Direct Determination of the Transfer Coefficient from Cyclic Voltammetry: Isopoints as Diagnostics

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Direct Determination of the Transfer Coefficient from Cyclic Voltammetry: Isopoints as Diagnostics

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Isopoints are observed when cyclic voltammograms recorded at several scan rates are all plotted on the same potential axis. The isopoint is the point where all curves intersect. Here, isopoints are used as a diagnostic under reversible and quasireversible electron transfer conditions. A method is presented for determining the transfer coefficient, α, using only the isopoint potential, switching potential, and peak potentials, all readily identifiable points on the voltammograms. It is not necessary to know the diffusion coefficients, standard rate constant, standard potential, electrode area, or solution concentration to apply this method. The isopoint method is applicable for differences in peak potentials of 0.073–0.145 V. The method is verified experimentally by comparing the values of α determined by the isopoint and convolution methods. A linearization of the dimensionless kinetic parameter, ψ, developed by Nicholson, with the difference in peak potentials is presented. It is also shown that the average of the peak potentials yields the half-wave potential within 1 mV for differences in the peak potential of less than approximately 0.145 V. All models were developed by computer simulation (Digisim).

In the mid-1960s, Nicholson and Shain[1] and Nicholson[2] developed the diagnostics used to interpret cyclic voltammetric responses under reversible and quasireversible electron transfer conditions. (Matsuda and Ayabe[3] had developed a method for interpreting the forward sweep in the mid-1950s.) The diagnostics developed by Nicholson and Shain are based on the peak potentials and currents and require the switching potentials to be far past the forward peak potential. Under quasireversible conditions, the diagnostics allow the determinations of a dimensionless kinetic parameter, ψ, which is dependent on the scan rate, the diffusion coefficients of the oxidized and reduced species, the standard heterogeneous rate constant, and the transfer coefficient. The transfer coefficient is a measure of the symmetry of the energy barrier for electron transfer and has a value between 0 and 1. The transfer coefficient can be determined from ψ if the diffusion coefficients and the standard rate constant are known. However, Nicholson points out that ψ is only weakly dependent on the transfer coefficient, so the determination will not be sensitive.

Nicholson and Shain[1] showed that the transfer coefficient can be determined from the peak potential and the potential at

half-maximum current if the scan rate can be increased sufficiently that the electron transfer process becomes irreversible. The transfer coefficient can be determined by potential step methods from the slopes of Tafel plots. To determine the rate constant by step methods, knowledge of the equilibrium potential is required.

In the mid-1970s, Oldham[4-6] and Savéant[7-9] and co-workers developed eloquent convolution or semiintegration methods to analyze cyclic voltammetric responses. The method can be used to evaluate the standard rate constant and the transfer coefficient if the diffusion coefficients, the formal potential, and the limiting convoluted current are known. After the current is semiintegrated, the limiting convoluted current is readily determined, but the analyses to determine the heterogeneous rate constant and the transfer coefficient are fairly sensitive to the value of the formal potential. The formal potential can be determined from the convoluted current.

The diagnostics developed by Nicholson and Nicholson and Shain to analyze voltammetric responses are based on four experimental observables: two peak potentials and two peak currents. With these four experimental observables, ψ can be extracted, but the kinetic information is embedded in ψ in a complex manner and cannot be extricated without additional information. If more experimental observables are identified on a voltammogram, it should be possible to extract additional information from the voltammogram. Here, we identify the isopoint as a useful diagnostic tool. Isopoints are observed when several cyclic voltammograms, recorded over the same potential range but at different scan rates, are all plotted on the same graph. Isopoints occur where all the voltammograms pass through a common point, as shown in Figure 1. These points are readily identifiable and, as shown below, can be used as a diagnostic to aid in extracting additional kinetic information from a voltammogram.

Here, we report on a method to determine the transfer coefficient directly from cyclic voltammetric data using the isopoint. The transfer coefficient is calculated using only the scan rate and four experimental observables: the switching potential, the two peak potentials, and the isopoint potential. The diffusion coefficients, standard rate constant, electrode area, solution concentration, and formal potential are not needed. The method applies for scan rates between 0.02 and 0.10 V/s and over a range of peak potential differences of 73–145 mV. (Under quasirevers-

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(1) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(2) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351–1355.
(3) Matsuda, H.; Ayabe, Y. *Z. Elektrochem.* **1955**, *59*, 494.

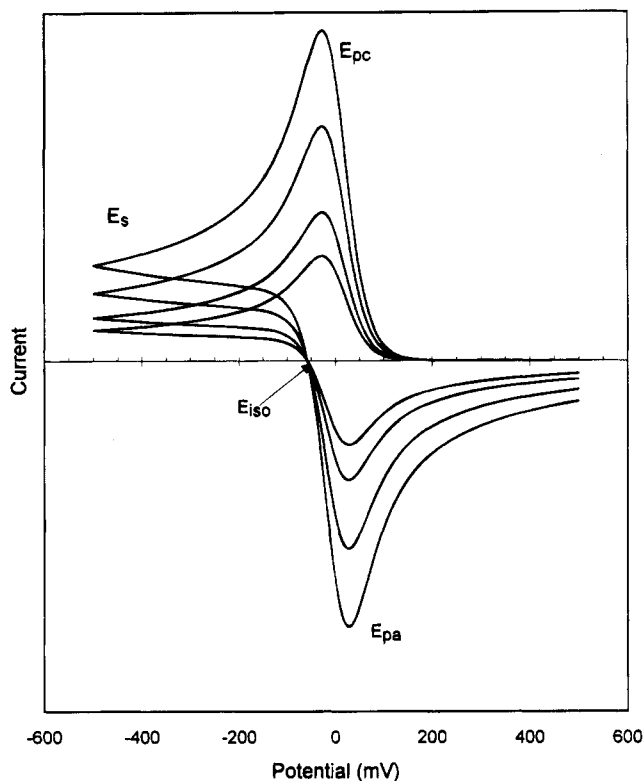(4) Oldham, K. B.; Spanier, J. *J. Electroanal. Chem.* **1970**, *26*, 331–341.
(5) Oldham, K. B. *Anal. Chem.* **1972**, *44*, 194–198.
(6) Oldham, K. B. *Anal. Chem.* **1973**, *45*, 39–44.
(7) Savéant, J. M.; Imbeaux, J. C. *J. Electroanal. Chem.* **1969**, *44*, 169–188.
(8) Savéant, J. M.; Tessier, D. *J. Electroanal. Chem.* **1975**, *65*, 57–66.
(9) Nadjo, L.; Savéant, J. M.; Tessier, D. *J. Electroanal. Chem.* **1974**, *52*, 403–412.

Figure 1. Simulated cyclic voltammograms for reversible hetero-geneous electron transfer kinetics. Voltammograms are shown for v = 0.01, 0.02, 0.05, and 0.10 V/s. The isopoint occurs at the intersection of the four sweeps on the reverse scan. For reversible kinetics, this occurs at zero current. The four potentials needed to evaluate α under quasireversible conditions are identified: E_{iso}, E_{pc}, E_{pa}, and E_s.

and input parameters to find the relationship between E_{iso} and the other experimental observables and parameters. The resulting relationship provides a means of determining the transfer coefficient, α. The data sets included results for between 62 and 306 cyclic voltammograms.

The method was verified experimentally by comparing the values determined for α by convolution voltammetry and the isopoint method. Cyclic voltammetric data were collected for the oxidation of 2.81 mM iron(III) perchlorate (Alfa) in 0.0936 M perchloric acid (Mallinckrodt). The concentration of iron perchlorate was determined from the limiting convoluted current. The 0.4591 cm^2 palladium electrode (Pine) was polished with 0.05 μm alumina (Buehler), rinsed in distilled water (Milli-Q) and concentrated nitric acid, and sonicated in distilled water to remove any embedded alumina particles. A calomel reference electrode (SCE) and a 6 cm^2 platinum screen counter electrode were used. The solution was thoroughly degassed with presaturated nitrogen. All measurements were made at room temperature. A Model 173 potentiostat (Princeton Applied Research) with a Model 276 interface card was used for cyclic voltammetry and chrono-amperometric studies. Cyclic voltammograms were recorded through an interfaced 486 computer (Gateway); current transients following a potential step were recorded on an IQ 300 digital oscilloscope (HiTechiques). Potential steps were performed in blank electrolyte to determine the solution resistance and double layer capacitance. The convolution method and isopoint method were applied to the same set of cyclic voltammograms.

RESULTS AND DISCUSSION

Reversible Electron Transfer Kinetics. Consider the following reaction at an electrode surface,

$$A + ne^- \rightleftharpoons B \qquad E^{\circ\prime} \qquad (1)$$
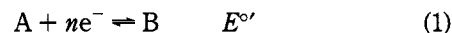
where $E^{\circ\prime}$ is the formal potential and n electrons are transferred. For a reversible system, the scan rate (v) is sufficiently slow that the electrode reaction is governed by the Nernst equation.[11] A set of reversible cyclic voltammograms is shown in Figure 1. All reversible cyclic voltammograms have the same shape indepen-dent of scan rate, diffusion coefficients, initial concentration of A, and electrode area. In a given cyclic voltammetric experiment, there is a set of experimentally controlled parameters: concentra-

ible conditions, Nicholson's method for determining ψ is ap-plicable for peak potential differences of 59–212 mV.) The transfer coefficient is determined immediately, and it can then be used in conjunction with ψ to separate out the other kinetic information. Room temperature and temperature-dependent mod-els are presented, and methods for correcting for solution resistance and capacitance are included. The behavior of isopoints under reversible conditions is also outlined. A linearization of Nicholson's ψ with reciprocal peak potential difference eliminates the need for a working curve in determining ψ. The limitations on calculating the reversible half-wave potential by averaging the peak potentials under quasireversible conditions are presented.

EXPERIMENTAL SECTION

All simulations were performed using a commercial program, Digisim (Bioanalytical Systems), written by Rudolph, Reddy, and Feldberg.[10] The cyclic voltammetric response for both reversible and quasireversible electron transfer kinetics was examined as a function of various input parameters, as listed in Table 1. Each parameter was varied, its effect on peak potentials and isopoints was identified, and the functional form of the relationship between the parameter and the experimental observables was determined. Using a spreadsheet (Excel-Microsoft) and the functional depen-dence of each parameter, a multivariable linear regression was then performed on the entire data set of experimental observables

(10) Rudolph, M.; Reddy, D. P.; Feldberg, S. W. *Anal. Chem.* **1994**, *66*, 589A–600A.

(11) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; Chapter 6.

tion of A (c_A^*, mol/cm³), electrode area (A, cm²), scan rate (v, V/s), and switching potential (E_s, V). There is also a set of parameters to be determined from the experiment: the ratio of the diffusion coefficients of the reactants and products, D_A/D_B, and the formal potential, $E^{\circ\prime} = E^\circ + (RT/nF) \ln(\gamma_A/\gamma_B)$, where E° is the standard potential, F and R are the Faraday constant and the gas constant, respectively, T is the temperature (K), and γ_A and γ_B are the activity coefficients of A and B, respectively.

Nicholson and Shain[1] developed the diagnostics used to interpret cyclic voltammograms for reversible kinetics. We focus on three principal diagnostics. First, for switching potentials far past $E^{\circ\prime}$, the peak slitting, ΔE_p, is 57 mV/n in the absence of resistance. Second, the current at any point on the cyclic voltammogram is proportional to $v^{1/2}$, so a plot of the peak current, i_p, versus $v^{1/2}$ is linear, where the slope can be used to determine D_A and the intercept should be zero:

$$i_p = 0.4463nFAc_A^*(nF/RT)^{1/2}v^{1/2}D_A^{1/2} \qquad (2)$$

Third, the forward peak potential, E_p^f, shifts on the potential axis depending on D_A/D_B, as

$$E_p^f - E_{1/2} = -1.109(RT/nF) \qquad (3)$$

where $E_{1/2} = E^{\circ\prime} + (RT/nF) \ln(D_B/D_A)^{1/2}$. $E_{1/2} = \frac{1}{2}(E_{pc} + E_{pa})$, where E_{pc} and E_{pa} are the peak potentials for the reduction and oxidation waves, respectively.

We have found that for a given E_s, the isopoint shifts in parallel with E_p^f on the potential axis as the ratio of the diffusion coefficients varies:

$$E_p^f - E_{iso} = 0.60(RT/nF) \ln[(F/RT)|E_s - E_p|] -$$
$$1.109(RT/nF) + (RT/2nF) \qquad (4)$$

with $r^2 = 0.9991$, and all potentials in volts. (Note, this equation is written for a reductive forward peak; for an oxidative forward peak, the sign of $E_p - E_{iso}$ will be reversed.) The isopoint occurs at zero current. Equation 4 was developed for $n = 1$ and 2, and provides an alternative method of finding n. At 298.2 K and $E_s - E_p = -0.300$ V, $E_p - E_{iso} = 0.0222$ V. $E_{iso} - E^{\circ\prime}$, as well as the shift in E_{iso} with D_A/D_B, follows directly from eqs 3 and 4, and $E_{1/2}$.
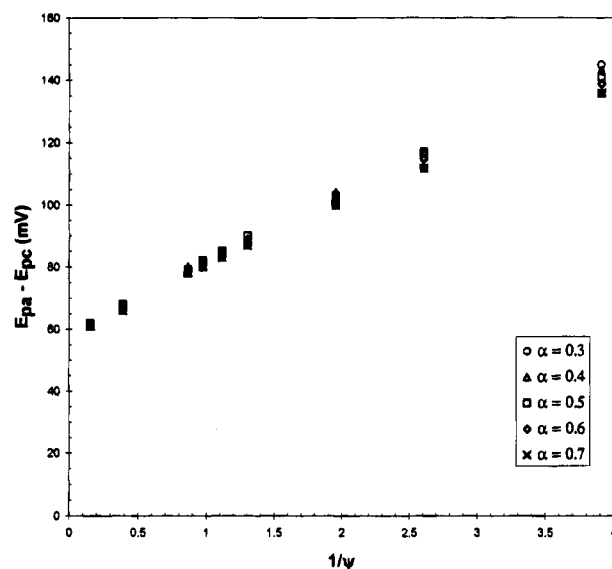
Quasireversible Electrode Kinetics. Consider a reaction at the electrode surface,

$$A + ne^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B \qquad E^{\circ\prime} \qquad (5)$$
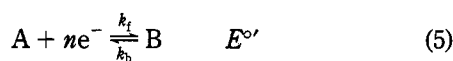
where k_f and k_b are the potential-dependent forward and reverse rate constants for the heterogenous electron transfer step. k_f and k_b are defined according to Butler Volmer models[12] as

$$k_f = k^\circ \exp[-\alpha(nF/RT)(E - E^{\circ\prime})] \qquad (6)$$

$$k_b = k^\circ \exp[(1 - \alpha)(nF/RT)(E - E^{\circ\prime})] \qquad (7)$$

(12) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; Chapter 2.

Figure 2. Linearization of ΔE_p with ψ^{-1}. The variation of ΔE_p with α is more significant at larger ψ^{-1}, but ΔE_p is not a strong function of ψ^{-1}, which means that the sensitivity of determining α from ΔE_p and ψ will be limited. $T = 298$ K, $n = 1$, and $D_A = D_B$.

where k° (cm/s) is the standard heterogeneous rate constant and α is the electron transfer coefficient ($0 \le \alpha \le 1$). k° is defined at $E = E^{\circ\prime}$, where $k^\circ = k_f = k_b$. The set of experimentally controlled parameters are the same as those for the reversible case: c_A^*, A, v, and E_s. The parameters to be determined include those listed for the reversible case (D_A/D_B and $E^{\circ\prime}$), as well as k° and α.

Cyclic voltammetric diagnostics to evaluate heterogeneous kinetics were developed by Nicholson.[2] The most common diagnostic for quasireversible kinetics is the peak splitting ($\Delta E_p = |E_{pc} - E_{pa}|$), where ΔE_p falls within the range

$$61/n \text{ mV} < \Delta E_p < 212/n \text{ mV} \qquad (8)$$

The dimensionless parameter characteristic of k° and α is ψ, where

$$\psi = \frac{(D_A/D_B)^{\alpha/2}k^\circ}{[(nF/RT)\pi v D_A]^{1/2}} \qquad (9)$$

In the method developed by Nicholson,[2] ψ is extracted from a working curve (ΔE_p vs ψ). Once ψ has been determined, k° can be calculated if D_A, D_B, α, and n are known. If D_B is not known, the usual assumption is that $D_A = D_B$, and, in this case, α does not have to be specified to find k°. If D_B is known, but α is not, usual practice is to approximate α as 0.5, as the determination of k° is not dramatically affected by $(D_A/D_B)^{\alpha/2}$. Although the method is intended to find ψ, Nicholson's method can be used to find α if D_A, D_B, n, and k° are known, but the determination is of limited precision because ψ and ΔE_p are not strong functions of α.

An alternative to Nicholson's working curve for finding ψ is presented here. A plot of ΔE_p vs ψ^{-1} is linear, as shown in Figure 2.

$$\Delta E_p(nF/RT) = M_1(1/\psi) + B_1 \qquad (10)$$

Equation 10 holds for $0.2 \le D_A/D_B \le 5$. As determined for $0.3 \le$

Table 2. Slopes (M_1) and Intercepts (B_1) Appropriate to $\Delta E_p(nF/Rt) = M_1(1/\psi) + B_1$ as a Function of α

α	M_1	B_1	std error in M_1	std error in B_1	corr coeff
0.3	0.872 66	2.2736	0.002 50	0.0036	0.9993
0.4	0.844 73	2.3366	0.005 77	0.0102	0.9962
0.5	0.842 80	2.3243	0.006 99	0.0118	0.9960
0.6	0.789 46	2.3791	0.007 50	0.0140	0.9959
0.7	0.751 93	2.3727	0.005 55	0.0104	0.9975

$\alpha \leq 0.6$, $M_1 = 0.841\,69 \pm 0.000\,32$ and $B_1 = 2.3189 \pm 0.0053$ for a data set of 306 voltammograms with a correlation coefficient of 0.9958; for $0.5 \leq \alpha \leq 0.7$, $M_1 = 0.7793 \pm 0.0050$ and $B_1 = 2.3862 \pm 0.0092$ as determined from data for 195 voltammograms with a correlation coefficient of 0.9922. Note, from Figure 2, there is a slight dependence on α for the slope and intercept of ΔE_p vs ψ^{-1}. This dependence introduces a small error in determining ψ^{-1}, which can be reduced by using the appropriate slope and intercept when determining ψ^{-1} at a specific value of α. Table 2 lists M_1 and B_1 for a range of α values. The equation of these lines was determined with $D_A = D_B = 5.0 \times 10^{-6}$ cm^2/s, $|E_p - E_s| \geq 0.250$ V, and $198.2 \leq T \leq 398.2$ K. The method outlined below to determine α relies on ψ, which can initially be approximated using eq 10 and values of M_1 and B_1 appropriate to either $0.3 \leq \alpha \leq 0.6$ or $0.5 \leq \alpha \leq 0.7$, as explained below. Once α is known, a more precise value of ψ can be determined using the values of M_1 and B_1 appropriate to the specific α, as listed in Table 2.

A commonly employed method in analyzing quasireversible cyclic voltammetric data is to approximate $E_{1/2}$ by averaging the peak potentials. An examination of this procedure shows that $E_{1/2} = \frac{1}{2}(E_{pc} + E_{pa})$ is correct within 1 mV for k° roughly greater than 0.002 cm/s. This corresponds to peak splitting of less than approximately 145 mV at 0.1 V/s. This limit of 145 mV is also the limit of applicability of the isopoint method for determining α.

For quasireversible kinetics, the isopoint occurs at currents, $i_{iso} \approx 0$. i_{iso} deviates from zero current as ψ decreases (the electron transfer reaction becomes less reversible). In all cases, $i_{iso} < 0.05 i_p$. di/dE is steep about E_{iso}, so for a single scan, E_{iso} can be roughly approximated by $E_{i=0}$ at $i = 0$ on the return sweep. E_{iso} is best determined as the intersection point of three or more cyclic voltammograms recorded at scan rates over half a decade of change. For quasireversible kinetics, when $i_{iso} = 0$, E_{iso} is the only point on the curve that obeys the Nernst equation:

$$i/nFA = k_f C_A(0,t) - k_b C_B(0,t) = 0 \qquad (11)$$

which, given eqs 6 and 7, yields

$$C_B(0,t)/C_A(0,t) = \exp[-(nF/RT)(E - E^{\circ\prime})] \qquad (12)$$

E_{iso}, like E_{pc} and E_{pa}, is a readily identifiable, experimentally measurable value but, as of yet, has not been exploited as a cyclic voltammetric diagnostic. Although ΔE_p vs ψ^{-1} shows only a slight dependence on α (Figure 2), $E_p(v) - E_{iso}$ vs ψ^{-1} shows a stronger dependence, as shown in Figure 3. As noted by Nicholson,[2] the effects of α on ΔE_p tend to cancel out because, as α varies, both peak potentials shift along the potential axis in the same direction. As shown in Figure 2, as ψ gets smaller and the irreversible regime is approached, the error associated with determining ψ
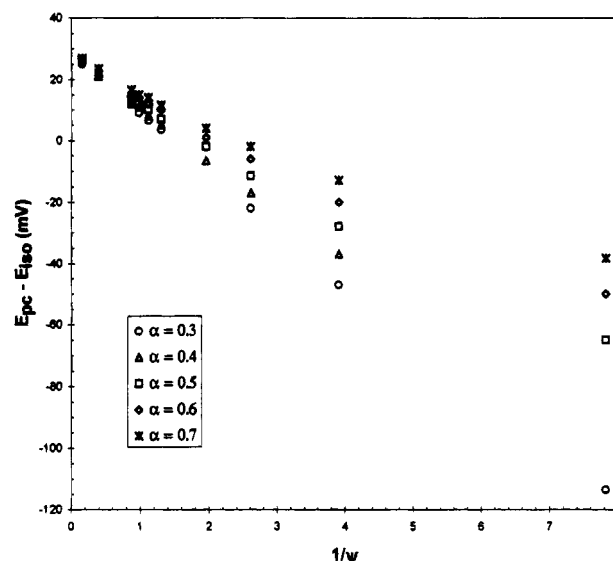
Figure 3. Variation of $E_p{}^f(v)$ with ψ^{-1} and α. $E_p{}^f(v) - E_{iso}$ is a strong function of ψ^{-1} and α. Because of this sensitivity, α is more precisely determined from $E_p{}^f(v) - E_{iso}$ than ΔE_p. $T = 298$ K, $n = 1$, and $D_A = D_B$.
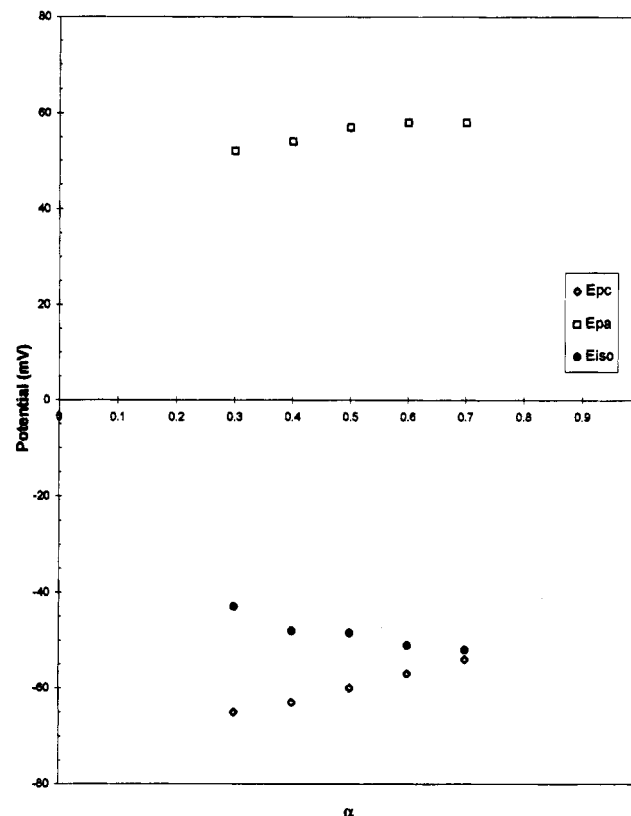

Figure 4. Variation in E_{iso}, E_{pa}, and E_{pc} with α for $k^{\circ} = 0.003$ cm/s. Because $\Delta E_p = |E_{pc} - E_{pa}|$ does not vary substantially with α, ΔE_p is not a sensitive method for determining α. $E_{pc} - E_{iso}$ is more sensitive to α for $0.3 < \alpha \leq 0.6$, and $E_{pa} - E_{iso}$ is more sensitive to α for $0.5 \leq \alpha \leq 0.7$. Thus, $E_{pc} - E_{iso}$ is used to find α for smaller α values, and $E_{pa} - E_{iso}$ is appropriate for higher α values. Note, discussion is appropriate to a system where the forward wave is a reduction. See text for discussion of forward oxidative wave. $T = 298$ K, $n = 1$, and $D_A = D_B$.

becomes greater because of variation[2] in ΔE_p with α. $E_p(v) - E_{iso}$ is more sensitive to α because, unlike E_{pc} and E_{pa}, the peak potentials and E_{iso} shift in different directions with α (see Figure 4). As α decreases, E_{pc} shifts negative and E_{iso} shifts positive; as

Table 3. Coefficients and Their Standard Errors for Eqs 14 and 16 as Well as Eqs 15 and 17

coeff	value	std error
For Eqs 14 and 16[a]		
M_1	0.8417	0.0003
B_1	2.3189	0.0053
M_2	−0.5838	0.0096
M_3	−0.06173	0.00265
M_4	0.7749	0.0219
B_2	−0.03151	0.00152
For Eqs 15 and 17[b]		
M_1'	0.7793	0.0050
B_1'	2.3862	0.0092
M_2'	0.2157	0.0021
M_3'	0.04868	0.00158
M_4'	0.7798	0.0129
B_2'	0.02832	0.00090

[a] $0.3 \leq \alpha \leq 0.6$; $T = 298.2$ K. [b] $0.5 \leq \alpha \leq 0.7$; $T = 298.2$ K.
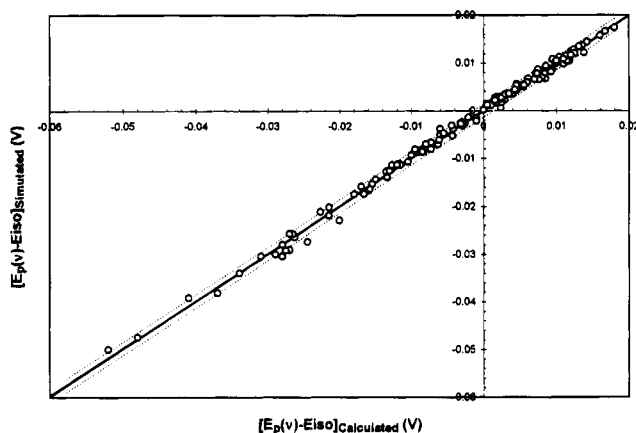
Figure 5. $E_p^f - E_{iso}$ as calculated from multivariable regression, as described by eq 14. Points and regression line are shown. Dotted lines are the allowed uncertainty of 1 mV in the determination of each of the peak potentials or 1.4 mV in ΔE_p.

α increases, E_{pa} shifts positive and E_{iso} shifts negative. Therefore, $E_p(v) - E_{iso}$ is a more sensitive probe of α than ΔE_p. The forward peak is more sensitive at smaller values of α ($0.3 \leq \alpha \leq 0.6$), and the reverse wave is more sensitive at larger values of α ($0.5 \leq \alpha \leq 0.7$).

The relationship between $E_p(v) - E_{iso}$ and ψ^{-1} takes the following form for both cases, whether $E_p(v)$ is the forward or reverse peak potential:

$$E_p(v) - E_{iso} = (1/\psi)(m\alpha + b)[(m'/v^{1/2}) + b'] - m'' \ln[|E_s - E_{1/2}|(F/RT)] + b'' \quad (13)$$

where ψ^{-1}, as defined by eq 10, can be replaced with $[(F/RT)\Delta E_p - B_1]/M_1$. (The values of M_1 and B_1 will depend on whether $0.3 \leq \alpha \leq 0.6$ or $0.5 \leq \alpha \leq 0.7$; see below.) The form of eq 13 was determined by independently regressing $E_p - E_{iso}$ vs ψ^{-1} with the functional forms of each α, v, and E_s. A different equation is found for the peak potential depending on whether the forward peak potential, $E_p^f(v)$, or the reverse peak potential, $E_p^r(v)$ is used. The final form of eq 13 and whether $E_p^f(v)$ or $E_p^r(v)$ is used depends on the value of α and the temperature. Each of the following equations applies for one-electron transfers. (Attempts to include multielectron transfers were not successful, probably

because of disproportionation reactions between the intermediate, reactant, and product.[13])

For $0.3 \leq \alpha \leq 0.6$ and $T = 298.2$ K,

$$(F/RT)(E_p^f(v) - E_{iso}) = (M_2/\psi)(1.24 - \alpha) + [M_3/(\psi v^{1/2})](1.24 - \alpha) + M_4 \ln[|E_s - E_{1/2}|(F/RT)] + B_2(F/RT) \quad (14)$$

For $0.5 \leq \alpha \leq 0.7$ and $T = 298.2$ K,

$$(F/RT)(E_p^r(v) - E_{iso}) = (M_2'/\psi)(1.25 + \alpha) + [M_3'/(\psi v^{1/2})](\alpha - 1.25) + M_4' \ln[|E_s - E_{1/2}|(F/RT)] + B_2'(F/RT) \quad (15)$$

The coefficients for these equations are listed in Table 3. The data sets used to determine the coefficients in eqs 14 and 15 contained data from 62 and 145 voltammograms, respectively; the respective correlation coefficients were $r^2 = 0.9979$ and $r^2 = 0.9932$. Note, eqs 14 and 15 are written for the forward wave corresponding to a reduction; if the forward wave is an oxidation, then replace $E_p^f(v) - E_{iso}$ and $E_p^r(v) - E_{iso}$ by $E_{iso} - E_p^f(v)$ and $E_{iso} - E_p^r(v)$, respectively. The final forms of eqs 14 and 15 were determined by a multivariable linear regression in ψ^{-1}, α, $v^{-1/2}$, and $\ln[|E_s - E^{o'}|(F/RT)]$. The quality of the fit for eq 14 is illustrated in Figure 5.

α can be determined by rearranging eqs 14 and 15.

For $0.3 \leq \alpha \leq 0.6$ and $T = 298.2$ K,

$$\alpha = 1.24 - \{(F/RT)(E_p^f(v) - E_{iso} - B_2) - M_4 \ln[|E_s - E_{1/2}|(F/RT)]\}/ \{([(F/RT)\Delta E_p - B_1]/M_1)(M_2 + M_3/v^{1/2})\} \quad (16)$$

For $0.5 \leq \alpha \leq 0.7$ and $T = 298.2$ K,

$$\alpha = \{(F/RT)(E_p^r(v) - E_{iso} - B_2') - M_4' \ln[|E_s - E_{1/2}| \times (F/RT)] + 1.25([(F/RT)\Delta E_p - B_1']/M_1')((M_3'/v^{1/2}) - M_2')\}/\{([(F/RT)\Delta E_p - B_1']/M_1')(M_2' + M_3'/v^{1/2})\} \quad (17)$$

As above, these equations are written for a reductive forward wave; if the forward wave is an oxidation, substitute $E_{iso} - E_p(v)$ for $E_p(v) - E_{iso}$ in eqs 16 and 17.

While eqs 16 and 17 appear complex, they allow α to be determined from two experimental parameters, E_s and v, and three experimental observables, $E_p^f(v)$, $E_p^r(v)$, and E_{iso}. $E_{1/2} = \frac{1}{2}[E_p^f(v) + E_p^r(v)]$. α can be determined without knowing ψ, D_A, D_B, and k^o. E_{iso} and E_p shift along the potential axis in parallel with D_A/D_B, as previously for the reversible case; therefore, eqs 16 and 17 are appropriate when D_A and D_B are not equal.

Equations 16 and 17 are valid at $T = 298.2$ K. For temperatures other than 298.2 K, more general forms of eqs 16 and 17 are as

(13) Hurd, R. M. *J. Electrochem. Soc.* **1962**, *109*, 327−332.

Table 4. Coefficients and Their Standard Errors for Eqs 18 and 19

coeff	value	std error
	For Eq 18[a]	
M_1	0.8417	0.0003
B_1	2.3189	0.0053
M_2	−0.5772	0.0080
M_3	−0.0725	0.0042
M_4	0.7018	0.0140
M_5	−1.035	0.038
M_6	0.00029	0.00008
	For Eq 19[b]	
M_1'	0.7793	0.0050
B_1'	2.3862	0.0092
M_2'	0.2148	0.0017
M_3'	0.04806	0.00130
M_4'	0.7608	0.0091
M_5'	1.1559	0.0242

[a] $0.3 \leq \alpha \leq 0.6$; $198.2 \leq T \leq 398.2$ K. [b] $0.5 \leq \alpha \leq 0.7$; $198.2 \leq T \leq 398.2$ K.

shown in eqs 18 and 19.

For $0.3 \leq \alpha \leq 0.6$,

$$\alpha = 1.24 - \{(F/RT)(E_p^f(v) - E_{iso}) - M_4 \ln[|E_s - E_{1/2}| \times (F/RT)] - M_5\}/\{([(F/RT)\Delta E_p - B_1']/M_1')[M_2 + (M_3/v^{1/2}) + (M_6(F/RT)/v^{1/2})]\} \quad (18)$$

For $0.5 \leq \alpha \leq 0.7$,

$$\alpha = \{(F/RT)(E_p^r(v) - E_{iso}) - M_4' \ln[|E_s - E_{1/2}| \times (F/RT)] - M_5' + 1.25([(F/RT)\Delta E_p - B_1']/M_1') \times ((M_3'/v^{1/2}) - M_2')\}/\{([(F/RT)\Delta E_p - B_1']/M_1') \times ((M_3'/v^{1/2}) - M_2')\} \quad (19)$$

The coefficients in eqs 18 and 19 were determined using data sets containing data for 134 and 209 voltammograms, respectively; the respective correlation coefficients are $r^2 = 0.9960$ and $r^2 = 0.9974$. The model for determining α, as shown above, was developed for $n = 1$, $198.2 \leq T \leq 398.2$ K and $0.02 \leq v \leq 0.1$ V/s. Table 4 lists coefficients to be used in eqs 18 and 19.

Resistance and Capacitance. The above model was developed without considering solution resistance (R) and double layer capacitance (C). Experimentally, however, the effects of resistance and capacitance will ultimately affect our ability to calculate α from the model proposed above. Methods of correcting for the resistance and capacitance are presented here.

Uncompensated resistance causes the peak splitting to increase, and analysis based on peak splitting will make kinetics appear to be slower than they would in the absence of resistance. Uncompensated resistance will limit the ability to calculate ψ^{-1} from ΔE_p, and so the peak splitting must be corrected for the resistance. The resistance and capacitance can be found experimentally by assuming a linear RC circuit and executing a small potential step (ΔE_{step}) either in a region where no electrolysis is occurring or in a blank electrolyte solution.[14] The measured

(14) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p 11.

current transient, $i_{step}(t)$, can be linearized to determine R and C; $\ln[i_{step}(t)] = \ln(\Delta E_{step}/R) - t/RC$. Once R is known, ΔE_p can be corrected by approximating the potential drop at each peak as

$$V_{drop} = i_p R \quad (20)$$

where i_p is the forward peak current. The forward and reverse peak potentials can be corrected by

$$E_p(corrd) = E_p(measd) + i_p R \quad (21)$$

where $E_p(corrd)$ is the peak potential corrected for R, $E_p(measd)$ is the peak potential measured from the cyclic voltammogram, and i_p is positive for a reduction. In this way, ΔE_p can be corrected as $\Delta E_p(corrd) = \Delta E_p(measd) - 2|i_p|R$, and α is well determined using $\Delta E_p(corrd)$. This correction works for $i_p R \leq 5$ mV, as a larger potential drop leads to >1 mV error in $\Delta E_p(corrd)$. With feedback methods, small electrodes, and low c_A^*, it should be possible to meet this constraint in solvents with dielectric constants greater than 20; under some conditions, solvents with lower dielectric constants may also satisfy this constraint. Because E_{iso} occurs near zero current, the potential shift in E_{iso} associated with uncompensated resistance is minimal.

The capacitance also needs to be considered when the isopoint method is used to calculate α. E_{iso} shifts along the potential axis with changing capacitance and can be corrected by using the following:

$$E_{iso}(corrd) = E_{iso}(measd) - 3 \text{ mV}\left(\frac{C/A}{20 \mu F}\right)\left(\frac{1 \text{ mM}}{c_A^*}\right)$$

$$T = 298.2 \text{ K} \quad (22)$$

where $E_{iso}(corrd)$ is the corrected E_{iso}, $E_{iso}(measd)$ is measured, and A is the electrode area. The 3 mV correction factor shown above in eq 22 changes with temperature. For $T = 198.2$ and 398.2 K, the correction factors are 2 and 4 mV, respectively. This suggests that the correction for temperature is $T \times 0.01$ mV. In the determination of α, $E_{iso}(corrd)$ is substituted for E_{iso}.

Limitations of Model. The model was developed for conditions listed in the Experimental Section, and the following is a list of the model constraints. First, the scan rates must be within the range of 0.020−0.100 V/s. Second, our range for quasireversible kinetics is slightly narrower than that characterized by Nicholson.[2] The isopoint method works for $0.25 \leq \psi \leq 1.5$ (or $73 \leq \Delta E_p \leq 145$ mV). Nicholson's method for finding ψ applies from the reversible through the quasireversible regime for $0.10 \leq \psi \leq 20$ (or $61 \leq \Delta E_p \leq 212$ mV). The applicability of the isopoint method is restricted as the system becomes more reversible. Third, one of the advantages of the isopoint method is that α can be determined even if D_A/D_B and $k°$ are not known. The isopoint method applies for $0.2 \leq D_A/D_B \leq 5$. Fourth, the voltage drop described by eq 20 should not exceed 5 mV if the peak potential difference is to be well corrected by eq 21. If the voltage drop exceeds 5 mV, the error in ΔE_p exceeds 1 mV. Fifth, the model is appropriate for a single electron transfer, $n = 1$. Sixth, as with any method of determining α, the isopoint method is sensitive to erroneous input. All potentials must be determined to within ±1 mV.

As the model was developed, α can be calculated to ± 0.03 if the values of α determined for several scan rates and several switching potentials are averaged. If only a single scan rate is used for a single switching potential, the uncertainty in α is ± 0.05.

In general, the model can be applied slightly outside of the constraints listed above. In cases where the model is applied too far outside its range of applicability, the model tends to fail fairly obviously. For example, if the model is applied for several scan rates and switching potentials, those within the constraints of the model will yield an average α value with minimal standard deviation. Those data sufficiently outside the applicable range of the model will yield substantially different values of α. If all the cyclic voltammograms are recorded under conditions outside the applicable range of the model, the calculated values of α will have substantial variation. Thus, while the method is fairly sensitive, when it is not applicable, it tends to fail in an obvious manner.

How to Measure α Using Cyclic Voltammetry.

(a) Run a series of cyclic voltammograms at three different scan rates, $0.02 \leq \nu \leq 0.1$ V/s, and scan at least 250 mV past the forward peak.

(b) Measure E_p^f, E_p^r, and E_{iso} from the cyclic voltammogram.

(c) Correct E_p^f and E_p^r for resistance using eq 21.

(d) Correct E_{iso} for capacitance using eq 22. (If temperature is other than room temperature, note comments below eq 22.)

(e) If $T \approx 298.2$ K, use eq 16 to determine α, using the appropriate coefficients listed in Table 3. If $T \neq 298.2$ K, use eq 18 to find α, using the coefficients listed in Table 4. If the forward wave corresponds to an oxidation, substitute $E_{iso} - E_p(\nu)$ for $E_p(\nu) - E_{iso}$ in eqs 16 and 18.

(f) If α is found to be greater than 0.6 using eq 16 (or eq 18), calculate α again using eq 17 (or eq 19, if $T \neq 298.2$ K). Appropriate coefficients are listed in Tables 3 and 4. Again, if the forward wave corresponds to an oxidation, substitute $E_{iso} - E_p(\nu)$ for $E_p(\nu) - E_{iso}$ in eqs 17 and 19.

(g) For best results, run cyclic voltammograms at several scan rates and several switching potentials. For each switching potential, determine E_{iso}. Average the resulting values of α.

Application of the Isopoint Method to Experimental Results.

The method was verified experimentally by determining α by the isopoint method and convolution voltammetry. Cyclic voltammograms were recorded for 2.81 mM iron(III) perchlorate in 0.0936 M perchloric acid at 50, 75, and 100 mV/s, under the conditions outlined in the Experimental Section. The solution resistance, R, and the double layer capacitance, C, were determined by 50 and 100 mV potential steps in the blank electrolyte,[14] over a potential range between 0.2 and 0.7 V vs SCE. The values found were $R = 2.34 \pm 0.39$ Ω, and $C = 10.6 \pm 0.07$ μF. The same set of voltammograms were analyzed by both methods.

The convolution method for analyzing cyclic voltammograms was developed independently by Oldham[4-6] and Saveant[7-9] and co-workers. The convoluted current, $I(E)$, is defined as

$$I(E) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(\tau)}{(t-\tau)^{1/2}}\,d\tau \qquad (23)$$

The digital algorithm developed by Lawson and Maloy[15] to convolute experimental current was employed. Once the applied

potential is sufficient to produce electrolysis at the mass transport limited rate, the convoluted current achieves a limiting value, I_{lim}, where

$$I_{lim} = nFAD_A^{1/2}c_A^* \qquad (24)$$

Because iron(III) perchlorate tends to adsorb water, its concentration (2.81 mM) was determined from I_{lim}. The diffusion coefficients of Fe(III) and Fe(II) in 1.0 M perchloric acid are reported as 5.5×10^{-6} and 6.5×10^{-6} cm^2/s, respectively.[16] Saveant and Tessier[8] showed that

$$-\ln\left[\frac{k_f(E)}{D_A^{1/2}}\right] = \ln\left[\frac{I_{lim} - I(E)[1 + \xi \exp((nF/RT)(E - E^{\circ\prime}))]}{i(E)}\right] \qquad (25)$$

where $\xi = (D_A/D_B)^{1/2}$ and $i(E)$ is the measured current. A plot of the right-hand side of eq 25 versus the applied potential, E, will be linear about $E^{\circ\prime}$, if Butler Volmer kinetics apply. The evaluation of the right-hand side of eq 25 is dependent on the evaluation of $E^{\circ\prime}$, which was determined from the convoluted current.[8] Note, for the convolution method, the determination of α is sensitive to the value of $E^{\circ\prime}$, unlike the isopoint method. It is possible to correct the convolution cyclic voltammogram for solution resistance and capacitance,[7,9,17] but because the resistance was so low, no correction was made.

For the three scan rates and a switching potential of 250 mV past the peak potential for the fastest scan rate, the convolution method yielded $\alpha = 0.446 \pm 0.023$. For the isopoint method, after correction for the resistance and capacitance (eqs 21 and 22), $\alpha = 0.441 \pm 0.003$ was found. These values are in excellent agreement. It is interesting to note that, at least in this case, the precision of the value found by the isopoint method is substantially greater than that found by convolution. Given D_A and D_B, k° can be calculated from eq 9. The convolution method yields $k^\circ = (2.1 \pm 0.2) \times 10^{-3}$ cm/s, while, once ψ was calculated using eq 10 and $M_1 = 0.844\,73$ and $B_1 = 2.233\,66$, appropriate to $\alpha = 0.4$ (see Table 2), the isopoint method yields $k^\circ = (2.7 \pm 0.4) \times 10^{-3}$ cm/s. Finally, it should be pointed out that the evaluation of α by the isopoint method is a simple procedure, requiring a few minutes, while the convolution method is a more complex procedure.

CONCLUSIONS

A method is presented for determining the transfer coefficient, α, from cyclic voltammetric results. Given scan rates between 0.020 and 0.100 V/s, the evaluation relies only on four experimental observables: the switching potential, the peak potentials, and the isopoint potential. It is not necessary to know concentrations, diffusion coefficients, electrode area, and standard rate constant. While the method presented here is slightly more restricted than Nicholson's method with respect to the range of applicable peak splittings ($73 \leq \Delta E_p \leq 145$ mV as opposed to 61

(15) Lawson, R. J.; Maloy, J. T. *Anal. Chem.* **1974**, *46*, 559–562.

(16) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker, Inc.: New York, 1969; p 220.

(17) Whitson, P. E.; Vanden Born, H. W.; Evans, D. H. *Anal. Chem.* **1973**, *45*, 1298–1306.

$\leq \Delta E_p \leq 212$ mV), it is readily applied and requires no other inputs than the experimentally measured potentials.

A linearization of the information presented by Nicholson to determine ψ (eq 9) is also presented. $E_{1/2} = {}^1/_2[E_{pc} + E_{pa}]$ has been shown to be correct within 1 mV for, roughly, $k° > 0.002$ cm/s (ΔE_p less than roughly 145 mV at 0.1 V/s). Diagnostics based on isopoints are presented for reversible electron transfers.

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