Scanning Electrochemical Microscopy. 20. Steady-State Measurements of the Fast Heterogeneous Kinetics in the Ferrocene/Acetonitrile System

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The application of the scanning electrochemical microscope (SECM) for steady-state measurements of fast heterogeneous kinetics is described. The method is based on the determination of the steady-state current vs potential curve for an electrode reaction at an ultramicroelectrode (radius a), held in close proximity (distance d) to a conductive substrate in a thin-layer cell arrangement. The technique developed can be used to study electrode reactions which are among the fastest known and were previously accessible only from transient measurements. The absence of complications in the measurements associated with solution resistance and charging current, typical for relaxation techniques, and the availability of a simple method of data analysis allow determination of reliable values of kinetic parameters. The standard rate constant, $k°$, for ferrocene oxidation in acetonitrile at a Pt electrode ($a = 1.08$ μm) was found to be 3.7 ± 0.6 cm/s, i.e., 2–4 times the values determined from fast scan cyclic voltammetry at ultramicroelectrodes. Two types of analytical approximations describing steady-state quasi-reversible voltammograms at a disk-shaped SECM microtip electrode in proximity to a conductive substrate are presented along with the exact solution in the form of a two-dimensional integral equation. The equivalence of these approximations at small tip–substrate separations is demonstrated. In general, this approach can be applied to the determination of $k°$, when the dimensionless parameter $k°d/D$ is less than 5 (where D is the diffusion coefficient).

Introduction

The continuing interest in fast electrode reactions (for recent examples see, e.g., refs 1–16) is due to two factors. First, these reactions usually represent the mechanistically simple case of essentially outer-sphere electron transfer (et). They are thus widely used as model experimental systems to examine various et theories[17,18] and to investigate the effects of solvent dynamics[11,19,20] and surface treatments.[16] Second, studies with ultramicroelectrodes (UME) revealed that many values of heterogeneous rate constants obtained earlier with larger (millimeter-sized) electrodes may be incorrect, mostly because of uncompensated IR drop in solution. The use of UME[21] along with sophisticated electronics[5,8] allows one to minimize this effect and to increase the reliability of the results. However, even with UMEs it is possible for the experimental kinetic data to be significantly perturbed by resistance effects, especially when attempting to determine the rate constant for a rapid electron transfer. One approach that has been used to ensure the absence of resistive contributions has been to show that independent measurements of reactions with supposedly known rate constants under identical conditions produce the same results; this has been applied, for example, for the reduction of C_{60} by an impedance analysis.[22]

To determine the heterogeneous rate constant, $k°$ (cm/s), the rate of mass transfer of electroactive material must be large compared to the heterogeneous et rate, i.e., $m \gtrsim k°$, where m is the mass-transfer coefficient appropriate for a particular technique. For a transient process with diffusion control, $m \approx \sqrt{D/t}$, so the study of fast reactions requires measurements at short times (t) (D is the diffusion coefficient). However, measurements at short times require complex instrumentation for control of potential and recording of current and they are often perturbed by contributions from double layer charging (capacitive currents) and from reactions of adsorbed electroactive species. These latter processes become more important as the characteristic time is decreased. In contrast to transient methods like cyclic voltammetry (CV), steady-state measurements[21,23] seem to be relatively problem-free in heterogeneous kinetic measurements. The IR drop for a micrometer-sized UME at steady-state is usually small (typically, less than 1 mV), there is negligible charging current or current attributed to adsorbed electroactive species, the data acquisition and analysis are very simple,[12] and filtering or background subtraction is usually unnecessary. Additionally, the shape of a steady-state voltammogram is very well defined and quite sensitive to artifacts; so minor impurity effects, surface fouling, or inadequate polishing can be detected by a lack of retracability. As in transient methods, steady-state measurements are only useful for studying fast heterogeneous reactions if a sufficiently high mass-transport rate can be achieved. In earlier studies with large electrodes, high mass transfer was attained through increases in solution convection, for example, with the rotating disk electrode $m \approx 0.62D^{2/3}\nu^{-1/6}\omega^{1/2}$ (where ω is the angular rotation velocity and ν is the kinematic viscosity). At ultramicroelectrodes, steady-state mass-transfer rates by diffusion can be high, as long as the electrode radius, a, is sufficiently small, i.e., $m \approx D/a$. However, to measure very rapid reactions, a submicron-sized UME[6,24,25] must be used, and these are not easy to make and are even more difficult to characterize with respect to size, shape, and configuration.[24] The geometry of such "nanodes"[6] may also be unsuitable for kinetics measurements.[26,27] A higher rate of mass transport in steady-state measurements with the same UME tip electrode can be obtained by using the SECM[28–30] with the UME held in close proximity (i.e., at a distance $d < a$) to a conductive substrate. In this case $m \approx D/d$. Previously we reported the application of this technique to studies of moderately fast electron transfer processes in both aqueous media[28,29] and highly resistive organic solvents.[30] Here the possibility of measurements of very fast heterogeneous kinetics will be discussed along with the related extensions of the SECM theory.

Theory

For a simple quasi-reversible electrode reaction O + ne^- → Red, the steady-state SECM problem includes a single Laplace equation:

$$\frac{\partial^2 C_O}{\partial Z^2} + \frac{\partial^2 C_O}{\partial R^2} + \frac{1}{R}\frac{\partial C_O}{\partial R} = 0 \tag{1}$$
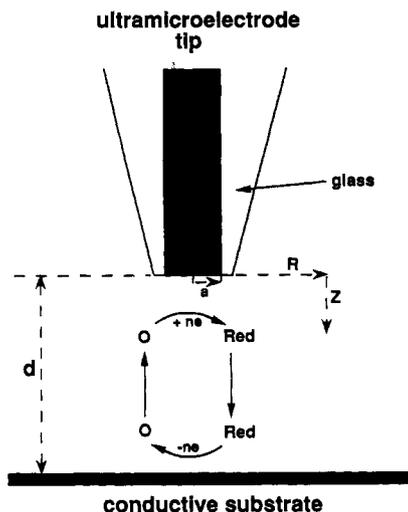
Figure 1. Schematic diagram of the SECM with a solid conductive substrate. The notation used to define the tip–substrate geometry is indicated.

for oxidized (or reduced) form of the mediator with the boundary conditions

tip surface $0 \leq R, Z = 0$;

$$J_T(R) = D_O\left[\frac{\partial C_O}{\partial Z}\right]_{Z=0} = -D_{Red}\left[\frac{\partial C_{Red}}{\partial Z}\right]_{Z=0} \quad (2)$$

substrate surface $0 \leq R, Z = d$; $C_O(R) = C_O^\circ$ (3)

where R and Z are spatial variables, $C(R,Z)$ is the concentration of electroactive species, C° is its bulk value, $C(R)$ is the surface concentration, and J is the diffusion flux density (Figure 1). The subscript O relates to the oxidized form and Red to the reduced form, and the subscript T refers to the tip electrode. The faradaic current density is

$$nFJ_T(R) = nF[k_f C_O(R) - k_b C_{Red}(R)] \quad (4)$$

and $J_T(R) = 0$ at $R > a$. The rate constants for reduction (k_f) and oxidation (k_b) at the tip are given by the Butler–Volmer relations[31]

$$k_f = k^\circ \exp[-\alpha nf(E - E^{\circ\prime})] \quad (5a)$$

$$k_b = k^\circ \exp[(1 - \alpha)nf(E - E^{\circ\prime})] \quad (5b)$$

where k° is the standard rate constant, E is the electrode potential, $E^{\circ\prime}$ is the formal potential, α is the transfer coefficient, n is the number of electrons transferred per redox event, and $f = F/RT$ (where F is the Faraday, R is the gas constant, and T is the temperature). The substrate is held at a sufficiently extreme potential that the electrode process there (Red $- ne^- \rightarrow$ O) is assumed to be diffusion controlled. The diffusion equation for the second form of the mediator (Red) is unnecessary because the concentrations of O and Red at steady state are interrelated by

$$C_O + C_{Red}D_{Red}/D_O = C^\circ \quad (6)$$

Using the Hanckel transform, as described previously,[32] one can solve the above problem in terms of dimensionless variables given by

$$r = R/a \quad (7)$$

$$L = d/a \quad (8)$$

$$c = 1 - C/C_O^\circ \quad (9)$$

$$j_T = J_T a/(DC_O^\circ) \quad (10)$$

to obtain

$$[1 - \pi j_T(r)/4\kappa']/\theta = \int_0^1 u j_T(u)\, du \int_0^\infty J_0(pr)\, J_0(pu)\, \tanh(pL)\, dp \quad (11)$$

$$i_T = -(\pi/2)\int_0^1 j_T(r) r\, dr \quad (12)$$

where J_0 is the Bessel function of the first kind of order zero,[33] $\kappa' = \pi a k^\circ \exp[-\alpha nf(E - E^{\circ\prime})]/(4D_O)$, and $\theta = 1 + \exp[nf(E - E^{\circ\prime})]D_O/D_{Red}$,[12] $i_T = I_T/I_{T,\infty}$, I_T is the tip current for the given L and E, and $I_{T,\infty}$ is the limiting current to the tip electrode far from any substrate expressed as[21]

$$I_{T,\infty} = 4nFDC^\circ a \quad (13)$$

The normalized steady-state current, $i_T(\kappa,\theta,L)$ is a trivariate function, whose representation would require very extensive tabulation. Alternatively one can use analytical approximations.

The numerical solution for a diffusion-controlled steady-state process under SECM conditions was reported previously.[34] Later analytical approximations[24] were obtained for both conductive and insulating substrates. For a conductive substrate

$$i_T(L) = 0.68 + 0.78377/L + 0.3315 \exp(-1.0672/L) \quad (14)$$

Equation 14 can be rewritten as

$$I_T(L) = 3.14a^2 nFC^\circ D/d + I_{T,\infty}[0.68 + 0.3315 \exp(-1.0672/L)] \quad (15)$$

The first term in this expression represents the current in a thin-layer cell (TLC) with a working electrode of surface area $A = \pi a^2$. The second term tends to $I_{T,\infty}$ as $L \rightarrow \infty$ (to about a 1% error associated with the fitting uncertainties and the finite thickness of the tip insulating sheath assumed in ref 34). This term represents the contribution of the microdisk steady-state current to the total current. This contribution is diminished by the blocking effect of the substrate and becomes negligibly small as $L \rightarrow 0$. Thus

$$I_T(L) = I_{TLC}(L) + I_{T,\infty}[0.68 + 0.3315 \exp(-1.0672/L)] \quad (16)$$

The reversible (nerstian) steady-state voltammogram for any electrode geometry obeys the following equation:[35]

$$I(E) = I_{dif}/\theta \quad (17)$$

where I_{dif} is the diffusion limiting current and θ is defined above. Thus for the SECM with a conductive substrate

$$I_T(E,L)/I_{T,\infty} = [0.68 + 0.78377/L + 0.3315 \exp(-1.0672/L)]/\theta \quad (18)$$

The simplest approximation for the quasi-reversible feedback current can be obtained assuming uniform accessibility of the tip surface, i.e., a uniform surface concentration of the electroactive species.[12] With this assumption the SECM is treated as a modified TLC with the diffusion limiting current expressed by eq 14. Under these conditions the approximate expression for the quasi-reversible steady-state voltammogram is[12]

$$I_T(E,L)/I_{T,\infty} = [0.68 + 0.78377/L + 0.3315 \exp(-1.0672/L)]/(\theta + 1/\kappa) \quad (19)$$

where the kinetic parameter

$$\kappa = k^\circ \exp[-\alpha nf(E - E^{\circ\prime})]/m_O \quad (20)$$

and the effective mass-transfer coefficient for SECM is

$$m_O = 4D_O(0.68 + 0.78377/L +$$

$$0.3315 \exp(-1.0672/L))/(\pi a) = I_T(L)/(\pi a^2 nFC^\circ) \quad (21)$$

Note that as $L \to \infty$, $m \approx D/a$, as expected. The approximation given by eq 19 is somewhat similar to the approximation for a microdisk voltammetric response by that of the equivalent size hemisphere.[36] In both cases, the assumption of uniform surface concentration is exact for a reversible electrode reaction (as $\kappa \to \infty$, eq 19 reduces to eq 18). With a decrease in reaction rate, eq 19 becomes less accurate. However, the errors are negligible at $L \ll 1$. In this case, the third term in brackets in eq 19 is much smaller than the second, leading to TLC behavior (i.e., uniform surface concentrations).

A better approximation can be obtained without the uniform accessibility assumption. According to ref 36, the quasi-reversible voltammogram at a microdisk can be calculated as

$$I_{disk}(E)/I_{T,\infty} = 1/\left[\theta\left(1 + \frac{\pi}{\kappa'\theta}\frac{2\kappa'\theta + 3\pi}{4\kappa'\theta + 3\pi^2}\right)\right] \quad (22)$$

The analogous equation for the TLC is[12,37]

$$I_{TLC}(E,L) = I_{TLC}(L)/(\theta + 1/\kappa) \quad (23)$$

and m_O in this case is

$$m_{TLC} = 2D_O D_{Red}/(D_O + D_{Red})d \quad (24)$$

Substitution of eqs 22 and 23 for the microdisk and TLC contributions to the SECM current leads to

$$i_T = \frac{0.78377}{L(\theta + 1/\kappa_{TLC})} + \frac{0.68 + 0.3315 \exp(-1.0672/L)}{\theta\left[1 + \frac{\pi}{\kappa'\theta}\frac{2\kappa'\theta + 3\pi}{4\kappa'\theta + 3\pi^2}\right]} \quad (25)$$

where $\kappa_{TLC} = 4\kappa' D_O/(\pi a m_{TLC})$. One can see from eq 25 that at large L the SECM response is essentially that of a single microdisk electrode, and the extent of reversibility of the steady-state voltammogram is determined by the parameter $\Lambda_T = k^\circ a/D$. At smaller L, however, TLC-type behavior is expected and another parameter, $\Lambda' = k^\circ d/D$, becomes the measure of apparent reversibility. Voltammograms calculated from eqs 19 and 25 are shown in Figure 2. Voltammograms for an essentially reversible process ($\Lambda' = 100$) are indistinguishable from each other and from the nernstian one obtained from eq 18 (curves 3). As expected, there are significant differences between the quasi-reversible curves computed from eqs 19 and 25 ($\Lambda' = 1$, curves 1). The difference becomes much smaller as either Λ' increases ($\Lambda' = 10$, curves 2) or L decreases (compare curves corresponding to the same Λ' in Figure 2a,b).

From eqs 11 and 12 (as well as from the approximate expressions 19 and 25), one can see that the tip current for any fixed L value is a function of two parameters, κ and θ. Consequently, three parameters, $\Lambda = k^\circ/m_O$, α, and $E^\circ{}'$, can be determined from the steady-state voltammogram using three values of quartile potentials, $E_{1/2}$, $E_{1/4}$, and $E_{3/4}$. A single table containing the above parameters for all possible pairs of $\Delta E_{1/4} = E_{1/4} - E_{1/2}$ and $\Delta E_{3/4} = E_{1/2} - E_{3/4}$ (see Table I in ref 12) is suitable for any kind of uniformly accessible electrode. To analyze voltammograms obtained with a nonuniformly accessible working electrode one needs to calculate an analogous table for that particular electrode geometry (such a table for a microdisk was also given in ref 12). For SECM this is not simple because i_T is a function of L; thus a special table has to be established for each particular L value. Although a computer program, available from the authors, allows one to generate such a table for any value of L, the use of the uniform approximation is simpler and probably adequate in most cases. In both cases, the effective mass-transfer coefficient can be calculated from eq 21, and after determination of $\Delta E_{1/4}$ and
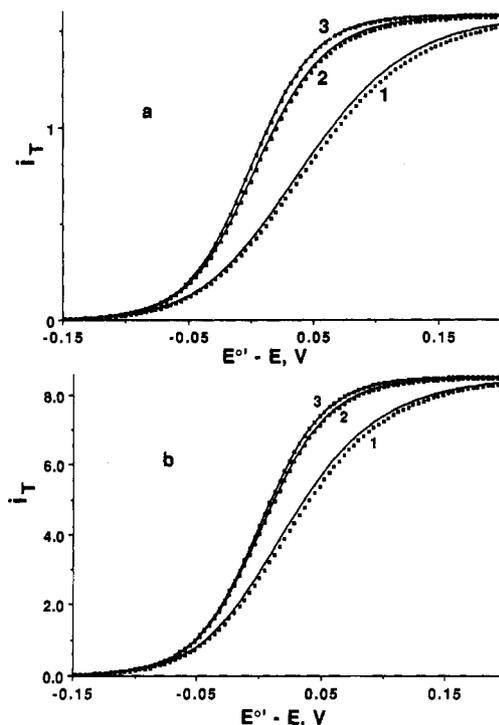
Figure 2. Steady-state voltammograms at different values of tip–substrate separation and different rates of the tip electrode reaction. (a) $L = 1$, (b) $L = 0.1$. $\alpha = 0.5$. Squares were calculated using the uniform accessibility approximation (eq 19); solid curves were obtained from eq 25 for $\Lambda' = 1$ (1), 10 (2), and 100 (3). Nernstian voltammograms are indistinguishable from curves 3.

$\Delta E_{3/4}$, the values of Λ, α, and $E^\circ{}' - E_{1/2}$ can be found in the corresponding table with $k^\circ = \Lambda m_O$.

Experimental Section

Chemicals. Ferrocene (Fluka Chemical Corp., Ronkonkoma, NY) was sublimed twice before use. Tetrabutylammonium tetrafluoroborate (TBABF₄, 99%, Aldrich Chemical Co., Milwaukee, WI) was dried for several hours at 100 °C prior to use. Acetonitrile (Burdick and Jackson, Muskegon, MI) was used as received. Solutions were deoxygenated with purified argon before each experiment.

Electrodes. An 11-μm-diameter carbon tip and 2- and 10-μm-diameter platinum microdisk tip electrodes were fabricated as described previously[38] and were polished with 0.05-μm alumina before each set of measurements. The glass sheath surrounding the smaller tip was beveled at a 45° angle so that the Pt surface was surrounded by a glass ring of about 10-μm thickness. In previous SECM measurements of heterogeneous kinetics,[29,30] the radius of the glass surrounding the tip was made as small as possible, i.e., $RG = r_{glass}/a \le 2$. In the present study, the RG value was about 10, and even with a good alignment of the tip with respect to the substrate, contact between the glass insulator and the substrate often occurred at a small distance, $d > 0$, between the tip and the substrate. Subsequently, very slow (e.g., 0.05 μm/s) movement of the tip towards the substrate led to a slight compression of the glass/Pt arrangement and thus to a decrease in d. This allowed a closer tip–substrate separation without current oscillations normally caused by vibrations at very small d (on the order of a hundred nanometers). We did not notice any significant difference between voltammograms obtained with and without contact between the glass sheath and the substrate (at the same d) except for the damping of current oscillations in the latter case. Data were acquired with either a two- or three-electrode configuration (with Pt gauze serving as a counterelectrode and a silver wire as a quasireference electrode) with similar results obtained in either mode. A 1.5-mm-diameter Pt disk
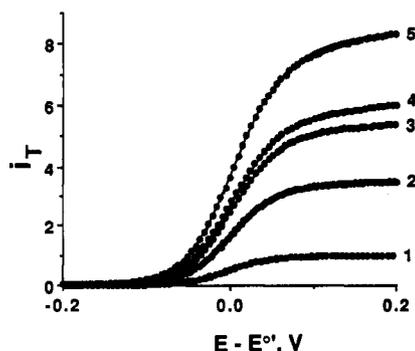
Figure 3. Tip steady-state voltammograms for the oxidation of 5.8 mM ferrocene in 0.52 M TBABF$_4$ in MeCN at a 1.08-μm radius Pt tip. Solid lines calculated from eq 25. Tip–substrate separation decreases from 1 to 5; see Table I for parameter values. The numbers on the curves correspond to those in Table I.

TABLE I: Kinetic Parameters for Oxidation of Ferrocene in Acetonitrile at Pt Tip Electrode ($a = 1.08 \mu$m) from SECM Steady-State Voltammograms ($\Delta E_{1/4} = E_{1/4} - E_{1/2}$, $\Delta E_{3/4} = \Delta E_{1/2} - E_{3/4}$, $\Delta E^{\circ\prime} = E^{\circ\prime} - E_{1/2}$)

| | | | | | k°, cm/s | | α | | $\Delta E^{\circ\prime}$ | |
no.	$\Delta E_{1/4}$	$\Delta E_{3/4}$	L	i_T	eq 19	eq 25	eq 19	eq 25	eq 19	eq 25
1	28.6	28.6	∞	1.0	(process is essentially reversible)					
2	30.5	32.3	0.27	3.55	3.4	2.4	0.48	0.49	5.4	5.5
3	31.4	34.7	0.17	5.47	4.5	3.5	0.38	0.39	6.5	6.5
4	32.3	36.9	0.14	6.10	4.1	3.3	0.36	0.36	7.9	8.0
5	32.9	38.5	0.10	8.53	5.1	4.3	0.35	0.35	9.1	9.1

(Bioanalytical Systems, West Lafayette, IN) was used as an unbiased substrate.

The SECM apparatus was described previously.[39] The measurements were performed in a 3-mL Teflon cell. Acetonitrile solutions were 5.8 mM in ferrocene and 0.5 M in TBABF$_4$. The voltammograms were obtained using an EI-400 four-electrode potentiostat (Ensman Instruments, Bloomington, IN) and a BAS-100A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) with scan rates of 10–20 mV/s.

Results and Discussion

The steady-state voltammograms at well-characterized carbon and platinum microdisk electrodes (5.5- and 5.0-μm radii, respectively, as confirmed by optical microscopy and independent electrochemical measurements) were employed to determine the diffusion coefficient of ferrocene. The value found $D = (1.7 \pm 0.05) \times 10^{-5}$ cm^2/s is in reasonable agreement with that found by fast-scan voltammetry for different supporting electrolytes.[2,3,40] We found the effective radius of the small platinum tip (nominally 1 μm) using the above value of D and eq 13 for the microdisk diffusion-limited current to be $a = 1.08 \mu$m.

Five steady-state voltammograms of ferrocene obtained at different tip–substrate separations are presented in Figure 3. The voltammograms were analyzed using the approach described previously.[12] The quartile potentials ($E_{1/4}$, $E_{1/2}$, and $E_{3/4}$) were determined from the digitized data, and the reproducibility of their differences, $\Delta E_{1/4} = E_{1/4} - E_{1/2}$ and $\Delta E_{3/4} = E_{1/2} - E_{3/4}$, was better than ± 0.5 mV. For an infinite L (the first voltammograms in Figure 3 and first set of data in Table I), both $\Delta E_{1/4}$ and $\Delta E_{3/4}$ values were equal to 28.6 mV, i.e., the voltammogram at a 1-μm radius microdisk far from the substrate was essentially nernstian. This suggests that the dimensionless parameter is $\Lambda_T > 10$,[12] and the lower limit for the rate constant is $k^\circ > 1.6$ cm/s.

Other voltammograms obtained with the tip in the proximity of the Pt substrate were analyzed with and without uniform approximation (eqs 19 and 25, respectively). For curve 2, the tip–substrate distance was fairly large ($L = 0.274$). The mass transfer in this case, although significantly faster than for a microdisk above, was still not sufficiently fast to satisfy the

criterion $\Lambda^\prime < 5$. The deviations of $\Delta E_{1/4}$ and $\Delta E_{3/4}$ from nernstian values were small, and the kinetic parameters found were not quite reliable. However, even at this relatively large L an analysis based on either eq 19 or eq 25 led to essentially the same values of α and $E^{\circ\prime}$, and the variation in k° was small. The last three sets of data, obtained at smaller tip–substrate separations, yielded very similar values for the kinetic parameters. The k° values obtained from eq 19 were about 20% higher, but this is probably within the range of experimental error. Thus, both eq 19 (with Table I in ref 12) and eq 25 (with a corresponding table computed for a given L) are suitable for evaluation of the electrode kinetics, which are fast for simple UME voltammetry (i.e., the tip CV with the UME far from the substrate is essentially nernstian). Obviously, the uniform approximation is most suitable for analysis of the SECM data obtained with a solid substrate, when $L \ll 1$. It is just these conditions that make an SECM experiment advantageous compared to simpler measurements with a microdisk electrode alone.

The k° value obtained (3.7 ± 0.6 cm/s) is approximately 2–4 times the value determined by fast scan voltammetry,[2,3,40] suggesting that even very careful compensation of the IR drop at UME cannot guarantee the desired accuracy of measurements when the heterogeneous kinetics are rapid. On the other hand, the value obtained is very close to that found from impedance analysis (2.6 cm/s at 285 K).[9] The transfer coefficient found ($\alpha = 0.37 \pm 0.02$) is somewhat lower than that theoretically expected ($\alpha = 0.5$). The much higher value of the rate constant ($k^\circ \simeq 10$ cm/s) predicted in ref 3 from steady-state voltammetry at 0.3–0.5-μm radius microdisks may result from imperfect geometry of such small UME. Another possible source of differences between the rate constants obtained from steady-state measurements and fast scan CV[2,3,40] at UME was noted by Lavagnini et al.[15] They demonstrated that the use of the Nicholson method[41] to analyze CV obtained at a microdisk electrode at intermediate scan rates (of the order of hundreds V/s[2,3,40]), without accounting for nonlinear diffusion, results in an underestimation of k°. A more sophisticated analysis of the same data[15] diminished the differences.

A simple way to check the validity of the experimental results and the reliability of the kinetic analysis is to note the constancy of the kinetic parameters with different values of d. While the mass-transfer rate increases with a decrease in the tip–substrate separation (i.e., from curve 3 to curve 5 in Figure 3), the heterogeneous rate constant and transfer coefficient should remain constant within the range of experimental error, as shown in Table I. Such a check is not possible for measurements at a single microelectrode alone, since the steady-state mass-transport rate can be changed only by using UMEs of different size.

We might note two sets of recent results which reported anomalously high[6] and low[13] values for the ferrocene system under conditions similar to those used here. The very high value of the rate constant, 220 cm/s, was obtained by using "nanodes", i.e., UME with reported radii of 16–18 Å. This value came from steady-state measurements with voltammograms fit to the microdisk theory,[36] and the authors suggested that the much lower values of k° obtained in other laboratories by conventional methods were limited by the time response of the technique and uncompensated IR drop. Such factors were also unimportant in our experiments. A problem with using very small electrodes (e.g., $a \ll 1 \mu$m) in heterogeneous kinetic studies is the difficulty in fabricating electrodes with known geometry and in characterizing these. As pointed out by others,[26,27] problems such as the recession of the electrode into a small chamber of surrounding insulator can lead to overestimation of k°.

On the other hand, a very low value for this rate constant (i.e., $k^\circ = 0.0194$ cm/s in MeCN with similar values for other solvents) was reported recently,[13] and similar results were obtained by several other groups (see refs 48–53 in ref 13) using conventional-
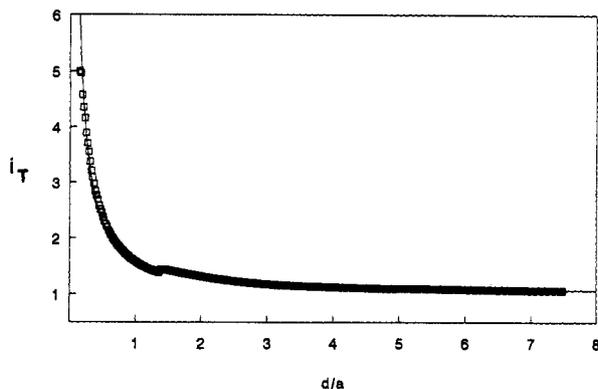
Figure 4. Normalized tip current–distance curve for a 1.08-μm radius Pt tip approaching a Pt substrate in a solution containing 5.8 mM ferrocene and 0.52 M TBABF$_4$ in MeCN. The tip was held at 0.9 V where the oxidation was diffusion controlled and approached the substrate at a rate of 0.1 μm/s. The theoretical curve (—) was computed from eq 16. The small discontinuity at L = 1.4 is an artifact caused by the piezo click.

sized electrodes. The authors suggested[13] that microelectrodes might produce much higher rate constants because of bad electrode–insulator seals and irregular geometries. However, a recent study[24] demonstrated that the shapes of SECM approach curves are very sensitive to tip geometry. Since any part of the tip surface exposed to solution due to an improper seal would not contribute to the feedback current in the same way as the true disk surface, any imperfection of this kind would result in irreconcilable deviations of i_T–d curves from the theory. In fact, no such deviations were observed and the agreement between the experimental and theoretical current–distance curves (Figure 4) was very good. It seems clear that measurements of fast kinetics at larger electrodes are prone to errors, e.g., due to uncompensated resistive drop. Many reported rate constants obtained by CV at larger electrodes are probably similarly too small, and we suggest that the ferrocene/MeCN system could be used to check a particular arrangement and experimental conditions to ensure the absence of resistive effects.

With respect to the SECM measurements reported here, one possible source of error would be deviations from ideal cell geometry. Such a situation could arise if the tip and substrate electrodes are not parallel to one another. However, misalignment of this type should be minimal since the relatively large ring of glass insulator at the tip (RG $\simeq$ 10) necessitates a parallel tip–substrate relationship by virtue of the very small tip–substrate electrode separations achieved in these measurements. Another possible deviation from ideal geometry would be a rounding of the tip due to polishing of the electrode. However, minimal contributions here were ensured by visible inspection of the tip using an optical microscope. The excellent agreement between experimental and theoretical approach curves (Figure 4) also confirms that the above effects are modest.

The second possible source of error would be convection in the tip–substrate gap due to vibrations of the tip and substrate electrodes. These vibrations, however, would manifest themselves primarily as current oscillations caused by rapid changes in the tip–substrate separation. Such fluctuations were observed in preliminary experiments but were eliminated in the present data by careful vibrational isolation of the SECM apparatus and the special damping approach described in the experimental section. In addition, the low sensitivity of the UME to convection is well-documented.[21]

Conclusions

Using the SECM with a micrometer-sized tip electrode, one can determine kinetic parameters of rapid heterogeneous reactions with the standard rate constant up to 10–20 cm/s from steady-state voltammetric curves. In these measurements, many typical

sources of experimental errors are eliminated, e.g., the IR drop and charging current are negligible, no data filtering or background correction need be used, and the possibility of distortions due to a poor seal of the microtip in glass can be excluded by an analysis of the current–distance curves. In this way the kinetic parameters for the oxidation of ferrocene in acetonitrile were determined. The comparison of the rate constant determined by this technique, $k° = 3.7 \pm 0.6$ cm/s, with values determined by fast scan voltammetry suggests that the latter technique, even with quite careful IR compensation, tends to underestimate the rate constant for very rapid reactions. In contrast, our $k°$ value agrees quite well with that obtained from impedance analysis.[9] The reproducible value of the transfer coefficient found here, $\alpha = 0.37 \pm 0.02$, is somewhat lower than that predicted by Marcus theory.

Three approximations for the SECM steady-state current were considered. The uniform approximation given by eq 19 is the most simple and least accurate. It is, however, suitable when the process studied is rapid and the tip–substrate separation is small. The analysis of the data is very simple and requires only two experimental values of differences between quartile potentials, with the formal potential and kinetic parameters immediately available from a general table. The approximation expressed by eq 25 is more accurate; however, an analysis based on this equation requires one to calculate a new table of parameters for each particular value of L (or to solve numerically a system of three nonlinear algebraic equations as described in ref 12). A FORTRAN program for such calculations can be obtained from the authors. Finally, a two-dimensional integral equation, eq 11, represents the exact solution of the problem, but it also must be solved anew for each value of L.

References and Notes

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