

Simulated Data for Electrochemical Determination of Rate Constants for Homogeneous Electron Transfer Reactions with a Second Order Homogeneous Follow-up Reaction. I: Coupling between Mediator and Reduced Form of the Substrate

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The kinetic eqns. for catalytic solution electron transfer followed by a second order coupling reaction: $A + e \rightleftharpoons B$; $B + C \rightarrow A + D$, k_1 ; $B + D \rightarrow \text{products}$, fast, have been solved by digital simulation for cyclic voltammetry (CV), linear sweep voltammetry (LSV) and double potential step chronoamperometry (DPSC). Simulated data for simple and fast measurements of the homogeneous electron transfer rate constant by four standard methods are presented. The methods allow measurements of k_1 for a broad range of fast and slow systems and have been tested on the anthracene/*t*-butyl bromide system and the anthracene/*sec*-butyl bromide system.

The key step in indirect electrolysis is the single electron transfer reaction in solution (SET) between an electrogenerated mediator and the substrate. The single electron transfer reaction has been known in inorganic chemistry for a long time,¹ but until the last two decades, only a few examples concerning organic systems were known.² In particular, the indirect reduction of aromatic and aliphatic halides with aromatic or heteroaromatic catalysts has been intensively studied (Refs. 3–6, and references therein).

The SET mechanism without follow-up reactions has been studied by most of the electrochemical techniques.⁷ First order or fast second order homogeneous electron transfer with a subsequent first order chemical reaction has been studied by polarography,^{7–9} linear-sweep volt-

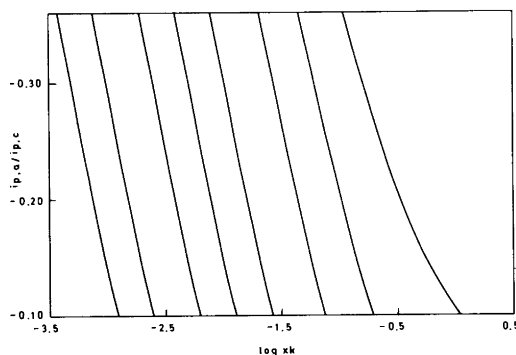


Fig. 1. The dependence of the current ratio $i_{p,a}/i_{p,c}$ on $\log xk$ for the method CV-1. $i_{p,c}$ and $i_{p,a}$ are the cathodic and anodic peak current measured when the switch potential is given by $E_{\text{switch}} = E_{A/B}^0 - 200$ mV. xk is the dimensionless kinetic parameter $xk = k_1 c_A^0 RT/Fv$. The curves are simulated for different c_2^0/c_1^0 ratios; from the right: 0.5, 1, 2, 5, 10, 20, 50 and 100.

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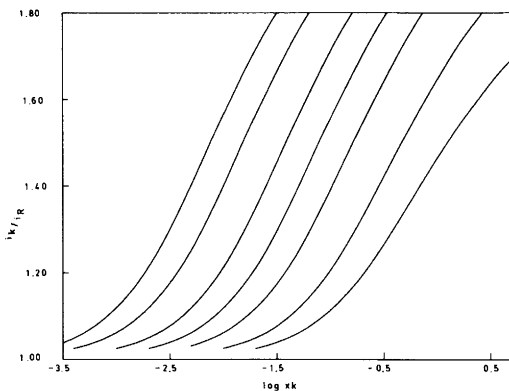


Fig. 2. The dependence of the current ratio i_k/i_R on $\log xk$ for the method LSV-1, i_R being the reversible peak current when only the mediator is present, whereas i_k is the peak current after the substrate has been added. xk is the dimensionless kinetic parameter $xk = k_1 c_A^0 RT/Fv$. The curves are simulated for different c_O^0/c_A^0 ratios; from right: 1, 2, 5, 10, 20, 50 and 100.

ammety (LSV) and cyclic voltammetry (CV),⁹⁻¹⁰ and by voltammetry at rotating disc electrodes.⁹

The purpose of this work was to find easy methods for determination of the rate constant for a second order SET reaction in the case where fast coupling between the products of the electrode reaction (mediator) and the products of the SET reaction takes place. Very often, the product of the first SET reaction is cleaved before the coupling reaction. However, the simulated data presented here cover both situations as long as the cleavage reaction is much faster than the SET reaction. Methods using data from the most popular electrochemical techniques, CV, LSV and double potential step chronoamperom-

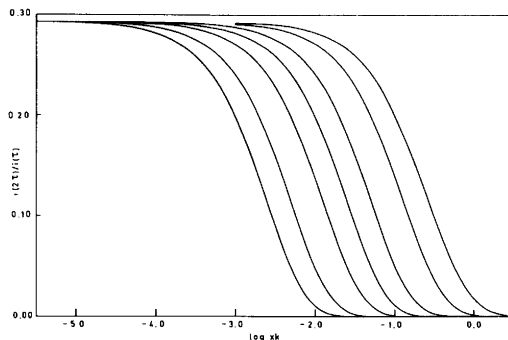


Fig. 3. The dependence of the current ratio $-i(2\tau)/i(\tau)$ on $\log xk$ for the method DPSC-1. xk is the dimensionless kinetic parameter $xk = k_1 c_A^0 \tau$. The curves are simulated for different c_O^0/c_A^0 ratios; from right: 1, 2, 5, 10, 20, 50 and 100.

etry (DPSC), are given. A similar LSV method has been described earlier by Savéant *et al.*^{3,4} Work on the case including competition by another electron transfer reaction is in progress.¹²

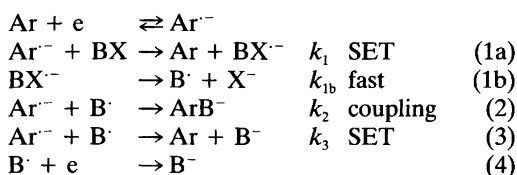
The methods proposed have been tested by measurements of the solution electron transfer rate for anthracene/*t*-butyl bromide and anthracene/*sec*-butyl bromide, i.e. cases where the coupling product is known to be the main product.⁶

Kinetic description

Several studies of the indirect reduction of alkyl halides by aromatic or heteroaromatic systems have been published in the last decade. In many cases, the reactions are adequately described by the following eqns. in which Ar/Ar^- is the mediator and BX is the alkyl halide:

Table 1. The 6th order polynomial fit for method CV-1.

c_O^0/c_A^0	C_0	C_1	C_2	C_3	C_4	C_5	C_6
0.5	1.6798	-30.920	225.83	-1057.2	2923.1	-4389.2	2749.1
1.0	-0.24277	-6.9123	31.728	-128.47	325.88	-468.77	284.65
2.0	-0.73397	-5.6606	25.461	-104.13	263.46	-376.78	226.09
5.0	-1.3098	-2.372	-11.935	126.31	-520.16	1008.3	-767.88
10.0	-1.5534	-4.6266	16.547	-50.484	75.184	-28.713	-35.315
20.0	-1.8513	-5.0522	22.784	-93.881	236.83	-336.79	200.33
50.0	-2.2574	-4.9783	22.134	-90.070	223.97	-313.93	183.76
100.0	-2.5616	-4.9465	21.880	-88.914	221.30	-311.32	183.29



In Ref. 6, it was shown by product analysis that the ratio between the coupling products and other products from B is most often greater than 10. For alkyl halides, only the primary alkyl halides showed lower ratios, e.g. anthracene/*n*-butyl bromide gave a ratio of 4.4. Consequently, we have chosen in this investigation to analyse the situation where the coupling reaction (2) is much

faster than the other reactions of B \cdot , so that we can then ignore reactions (3) and (4). Thus, the investigated process is no longer catalytic, but is merely a two-electron reductive addition process.

In this treatment we have made the following assumptions: The rate-determining step is the forward homogeneous electron transfer (1a), whereas (1b) and (2) are both much faster; consequently, the steady-state approximation applies to BX \cdot and B \cdot . Furthermore, it was assumed that the diffusion coefficients of all species are equal and that the heterogeneous electron transfer Ar/Ar \cdot is fast and therefore governed by Nernst's law.

Table 2. Rate constants for electron transfer from anthracene to *t*-butyl bromide in 0.1 M Bu $_4$ NBF $_4$ /DMF at $T = 21.4^\circ\text{C}$.

Method LSV-1

c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	i_p/i_R	$10^3 k_f/\text{M}^{-1} \text{s}^{-1}$
2.0	10.0	0.98	1.65	
2.0	10.0	1.97	1.48	2.78
2.0	10.0	4.90	1.25	

Method CV-1

c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	$-i_{p,a}/i_{p,c}$	$10^3 k_f/\text{M}^{-1} \text{s}^{-1}$	$10^3 \langle k_1 \rangle/\text{M}^{-1} \text{s}^{-1}$
2.0	10.0	19.7	0.109	4.71	
2.0	10.0	29.5	0.198	4.54	
2.0	10.0	39.3	0.267	4.47	4.61(0.13)
2.0	10.0	49.0	0.314	4.54	
2.0	10.0	58.8	0.353	4.57	
2.0	10.0	73.7	0.389	4.82	

Method DPSC-1

c_A^0/mM	c_C^0/c_A^0	τ/ms	$-i(2\tau)/i(\tau)$	$10^3 k_f/\text{M}^{-1} \text{s}^{-1}$	$10^3 \langle k_1 \rangle/\text{M}^{-1} \text{s}^{-1}$
2.0	10.0	4.9	0.076	3.70	
2.0	10.0	3.0	0.123	3.77	
2.0	10.0	2.8	0.128	3.84	3.87(0.15)
2.0	10.0	2.3	0.144	3.98	
2.0	10.0	2.0	0.155	4.08	

Method DPSC-2

$c_A^0 = 2.0 \text{ mM}$, $c_C^0/c_A^0 = 10.0$, $\tau_{0.5} = 2.22 \text{ ms}$, $k_1 = 3990 \text{ M}^{-1} \text{ s}^{-1}$.

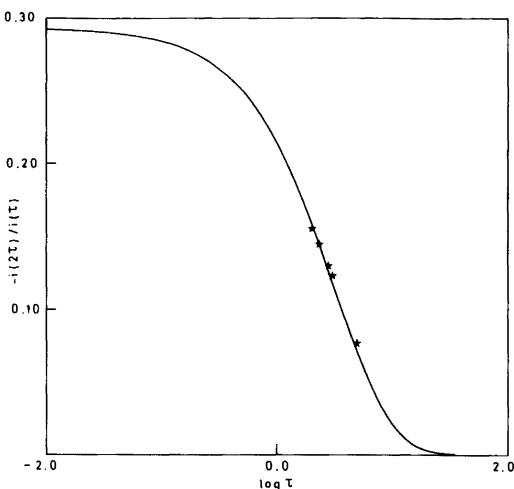
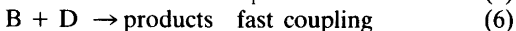
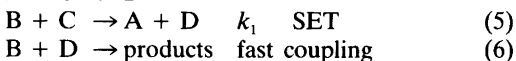
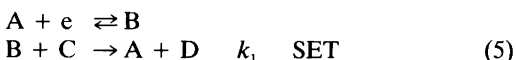


Fig. 4. Illustration of the use of method DPSC-1. The points (*) were experimentally determined by DPSC for the anthracene/*t*-butyl bromide system. The experiments were made in 0.1 M Bu₄NBF₄/DMF with c_A^o = 2.0 mM and c_C^o = 20.0 mM at T = 21.4 °C. The best fit of the experimental data to the simulated curve for c_C^o/c_A^o = 10 is for log xk = log τ + 0.89, where the pulse time, τ, is measured in s. From this relation and k₁ = 10^{(-log(c_A^o) + 0.89)} M⁻¹ s⁻¹ we find when c_A^o = 2.0 mM that k₁ = 3.88 × 10³ M⁻¹ s⁻¹.

The steady-state approximation for BX⁻ and B⁻ results in the following equality:

$$k_1 c_{Ar^-} c_{BX^-} = k_{1b} c_{BX^-} = k_2 c_{Ar^-} c_B$$

In this situation, the reaction scheme can be written in general terms as eqns. (5) and (6) we and can



describe the scheme mathematically by the differential eqns. (7), (8) and (9) with the normal boundary conditions for the electrochemical techniques:

$$dc_A/dt = Dd^2c_A/dx^2 + k_1 c_B c_C \tag{7}$$

$$dc_B/dt = Dd^2c_B/dx^2 - 2k_1 c_B c_C \tag{8}$$

$$dc_C/dt = Dd^2c_C/dx^2 - k_1 c_B c_C \tag{9}$$

For t = 0, x ≥ 0; x = ∞, t ≥ 0:

$$c_A = c_A^o, c_B = 0, c_C = c_C^o;$$

when x = 0, t ≥ 0:

$$\text{CV: } c_A/c_B = \exp(F/RT(E - E_{A/B}^o));$$

$$\text{DPSC: } 0 < t \leq \tau, c_a = 0; \tau < t \leq 2\tau, c_B = 0;$$

$$i = FDA(dc_A/dx).$$

The following dimensionless parameters are introduced:

$$a = c_A/c_A^o, b = c_B/c_A^o, c = c_C/c_A^o, c^o = c_C^o/c_A^o$$

$$\text{CV: } \theta = \left(\frac{Fv}{RT}\right) t, \xi = -\frac{F}{RT}(E - E_{A/B}^o)$$

$$y = \left(\frac{Fv}{DRT}\right)^{1/2} x, \lambda_1 = \left(\frac{RT}{F}\right) \left(\frac{k_1 \cdot c_A^o}{v}\right)$$

$$\text{DPSC: } \theta = \frac{t}{\tau}, y = \frac{x}{(\tau \cdot D)^{1/2}}$$

$$\lambda_1 = k_1 c_A^o \cdot \tau$$

$$\psi = \frac{i}{FDA}$$

The differential eqns. and the boundary conditions can now be written in dimensionless form as follows:

$$da/d\tau = d^2a/dy^2 + \lambda_1 bc \tag{10}$$

$$db/d\tau = d^2b/dy^2 - 2\lambda_1 bc \tag{11}$$

$$dc/d\tau = d^2c/dy^2 - \lambda_1 bc \tag{12}$$

$$\theta = 0, y \geq 0; y = \infty, \theta \geq 0;$$

$$a = 1, b = 0, c = c^o;$$

$$y = 0, \theta \geq 0;$$

$$\text{CV: } a/b = \exp(-\xi);$$

$$\text{DPSC: } 0 < \theta \leq 1, a_{y=0} = 0; 1 < \theta \leq 2, b_{y=0} = 0;$$

$$\psi = (da/dy)_{y=0} = -(db/dy)_{y=0}.$$

Experimental

Reagents. The supporting electrolyte, Bu₄NBF₄, and solvent, DMF, were purified by standard procedures. The anthracene was used as received but the *t*-butyl bromide and the *sec*-butyl bromide were distilled before use. No electroactive impurities could be detected.

Table 3. Rate constants for electron transfer from anthracene to *sec*-butyl bromide in 0.1 M Bu₄NBF₄/DMF at *T* = 25 °C.

Method LSV-1

c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	i_A/i_R	$10^3 k_f/\text{M}^{-1} \text{s}^{-1}$
1.98	2.0	0.050	1.75	1.66
1.98	2.0	0.200	1.49	
1.98	2.0	0.497	1.29	
1.98	2.0	0.996	1.17	
1.60	50	0.497	1.87	1.93
1.60	50	1.99	1.69	
1.60	50	4.98	1.51	
1.60	50	19.8	1.23	

Method CV-1

c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	$-i_{p,a}/i_{p,c}$	$10^3 k_f/\text{M}^{-1} \text{s}^{-1}$	$10^3 \langle k_1 \rangle / \text{M}^{-1} \text{s}^{-1}$
1.98	2.0	1.99	0.170	1.96	1.92(0.04)
1.98	2.0	2.98	0.262	1.89	
1.98	2.0	3.98	0.322	1.91	
1.95	5.0	4.97	0.149	2.01	2.09(0.06)
1.95	5.0	7.95	0.237	2.14	
1.95	5.0	10.94	0.313	2.11	
1.90	10.0	10.94	0.163	2.06	2.06(0.02)
1.90	10.0	16.80	0.261	2.04	
1.90	10.0	22.8	0.327	2.08	
1.60	50	59.4	0.189	2.31	2.43(0.12)
1.60	50	79.4	0.244	2.42	
1.60	50	119.0	0.326	2.55	

Method DPSC-1

c_A^0/mM	c_C^0/c_A^0	τ/ms	$-i(2\tau)/i(\tau)$	$10^3 k_f/\text{M}^{-1} \text{s}^{-1}$	$10^3 \langle k_1 \rangle / \text{M}^{-1} \text{s}^{-1}$
1.98	2.0	20.0	0.143	2.42	2.49(0.08)
1.98	2.0	18.4	0.148	2.46	
1.98	2.0	16.9	0.152	2.58	
1.95	5.0	10.3	0.120	2.28	2.35(0.09)
1.95	5.0	7.37	0.149	2.46	
1.95	5.0	6.03	0.170	2.33	
1.90	10.0	5.00	0.131	2.20	2.31(0.10)
1.90	10.0	3.99	0.148	2.34	
1.90	10.0	2.99	0.170	2.31	

Method DPSC-2

$c_A^0 = 1.90 \text{ mM}$, $c_C^0/c_A^0 = 10.0$, $\tau_{0.5} = 4.05 \text{ ms}$, $k_1 = 2301 \text{ M}^{-1} \text{ s}^{-1}$.

Instrumentation and data handling procedures. The potentiostat was a home-built adder type with a semiautomatic IR-compensator. The potentiostat was driven by a HP 8116A programmable function generator. The current and potential signals were digitized by two parallel running 12 bit A/D converters from Burr-Brown (803), 16 kb ram being available to each digitized signal.

The digital acquisition system was connected to an Olivetti M24 personal computer. The computer was programmed for data treatment for the different techniques. In CV, the programme finds the baseline for the forward scan by linear regression and subtracts the charging currents from the absolute measured peak current.²¹ The peak point is found manually with the help of a cursor system. The peak currents are calculated as the mean value of 10 points around the peak point.

Each experiment was repeated three times and the average value and the variance calculated for the scan rate, peak currents and peak current ratio.

The DPSC programme calculates $i(\tau)$ and $i(2\tau)$ as the mean values of the last 20 data points before the potential shifts. The normalized current ratio was calculated as $R = i(2\tau)/0.2928i(\tau)$, each experiment being repeated three times and the average value and the variance calculated for the pulse time and the normalized current ratio. The acquisition system and data treatment programmes are described in detail in Ref. 22.

The electrochemical cell. The measurements were conducted in DMF solutions containing 0.1 M Bu₄NBF₄. The reference electrode was Ag/Ag⁺ in DMF, constructed in the manner described by Moe.²³ A modified cylindrical tube was used (25 ml volume) with a joint to accommodate a teflon plug which served as a holder for the three electrodes. The temperature sensor and nitrogen inlet had separate entrance through two arms fixed on the cylindrical tube.

Simulations. The simulations were performed on an Olivetti M24 personal computer programmed in Turbo Pascal. The figures were plotted by a HP 7475 plotter.

Results and discussion

In the digital simulations, the explicit point method^{13,14} was used, described in detail by Britz.¹⁵ The stability factor ($D\Delta t/\Delta x^2$) was kept equal to 0.45 in all cases. The integration was performed by a 4th order classical Runge-Kutta method¹⁶ (for application to electrochemistry, see Refs. 17 and 18).

In all simulations, a 6-point approximation of the flux was applied.¹⁹ The approximation is based on the assumption that the concentration profile near the electrode surface can be adequately described by a third order polynomial. The eqn. for the flux is: $(da/dx)_{x=0} = (-137a_1 + 300(a_2 - a_3) + 200a_4 - 75a_5 + 12a_6)/(60\Delta x)$, where a_1 is the concentration of A at the surface.

The CV experiments were all simulated with $E_{\text{start}} = E_{\text{A/B}}^\circ + 200$ mV and $E_{\text{switch}} = E_{\text{A/B}}^\circ - 200$ mV. Additional simulations have shown that the peak current ratios are not very sensitive (<1%) to E_{switch} as long as $E_{\text{A/B}}^\circ - 190$ mV < $E_{\text{switch}} < E_{\text{A/B}}^\circ - 210$ mV. The CV experiments were simulated with 8000 timesteps corresponding to 0.1 mV/timestep. DPSC was simulated with a total of 2000 timesteps.

Method CV-1. The simulated CV data can be treated by two different methods. The first involves the ratio of the anodic peak current to the cathodic peak current, $i_{p,a}/i_{p,c}$, which is plotted versus $\log(xk)$ in Fig. 1 for various ratios of c_A°/c_C° . The kinetic parameter xk is given by: $xk = k_1 c_A^\circ / (38.92 \cdot v)$, where k_1 is in M⁻¹s⁻¹, c_A° in M, v in Vs⁻¹ and 38.92 is the value of F/RT at 25°C.

Experimentally, it was found that the interval $0.1 < -i_{p,a}/i_{p,c} < 0.36$ gave the most reliable and accurate results. In this interval, a 6th order polynomial was fitted to $i_{p,a}/i_{p,c}$ and the coefficients are given in Table 1. Thus, the xk value can be calculated from experimental ratios, $r = i_{p,a}/i_{p,c}$ by:

$$\log(xk) = C_6 r^6 + C_5 r^5 + C_4 r^4 + C_3 r^3 + C_2 r^2 + C_1 r + C_0.$$

The polynomial gives a precision in $\log(xk)$ of 1 at the fourth decimal.

The second way to use the simulated CV data makes use only of the information on the first sweep, corresponding to information from the LSV technique.

Method LSV-1. The method is indirect, i.e. involves two experiments: the first in order to measure the reversible reduction peak current i_R when only the mediator is present, and the second to measure the kinetic peak current i_k after the substrate has been added. The ratio of i_k/i_R is plotted versus $\log(xk)$ in Fig. 2 for various values of c_A^0/c_A^* .

When xk has been determined from Fig. 1, Fig. 2 or Table 1, the rate constant can easily be calculated from: $k_1 = xk \cdot 38.92 \cdot v/c_A^0 \text{ M}^{-1}\text{s}^{-1}$.

DPSC experiments. These were simulated with the assumption that the reduction of A was diffusion-controlled during the first potential step ($c_{A, x=0} = 0$) and the oxidation of B was diffusion-controlled during the second step potential ($c_{B, x=0} = 0$). This is the case when the potential is stepped 300 mV more negative and 300 mV more positive than $E_{A/B}^0$, respectively.

Method DPSC-1. The third method for determining the rate constants is the usual method for DPSC, i.e. measuring the ratio $i(2\tau)/i(\tau)$ of the current at the end of the second step, $i(2\tau)$, to the current at the end of the first step, $i(\tau)$. This ratio is plotted versus $\log(xk)$ in Fig. 3. In this case the kinetic parameter is: $xk = k_1 c_A^0 \tau$, with c_A^0 in M and τ in s.

When xk has been determined from a fit of experimental values to the curve, the rate constant can be calculated according to: $k_1 = xk/(c_A^0 \tau) \text{ M}^{-1}\text{s}^{-1}$.

Method DPSC-2. The fourth and last method for finding the rate constant is to use the approach of Bard *et al.*²⁰ where the pulse time, τ , is experimentally varied until the normalized current ratio, $-i(2\tau)/(i(\tau) \cdot 0.2928)$, is equal to 0.5 for $c_A^0/c_A^* \geq 10$. At that point the rate constant is given by: $k_1 = 0.1771/(c_A^0 \tau) \text{ M}^{-1}\text{s}^{-1}$.

We have studied experimentally the coupling reaction using anthracene, *t*-butyl bromide and *sec*-butyl bromide. From preparative electrolysis and subsequent product distribution analysis by GLC and NMR, it was found for the anthracene/*t*-butyl bromide system that the coupling reaction is 36 times faster than the competing side reactions, whereas for the anthracene/*n*-butyl bromide system the coupling reaction is only 4.4 times faster than the side reactions.⁶ By interpolation, the coupling reaction is expected to be at least 10 times faster than the side reaction for the

anthracene/*sec*-butyl bromide system. In cases such as this it is possible to neglect the side reactions and focus on the coupling reaction.

For the anthracene/*t*-butyl bromide system the experimental $i(2\tau)/i(\tau)$ values are plotted together with the simulated curve in Fig. 4. Table 2 gives the k_1 values determined by the four different methods. Values of k_1 for the anthracene/*sec*-butyl bromide system are given in Table 3.

The observed k_1 values are all in the same range except for the LSV method. This seems to be a general trend, since we have observed the same difference in other investigations. The reason could be that the CV and DPSC results depend on the degree of reversibility, while the LSV results are calculated from the current enhancement from purely reversible to purely irreversible conditions. In the tables, it is seen that the deviations between the CV or DPSC results and the LSV results are greatest for the relatively slow reactions. This may be due to the effect of convection because of the low scan rate, or it may simply be that a small error in the current ratio affects the rate constant most at the low end of the working curve. This indicates that the faster the reaction, the better is the LSV method, i.e., best when the response is irreversible at a reasonable scan rate. Finally, another case where the LSV method is the method of choice is when another electrochemical reaction takes place at a potential after the investigated couple in a way that affects the background current for the reverse current in CV or DPSC.

Conclusion

The rate constant for the coupling mechanism for solution electron transfer reactions can be determined in a simple and easy way. The proposed methods complement each other in two respects: First, one method (LSV) is best for fast reactions and the other methods (CV and DPSC) are best for medium fast and slow reactions; second, the LSV method may be used when further electrochemical reactions interfere with the current ratios for the direct methods.

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