i.e., for the modified diffusion-controlled system) the semiderivative is: \(^{12}\)
\[ e(E) = \frac{nFm^*}{4RT} \text{sech}^2 \left[ \frac{nF}{2RT}(E-E^{R}_{1/2}) + \frac{1}{2} \ln(1+1/K) \right] \]  
(eqnn. 9)

where the peak potential at the peak maximum in this system is shifted cathodically as compared to the system without preceding homogeneous kinetics by an amount:
\[ \Delta E_p = \frac{RT}{nF} \ln(1+1/K) \]  
(eqnn. 10)

The full width at half maximum (FWHM) for the semiderivative of the system described by either Eqnn. 6 or 9 is: \(^{11}\)
\[ \text{FWHM} = \frac{90.6}{n} \text{mV} \]  
(eqnn. 11)

For non-reversible charge transfers Imbeaux and Saveant\(^{10}\) derived equations relating the semiintegral and the l.s.v. current to applied potential. Goto and Oldham\(^{13}\) have derived an analytic expression relating the semiintegral to a series solution involving the applied potential and have shown a qualitative agreement between theory and experiment. Dalrymple-Alford, et al.,\(^{11}\) extended this work to the semiderivative, showing that the semiderivative of an l.s.v. wave exhibiting irreversible charge transfer kinetics was a nearly symmetric peak, beginning and ending at the baseline, with a FWHM given by
FWHM = $\frac{75.5}{a_n}$ mV \hfill (eqn. 12)

and a peak potential $E_p$ given by:

$E_p = E_{1/2} - \frac{RT}{2a_nF} \ln \left( \frac{nF}{a_RT} \right) + 0.055 \left( \frac{RT}{a_nF} \right) + \frac{RT}{a_nF} \ln \Lambda$ \hfill (eqn. 13)

From Fig. 1 of Ref. 11 the semiderivative of an irreversible charge transfer is seen to be similar in appearance to a sech$^2$ function and some success might therefore be expected in using the technique developed for curve fitting of reversible systems\textsuperscript{6} to fit semiderivatives of waves of non-reversible charge transfer systems.

For the system exhibiting homogeneous kinetics in the pure kinetic zone Imbeaux and Saveant\textsuperscript{10} have derived a relation between current, semiintegral and applied potential as:

$E = E_{1/2} - \frac{RT}{2nF} \ln k_b + \frac{RT}{nF} \ln \left[ \frac{i_L - i(E)}{m(E)} \right]$ \hfill (eqn. 14)

where $i(E)$ is the observed current, $i_L$ is the limiting current observed at large negative potentials, and $m(E)$ is the semiintegral. From Eqn. 14 an expression analogous to Eqn. 6 can be derived:

$$\frac{4 m^2(E)(i_L - i(E))^2}{[m^2(E) + (i_L - i(E))^2]^2} = \text{sech}^2 \left[ \frac{nF}{RT} \left( E - E_{1/2} + \frac{RT}{2nF} \ln k_b \right) \right]$$ \hfill (eqn. 15)

This function has a maximum at the potential:

$E_p = E_{1/2} - \frac{RT}{2nF} \ln k_b$ \hfill (eqn. 16)

has a peak height of 1 at the peak maximum, and has FWHM given by:

$\text{FWHM} = \frac{45.3}{n} \text{mV}$ \hfill (eqn. 17)

For non-reversible homogeneous kinetic systems expressions relating semi-integral, current and applied potential\textsuperscript{10} are so complex as to not be useful
at the present time. It is doubted that curve fitting of waves of these systems will be successful.

EXPERIMENTAL

The effectiveness of the curve fitting techniques for different electrochemical systems was determined by application to artificial data. Synthetic l.s.v. waves for systems with non-reversible charge transfer kinetics were constructed using the finite difference method of digital simulation, as described by Feldberg and others.\textsuperscript{14,15} This method involves the creation of a series of discrete volume elements that represent the concentration of species at specified distances from the electrode surface. The concentrations in the various volume elements are changed iteratively with time with respect to diffusion, charge transfer and whatever homogeneous reactions may be occurring in the system.

The data files created for the study of the application of semidifferential voltammetric curve fitting to systems showing non-reversible charge transfer kinetics are summarized in Table I. The program used to do this finite difference simulation was a FORTRAN program named DIGIT. This program, like all others, was run on a DEC LSI-11/23 CPU with floppy disk data storage and 128 K words of memory. All files contain one peak, have potential ranges from 0.0 V to -1.0 V, and use \( \alpha = 0.5, E^0 = -0.5 \) V, and \( n = 2 \). All files are 512 points long and required 512 iterations for construction; this process required about 85 seconds of CPU time.

After creation, the artificial l.s.v. files were semidifferentiated by a FORTRAN program employing the Grünwald method as given by Oldham and Spanier.\textsuperscript{16} The semidifferentiated files were used as input for the curve fitting program BIMFIT,\textsuperscript{6} which is based on the sequential simplex algorithm. This program uses as a fitting function
\[ f(E) = A \sech^2[B(E-C)] \] (eqn. 18)

The variable \( A \) is called the returned peak height and is the height at the peak maximum, and \( B \) is related to the FWHM of the \( \sech^2 \) peak by \( \text{FWHM} = 1.7627/B \). The FWHM is called the peak width. Finally, \( C \) is called the peak potential and is the potential of the \( \sech^2 \) peak at the peak maximum. As input, BIMFIT requires only the number of peaks in the semidifferentiated voltammogram and the file itself. The use of BIMFIT in fitting \( \sech^2 \) peaks and in resolving overlapped electrochemically reversible peaks has been reported previously.\(^6\) The minimization routine was modified to terminate when the sum of squares of residuals at the vertices of the simplex was less than \( 1.0 \times 10^{-12} \). Times for fitting of single peaks were on the order of 50-80 seconds. Returned peak parameters for the BIMFIT fitting of semiderivatives of the charge transfer kinetic data files are shown in Table I.

In addition to the single wave files just described, synthetic semiderivative voltammograms of overlapping waves corresponding to systems with reversible and non-reversible charge transfer kinetics were created. This was done to demonstrate the effectiveness of semidifferential voltammetric curve fitting in fitting systems with non-reversible charge transfer kinetics. These waves were constructed by adding \( \sech^2 \) functions with specified peak potentials, heights and widths to the semiderivatives of the files in Table I. The added \( \sech^2 \) function was in all cases of approximately the same height as the wave to which it was added, was of 45.3 mV in width (equivalent to a reversible 2-electron wave), and was given a peak potential either 35, 50, or 70 mV cathodic to the peak potential of the file to which it was added. After creation, the file of overlapped semiderivative peaks was used as input to BIMFIT, and also to a version of BIMFIT called CNWSBM. This
second program is the same as BIMFIT except that the peak widths are con-
strained to an input value. In this study, peak widths input to CNWSBM were
the returned peak widths taken from application of BIMFIT to the
semiderivatives of the single peak charge transfer kinetic systems.

The finite difference digital simulation works well on the LSI-11/23 for
systems with only charge transfer kinetics, or for systems with charge trans-
fer and slow homogeneous kinetics. For systems with rapid kinetics, however,
a very large number of iterations is needed to achieve accurate results, and
the CPU time necessary to generate these peaks becomes long. For this reason
the numerical integration method of Nicholson and Sham\textsuperscript{17} was employed for
the simulation of systems with rapid kinetics. In this method, the partial
differential equations and boundary conditions describing the CE mechanism are
first solved to set an integral equation in time:

\[ 1 - \int_0^{\alpha t} \frac{\psi(z)dz}{\sqrt{\alpha t - z}} = \frac{1 + K}{K} \theta S_\lambda(\alpha t) \int_0^{\alpha t} \frac{\psi(z)dz}{\sqrt{\alpha t - z}} + \frac{1}{K} \int_0^{\alpha t} \exp(-\lambda(\alpha t - z)\psi(z)dz \quad (\text{eqn. 19}) \]

where \( a = nFv/RT, \theta = \exp[nF/RT(E - E_{1/2})], E_i \) is the initial
potential, and \( S_\lambda(\alpha t) = \exp(-\alpha t) \).

The solution desired is the value of \( \psi(\alpha t) \). Consider that the entire
interval from 0 to \( \alpha t \) is divided into \( n \) subintervals each of length \( \delta = \alpha t/n; \)
from this it is seen that the value of \( \psi(n\delta) \) is desired, where \( n \) is some
integer. Suppose that all the \( \psi(k\delta), k = 1, 2, \ldots, n-1 \) are already known. The
substitution \( z = k\delta \) is made into all the integrals of Eqn. 19, and these now
have the form

\[ \int_0^{\alpha t} \frac{f(z)\psi(z)dz}{\sqrt{\alpha t - z}} = \sqrt{\delta} \int_0^n \frac{f(k\delta)\psi(k\delta)dk}{\sqrt{n-k}} \quad (\text{eqn. 20}) \]

These integrals cannot be evaluated in this form, as a singularity exists at
\( n = k \). This singularity is removed by integration by parts, and the resulting
integral is in the form of a Riemann-Stieltjes integral,\(^{13}\) where it is assumed that the integral of \(f(\kappa \delta)/ n-k\) exists, and \(s(\kappa \delta)\) is that integral. The Riemann-Stieltjes integral may be recast as a finite sum

\[
\int_0^n \! g(k \delta) \, d\psi(k \delta) = \sum_{k=1}^{n} g(k \delta) [\psi(k \delta) - \psi((k-1) \delta)]
\]  
(eqn. 21)

After substituting the corresponding sum in for all the integrals in Eqn. 20, the resulting equation is solved for \(\psi(n \delta)\). As all the \(\psi(k \delta)\) are known, the value of \(\psi(n \delta)\) follows immediately. The process is extended to determine \(\psi((n+1) \delta)\), and continued until the desired termination.

The data files created for the study of the suitability of the semidifferential voltammetric curve fitting technique for systems involving homogeneous kinetics are shown in Table II. The program DIGIT was used to create files K through P; the FORTRAN program NSSOL, employing Nicholson and Shain's method, was used for the creation of files Q through CC. All files extend from 0.0 V to -1.0 V, use \(E_{1/2} = -0.5\) V and \(n = 2\), and set the equilibrium constant \(K = k_f/k_b = 10^{-4}\). All files were 512 points long and required 512 iterations; both programs required about 180 seconds of CPU time per file.

After creation, files were semidifferentiated and used as input to BIMFIT. In addition some of the homogeneous kinetic data files were semi-integrated, and operated on according to Eqn. 15. This process will be referred to here simply as convolution, and files derived from this process will be called convoluted files. The program used to accomplish this was a FORTRAN program named KPSEMI, and the routine used for semi-integration was also based on the Grünwald algorithm. The resultant convoluted files were written to disk, and used as input to BIMFIT. Table II shows single peak results for sech\(^2\) fits to semidifferentiated homogeneous kinetic data files, and Table III shows results of sech\(^2\) fits to convoluted homogeneous kinetic data files.
RESULTS AND DISCUSSION

Charge Transfer Kinetics

The effectiveness of any curve fitting technique for a system may be judged by how well returned peak parameters obey relations derived from theory. For the semidifferential voltammetric curve fittings technique as applied to charge transfer kinetic systems, this first implies that the semi-derivative is \( \text{sech}^2 \) in form, (as is stated by Eqn. 6 for reversible charge transfer systems). The first condition of validity of semidifferential voltammetric curve fitting for any system must be the return of a coefficient of determination, or \( R^2 \) value, close to 1.

The semidifferential voltammetric curve fittings technique will be considered valid for a given non-reversible charge transfer system only when, in addition to the return of \( R^2 \) close to 1, returned peak parameters agree with parameters derived from theoretical relations. Useable relations with which to judge the effectiveness of semidifferential voltammetric curve fitting exist only for reversible and irreversible charge transfer kinetic systems. The relations that may be so used are Eqns. 8 and 11 for reversible charge transfers and Eqns. 12 and 13 for irreversible charge transfers. From Eqns. 8 and 11, if semidifferential voltammetric curve fitting is valid for reversible charge transfer systems, returned peak potentials and widths for these systems will be \(-0.500 \) V and \(45.3 \) mV, respectively. If semidifferential voltammetric curve fitting is to be valid for irreversible charge transfer systems, the returned peak widths for these systems will be \(75.5 \) mV, as given by Eqn. 12, and a linear least squares fit of returned peak potential vs. \( \ln \Lambda \) for these systems will have a slope of \(25.7 \) mV, and an intercept of \(-0.435 \) V, as given by Equation 13.
The returned fit parameters for all charge transfer systems studied are shown in Table I. From the definitions of charge transfer reversibility and irreversibility, files I and J are seen to be reversible, while files A and B are irreversible. A linear least squares fit of returned $E_p$ vs. $\ln \Lambda$ for files A and B save a slope of 25.7 mV and an intercept of -0.4313 V. Comparisons of these values and the returned peak parameters for files A, B, I, and J with the values predicted above show close agreement between fit and theoretical parameters for both reversible and irreversible charge transfer systems. Coefficients of determination are close to 1 for the four files. Both conditions of validity are fulfilled for the application of semidifferential voltammetric curve fitting to both reversible and irreversible charge transfer systems.

There are no simple relations with which returned peak potentials or widths can be used to judge the effectiveness of semidifferential voltammetric curve fitting for systems with quasi-reversible charge transfer kinetics. Because the returned $R^2$ values get closer to 1 as $\Lambda$ is increased, and because quasi-reversible systems become more and more reversible as $\Lambda$ is increased, one might expect semiderivatives of waves of these systems to become more and more $\text{sech}^2$ in shape as $\Lambda$ is increased. The semidifferential voltammetric curve fitting technique is expected to better fit these semiderivatives than in the completely irreversible case.

There is another way to show that semidifferential voltammetric curve fitting is valid for non-reversible charge transfer systems. One may overlap semiderivatives of waves for these systems with $\text{sech}^2$ functions and use semidifferential voltammetric curve fittings to resolve the overlapped peaks. The accuracy with which parameters are returned from the fused peak waves gives an indication of the suitability of semidifferential voltammetric curve fitting.
fittings for the curve fitting of the wave for the quasi-reversible system, and incidentally gives an indication of how well peak resolution of such overlapped systems may work.

Towards this end, the accuracy of resolution is rather arbitrarily defined as

\[ \text{accuracy} = 1 - \frac{1}{\text{NP}} \sum_{i=1}^{P} \left| \frac{(\text{Returned peak parameter} - \text{true peak parameter})}{\text{True Peak Parameter}} \right| \]  (eqn. 22)

where NP is the number of peaks, and P is the number of parameters, 3 x NP. Because the peak potential is referenced to an arbitrary zero, the residual in peak potential is not divided by the true peak potential; rather, it is divided by the true peak width, giving (perhaps) a less biased estimate of the accuracy. Failure of resolution is defined as the return of accuracy less than 0.85; this corresponds to a maximum relative error in each of the returned parameters of 5%.

A plot of accuracy vs. increasing A is shown in Fig. 1. Note that the abscissa is not to any scale, but rather reflects only an ordering of accuracy with increasing A. With the exception of several anomalous points in the plot of accuracy vs. increasing A for systems with peak potentials separated by 35 mV, these plots of accuracy monotonically increase with A. This implies that fits of semiderivatives of waves of non-reversible charge transfer kinetic systems improve with increasing A and, therefore, the \( \text{sech}^2 \) function is a good fitting function over the entire range of charge transfer kinetic behavior.

It is interesting that accuracy does not always increase monotonically with increasing A, and that accuracy does not always increase with increasing peak separation. This may be the result of the obtaining of a false minimum by BIMFIT. If the peak potential of a fit peak is changed slightly, the \( R^2 \)
between experimental peak and fit peak changes greatly. If fit peak height and width are changed simultaneously so as to increase height and decrease width (or vice versa) the returned $R^2$ changes only slightly. The small non-sech$^2$ nature of a semiderivative of a wave for a non-reversible charge transfer system could, in the right circumstances cause large errors in returned peak heights and widths.

One way to negate this effect is to constrain the peak widths in the fitting program, using input values from single peak data. This is equivalent to the empirical approaches employed in the past.$^1$-$^3$ Figure 2 shows a plot of accuracy vs. increasing $\Lambda$ for constrained width fits. These curves always change monotonically with increasing $\Lambda$, except for some small fluctuations at accuracy very near 1. Since the ordering of accuracy with peak separation goes almost monotonically from most overlapped to least overlapped systems for a given $\Lambda$, these results indicate that a great deal of the apparent false minimum effect has been eliminated. If failure is defined as the return of peak parameters which generate an accuracy $< 0.90$, peak resolution succeeds for all files except for the totally irreversible systems at 35 mV peak separation.

**Homogeneous Kinetics**

The effectiveness of both semidifferential voltammetric curve fitting and convolutive voltammetric curve fitting for systems with non-reversible homogeneous kinetics is judged in the same way as is semidifferential voltammetric curve fitting for systems with non-reversible charge transfer kinetics. The methods are valid for only those systems where returned fit parameters are close to those predicted from theory and returned $R^2$ values are close to 1.

Relations that may be used for the evaluation of semidifferential voltammetric curve fitting for systems with reversible homogeneous kinetics are Eqns. 8, 10, and 11. From Eqn. 8, a pure diffusion-controlled system has
a semiderivative with a peak potential equal to the reversible half-wave potential, which for all systems studied is \(-0.5000\) V. For an equilibrium constant of \(10^{-4}\), \(\Delta E_p\) from Eqn. 10 is \(0.118\) V; thus, the peak potential of the semiderivative of a modified diffusion system in this study should be \(-0.618\) V. Peak widths of semiderivatives of systems with either form of reversible behavior should be \(45.3\) mV. For the semidifferential voltammetric curve fitting to be considered valid in either zone of kinetic behavior, returned peak parameters must be close to these.

Table II gives returned peak parameters and \(R^2\) for the application of semidifferential voltammetric curve fitting to all the homogeneous kinetic systems studied in this investigation. From the definition of the homogeneous kinetic zones of behavior, and from the definition of homogeneous kinetic reversibility, files K and L should be reversible with pure diffusion-controlled behavior, and files AA, BB, and CC should be reversible with modified diffusion-controlled behavior. Returned parameters for these files, and for file Z also, show both good agreement with theoretical parameters and \(R^2\) values close to 1. The limits of validity of the semidifferential voltammetric curve fitting technique as applied to systems with preceding homogeneous kinetics can be said to extend to the boundaries of the pure and modified diffusion-controlled zones as defined by Saveant and Vianello.

The returned \(R^2\) values for the application of semidifferential voltammetric curve fitting to systems in the kinetically controlled regime suggests that semidifferential voltammetric curve fitting is not valid for the curve fitting of waves for these systems. One relation which is applicable for testing the validity of semidifferential voltammetric curve fitting for these systems is a relation for peak height given by Nicholson and Shain:\(^1\)

\[
\frac{1}{T_K} = \frac{1.02}{T_d} + \frac{0.471}{T_d^{0.5}} \frac{1}{\rho_k} \tag{eqn. 23}
\]
where $i_K$ is the peak height of an l.s.v. wave for a system with preceding homogeneous kinetics, and $i_d$ is the peak height of an l.s.v. wave in the limit of large $\lambda$ for the same equilibrium constant and is called the diffusion current.

Linear least squares fits of $1/i_K$ vs. $1/\sqrt{\lambda}$ were made for $i_K$ taken as the interpolated peak height of the synthetic homogeneous kinetic wave, and for $i_K$ taken as the returned peak height from the application of semidifferential voltammetric curve fitting to the same synthetic homogeneous kinetic wave. Slopes and intercepts are related to $i_K$ and $K$ through Eqn. 23. Table III shows the actual $i_K$ (taken as 0.4463 for a reversible wave given by Nicholson and Sham) and $K$, and the $i_K$ and $K$ calculated from slopes and intercepts of the linear least squares fits. Calculated $i_K$ and $K$ for both fits agree well with the actual $i_K$ and $K$, although the results found from heights returned by semidifferential voltammetric curve fitting are somewhat low in both cases. Thus, although the $R^2$ values are poor, the error in the returned peak height is small.

Figure 3 shows the semiderivative of a kinetically controlled system and the reconstructed sech$^2$ fit to that system. For the first part of the wave, including the peak, the sech$^2$ function fits fairly well; it is only at more negative potentials, where the homogeneous kinetics have more of an effect, that the greater portion of the misfit occurs. Even though returned peak heights are in error only by a small amount, the semidifferential voltammetric curve fittings technique is not a valid approach for fitting homogeneous kinetic systems in the kinetically controlled regime.

In the limiting case of pure kinetic behavior the convolutive voltammetric curve fitting technique may be applied. Convolutive voltammetric curve fitting is also considered valid for fits with returned $R^2$ close to 1.
and for returned fit parameters close to those predicted from convolutive voltammetric theory. In this case, applicable relations for the testing of convolutive voltammetric curve fitting's validity are Eqn. 16 for the peak potential and Eqn. 17 for the peak width. For the systems studied in this investigation, returned peak widths must be close to 22.6 mV, and plotted points of returned $E_p$ vs. $\ln k_b$ must be close to the line predicted by Eqn. 16 for convolutive voltammetric curve fitting to be valid for a given wave.

Figure 4 shows the fit obtained by applying convolutive curve fitting to the same system shown in Figure 3. Here, the fit is excellent over the entire range of the wave.

Table IV shows the results from application of convolutive voltammetric curve fitting to several data files that, from the previous definition of pure kinetic behavior for $K = 10^{-4}$, should be near to or in the zone of pure kinetic behavior. Figure 5 shows plotted points of returned $E_p$ vs. $\ln k_b$ for most of the files of Table III, and also shows the straight line expected from Eqn. 16. Examination of Fig. 5 and of the returned peak heights, widths, and $R$ values in Table IV show that returned peak parameters agree well with theoretical parameters for files Q through W, and perhaps for file X also. This corresponds to an area of validity ranging from $\lambda = 1$ to $\lambda = 10^4$ for the convolutive voltammetric curve fitting technique. This agrees fairly well with the boundaries of pure kinetic behavior given by Saveant and Vianello, and suggests that convolutive voltammetric curve fitting is valid for systems with pure kinetic homogeneous kinetic behavior.

CONCLUSIONS

The semidifferential voltammetric curve fitting technique can be used successfully for all systems showing heterogeneous charge transfer kinetics. This allows one to fit electrochemical peaks for most metals and
many organic compounds to a simple three parameter model in which each parameter is related to theoretical electrochemical parameters. Additionally, the semidifferential voltammetric curve fitting technique can be extended to systems which show diffusion-controlled homogeneous kinetics. In the limit of labile kinetics (very rapid dissociation), the peak position is related to the redox potential of the electroactive species and the equilibrium constant of the dissociation. In the limit of non-labile kinetics (very slow dissociation), the peak position is related to only the redox potential. Only for quasi-labile complexes, where the kinetics of dissociation control the shape of the LSV curve, the semidifferential curve fitting method fails.

Fortunately, most of these complexes (those showing pure-kinetic control) can be fit quantitatively using the method of convolutive voltammetric curve fitting. Thus, by combining these two techniques, it is possible to fit essentially all systems with either heterogeneous charge transfer kinetics or homogeneous complex dissociation kinetics, to a model based totally on theoretical electrochemical parameters.
LITERATURE CITED

Credit

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Acknowledgement

The authors thank T.F. Brown for useful discussions and comments throughout the course of this work.
Table I. Definition of systems and returned fit parameters for the application of s.v.c.f. to charge transfer kinetic systems involving a single peak.

<table>
<thead>
<tr>
<th>Filename</th>
<th>A</th>
<th>Potential (V)</th>
<th>Height</th>
<th>Width (mV)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.000128</td>
<td>-0.6614</td>
<td>1.8486</td>
<td>76.00</td>
<td>0.9980</td>
</tr>
<tr>
<td>B</td>
<td>0.00128</td>
<td>-0.6023</td>
<td>1.8500</td>
<td>75.98</td>
<td>0.9980</td>
</tr>
<tr>
<td>C</td>
<td>0.0128</td>
<td>-0.5441</td>
<td>1.9377</td>
<td>73.26</td>
<td>0.9990</td>
</tr>
<tr>
<td>D</td>
<td>0.0257</td>
<td>-0.5289</td>
<td>2.0775</td>
<td>68.50</td>
<td>0.9996</td>
</tr>
<tr>
<td>E</td>
<td>0.0642</td>
<td>-0.5143</td>
<td>2.3944</td>
<td>59.25</td>
<td>0.9999</td>
</tr>
<tr>
<td>F</td>
<td>0.128</td>
<td>-0.5078</td>
<td>2.6525</td>
<td>53.37</td>
<td>0.9999</td>
</tr>
<tr>
<td>G</td>
<td>0.642</td>
<td>-0.5019</td>
<td>3.0051</td>
<td>47.09</td>
<td>0.9999</td>
</tr>
<tr>
<td>H</td>
<td>1.28</td>
<td>-0.5011</td>
<td>3.0635</td>
<td>46.22</td>
<td>0.9999</td>
</tr>
<tr>
<td>I</td>
<td>12.8</td>
<td>-0.5004</td>
<td>3.1193</td>
<td>45.41</td>
<td>0.9999</td>
</tr>
<tr>
<td>J</td>
<td>128</td>
<td>-0.5003</td>
<td>3.1252</td>
<td>45.32</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

aOther parameters defining the systems are discussed in the text.
bAs defined in text.
cArbitrary units.
Table II. Definition of systems\textsuperscript{a} and returned fit parameters for the application of s.v.c.f. to homogeneous kinetic systems involving a single peak.

<table>
<thead>
<tr>
<th>Filename</th>
<th>$\lambda^b$</th>
<th>Potential (V)</th>
<th>Height\textsuperscript{c}</th>
<th>Width (mV)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.00100</td>
<td>-0.5003</td>
<td>$2.211 \times 10^{-4}$</td>
<td>45.40</td>
<td>0.9999</td>
</tr>
<tr>
<td>L</td>
<td>0.0100</td>
<td>-0.5007</td>
<td>$2.219 \times 10^{-4}$</td>
<td>46.24</td>
<td>0.9958</td>
</tr>
<tr>
<td>M</td>
<td>0.0500</td>
<td>-0.5023</td>
<td>$2.284 \times 10^{-4}$</td>
<td>48.78</td>
<td>0.9338</td>
</tr>
<tr>
<td>N</td>
<td>0.100</td>
<td>-0.5042</td>
<td>$2.409 \times 10^{-4}$</td>
<td>50.35</td>
<td>0.8457</td>
</tr>
<tr>
<td>O</td>
<td>0.200</td>
<td>-0.5075</td>
<td>$2.639 \times 10^{-4}$</td>
<td>52.82</td>
<td>0.7315</td>
</tr>
<tr>
<td>P</td>
<td>0.500</td>
<td>-0.5159</td>
<td>$3.351 \times 10^{-4}$</td>
<td>58.75</td>
<td>0.6316</td>
</tr>
<tr>
<td>Q</td>
<td>1.00</td>
<td>-0.5234</td>
<td>$4.543 \times 10^{-4}$</td>
<td>75.70</td>
<td>0.6064</td>
</tr>
<tr>
<td>R</td>
<td>2.00</td>
<td>-0.5276</td>
<td>$6.428 \times 10^{-4}$</td>
<td>75.49</td>
<td>0.6065</td>
</tr>
<tr>
<td>S</td>
<td>3.00</td>
<td>-0.5301</td>
<td>$7.869 \times 10^{-4}$</td>
<td>74.56</td>
<td>0.6055</td>
</tr>
<tr>
<td>T</td>
<td>5.00</td>
<td>-0.5334</td>
<td>$1.018 \times 10^{-3}$</td>
<td>74.78</td>
<td>0.6065</td>
</tr>
<tr>
<td>U</td>
<td>10.0</td>
<td>-0.5379</td>
<td>$1.437 \times 10^{-3}$</td>
<td>75.34</td>
<td>0.6090</td>
</tr>
<tr>
<td>V</td>
<td>100.</td>
<td>-0.5530</td>
<td>$4.389 \times 10^{-3}$</td>
<td>55.64</td>
<td>0.5687</td>
</tr>
<tr>
<td>W</td>
<td>$1.00 \times 10^3$</td>
<td>-0.5781</td>
<td>$1.266 \times 10^{-2}$</td>
<td>78.72</td>
<td>0.6720</td>
</tr>
<tr>
<td>X</td>
<td>$1.00 \times 10^4$</td>
<td>-0.5913</td>
<td>$3.875 \times 10^{-2}$</td>
<td>82.00</td>
<td>0.6964</td>
</tr>
<tr>
<td>Y</td>
<td>$1.00 \times 10^6$</td>
<td>-0.6182</td>
<td>$0.3044$</td>
<td>90.57</td>
<td>0.8407</td>
</tr>
<tr>
<td>Z</td>
<td>$1.00 \times 10^8$</td>
<td>-0.6203</td>
<td>$1.340$</td>
<td>59.16</td>
<td>0.9851</td>
</tr>
<tr>
<td>AA</td>
<td>$1.00 \times 10^{10}$</td>
<td>-0.6196</td>
<td>$2.067$</td>
<td>47.11</td>
<td>0.9998</td>
</tr>
<tr>
<td>BB</td>
<td>$1.00 \times 10^{11}$</td>
<td>-0.6195</td>
<td>$2.156$</td>
<td>45.98</td>
<td>0.9999</td>
</tr>
<tr>
<td>CC</td>
<td>$1.00 \times 10^{12}$</td>
<td>-0.6195</td>
<td>$2.185$</td>
<td>45.61</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Other parameters defining the systems are discussed in the text.

\textsuperscript{b}As defined in text.

\textsuperscript{c}Arbitrary units.
Table III. Actual and determined diffusion currents and equilibrium constants for the homogeneous kinetic systems studied.

<table>
<thead>
<tr>
<th></th>
<th>Actual values</th>
<th>Interpolated values(^a)</th>
<th>S.v.c.f. values(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>0.4463</td>
<td>0.446</td>
<td>0.432</td>
</tr>
<tr>
<td>(K)</td>
<td>(1.00 \times 10^{-4})</td>
<td>(1.01 \times 10^{-4})</td>
<td>(0.757 \times 10^{-4})</td>
</tr>
</tbody>
</table>

\(^a\)Values are determined from linear least squares fits of \(1/\sqrt{A}\) to \(1/i_k\), where \(i_k\) is the peak height of the l.s.v. wave determined from parabolic interpolation.

\(^b\)Values are determined from linear least squares fits of \(1/\sqrt{A}\) to \(1/i_k\), where \(i_k\) is the returned peak height from s.v.c.f. Five points were used to generate the least-squares result, with rate constants ranging from \(10^6\) to \(10^{10}\); the regression coefficient was 0.9999.
Table IV. Returned peak parameters for convolutive voltammograms of homogeneous kinetic systems\(^a\) involving a single peak.

<table>
<thead>
<tr>
<th>Filename</th>
<th>Potl. (V)</th>
<th>Height(^b)</th>
<th>Width (mV)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-0.5341</td>
<td>0.9856</td>
<td>73.52</td>
<td>0.9396</td>
</tr>
<tr>
<td>O</td>
<td>-0.4707</td>
<td>0.0062</td>
<td>3.74</td>
<td>0.0001</td>
</tr>
<tr>
<td>P</td>
<td>-0.5107</td>
<td>1.003</td>
<td>13.10</td>
<td>0.9935</td>
</tr>
<tr>
<td>Q</td>
<td>-0.5279</td>
<td>1.001</td>
<td>22.50</td>
<td>0.9999</td>
</tr>
<tr>
<td>R</td>
<td>-0.5323</td>
<td>1.001</td>
<td>22.49</td>
<td>0.9999</td>
</tr>
<tr>
<td>S</td>
<td>-0.5349</td>
<td>1.000</td>
<td>22.48</td>
<td>0.9999</td>
</tr>
<tr>
<td>T</td>
<td>-0.5382</td>
<td>1.0000</td>
<td>22.44</td>
<td>0.9999</td>
</tr>
<tr>
<td>U</td>
<td>-0.5426</td>
<td>1.0000</td>
<td>22.38</td>
<td>0.9999</td>
</tr>
<tr>
<td>V</td>
<td>-0.5571</td>
<td>1.001</td>
<td>22.07</td>
<td>0.9999</td>
</tr>
<tr>
<td>W</td>
<td>-0.5710</td>
<td>1.003</td>
<td>21.12</td>
<td>0.9996</td>
</tr>
<tr>
<td>X</td>
<td>-0.5833</td>
<td>1.006</td>
<td>18.75</td>
<td>0.9956</td>
</tr>
<tr>
<td>Y</td>
<td>-0.5963</td>
<td>1.239</td>
<td>5.08</td>
<td>0.0846</td>
</tr>
</tbody>
</table>

\(^a\)As defined in Table II.

\(^b\)Arbitrary units.
FIGURE CAPTIONS

Figure 1: Plots of curve fitting accuracy vs. increasing dimensionless heterogeneous rate constant $\Lambda$, for parameters returned from BIMFIT fits of overlapped semiderivatives of non-reversible charge transfer systems. The abscissa has been expanded for clarity. Triangles are accuracies for overlapped systems with peak potentials 35 mV apart, squares are accuracies for peaks 50 mV apart, and crosses are accuracies for systems 70 mV apart.

Figure 2: Plots of curve fitting accuracy vs. increasing dimensionless heterogeneous rate constant $\Lambda$. Here, accuracies are determined from CNWSBM fits. Input peak widths to CNWSBM are taken from BIMFIT fits to single peak data. Symbols are as in Fig. 1.

Figure 3: Semiderivative wave and fit sech$^2$ function for file X.

Figure 4: Convolutive voltammetric wave fit to file X. Both file X and fit are shown.

Figure 5: Plot of returned $E_p$ as a function of $\ln k_b$. The line gives the expected $E_p$ as a function of $\ln k_b$ calculated from Equation 16.
Figure 3

POTENTIAL (VOLTS)

PEAK HEIGHT x 0.1 (ARBITRARY UNITS)
Figure 5: Graph showing the relationship between peak potential (volts) and $\ln k_b$. The graph plots points that indicate a linear relationship between the two variables.
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