Direct determination of diffusion coefficients by chronoamperometry at microdisk electrodes

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Abstract

The chronoamperometric response at a microdisk is used for the direct determination of the diffusion coefficient of an electroactive species. The method does not require knowledge of the bulk concentration and the number of electrons participating in the electrode reaction, and requires only a value for the disk radius. Subsequent determination of the number of electrons (n) for an electrode reaction or the concentration of electroactive species is also possible. This approach is demonstrated with the evaluation of the diffusion coefficient of $Fe(CN)_6^{4-}$ in KCl and that of borohydride ion in NaOH. In both cases, the values of n found remained constant over a wide time range and correspond to those expected for these processes.

INTRODUCTION

Electrochemical methods are widely used to determine diffusion coefficients (D) of electroactive species by carrying out electrode reactions under conditions where the rate of the process is controlled by mass transfer. In most of these, e.g., potential-step chronoamperometry or chronocoulometry at a planar electrode, determination of D for an oxidized species O, by carrying out the electrode reaction $O + n\ e^- \rightarrow R$ requires knowledge of the number of electrons transferred in the electrode reaction (n), the electrode area (A) and the bulk concentration of electroactive species, O (c^*). Moreover, in studying new electrode reactions, one would often like to determine n without knowing D. This can be done by coulometric methods [1], but these are usually more demanding than voltammetric techniques. In this paper we propose a simple technique for the direct determination of D independent of n, A and c^*, based on treatment of the chronoamperogram obtained with a microdisk electrode that requires only knowledge of the disk radius

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(*a*). Armed with this value of *D*, *n* can be determined from the same data, if c^* is known.

D is usually evaluated by the following electrochemical measurements: (1) limiting currents at rotating disk, dropping mercury, or microdisk electrodes; (2) peak currents for reversible cyclic voltammetric waves; (3) slopes of $i-t^{-1/2}$ curves in potential-step chronoamperometry (or $i-t^{1/2}$ in chronocoulometry); (4) transition times in chronopotentiometry [1,2]. We devised the approach described here during a study of the chronoamperometric response of the tip current of a scanning electrochemical microscope (SECM) [3]. With the SECM, one usually normalizes the tip current with respect to its steady state value with the tip far away from a substrate; i.e., with respect to

$$i_{\mathrm{d,ss}} = 4nFDc^*a \tag{1}$$

We showed that one could extract *D*, independent of *n*, *A*, and c^*, directly from the normalized transient SECM current. We show here that this is also true for the normalized response of an ultramicroelectrode alone, since an analysis of the analytical expression for the microdisk chronoamperometry shows that the faradaic current is proportional to $nAD^{1/2}c^*$ at very short times and to $nADc^*$ at long times.

The idea of determining *D* by comparing transient data with steady state data has been a subject of several publications [4–6] and was recently the object of an extensive study by Amatore and coworkers [7]. In most cases, however, these studies required at least two separate measurements, e.g., with electrodes of different sizes or geometries (planar electrode, RDE, microdisk), or by different techniques (chronoamperometry, steady state voltammetry) and sometimes necessitated the use of a standard electroactive species added to the solution. An alternative approach to determination of *D*, without knowledge of *n* and c^*, involves determination of the time required for a product (R) produced at a generator electrode to transit to a closely spaced collector electrode, e.g., in an array of individually addressable microelectrodes [8], rotating ring–disk electrode [9], or SECM [3]. This approach, however, requires a rather specialized electrode assembly and stability of species R. To our knowledge, no one has proposed a direct determination of *D* from a single chronoamperogram recorded on a microdisk for the species of interest.

EXPERIMENTAL

Reagents

$K_4Fe(CN)_6 \cdot 3\ H_2O$ (MCB Manufacturing Chemists Inc., Cincinnati, OH), KCl and NaOH (Baker Analyzed, J.T. Baker Inc., Phillipsburg, NJ), and $NaBH_4$ (Aldrich Chemical Company, Milwaukee, WI) were used without further purification. All solutions were prepared with deionized water (Milli-Q, Millipore Corp.).

Electrodes

For the experiment with $Fe(CN)_6^{4-}$ the reference electrode was a Pt wire and the working electrode was a 25 μm diameter Pt microdisk (Goodfellow Metals Ltd,

Cambridge, UK) encased in glass. For the experiment with borohydride the reference electrode was a $Hg/Hg_2SO_4/sat.$ K_2SO_4 electrode and the working electrode was a 50 μm diameter Au microdisk (Goodfellow Metals Ltd.) encased in glass. Before each experiment, the microdisk was polished on a Nylon cloth with 0.25 μm diamond paste (Buehler Ltd, Lake Bluff, IL).

Apparatus

The potential of the working electrode, in a two electrode configuration, was controlled by a Princeton Applied Research (PAR) model 175 programmer and the current was monitored with a home-built current follower with a rise time of about 100 μs. The chronoamperometric response was recorded with a Norland 3001A/DMX digital processing oscilloscope with a model 3226B (2 μs, 10 bit) acquisition module (Norland Corporation, Fort Atkinson, WI).

THEORY

Spherical approximation to the microdisk

To analyze the microdisk chronoamperometric response, one can use, as an initial approximation, a semi-analytical approach based on the analogy between the diffusion to a sphere and that to a disk. Oldham [10,11] compared the current response of a microdisk to that of a microsphere and showed that the diffusion controlled current to a microdisk of radius a is the same as that at a hemisphere of radius, r_s, $r_s = 2a/\pi$. The current at a sphere is [1]

$$i_s(t) = \frac{nFAD^{1/2}c^*}{\pi^{1/2}t^{1/2}} + \frac{nFADc^*}{r_s} \qquad (2)$$

The analogous equation for a microdisk is

$$i_d(t) = \pi^{1/2}nFD^{1/2}c^*a^2t^{-1/2} + 4nFDc^*a \qquad (3)$$

Normalizing eqn. (3) with respect to the steady state current, eqn. (1), yields

$$i_d(t)/i_{d,ss} = (\pi^{1/2}/4)a(Dt)^{-1/2} + 1 \qquad (4)$$

From eqn. (4), $i_d(t)/i_{d,ss}$ is clearly a linear function of $1/\sqrt{t}$. The procedure for the direct measurement of D involves recording an i–t curve with a microdisk electrode over a time window which spans the transient and the steady state regions. The chronoamperometric data are then normalized with respect to the steady state current. A plot of $i_d(t)/i_{d,ss}$ vs. $1/\sqrt{t}$ is a straight line with an intercept of one and slope, S. If a is known, one can evaluate D:

$$D = \pi a^2/16S^2 \qquad (5)$$

This procedure allows the direct determination of D. If c^* is known, the values $i_{d,ss}$, D, and a can be used to compute n from eqn. (1).

As shown in eqn. (6), the accuracy of this technique depends greatly on the uncertainty in the value of the disk radius (Δa) and the slope, S.

$$\Delta D/D = 2[(\Delta a/a) + (\Delta S/S)] \tag{6}$$

At this point we investigate the validity of eqn. (4) as well as the optimum time domain required for accurate measurement of D. Previous studies [10,12,13] have shown that at very short times ($Dt/a^2 < 10^{-4}$, for $< 1\%$ error) (and assuming no kinetic limitations), semi-infinite linear diffusion to and from a microdisk takes place, and that the diffusion controlled current obeys the Cottrell equation [1] (first term in eqn. 3). At long times ($Dt/a^2 > 10^2$, for $< 1\%$ error), a quasi-spherical diffusion field leads to a steady state current (last term in eqn. 3). Thus it is clear that eqn. (3) predicts the current to a microdisk at very short and long times, but undoubtedly leads to poor estimations in the intermediate time window.

For a more precise description of the current to a microdisk, we recall an expression suggested by Shoup and Szabo [12]

$$\frac{i_d(t)}{i_{d,ss}} = \frac{\pi}{4} + \frac{\pi^{1/2}}{4}\left(\frac{Dt}{a^2}\right)^{-1/2} + \left(1 - \frac{\pi}{4}\right)\exp\left(-\frac{\pi^{1/2} - 8\pi^{-3/2}}{4 - \pi}\left(\frac{Dt}{a^2}\right)^{-1/2}\right) \tag{7}$$

$$\frac{i_d(t)}{i_{d,ss}} = 0.7854 + 0.4431\tau^{-1/2} + 0.2146\exp(-0.3911\tau^{-1/2}) \tag{8}$$

$$\tau = Dt/a^2 \tag{9}$$

This equation is based on a fit to the short and long time analytical solutions [13] of the microdisk chronoamperometric response and was found to be exact within 0.6% at all times [12].
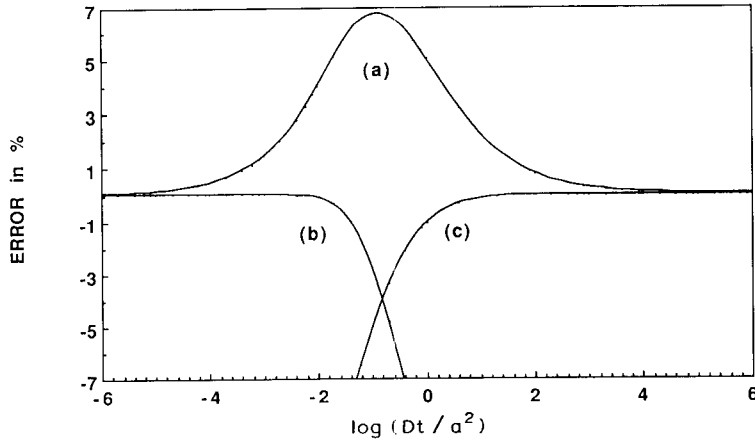

Fig. 1. Plot of the relative error of (a) eqn. (4), (b) eqn. (12), and (c) eqn. (13); compared to eqn. (8) as a function of the dimensionless time.

Figure 1, curve (a) shows a comparison between eqn. (4) and eqn. (8). As predicted, eqn. (4) is valid at very short and long times; it also shows that the maximum deviation, 6.8%, occurs for a dimensionless time, τ, of about 0.1 (i.e., $t = 0.1a^2/D$). Thus within the experimental time window commonly used, eqn. (4) leads to a poor fit with the theory; for t within 4×10^{-4} a^2/D and 60 a^2/D the relative error of eqn. (4) is greater than 1%.

Linear expressions for the transient at short and long times

Let us recall the short time and long time expressions that were used to derive eqn. (7). At short times we have (see eqn. 5 of ref. 12)

$$\frac{i_d(t)}{i_{d,ss}} = \frac{\pi}{4} + \frac{\pi^{1/2}}{4}\left(\frac{Dt}{a^2}\right)^{-1/2} + O(t) \tag{10}$$

and at long times (see eqn. 4 of ref. 12)

$$\frac{i_d(t)}{i_{d,ss}} = 1 + \frac{2}{\pi^{3/2}}\left(\frac{Dt}{a^2}\right)^{-1/2} + O(t^{-3/2}) \tag{11}$$

In both cases the second terms are linear functions of $1/\sqrt{t}$. These equations can be used for the direct determination of D. At short times

$$i_d(t)/i_{d,ss} = 0.7854 + \left(\pi^{1/2}/4\right)a(Dt)^{-1/2} \tag{12}$$

and at long times

$$i_d(t)/i_{d,ss} = 1 + \left(2/\pi^{3/2}\right)a(Dt)^{-1/2} \tag{13}$$

In Fig. 1, curve (b) shows a comparison between eqn. (12) and eqn. (8) whereas curve (c) shows a comparison between eqn. (13) and eqn. (8). If the final time (t_f) is less than 0.04 a^2/D the current ratio given by eqn. (12) is within 1% of that given by eqn. (8) and if the initial time (t_i) is greater than a^2/D the current ratio given by eqn. (13) is within 1% of that given by eqn. (8).

Thus there are three expressions where the transient normalized with respect to the steady state current is a linear function of the inverse square root of time. Equation (4) is valid at all times and at worst is exact to within 6.8%, eqn. (12) is valid at short times and is exact within 1% for t_f less than 0.04 diffusion time, and eqn. (13) is valid at long times and is exact within 1% for t_i greater than one diffusion time. Any of these equations can be used for the direct determination of D. However, for the very short time region (e.g., the Cottrell region or eqn. 12), errors in the measured current can arise from contributions from double layer charging, finite rise times of the potentiostat and current follower, amplifier overload, and finite heterogeneous electron transfer kinetics. Of course, at all times, it is possible to fit the experimental current ratio to the more exact eqn. (8). However, this procedure requires a one dimensional non-linear regression which is more tedious than the linear approach involving the approximate equations.

Microsphere electrodes

For a microsphere, eqn. (2) is exact. Thus, normalizing this expression with respect to the steady state, we find

$$i_s(t)/i_{s,ss} = 1 + r_s/(\pi D t)^{1/2} \tag{14}$$

For a sphere, a plot of $i_s(t)/i_{s,ss}$ against $1/\sqrt{t}$ yields a straight line with slope, $S = r_s/(\pi D)^{1/2}$ which can be used for the direct determination of D. Note that eqn. (14) holds, in principle, for any spherical electrode, even one with a larger radius, e.g., the hanging mercury drop electrode. With electrodes of larger radii, however, the steady state current is only attained at long times and under these conditions natural convection inevitably disturbs the measured current and leads to serious errors in $i_{s,ss}$ [14]. Thus, although the approach suggested here was available many years ago, it is only with the advent of microelectrodes that this technique has become feasible. It would be especially useful with mercury microsphere electrodes [15].

All the equations given above are based on the assumption that a transient is recorded with zero concentration of the electroactive substance at the electrode surface (c^s). This assumption is generally accepted by the authors calculating transients provided by large potential steps at microdisks [12,13]. Actually, the decrease in c^s is not instantaneous and depends upon the rate of heterogeneous electron transfer. On a microelectrode this process is more significant than on a plane. As has been shown previously [16], this may lead to substantial deviation from the Cottrell equation at the very early stages of the transient. The time region in which this deviation occurs is determined by the values of kinetic parameters of the electrode process, the disk radius, and the potential applied. Our calculations for the electrochemical system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ ($k^\circ \approx 0.1$ cm s^{-1}) showed that with $a = 12.5$ μm and $E = E^\circ - 200$ mV (where E° is the formal potential), this effect should be observed at times less than 1 ms. However, if $E = E^\circ - 150$ mV, this time is 0.01 s. If the initial part of the chronoamperogram deviates from a linear dependence of $i(t)/i_{ss}$ vs $1/\sqrt{t}$, the time window used to determine D should be changed.

If the experimental conditions prevent applying a sufficiently high potential to the electrode, to drive c^s to zero, both values $i(t)$ and i_{ss} would contain the additional multiplier ($c^* - c^s$). Equations (4), (12), (13), and (14) are still valid, since this term should cancel upon normalization.

RESULTS AND DISCUSSION

Oxidation of $Fe(CN)_6^{4-}$ in KCl

To assess the applicability of this approach, diffusion controlled microdisk transients were recorded for the oxidation of $Fe(CN)_6^{4-}$ in KCl, over different time regions using sampling rates of one point every 100 μs, 1 ms, or 10 ms. Experimental results are shown in Figs. 2–5. In these figures, the experimental ratio $i_d(t)/i_{d,ss}$ is plotted against $1/\sqrt{t}$ and in each case, the experimental points show that
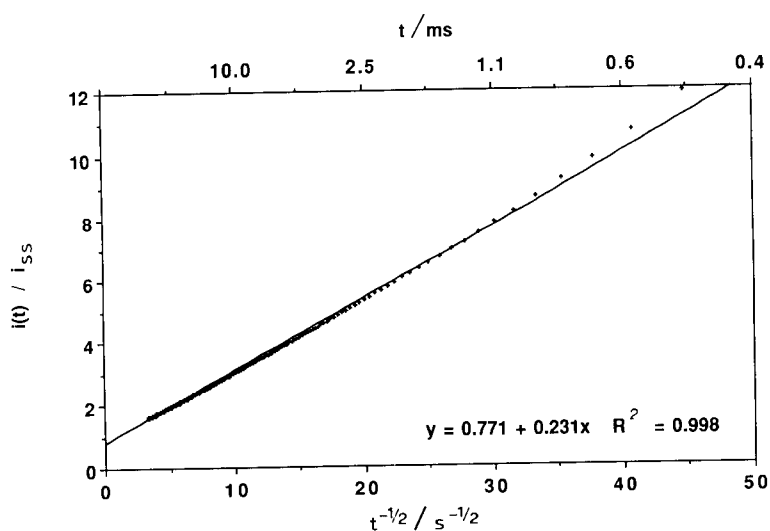
Fig. 2. Plot of the experimental ratio $i_d(t)/i_{d,ss}$ against the inverse square root of time for the oxidation of 48.3 mM $Fe(CN)_6^{4-}$ in 1 M KCl with a 13 μm radius Pt microdisk. Short time region: the sampling rate is 100 μs per point. The results of the linear regression are also shown.

$i_d(t)/i_{d,ss}$ is a linear function of $1/\sqrt{t}$, thus agreeing with the theoretical predictions. A linear regression was used to compute the slope S and the intercept over each time region. These are given in Table 1 along with values of D and n calculated by the approximate equations appropriate for the time regime. The disk
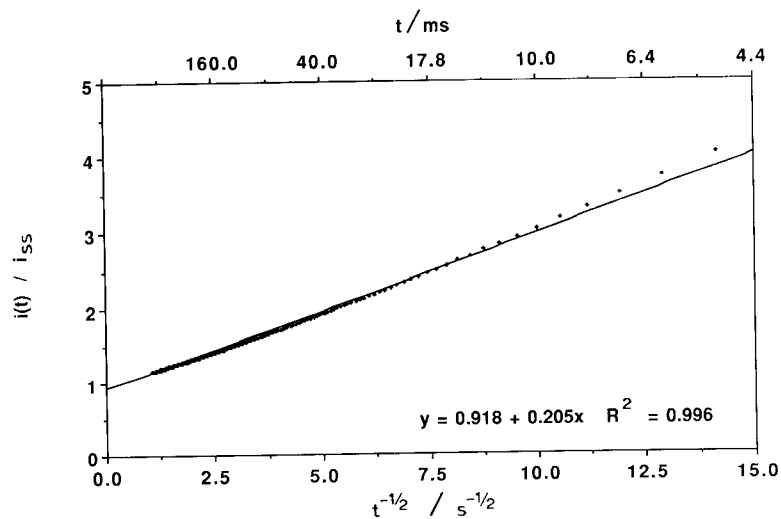

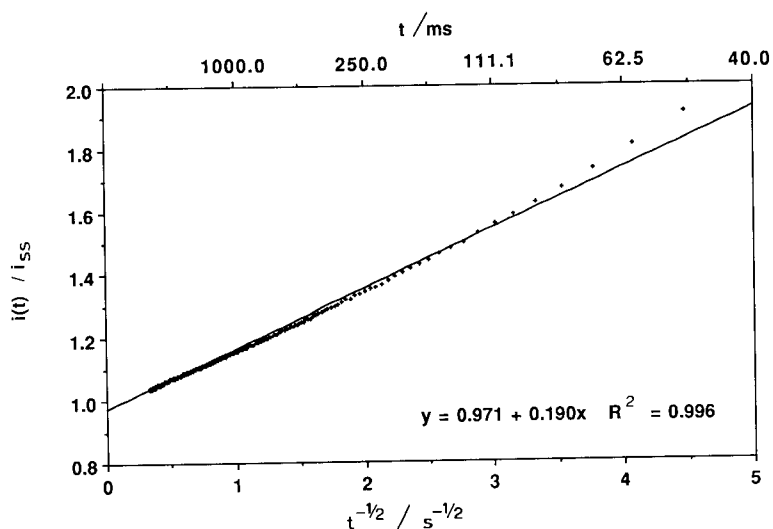Fig. 3. Same as in Fig. 2. Intermediate time region: the sampling rate is 1 ms per point.

Fig. 4. Same as in Fig. 2. Long time region: the sampling rate is 10 ms per point.

radius, $a = 13.0 \pm 0.3$ μm, was determined by recording the limiting currents on steady state voltammograms for the oxidation of 4 mM $Fe(CN)_6^{4-}$ in 1 M KCl (under these conditions, the diffusion coefficient of $Fe(CN)_6^{4-}$ is reported [2] to be 6.32×10^{-6} cm^2 s^{-1}); observations with an optical microscope confirmed the value
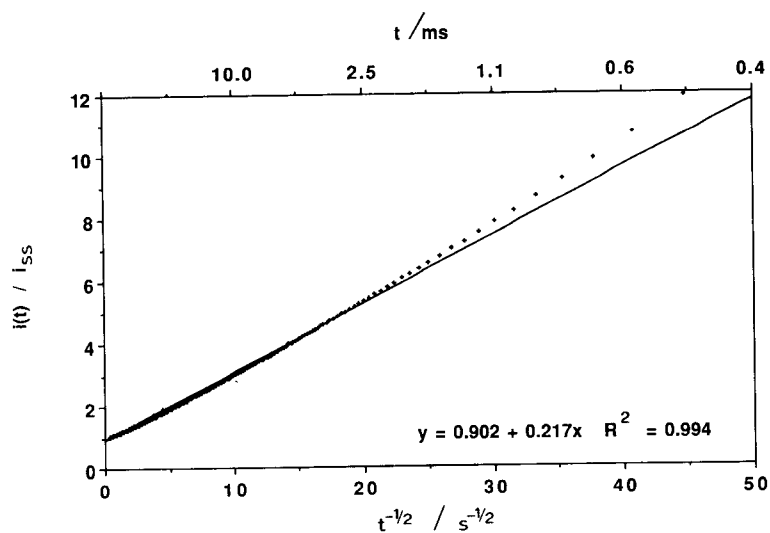

Fig. 5. Transients shown in Figs. 2–4 are combined to show the response of the microdisk over the complete time range. The results of the linear regression applied to the whole transient are also shown.

TABLE 1

Experimental and calculated results for the oxidation of $Fe(CN)_6^{4-}$ in 1 M KCl. $c^* = 48.3 \times 10^{-6}$ mol cm^{-3} and $a = 13 \times 10^{-4}$ cm. In each case n was calculated with the equation: $n = i_{d,ss}/4FDc^*a$

Figure	Transient time region	$i_{d,ss}/$ nA	$S/$ s$^{1/2}$	intercept	$10^6 D/$ cm^2 s^{-1}	n	Equation
2	0.5–89.6 ms	151	0.231	0.771	6.22	1.00	12
3	5–896 ms	153	0.205	0.918	7.90	0.80	12
					5.19	1.22	13
4	0.05–8.96 s	152	0.190	0.971	6.04	1.04	13
5	0.5 ms–8.96 s	152	0.217	0.902	7.05	0.89	4

measured electrochemically. The results in Table 1 show that eqn. (12) at short times, and eqn. (13) at long times, yield values for D and n in very good agreement with the expected ones. At intermediate times, however, eqns. (12) and (13) yield values for D and n that bracket the expected ones. For the whole transient, the spherical approximation, eqn. (4), leads to about an 11% error for D and n. This approximate equation must be used with care. A 10% error on D may not be significant, but a 10% error in n, while usually unimportant when $n = 1$, is certainly not acceptable when $n = 8$, as will be seen in the study of the oxidation of the borohydride ion. In all cases, the intercepts computed with the linear regression are in good agreement with the theoretical predictions. The value of the intercept can be used as a diagnostic criterion. If the computed value does not match the theoretical one, the equation employed in the given experimental time region should be changed. As mentioned above, the best fit to the experimental data should be obtained using a non-linear regression of eqn. (8) which is precise at any time. Actually this procedure led to the values $D = 6.9 \times 10^{-6}$ cm^{2}s^{-1}, $n = 0.91$, which are less accurate than the results shown in Table 1. These results support the use of eqns. (12) and (13) since, contrary to a linear regression, a non-linear regression may yield several sets of parameters which satisfy the best fit criteria.

While the linear procedure is applicable to simple diffusion controlled electron transfer reactions, it is difficult to estimate the applicability of the technique described to the study of multistep electrode processes with coupled chemical reactions. For example, for ECE mechanisms, dependence of i vs. $t^{-1/2}$ may be non-linear at planar or spherical electrodes [2,17].

Oxidation by BH_4^- in NaOH

We also applied this method to the electrooxidation of borohydride ion in alkaline solutions at a gold electrode. The mechanism of this process is complicated with borate as the product with the number of electrons involved in the overall reaction equal to 8 [18–21]. The cyclic voltammogram (CV) of this process at a large gold electrode consists of a single peak typical of a simple irreversible electrooxida-
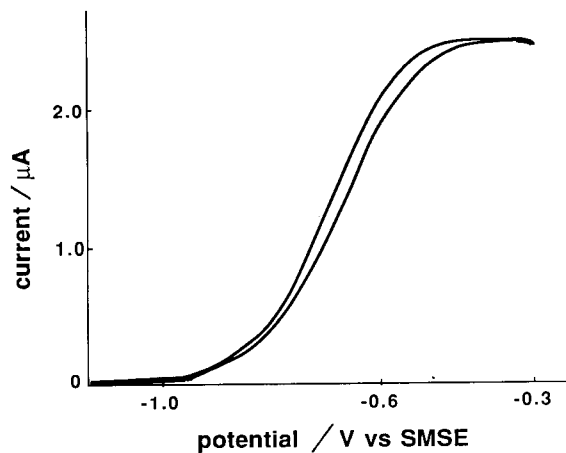
Fig. 6. Steady state linear sweep voltammogram recorded on a 25 μm radius gold microdisk for the oxidation of 20 mM sodium borohydride in 1 M NaOH. The scan rate was 5 mV s^{-1}.

tion [21]. The steady state CV at a Au microdisk, Fig. 6, also shows a simple and regular shape, suggesting that the shape of a microdisk current transient may also be similar to that of a simple electrode reaction.

Concentrated NaOH (1.0 M) was used as supporting electrolyte for recording the borohydride transients. This allowed the use of a high concentration of NaBH$_4$
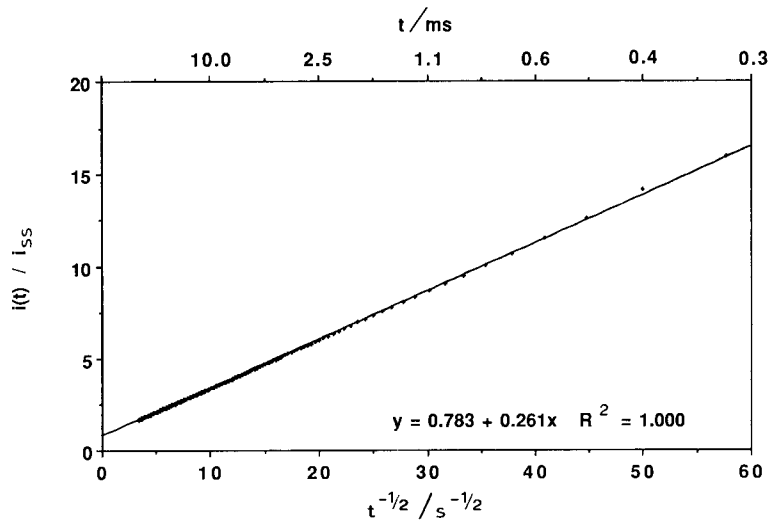

Fig. 7. Plot of the experimental ratio $i_d(t)/i_{d,ss}$ against the inverse square root of time for the oxidation of 20 mM BH$_4^-$ in 1 M NaOH with a 25 μm gold microdisk. Short time region: the sampling rate is 100 μs per point. The results of the linear regression are also shown.
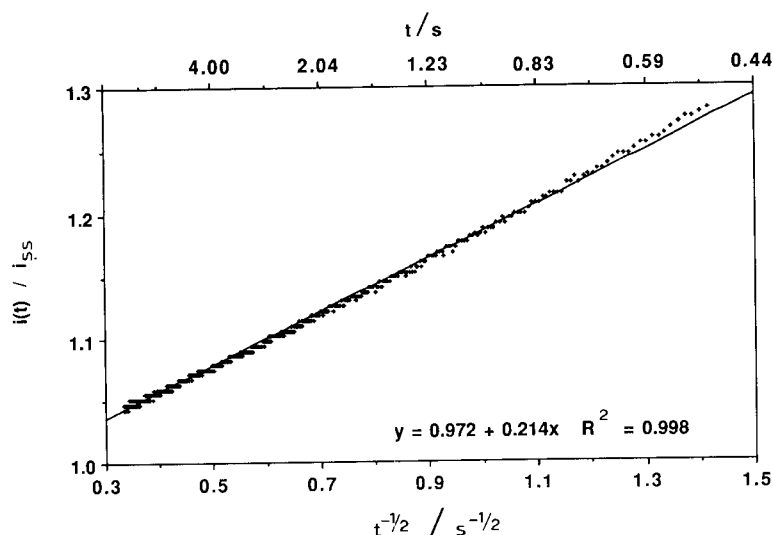
Fig. 8. Same as in Fig. 7. Long time region: the sampling rate is 10 ms per point.

(0.02 M) thus minimizing problems connected with charging current. Moreover, the high pH value suppressed hydrolysis of borohydride completely [18–20]. Recorded chronoamperograms showed a linear dependence of i vs $t^{-1/2}$ at both short (Fig. 7) and long times (Fig. 8). Excellent agreement of the intercept values with the theoretical ones (see eqns. 12 and 13) demonstrates the adequacy of the description of these transients by the approximate equations proposed for a simple electrode process. The values of D obtained for the short-time and long-time dependences $(1.66 \times 10^{-5}$ cm^2 s^{-1} and 1.76×10^{-5} cm^2 s$^{-1})$ agree quite well. A D value of 1.68×10^{-5} cm^2 s^{-1} was obtained by non-linear regression of the whole transient with the Shoup–Szabo equation, eqn. (8). Note that the overall electrode reaction converting BH_4^- to BO_2^- via exchange of 8 e$^-$ and 8 H$^+$, cleavage of 4 B–H bonds and formation of 2 B–O bonds clearly involves a number of steps (EC ... reactions). The fact that the data at very short times ($\leqslant 400$ μs) agree quite well with that at long times suggests that the rates of intervening chemical steps are high.

Only a few experimental reports of D for borohydride have appeared. Some seem unreasonable (e.g., $D = 10^{-4}$ cm^2 s^{-1}, ref. 22), and none has been obtained in the electrolyte used here. However, the result of Gardiner and Collat [18,19] ($D = 2.1 \times 10^{-5}$ cm^2 s^{-1} in 0.01 M NaOH) is quite close. The n value for the electrode reaction was calculated by eqn. (1) using two short-time and two long-time dependences. The obtained $n = 7.5 \pm 0.5$ is close to the expected value for the half-reaction

$$BH_4^- + 2 H_2O \rightarrow BO_2^- + 8 H^+ + 8 e^- \tag{15}$$

and confirms the correctness of the proposed procedure.

CONCLUSION

We have described a simple technique that allows independent determination of D and n values. Two applications of this technique are suggested. The measurement of the diffusion coefficient of the species participating in a simple electrochemical reaction, is simple, accurate, and rapid. Determination of the parameters of a complicated process, the exact mechanism of which may be unknown, is possible, as long as diffusion is the rate determining step. Subsequent determination of n may then be useful for studying the mechanism of this process. The estimation of n values and D values for several stages of the complicated process may also be possible, when different steady states correspond to different stages. Note that this approach may be useful in some circumstances for the estimation of concentration (when n is known) without calibration with standards, by determination of D from the transient and c^* from the steady state current. For example this procedure may be useful when standards are not available.

REFERENCES

1 A.J. Bard and L. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
2 R.N. Adams, Electrochemistry at Solid Electrodes, Marcel Dekker, New York, 1969.
3 A.J. Bard, G. Denuault, B.C. Dornblaser, R.A. Friesner and L.S. Tuckerman, Anal. Chem., in press.
4 C. Biondi and L. Bellugi, J. Electroanal. Chem., 24 (1970) 263.
5 M. Kakihana, H. Ikeuki and G.P. Sato, J. Electroanal. Chem., 117 (1981) 201.
6 A.S. Baranski, W.R. Fawcett and C.M. Gilbert, Anal. Chem., 57 (1985) 166.
7 C. Amatore, M. Azzali, P. Calas, A. Jutand, C. Lefrou and Y. Rollin, J. Electroanal. Chem., 288 (1990) 45.
8 S. Licht, V. Cammarata and M.S. Wrighton, J. Phys. Chem., 94 (1990) 6133.
9 W.J. Albery and M.L. Hitchman, Ring–Disc Electrodes, Clarendon Press, Oxford, 1971, p. 105.
10 K.B. Oldham, J. Electroanal. Chem., 122 (1981) 1.
11 K.B. Oldham and C.G. Zoski, J. Electroanal. Chem., 256 (1988) 11.
12 D. Shoup and A. Szabo, J. Electroanal. Chem., 140 (1982) 237.
13 K. Aoki and J. Osteryoung, J. Electroanal. Chem., 122 (1981) 19.
14 I.M. Kolthoff and J.J. Lingane, Polarography, Interscience, New York, 1952, Vol. 1, p. 33.
15 K.R. Wehmeyer and R.M. Wightman, Anal. Chem., 57 (1985) 1989.
16 M.V. Mirkin and A.P. Nilov, J. Electroanal. Chem., 283 (1990) 35.
17 G.S. Alberts and I. Shain, Anal. Chem., 35 (1963) 1859.
18 J.A. Gardiner and J.W. Collat, Inorg. Chem., 4 (1965) 1208.
19 J.A. Gardiner and J.W. Collat, J. Am. Chem. Soc., 87 (1965) 1962.
20 J.H. Morris, H.J. Gysling and D. Reed, Chem. Rev., 85 (1985) 51.
21 M.V. Mirkin and A.J. Bard, Anal. Chem., 63 (1991) 532.
22 E.D. Marshall and R.A. Widing, US AEC Report, A.E.C.D., 1950, p. 2914.