Simple Analysis of Quasi-Reversible Steady-State Voltammograms

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The kinetic parameters (k° and α) of a uncomplicated quasi-reversible electrochemical reaction studied by any steady-state voltammetric technique can be found directly from the values of two easily accessible experimental parameters, ($E_{1/4} - E_{1/2}$) and ($E_{1/2} - E_{3/4}$), where $E_{1/2}$ is the experimental half-wave potential and $E_{1/4}$ and $E_{3/4}$ are voltammetric quartile potentials. For any type of steady-state (or pseudo-steady-state) current–potential curve obtained with a uniformly accessible working electrode, e.g., voltammetry at a rotating disk or hemispherical microelectrode, polarography, sample current voltammetry, and thin-layer voltammetry, a table is given which shows the kinetic parameters, i.e., standard rate constant, k°, and the transfer coefficient, α, and also the formal potential, $E^{\circ\prime}$, from the two above experimental values. An analogous table is presented for the nonuniformly accessible microdisk electrode. Unlike previously reported approaches, an independent evaluation of the standard (formal) potential is unnecessary. This analysis also does not rely on values of the electrode surface area and the bulk concentration of electroactive species which usually decrease the accuracy of the results. The application of the proposed methodology to other electrochemical systems including scanning electrochemical microscopy (SECM) and ultramicroelectrodes shaped as a cone or spherical segment is also discussed.

INTRODUCTION

This paper deals with a quick and simple method for extracting the heterogeneous electron-transfer kinetic parameters (k°, α) and the formal potential ($E^{\circ\prime}$) from the steady-state voltammogram of a quasi-reversible reaction. While the treatment of Nernstian and totally irreversible waves is straightforward, that for quasi-reversible reactions is more difficult.[1] For example, as discussed below, no simple method exists for estimation of k° from a steady-state voltammogram that is equivalent to the approach used in cyclic voltammetry (CV), where k° can be estimated from the variation of the splitting between the forward and reverse peak potentials (ΔE_p) as a function of scan rate.[2]

There are several ways of obtaining a time-independent (steady-state or pseudo-steady-state) response. For example, in classical polarography,[1,3] the current, i, is time-dependent, but by measuring i at a fixed lifetime of a drop (or at a fixed sampling interval, as in tast-polarography), one can obtain a pseudo-steady-state current–potential curve, i.e., the polarogram. An analogous method using a stationary working electrode is sampled-current voltammetry.[1] True steady-state voltammograms are obtained at a rotating-disk electrode (RDE),[4] as well as with thin-layer electrochemical cells.[5] The recent widespread use of ultramicroelectrodes (UME)[6] has led to a renewed interest in steady-state voltammetry. A number of different types of UME have been used, e.g., hemisphere,[7,8] microdisk,[7] ring,[9] spherical segment,[10] cone,[11] and those employed with the scanning electrochemical microscope.[12] Steady-state voltammetry is one of the best techniques for studying fast electrochemical kinetics.[1,5-7,13-17] Its important advantages over the relaxation methods, such as CV, include the absence of the limitations caused by the charging current (and also ohmic potential drop in the case of UME experiments), insensitivity to low levels of reactant adsorption, relative simplicity of data acquisition, and high accuracy and reproducibility of the results.

Unlike transient methods, the theory for steady-state techniques is relatively simple. For those of the above mentioned electrochemical systems which employ a uniformly accessible working electrode, analytical expressions (exact or approximate) are available for computing quasi-reversible current–potential curves. Simple analytical expressions for steady-state voltammetry at a (nonuniformly accesible) microdisk electrode[17] and for a hemisphere[18] have been proposed, and analogous approaches have been described earlier, e.g., for quasi-reversible polarographic waves.[19,20] However, the kinetic analysis of steady-state quasi-reversible voltammograms is cumbersome and inconvenient. For example, the analysis of polarographic data[19,20] is based on a not-very-accurate graphical extrapolation and requires independent determination of the reversible half-wave potential. Similar procedures have been proposed for the RDE[21] and for normal-pulse polarography.[1] An even more difficult graphical analysis of a microdisk voltammogram[15] involves an approximation and a linear least squares analysis of the

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"slightly curved" working curves. Another analysis of the microdisk equation included five different situations (from "reversible/near reversible" to "near irreversible/irreversible" electrode reactions) and four two-parameter families of working curves.[17] For some cases this analysis requires data obtained with different radius electrodes and, for quasi-reversible systems, an independent determination of the formal potential. This determination is not always straightforward, and even a small error in $E^{\circ\prime}$ can lead to significant errors in the kinetic parameters. We demonstrate below that $E^{\circ\prime}$ can be easily obtained from a quasi-reversible voltammogram at a single electrode.

In this paper we present a unified treatment that holds for the steady-state quasi-reversible voltammogram for an uncomplicated electron-transfer reaction at a uniformly accessible electrode and also for a microdisk. The next section describes the equations and the approach used to generate the tables for the analysis of voltammograms. The reader interested only in the application of this method can consult the Results and Discussion which describes the use of these tables for several different electrochemical methods.

THEORY

Uniformly Accessible Electrodes. Consider a quasi-reversible uncomplicated electrochemical reaction Ox + ne ⇄ Red with only Ox initially present in solution, at a concentration, c_O^*. The following well-known formulation holds for any steady-state (or pseudo-steady-state) measurements at a uniformly accessible electrode (see, for example, ref 22):

$$\begin{aligned} i &= nFA(c_O k_f - c_R k_b) \\ &= nFAm_O(c_O^* - c_O) \\ &= nFAm_R c_R \end{aligned} \tag{1}$$

where i is the steady-state faradaic current, n is the number of electrons involved in the electrode reaction, F is Faraday's constant, A is the electrode surface area, c_O and c_R are the surface concentrations of the electroactive species, k_f and k_b are forward (cathodic) and backward (anodic) heterogeneous rate constants, and m_O and m_R are mass-transfer coefficients for the given electrochemical method. From eq 1

$$\frac{i}{nFA} = \left(c_O^* - \frac{i}{nFAm_O}\right)k_f - \frac{i}{nFAm_R}k_b \tag{2}$$

or

$$i = \frac{nFAc_O^* k_f}{1 + k_f/m_O + k_b/m_R} \tag{3}$$

Substituting into eq 3 the value of the limiting current, i_d, given by

$$i_d = nFAm_O c_O^* \tag{4}$$

one obtains

$$\frac{i}{i_d} = \frac{1}{1 + m_O/k_f + m_O k_b/(m_R k_f)} \tag{5}$$

Equation 5 can be rewritten assuming Butler–Volmer kinetics of the electrode reaction, i.e., $k_f = k^\circ \exp[-\alpha nf(E - E^{\circ\prime})]$ and $k_b = k^\circ \exp[(1-\alpha)nf(E - E^{\circ\prime})]$, where $f = F/RT$ and E is the potential of the electrode

$$\frac{i}{i_d} = \frac{1}{1 + m_O \exp[\alpha nf(E - E^{\circ\prime})]/k^\circ + (m_O/m_R)\exp[nf(E - E^{\circ\prime})]} \tag{6}$$

We now use slightly modified notation for equations analogous to eq 6 for a hemisphere[18] and a microdisk electrode[17] to write

$$\theta = 1 + \frac{m_O}{m_R}\exp(nf(E - E^{\circ\prime})) \tag{7}$$

$$\kappa = k^\circ \exp(-\alpha nf(E - E^{\circ\prime}))/m_O \tag{8}$$

$$\frac{i}{i_d} = \frac{1}{\theta + 1/\kappa} \tag{9}$$

Now consider the potential $E_{1/p}$, where $i_d/i_{1/p} = p$

$$\frac{i_{1/p}}{i_d} = \frac{1}{\theta_{1/p} + 1/\kappa_{1/p}} = \frac{1}{p} \tag{10}$$

or

$$\theta_{1/p} + 1/\kappa_{1/p} = p \tag{11}$$

where all variables with a subscript "$1/p$" correspond to $E_{1/p}$. Specifically, for the half-wave potential, $E_{1/2}$

$$\theta_{1/2} + 1/\kappa_{1/2} = 2 \tag{12}$$

$$\theta_{1/2} = 1 + \frac{m_O}{m_R}\exp[nf(E_{1/2} - E^{\circ\prime})] \tag{13}$$

$$\kappa_{1/2} = k^\circ \exp[-\alpha nf(E_{1/2} - E^{\circ\prime})]/m_O \tag{14}$$

From eqs 7, 8, 12, and 13 one can easily derive

$$\kappa_{1/p} = k^\circ \exp[-\alpha nf(E_{1/p} - E^{\circ\prime})]/m_O = \kappa_{1/2}\epsilon_{1/p}^{-\alpha} \tag{15}$$

$$\theta_{1/p} = 1 + \frac{m_O}{m_R}\exp[nf(E_{1/p} - E^{\circ\prime})] = (\theta_{1/2} - 1)\epsilon_{1/p} + 1 \tag{16}$$

where

$$\epsilon_{1/p} = \exp[nf(E_{1/p} - E_{1/2})] \tag{17}$$

Equation 11 can be written for two quartile potentials, $E_{1/4}$ and $E_{3/4}$:

$$\theta_{1/4} + 1/\kappa_{1/4} = 4 \tag{18}$$

$$\theta_{3/4} + 1/\kappa_{3/4} = {}^4/_3 \tag{19}$$

Taking into account eqs 15 and 16, one can combine eqs 12, 18, and 19 to obtain a system of three non-linear equations

$$\begin{aligned} &\theta_{1/2} + 1/\kappa_{1/2} = 2 \\ &(\theta_{1/2} - 1)\epsilon_{1/4} + 1 + \epsilon_{1/4}^{\alpha}/\kappa_{1/2} = 4 \\ &(\theta_{1/2} - 1)\epsilon_{3/4} + 1 + \epsilon_{3/4}^{\alpha}/\kappa_{1/2} = {}^4/_3 \end{aligned} \tag{20}$$

or

(22) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 290.

$$\theta_{1/2} + 1/\kappa_{1/2} = 2 \tag{21a}$$

$$\epsilon_{1/4}\theta_{1/2} + {\epsilon_{1/4}}^{\alpha}/\kappa_{1/2} = 3 + \epsilon_{1/4} \tag{21b}$$

$$\epsilon_{3/4}\theta_{1/2} + {\epsilon_{3/4}}^{\alpha}/\kappa_{1/2} = {}^1/_3 + \epsilon_{3/4} \tag{21c}$$

where $\epsilon_{1/4}$ and $\epsilon_{3/4}$ are given by eq 17.

Multiplying eq 21a by ${\epsilon_{1/4}}^{\alpha}$ and ${\epsilon_{3/4}}^{\alpha}$ with successive subtraction of it from eqs 21b and 21c leads to two equations which do not contain $\kappa_{1/2}$

$$\theta_{1/2}(\epsilon_{1/4} - {\epsilon_{1/4}}^{\alpha}) + 2{\epsilon_{1/4}}^{\alpha} = 3 + \epsilon_{1/4} \tag{22a}$$

$$\theta_{1/2}(\epsilon_{3/4} - {\epsilon_{3/4}}^{\alpha}) + 2{\epsilon_{3/4}}^{\alpha} = {}^1/_3 + \epsilon_{3/4} \tag{22b}$$

From eq 22a we find

$$\theta_{1/2} = \frac{3 + \epsilon_{1/4} - 2{\epsilon_{1/4}}^{\alpha}}{\epsilon_{1/4} - {\epsilon_{1/4}}^{\alpha}} \tag{23}$$

Substituting eq 23 into eq 22b yields

$${\epsilon_{1/4}}^{\alpha}(1 - 3\epsilon_{3/4}) + 3{\epsilon_{3/4}}^{\alpha}(\epsilon_{1/4} - 3) + 9\epsilon_{3/4} - \epsilon_{1/4} = 0 \tag{24}$$

Solving eq 24 numerically, one obtains α, which in turn allows $\theta_{1/2}$ to be obtained from eq 23 and then $\kappa_{1/2}$ by

$$\kappa_{1/2} = \frac{1}{2 - \theta_{1/2}} \tag{25}$$

Then

$$n(E^{\circ\prime} - E_{1/2}) = -\frac{1}{f}\ln((\theta_2 - 1)m_R/m_O) \tag{26}$$

and

$$k^\circ = \kappa_{1/2} m_O \exp[\alpha n f(E_{1/2} - E^{\circ\prime})] \tag{27}$$

Nonuniformly Accessible Electrodes: Microdisk Electrode. In the case of an electrode whose surface is not uniformly accessible, the surface concentrations, c_O and c_R, are functions of position, e.g., r for a disk electrode, and condition 1 does not hold. Here an analytical approximation is needed to replace the exact eq 9. An approximate equation describing quasi-reversible steady-state voltammograms at a microdisk with a maximum error less than 0.3%[17,18] is

$$\theta i/i_d = \left[1 + \frac{\pi}{\kappa'\theta}\frac{2\kappa'\theta + 3\pi}{4\kappa'\theta + 3\pi^2}\right]^{-1} \tag{28}$$

where θ is still defined by eq 7 with $m_O/m_R = D_O/D_R$

$$\kappa' = \frac{\pi d k^\circ}{8D_O}\exp[-\alpha n f(E - E^{\circ\prime})] \tag{29}$$

and d is the superficial diameter of the electrode ($d = 2a$, where a is the disk radius[18]). Equations 16 and 17 still hold for $\theta_{1/2}$, and eqs 14 and 15 can be rewritten for κ' as follows:

$$\kappa'_{1/2} = \frac{\pi d k^\circ}{8D_O}\exp[-\alpha n f(E_{1/2} - E^{\circ\prime})] \tag{30}$$

$$\kappa'_{1/p} = \frac{\pi d k^\circ}{8D_O}\exp[-\alpha n f(E_{1/p} - E^{\circ\prime})] = \kappa'_{1/2}{\epsilon_{1/p}}^{-\alpha} \tag{31}$$

Combining eqs 16, 17, 28, 30, and 31 yields

$$\kappa'_{1/2}(8\kappa'_{1/2}\theta_{1/2} + 6\pi^2 - 4{\kappa'_{1/2}}\theta_{1/2}^2 - (3\pi^2 + 2\pi)\theta_{1/2}) = 3\pi^2$$

$$\kappa'_{1/2}{\epsilon_{1/4}}^{-\alpha}\{16{\epsilon_{1/4}}^{-\alpha}\kappa'_{1/2}[(\theta_{1/2} - 1)\epsilon_{1/4} + 1] + 12\pi^2 - 4\kappa'_{1/2}{\epsilon_{1/4}}^{-\alpha}[(\theta_{1/2} - 1)\epsilon_{1/4} + 1]^2 - (3\pi^2 + 2\pi)[(\theta_{1/2} - 1)\epsilon_{1/4} + 1]\} = 3\pi^2 \tag{32}$$

$$\kappa'_{1/2}{\epsilon_{3/4}}^{-\alpha}\{16\kappa'_{1/2}{\epsilon_{3/4}}^{-\alpha}[(\theta_{1/2} - 1)\epsilon_{3/4} + 1]/3 + 4\pi^2 - 4\kappa'_{1/2}{\epsilon_{3/4}}^{-\alpha}[(\theta_{1/2} - 1)\epsilon_{3/4} + 1]^2 - (3\pi^2 + 2\pi)[(\theta_{1/2} - 1)\epsilon_{3/4} + 1]\} = 3\pi^2$$

This system is too cumbersome for analytical transformations. However, the numerical solution provides the values of α, $\kappa'_{1/2}$, and $\theta_{1/2}$, and subsequently $E^{\circ\prime}$ and k° according to eqs 26 and 30.

RESULTS AND DISCUSSION

Uniformly Accessible Electrodes. Equal Diffusion Coefficients. Equation 24 was solved using the ZREAL subroutine from the IMSL Program Library.[23] The results are presented in Table I. Each column of the table corresponds to a given value of $n(E_{1/4} - E_{1/2})$ in the range 29.9–294 mV. Each triplet of rows corresponds to the value of $n(E_{1/2} - E_{3/4})$ indicated in the left cell. The upper row in each group contains the values of the dimensionless rate constant $\lambda = k^\circ/m_O$, the second contains the α value, and the third contains $n(E^{\circ\prime} - E_{1/2})$. To determine these kinetic parameters from steady-state voltammograms at any uniformly accessible electrode, one finds the potentials $E_{1/4}$, $E_{1/2}$, and $E_{3/4}$ and calculates the differences $(E_{1/4} - E_{1/2})$ and $(E_{1/2} - E_{3/4})$. The values of the kinetic parameters can then be found in Table I at the intersection of the corresponding column and row. While the α and $E^{\circ\prime}$ values found from Table I are independent of the employed steady-state technique, the k° determination requires the knowledge of m_O which is related to the particular electrochemical method.

To make Table I easy to use, we chose the potential scale in the form $n(E_i - E_{1/2})$ instead of more general dimensionless scale $nf(E_i - E_{1/2})$ and assumed $f = \ln(10)/0.059$ corresponding to $T = 298$ K. To analyze voltammograms obtained at a different temperature, T, one should multiply the potentials in Table I by the factor 298/T.

The highest value of λ which can be determined by this method is about 10, in agreement with ref 17. There is also a lower limit of $\lambda \sim 0.04$, which corresponds to an effectively irreversible process.[17] This limitation is connected with the impossibility of the determination of $E^{\circ\prime}$ from a totally irreversible polarization curve. If $E^{\circ\prime}$ is known, other parameters of an irreversible electrode reaction can be found easily.

Unequal Diffusion Coefficients. Although the data in Table I were computed by assuming $m_O = m_R$ (or $D_O = D_R$), only minor modifications are necessary when the difference between D_O and D_R is significant. First, eq 24 does not contain m_O and m_R values. Consequently, the values of α given in Table I as well as $\theta_{1/2}$ and $k_{1/2}$ values obtained from eqs 23 and 25 are independent of m_R/m_O. One can rewrite eq 26 in the form

$$n(E^{\circ\prime} - E_{1/2}) = -\frac{1}{f}\ln((\theta_2 - 1)m_R/m_O) = -\frac{1}{f}\ln(\theta_2 - 1) - \frac{1}{f}\ln(m_R/m_O)$$

$$= n(E^{\circ\prime} - E_{1/2})|_{m_R = m_O} + \frac{1}{f}\ln(m_O/m_R) \tag{33}$$

where $(E^{\circ\prime} - E_{1/2})|_{m_R = m_O}$ is given in Table I for corresponding

(23) IMSL MATH/LIBRARY. FORTRAN Subroutines for Mathematical Applications, version 1.1, IMSL Inc.: Houston, 1989.

values of $(E_{1/4} - E_{1/2})$ and $(E_{1/2} - E_{3/4})$. To take into account the inequality of the diffusion coefficients one should add the term $1/f \ln (m_O/m_R)$ to that value. Clearly, the error in $E^{\circ\prime}$ resulting from neglecting the inequality of m_O and m_R is equal to this additional term.

Analogously, from eq 27

$$k^\circ = k_{1/2} m_O \exp(\alpha n f (E_{1/2} - E^{\circ\prime})|_{m_R \neq m_O})$$
$$= k^\circ|_{m_R = m_O} \exp[\alpha n f (E^{\circ\prime}|_{m_R = m_O} - E^{\circ\prime}|_{m_R \neq m_O})]$$
$$= k^\circ|_{m_R = m_O} (m_R/m_O)^\alpha \quad (34)$$

where $k^\circ|_{m_R = m_O}$ is calculated from Table I.

Example 1. Hemispherical Microelectrode. For a hemispherical electrode, the mass-transfer coefficients are $m_O = D_O/r_0 = D_O\pi/d$ and $m_R = D_R/r_0 = D_R\pi/d$, where r_0 is the electrode radius and $d = \pi r_0$ is its superficial diameter. With these expressions, eqs 7–9 determine the shape of a quasi-reversible voltammogram at a hemisphere.[18] Thus the kinetic parameters can be found from Table I for given values of $(E_{1/4} - E_{1/2})$ and $(E_{1/2} - E_{3/4})$. The standard rate constant in this case is

$$k^\circ = \lambda m_O = \pi\lambda D_O/d = \lambda D_O/r_0 \quad (35)$$

The corrections (33) and (34) should be introduced if $D_R \neq D_O$.

Example 2. Rotating Disk Electrode. With $m_O = 0.61 D_O^{2/3} \nu^{-1/6} \omega^{1/2}$ and $m_R = 0.61 D_R^{2/3} \nu^{-1/6} \omega^{1/2}$, where ν is the

Table I. Kinetic Parameters from the Steady-State Voltammogram at a Uniformly Accessible Electrode ($\Delta E_{1/4} = E_{1/4} - E_{1/2}$, $\Delta E_{3/4} = \Delta E_{1/2} - E_{3/4}$; $\lambda = k^\circ/m_O$, $\Delta E^{\circ\prime} = E^{\circ\prime} - E_{1/2}$)

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	29.5	30.0	30.5	31.0	31.5	32.0	32.5	33.0	33.5	34.0	34.5	35.0	35.5	36.0	36.5	37.0	37.5	38.0	38.5	39.0	39.5
31.0	λ	10.0	4.89	1.95																		
	α	0.34	0.59	0.77																		
	$n\Delta E^{\circ\prime}$	2.6	5.1	11.6																		
31.5	λ	11.3	6.23	3.29	1.38																	
	α	0.22	0.46	0.64	0.78																	
	$n\Delta E^{\circ\prime}$	2.3	4.1	7.5	15.4																	
32.0	λ	12.3	7.22	4.28	2.37	1.03																
	α	0.12	0.36	0.54	0.67	0.79																
	$n\Delta E^{\circ\prime}$	2.1	3.6	5.9	10.0	19.4																
32.5	λ	13.1	7.98	5.04	3.14	1.80	0.81															
	α	0.03	0.27	0.45	0.58	0.70	0.79															
	$n\Delta E^{\circ\prime}$	2.0	3.3	5.1	7.9	12.8	23.5															
33.0	λ		8.58	5.65	3.74	2.41	1.42	0.66														
	α		0.19	0.37	0.50	0.62	0.71	0.79														
	$n\Delta E^{\circ\prime}$		3.1	4.6	6.8	10.1	15.6	27.4														
33.5	λ		9.07	6.14	4.24	2.90	1.92	1.15	0.54													
	α		0.13	0.30	0.44	0.55	0.64	0.72	0.78													
	$n\Delta E^{\circ\prime}$		2.9	4.3	6.1	8.7	12.4	18.6	31.3													
34.0	λ		9.47	6.54	4.64	3.31	2.32	1.56	0.96	0.46												
	α		0.07	0.24	0.37	0.48	0.58	0.65	0.72	0.78												
	$n\Delta E^{\circ\prime}$		2.8	4.1	5.7	7.7	10.6	14.8	21.5	35.1												
34.5	λ		9.80	6.88	4.98	3.65	2.67	1.91	1.31	0.81	0.40											
	α		0.02	0.19	0.32	0.43	0.52	0.60	0.66	0.72	0.77											
	$n\Delta E^{\circ\prime}$		2.8	3.9	5.3	7.1	9.5	12.7	17.2	24.5	38.8											
35.0	λ			7.17	5.28	3.95	2.96	2.20	1.60	1.11	0.70	0.35										
	α			0.14	0.27	0.38	0.47	0.55	0.61	0.67	0.72	0.76										
	$n\Delta E^{\circ\prime}$			3.8	5.1	6.7	8.7	11.3	14.8	19.7	27.5	42.3										
35.5	λ			7.42	5.53	4.20	3.21	2.46	1.86	1.37	0.96	0.62	0.31									
	α			0.10	0.23	0.33	0.42	0.50	0.57	0.62	0.67	0.72	0.76									
	$n\Delta E^{\circ\prime}$			3.7	4.9	6.3	8.1	10.4	13.2	17.0	22.2	30.4	45.7									
36.0	λ			7.63	5.74	4.42	3.44	2.68	2.08	1.59	1.19	0.84	0.55	0.28								
	α			0.06	0.19	0.29	0.38	0.46	0.52	0.58	0.63	0.67	0.71	0.75								
	$n\Delta E^{\circ\prime}$			3.6	4.7	6.1	7.7	9.7	12.1	15.1	19.2	24.7	33.2	48.9								
36.5	λ			7.82	5.93	4.61	3.63	2.87	2.27	1.79	1.38	1.04	0.75	0.49	0.25							
	α			0.02	0.15	0.26	0.34	0.42	0.48	0.54	0.59	0.64	0.68	0.71	0.74							
	$n\Delta E^{\circ\prime}$			3.5	4.6	5.9	7.4	9.1	11.3	13.9	17.1	21.4	27.2	36.0	52.1							
37.0	λ				6.10	4.78	3.80	3.04	2.45	1.96	1.56	1.21	0.92	0.67	0.44	0.23						
	α				0.12	0.22	0.31	0.38	0.45	0.51	0.56	0.60	0.64	0.67	0.71	0.73						
	$n\Delta E^{\circ\prime}$				4.5	5.7	7.1	8.7	10.6	12.9	15.7	19.1	23.6	29.7	38.7	55.1						
37.5	λ				6.25	4.93	3.95	3.20	2.60	2.11	1.71	1.37	1.08	0.83	0.60	0.40	0.22					
	α				0.09	0.19	0.28	0.35	0.42	0.47	0.52	0.57	0.60	0.64	0.67	0.70	0.73					
	$n\Delta E^{\circ\prime}$				4.4	5.5	6.9	8.4	10.1	12.2	14.6	17.5	21.2	25.8	32.1	41.4	58.0					
38.0	λ				6.38	5.06	4.09	3.33	2.74	2.25	1.85	1.51	1.22	0.97	0.75	0.55	0.37	0.20				
	α				0.06	0.16	0.25	0.32	0.39	0.44	0.49	0.53	0.57	0.61	0.64	0.67	0.70	0.72				
	$n\Delta E^{\circ\prime}$				4.3	5.4	6.7	8.1	9.7	11.6	13.8	16.3	19.4	23.2	28.0	34.5	44.0	60.8				
38.5	λ				6.50	5.18	4.21	3.46	2.86	2.38	1.97	1.64	1.35	1.09	0.87	0.68	0.50	0.34	0.19			
	α				0.04	0.14	0.22	0.30	0.36	0.41	0.46	0.51	0.54	0.58	0.61	0.64	0.67	0.69	0.71			
	$n\Delta E^{\circ\prime}$				4.3	5.3	6.5	7.9	9.4	11.1	13.1	15.4	18.1	21.3	25.2	30.2	36.9	46.5	63.5			
39.0	λ				6.61	5.29	4.32	3.57	2.97	2.49	2.09	1.75	1.46	1.21	0.99	0.80	0.62	0.46	0.32	0.18		
	α				0.01	0.11	0.20	0.27	0.33	0.39	0.44	0.48	0.52	0.55	0.58	0.61	0.64	0.66	0.68	0.70		
	$n\Delta E^{\circ\prime}$				4.2	5.2	6.4	7.7	9.1	10.7	12.5	14.6	17.0	19.9	23.2	27.3	32.4	39.2	49.0	66.1		
39.5	λ					5.39	4.42	3.67	3.08	2.59	2.19	1.85	1.56	1.31	1.10	0.90	0.73	0.57	0.43	0.30	0.17	
	α					0.09	0.17	0.25	0.31	0.36	0.41	0.45	0.49	0.53	0.56	0.59	0.61	0.64	0.66	0.68	0.70	
	$n\Delta E^{\circ\prime}$					5.2	6.3	7.5	8.9	10.4	12.1	14.0	16.2	18.7	21.6	25.1	29.3	34.5	41.4	51.4	68.7	
40.0	λ					5.48	4.51	3.76	3.17	2.69	2.28	1.95	1.66	1.41	1.19	1.00	0.83	0.67	0.53	0.40	0.28	0.16
	α					0.07	0.15	0.22	0.29	0.34	0.39	0.43	0.47	0.50	0.53	0.56	0.59	0.61	0.63	0.65	0.67	0.69
	$n\Delta E^{\circ\prime}$					5.1	6.2	7.3	8.7	10.1	11.7	13.5	15.5	17.8	20.4	23.4	27.0	31.3	36.6	43.6	53.7	71.1

Table I (Continued)

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	34	39	44	49	54	59	64	69	74	79	84	89	94
45.0	λ	2.91	0.96	0.18										
	α	0.22	0.49	0.61										
	$n\Delta E^{o'}$	9.7	26.0	74.0										
50.0	λ	3.22	2.31	0.59	0.15									
	α	0.12	0.37	0.49	0.55									
	$n\Delta E^{o'}$	9.0	21.1	40.2	90.3									
55.0	λ	3.41	1.53	0.82	0.43	0.13								
	α	0.06	0.30	0.41	0.47	0.51								
	$n\Delta E^{o'}$	8.7	19.1	32.9	53.1	104								
60.0	λ	3.52	1.67	0.98	0.60	0.35	0.12							
	α	0.03	0.24	0.35	0.41	0.44	0.47							
	$n\Delta E^{o'}$	8.5	18.0	29.6	44.2	64.8	116							
65.0	λ	3.59	1.77	1.09	0.73	0.49	0.31	0.12						
	α	.003	0.20	0.30	0.36	0.40	0.42	0.43						
	$n\Delta E^{o'}$	8.4	17.3	27.7	39.8	54.6	75.4	127						
70.0	λ		1.85	1.18	0.82	0.59	0.42	0.28	0.12					
	α		0.17	0.27	0.32	0.36	0.38	0.39	0.40					
	$n\Delta E^{o'}$		16.9	26.5	37.2	49.5	64.4	85.1	136					
75.0	λ		1.90	1.24	0.89	0.67	0.51	0.38	0.27	0.12				
	α		0.15	0.24	0.29	0.32	0.34	0.36	0.37	0.37				
	$n\Delta E^{o'}$		16.6	25.7	35.5	46.4	58.6	73.5	94.1	145				
80.0	λ		1.95	1.30	0.95	0.73	0.57	0.45	0.35	0.25	0.12			
	α		0.13	0.22	0.27	0.30	0.32	0.33	0.34	0.35	0.35			
	$n\Delta E^{o'}$		16.3	25.1	34.3	44.2	55.1	67.3	82.0	103	154			
85.0	λ		1.98	1.34	1.00	0.78	0.63	0.51	0.42	0.33	0.25	0.13		
	α		0.12	0.20	0.25	0.27	0.29	0.31	0.32	0.32	0.33	0.33		
	$n\Delta E^{o'}$		16.2	24.6	33.4	42.7	52.6	63.3	75.4	90.1	110	161		
90.0	λ		2.01	1.38	1.04	0.82	0.67	0.56	0.47	0.39	0.32	0.24	0.13	
	α		0.11	0.18	0.23	0.26	0.27	0.29	0.30	0.30	0.31	0.31	0.31	
	$n\Delta E^{o'}$		16.0	24.2	32.7	41.5	50.8	60.5	71.2	83.2	97.8	118	169	
95.0	λ		2.03	1.41	1.07	0.86	0.71	0.60	0.51	0.44	0.37	0.31	0.24	0.13
	α		0.10	0.17	0.21	0.24	0.26	0.27	0.28	0.28	0.29	0.29	0.29	0.30
	$n\Delta E^{o'}$		15.9	23.9	32.2	40.6	49.4	58.5	68.2	78.7	90.7	105	125	176

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	39	49	59	69	79	89	99	109	119	129	139	149	159	169	179	189
100.0	λ	2.05	1.10	0.75	0.55	0.41	0.30	0.13									
	α	0.09	0.20	0.24	0.26	0.27	0.28	0.28									
	$n\Delta E^{o'}$	15.8	31.7	48.3	65.9	86.0	112	183									
110.0	λ	2.08	1.15	0.81	0.62	0.49	0.38	0.29	0.14								
	α	0.08	0.18	0.22	0.24	0.25	0.25	0.25	0.26								
	$n\Delta E^{o'}$	15.7	31.0	46.6	62.7	80.1	99.9	126	197								
120.0	λ	2.10	1.19	0.85	0.67	0.54	0.45	0.36	0.28	0.15							
	α	0.07	0.16	0.20	0.21	0.22	0.23	0.23	0.23	0.24							
	$n\Delta E^{o'}$	15.6	30.5	45.5	60.6	76.4	93.4	113	139	210							
130.0	λ	2.12	1.22	0.89	0.71	0.59	0.50	0.42	0.35	0.28	0.15						
	α	0.06	0.15	0.18	0.20	0.21	0.21	0.21	0.22	0.22	0.22						
	$n\Delta E^{o'}$	15.5	30.1	44.6	59.1	73.9	89.4	106	126	152	222						
140.0	λ	2.13	1.25	0.92	0.74	0.62	0.54	0.46	0.40	0.34	0.28	0.16					
	α	0.06	0.13	0.17	0.18	0.19	0.20	0.20	0.20	0.20	0.20	0.20					
	$n\Delta E^{o'}$	15.5	29.8	43.9	57.9	72.0	86.6	102	119	138	164	235					
150.0	λ	2.14	1.27	0.95	0.77	0.66	0.57	0.50	0.44	0.39	0.34	0.28	0.17				
	α	0.05	0.12	0.15	0.17	0.18	0.18	0.18	0.19	0.19	0.19	0.19	0.19				
	$n\Delta E^{o'}$	15.4	29.6	43.4	57.0	70.6	84.5	98.8	114	131	150	176	247				
160.0	λ	2.15	1.28	0.97	0.80	0.68	0.60	0.54	0.48	0.43	0.38	0.33	0.28	0.17			
	α	0.05	0.12	0.14	0.16	0.17	0.17	0.17	0.17	0.18	0.18	0.18	0.18	0.18			
	$n\Delta E^{o'}$	15.4	29.4	43.0	56.3	69.5	82.9	96.6	111	126	142	162	188	258			
170.0	λ	2.16	1.30	0.99	0.82	0.71	0.63	0.56	0.51	0.46	0.42	0.37	0.33	0.28	0.18		
	α	0.05	0.11	0.13	0.15	0.16	0.16	0.16	0.16	0.16	0.17	0.17	0.17	0.17	0.17		
	$n\Delta E^{o'}$	15.3	29.2	42.6	55.7	68.6	81.6	94.8	108	123	138	154	173	199	270		
180.0	λ	2.17	1.31	1.01	0.84	0.73	0.65	0.59	0.54	0.49	0.45	0.41	0.37	0.32	0.28	0.18	
	α	0.04	0.10	0.13	0.14	0.15	0.15	0.15	0.15	0.156	0.16	0.16	0.16	0.16	0.16	0.16	
	$n\Delta E^{o'}$	15.3	29.1	42.3	55.2	67.9	80.6	93.4	107	120	134	149	166	185	211	281	
190.0	λ	2.17	1.33	1.02	0.86	0.75	0.67	0.61	0.56	0.51	0.47	0.43	0.40	0.36	0.32	0.28	0.18
	α	0.04	0.10	0.12	0.13	0.14	0.14	0.14	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
	$n\Delta E^{o'}$	15.3	28.9	42.0	54.7	67.3	79.7	92.3	105	118	131	145	160	177	196	222	293

Table I (Continued)

$n\Delta E_{3/4}$,mV	Parameter	$n\Delta E_{1/4}$,mV 54	74	94	114	134	154	174	194	214	234	254	274	294
200.0	λ	1.19	0.82	0.66	0.56	0.48	0.41	0.34	0.25					
	α	0.10	0.13	0.14	0.14	0.14	0.14	0.14	0.14					
	$n\Delta E^{\circ\prime}$	35.4	60.6	85.2	110	136	164	197	254					
220.0	λ	1.18	0.84	0.69	0.60	0.52	0.46	0.40	0.33	0.25				
	α	0.10	0.12	0.12	0.13	0.13	0.13	0.13	0.13	0.13				
	$n\Delta E^{\circ\prime}$	35.1	59.9	83.8	108	132	158	186	220	276				
240.0	λ	1.20	0.87	0.72	0.63	0.56	0.50	0.44	0.39	0.33	0.26			
	α	0.09	0.11	0.11	0.12	0.12	0.12	0.12	0.12	0.12	0.12			
	$n\Delta E^{\circ\prime}$	34.9	59.3	82.8	106	130	154	180	208	242	298			
260.0	λ	1.21	0.89	0.75	0.66	0.59	0.53	0.48	0.43	0.38	0.33	0.26		
	α	0.08	0.10	0.10	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11		
	$n\Delta E^{\circ\prime}$	34.7	58.8	82.1	105	128	152	176	202	230	264	320		
280.0	λ	1.22	0.91	0.77	0.68	0.61	0.56	0.51	0.46	0.42	0.37	0.33	0.26	
	α	0.07	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	
	$n\Delta E^{\circ\prime}$	34.5	58.5	81.4	104	127	150	173	198	224	252	286	342	
300.0	λ	1.24	0.92	0.79	0.70	0.64	0.58	0.54	0.49	0.45	0.41	0.37	0.33	0.26
	α	0.07	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
	$n\Delta E^{\circ\prime}$	34.4	58.2	80.9	103	126	148	171	195	219	245	274	307	364

kinematic viscosity and ω is the rotation rate,[22] eq 35 for the RDE becomes

$$k^\circ = \lambda m_O = 0.61 D_O^{2/3} \nu^{-1/6} \omega^{1/2} \lambda$$
$$= \lambda i_d/(nFAc_O^*) \quad (36)$$

Example 3. dc Polarography. For dc polarography, within the framework of the Ilkovic approximation, $m_O = \sqrt{7D_O/(3\pi\tau)}$ and $m_R = \sqrt{7D_R/(3\pi\tau)}$, where τ is the sampling interval (these are expressions for instantaneous polarographic current). Thus

$$k^\circ = \lambda\sqrt{7D_O/(3\pi\tau)} \quad (37)$$

More precise results can probably be obtained with the spherical correction introduced into expressions for mass-transfer coefficients.

Example 4. Sampled Current Voltammetry. For sampled current voltammetry at a planar electrode $m_O = \sqrt{D_O/(\pi t)}$ and $m_R = \sqrt{D_R/(\pi t)}$, where t is the sampling time and

$$k^\circ = \lambda\sqrt{D_O/(\pi t)} \quad (38)$$

Clearly, choosing the smallest possible value of t (with the smallest t limited by interference of charging current and adsorption), one can combine the advantages of fast transient measurements with the simplicity of the steady-state data analysis.

Example 5. Thin-Layer Steady-State Voltammetry. The mass-transfer coefficients, according to ref 5, are $m_O = m_R = 2D_OD_R/l(D_O + D_R)$ where l is the thickness of the cell. Consequently

$$k^\circ = \frac{2D_OD_R}{l(D_O + D_R)}\lambda \quad (39)$$

Nonuniformly Accessible Electrodes: Microdisk Electrode. The system (eq 32) for a microdisk electrode was solved numerically using the NEQNJ subroutine from the IMSL Program Library.[23] The design of Table II containing the computational results is analogous to that in Table I, and the calculation of the kinetic parameters proceeds in the same way. Because the definition of the mass-transfer coefficient for a nonuniformly accessible microdisk is not straightforward, we chose the simplest expression for the kinetic parameter $\lambda = ak^\circ/D_O$. Correspondingly, k° can be found by substituting the λ value from Table II into the formula

$$k^\circ = D_O\lambda/a \quad (40)$$

The corrections for unequal diffusion coefficients are still given by eqs 33 and 34 with $m_O/m_R = D_O/D_R$, and the factor of $298/T$ is necessary when $T \neq 298$ K. To see the similarity between the microdisk and the equivalent size hemisphere[18] one should multiply the λ values in Table II by the factor of $\pi/2$.

Since the above analysis and that by Oldham et al.[17] are based on the same approximate equation, eq 28, they should extract the same values of kinetic parameters from experimental data. As an example, let us consider $|E_{1/2} - E_{1/4}| = 55$ mV and $|E_{3/4} - E_{1/2}| = 60$ mV. From Table II, $\lambda = 0.25$, $\alpha = 0.50$, and $E^{\circ\prime} = E_{1/2} + 88$ mV. Using this $E^{\circ\prime}$ value and $|E_{3/4} - E_{1/4}| = 115$ mV, one can find from Figure 2 of ref 17, $\alpha \approx 0.5$ and $\log(\pi\lambda/4) = -0.7$, i.e., $\lambda \approx 0.25$, in agreement with the results above.

How To Use Tables I and II. Clearly, not all values of $\Delta E_{1/4}$ and $\Delta E_{3/4}$ are suitable for kinetic analysis. Many cells in Tables I and II are empty because corresponding values of quartile potentials are in contradiction with the theory (e.g., $\Delta E_{1/4}$ cannot be larger than $\Delta E_{3/4}$). Not all allowed pairs of $\Delta E_{1/4}$ and $\Delta E_{3/4}$ provide reliable values of the kinetic parameters. For example, assuming $\Delta E_{3/4} = 31$ mV for a one-electron process at a microdisk, one can see that the variation of $\Delta E_{1/4}$ in a narrow range, from 30 to 30.5 mV, would lead to an almost 1 order-of-magnitude increase in k° and about 20 mV variation in $E^{\circ\prime}$. This happens because the chosen values of the quartile potentials correspond to an almost reversible steady-state voltammogram; in this case one can evaluate the range of the reaction rate but not study its kinetics quantitatively. Thus one should avoid using voltammograms obtained at a microdisk with either $\Delta E_{1/4} \leq 31$ mV or $\Delta E_{3/4} \leq 32$ mV for quantitative analysis. For uniformly accessible electrodes the analogous limits are a little lower, $\Delta E_{1/4} \approx 30.5$ mV and $\Delta E_{3/4} \approx 31$ mV. To judge the applicability of a particular voltammogram (i.e., the microelectrode size or the chosen mass-transfer rate) for kinetic measurements and to evaluate precision, one should estimate uncertainties in $\Delta E_{1/4}$ and $\Delta E_{3/4}$ values and check Table I or II to see how significant are the variations of λ, α, and $E^{\circ\prime}$ caused by these uncertainties. In our microelectrode experiments, we found that a reproducibility of $\Delta E_{1/4}$ and $\Delta E_{3/4}$ within ±0.5 mV can easily be achieved when one analyzes digitized data or uses an X–Y recorder with a voltage scale of 5–10 mV/cm. The accuracy of determined parameters can also be improved by recording several voltammograms and averaging the values of $\Delta E_{1/4}$ and $\Delta E_{3/4}$.

Because of space limitations we could not tabulate parameters for all $\Delta E_{1/4}$ and $\Delta E_{3/4}$ values of 0.5-mV separation (as is done for the interval from 30 to 40 mV where higher precision is required). Therefore, experimentally found $\Delta E_{1/4}$ and $\Delta E_{3/4}$ can fall between the tabulated values. Supplementary material to this paper contains extensive tables for a uniformly accessible electrode and for a microdisk covering the range of $\Delta E_{3/4}$ from 41 to 90 mV. Sufficiently close spacing of tabulated parameters in these tables limits errors associated with interpolation to a few percent.

It is also possible to carry out linear interpolation between the neighboring tabulated values of corresponding parameters in Tables I and II. Two different cases may occur: (a) One of the $\Delta E_{1/4}$ and $\Delta E_{3/4}$ values is equal to a tabulated value, while another one (E) is bounded between two values, E_{I} and E_{II}. Then any parameter (P, where $P = \lambda$, α, or $n\Delta E^{\circ\prime}$) corresponding to E can be found according to the formula

$$P = P(E_{\mathrm{I}}) + (P(E_{\mathrm{II}}) - P(E_{\mathrm{I}}))(E - E_{\mathrm{I}})/(E_{\mathrm{II}} - E_{\mathrm{I}}) \quad (41)$$

For example, if $\Delta E_{1/4} = 40$ mV and $\Delta E_{3/4} = 72$ mV, find the corresponding λ value from Table II. In this case $E = 72$ mV, $E_{\mathrm{I}} = 70$ mV, $E_{\mathrm{II}} = 75$ mV, $\lambda(E_{\mathrm{I}}) = 2.35$, $\lambda(E_{\mathrm{II}}) = 2.46$. According to eq 41, $\lambda = 2.35 + (2.46 - 2.35)(72 - 70)/(75 - 70) = 2.39$. Calculation of α and $n\Delta E^{\circ\prime}$ is completely analogous. (b) Neither the $\Delta E_{1/4}$ nor the $\Delta E_{3/4}$ value can be found in the table. If $\Delta E_{1/4}$ is bounded between E_{I} and E_{II} and $E_{3/4}$ is bounded between E_{III} and E_{IV}, a somewhat more complicated linear two-dimensional interpolation is required to find—

Table II. Kinetic Parameters from the Steady-State Voltammogram at a Microdisk Electrode ($\Delta E_{1/4} = E_{1/4} - E_{1/2}$, $\Delta E_{3/4} = \Delta E_{1/2} - E_{3/4}$; $\lambda = ak^{\circ}/D_{\mathrm{O}}$, $\Delta E^{\circ\prime} = E^{\circ\prime} - E_{1/2}$

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	30.0	30.5	31.0	31.5	32.0	32.5	33.0	33.5	34.0	34.5	35.0	35.5	36.0	36.5	37.0	37.5	38.0
31.0	λ	4.17	0.84															
	α	0.78	0.94															
	$n\Delta E^{\circ\prime}$	9.0	27.0															
31.5	λ		3.49	1.49														
	α		0.77	0.87														
	$n\Delta E^{\circ\prime}$		10.5	19.3														
32.0	λ		6.12	1.45	0.40													
	α		0.61	0.86	0.92													
	$n\Delta E^{\circ\prime}$		6.8	19.6	41.4													
32.5	λ		5.21	3.89	0.81	0.20												
	α		0.63	0.68	0.88	0.92												
	$n\Delta E^{\circ\prime}$		7.7	9.9	28.6	56.9												
33.0	λ			5.34	2.50	0.43	0.08											
	α			0.58	0.74	0.89	0.91											
	$n\Delta E^{\circ\prime}$			7.8	13.8	40.6	81.5											
33.5	λ			6.45	3.74	1.55	0.12											
	α			0.49	0.64	0.79	0.90											
	$n\Delta E^{\circ\prime}$			6.7	10.4	19.4	71.9											
34.0	λ			7.36	4.67	2.70	0.77	0.17										
	α			0.41	0.55	0.68	0.83	0.88										
	$n\Delta E^{\circ\prime}$			6.1	8.8	13.3	30.4	64.0										
34.5	λ				5.43	3.49	1.97	0.33	0.15									
	α				0.48	0.60	0.71	0.86	0.87									
	$n\Delta E^{\circ\prime}$				7.9	11.1	16.8	47.8	67.5									
35.0	λ			8.76	6.07	4.13	2.67	1.46	0.25									
	α			0.29	0.42	0.54	0.64	0.74	0.85									
	$n\Delta E^{\circ\prime}$			5.3	7.2	9.8	13.7	20.9	55.2									
35.5	λ				6.62	4.68	3.22	2.08	1.09									
	α				0.37	0.48	0.58	0.67	0.76									
	$n\Delta E^{\circ\prime}$				6.8	9.0	12.0	16.5	25.5									
36.0	λ			9.79	7.10	5.15	3.69	2.57	1.65	0.81								
	α			0.19	0.32	0.43	0.52	0.61	0.69	0.77								
	$n\Delta E^{\circ\prime}$			4.9	6.4	8.4	10.9	14.3	19.6	30.8								
36.5	λ			10.2	7.52	5.57	4.11	2.98	2.08	1.32	0.61							
	α			0.15	0.27	0.38	0.48	0.56	0.63	0.70	0.78							
	$n\Delta E^{\circ\prime}$			4.7	6.1	7.9	10.1	12.9	16.8	22.9	36.6							
37.0	λ				7.89	5.94	4.47	3.34	2.44	1.71	1.08	0.47						
	α				0.23	0.34	0.43	0.51	0.59	0.65	0.72	0.78						
	$n\Delta E^{\circ\prime}$				5.9	7.5	9.5	11.9	15.1	19.5	26.5	42.8						
37.5	λ				8.22	6.26	4.79	3.66	2.76	2.04	1.42	0.89	0.36					
	α				0.20	0.30	0.39	0.47	0.54	0.61	0.67	0.72	0.78					
	$n\Delta E^{\circ\prime}$				5.7	7.2	9.0	11.2	13.9	17.4	22.2	30.1	49.3					
38.0	λ				8.51	6.55	5.08	3.94	3.04	2.32	1.72	1.20	0.74	0.28				
	α				0.17	0.27	0.36	0.44	0.51	0.57	0.62	0.68	0.73	0.78				
	$n\Delta E^{\circ\prime}$				5.6	7.0	8.7	10.6	13.0	15.9	19.7	25.1	33.9	56.0				
38.5	λ					6.81	5.34	4.20	3.30	2.57	1.97	1.47	1.03	0.62	0.23			
	α					0.24	0.32	0.40	0.47	0.53	0.59	0.64	0.68	0.73	0.78			
	$n\Delta E^{\circ\prime}$					6.8	8.4	10.2	12.3	14.9	18.0	22.2	28.1	37.8	62.8			
39.0	λ					7.05	5.57	4.43	3.53	2.80	2.20	1.70	1.27	0.88	0.53	0.18		
	α					0.21	0.29	0.37	0.44	0.50	0.55	0.60	0.65	0.69	0.73	0.77		
	$n\Delta E^{\circ\prime}$					6.6	8.1	9.8	11.7	14.0	16.8	20.2	24.7	31.1	41.7	69.6		
39.5	λ					7.27	5.79	4.64	3.73	3.00	2.40	1.90	1.48	1.10	0.77	0.46	0.15	
	α					0.18	0.27	0.34	0.41	0.47	0.52	0.57	0.61	0.65	0.69	0.73	0.76	
	$n\Delta E^{\circ\prime}$					6.5	7.9	9.5	11.3	13.4	15.8	18.8	22.5	27.3	34.1	45.6	76.6	
40.0	λ					7.46	5.98	4.83	3.92	3.19	2.59	2.09	1.66	1.29	0.97	0.68	0.40	0.12
	α					0.15	0.24	0.31	0.38	0.44	0.49	0.54	0.58	0.62	0.66	0.69	0.73	0.76
	$n\Delta E^{\circ\prime}$					6.4	7.7	9.2	10.9	12.8	15.1	17.7	20.8	24.7	29.9	37.2	49.5	83.9

Table II (Continued)

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	35	40	45	50	55	60	65	70	75	80	85	90
45.0	λ	3.31	0.77										
	α	0.33	0.60										
	$n\Delta E^{o\prime}$	13.1	37.4										
50.0	λ	3.95	1.40	0.44									
	α	0.21	0.46	0.58									
	$n\Delta E^{o\prime}$	11.6	26.6	56.3									
55.0	λ	4.33	1.78	0.84	0.31								
	α	0.13	0.37	0.48	0.54								
	$n\Delta E^{o\prime}$	11.0	23.1	40.3	73.2								
60.0	λ	4.57	2.03	1.10	0.60	0.25							
	α	0.09	0.30	0.41	0.47	0.50							
	$n\Delta E^{o\prime}$	10.6	21.4	34.8	53.2	88.3							
65.0	λ		2.22	1.29	0.80	0.48	0.22						
	α		0.25	0.35	0.41	0.45	0.47						
	$n\Delta E^{o\prime}$		20.4	32.0	46.1	65.1	102						
70.0	λ		2.35	1.43	0.95	0.64	0.42	0.19					
	α		0.22	0.31	0.37	0.40	0.42	0.44					
	$n\Delta E^{o\prime}$		19.7	30.3	42.3	56.6	76.1	116					
75.0	λ		2.46	1.54	1.07	0.77	0.55	0.37	0.18				
	α		0.19	0.28	0.33	0.36	0.39	0.40	0.41				
	$n\Delta E^{o\prime}$		19.2	29.1	39.9	52.0	66.6	86.3	129				
80.0	λ		2.54	1.63	1.16	0.86	0.65	0.49	0.34	0.17			
	α		0.17	0.25	0.30	0.33	0.35	0.37	0.38	0.38			
	$n\Delta E^{o\prime}$		18.9	28.3	38.2	49.1	61.3	75.9	96.0	141			
85.0	λ		2.60	1.71	1.24	0.94	0.74	0.58	0.45	0.32	0.16		
	α		0.15	0.23	0.28	0.31	0.33	0.34	0.35	0.36	0.36		
	$n\Delta E^{o\prime}$		18.6	27.6	37.0	47.0	57.9	70.1	84.8	105	155		
90.0	λ		2.65	1.77	1.30	1.01	0.81	0.66	0.53	0.42	0.31	0.15	
	α		0.14	0.21	0.26	0.29	0.31	0.32	0.33	0.33	0.34	0.34	
	$n\Delta E^{o\prime}$		18.4	27.1	36.1	45.5	55.4	66.2	78.4	93.2	114	168	
95.0	λ		2.70	1.82	1.36	1.07	0.87	0.72	0.60	0.49	0.40	0.30	0.13
	α		0.13	0.20	0.24	0.27	0.29	0.30	0.31	0.31	0.32	0.32	0.32
	$n\Delta E^{o\prime}$		18.3	26.7	35.4	44.3	53.6	63.5	74.2	86.4	01.3	123	184

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190
100.0	λ	2.73	1.41	0.92	0.66	0.47	0.29										
	α	0.12	0.23	0.27	0.29	0.30	0.31										
	$n\Delta E^{o\prime}$	18.1	34.8	52.2	71.2	94.2	131										
110.0	λ	2.79	1.49	1.01	0.75	0.57	0.43	0.28									
	α	0.10	0.20	0.24	0.26	0.27	0.28	0.28									
	$n\Delta E^{o\prime}$	17.9	34.0	50.2	67.2	86.0	109	147									
120.0	λ	2.83	1.55	1.08	0.83	0.66	0.53	0.41	0.27								
	α	0.09	0.18	0.22	0.24	0.25	0.25	0.25	0.26								
	$n\Delta E^{o\prime}$	17.8	33.3	48.8	64.6	81.3	99.9	123	162								
130.0	λ	2.86	1.60	1.14	0.89	0.72	0.60	0.49	0.39	0.27							
	α	0.08	0.17	0.20	0.22	0.23	0.23	0.23	0.24	0.24							
	$n\Delta E^{o\prime}$	17.7	32.8	47.7	62.7	78.1	94.6	113	136	178							
140.0	λ	2.89	1.64	1.19	0.94	0.78	0.66	0.56	0.47	0.38	0.26						
	α	0.07	0.15	0.18	0.20	0.21	0.21	0.22	0.22	0.22	0.22						
	$n\Delta E^{o\prime}$	17.6	32.5	46.9	61.3	75.9	91.1	108	126	150	193						
150.0	λ	2.91	1.68	1.23	0.99	0.83	0.71	0.62	0.53	0.46	0.37	0.26					
	α	0.07	0.14	0.17	0.19	0.19	0.20	0.20	0.20	0.20	0.20	0.21					
	$n\Delta E^{o\prime}$	17.5	32.2	46.3	60.2	74.3	88.6	104	120	139	163	209					
160.0	λ	2.93	1.71	1.27	1.03	0.87	0.76	0.66	0.59	0.51	0.44	0.37	0.25				
	α	0.06	0.13	0.16	0.17	0.18	0.19	0.19	0.19	0.19	0.19	0.19	0.19				
	$n\Delta E^{o\prime}$	17.5	31.9	45.8	59.4	73.0	86.7	101	116	132	151	175	225				
170.0	λ	2.94	1.73	1.30	1.06	0.91	0.80	0.71	0.63	0.56	0.50	0.43	0.36	0.25			
	α	0.06	0.12	0.15	0.16	0.17	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18			
	$n\Delta E^{o\prime}$	17.4	31.7	45.3	58.7	71.9	85.2	98.9	113	128	144	163	188	242			
180.0	λ	2.96	1.76	1.32	1.09	0.94	0.83	0.74	0.67	0.60	0.54	0.49	0.43	0.36	0.24		
	α	0.06	0.12	0.14	0.15	0.16	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17		
	$n\Delta E^{o\prime}$	17.4	31.5	45.0	58.1	71.1	84.0	97.2	111	125	140	156	175	200	259		
190.0	λ	2.97	1.78	1.35	1.12	0.97	0.86	0.78	0.70	0.64	0.58	0.53	0.48	0.42	0.36	0.24	
	α	0.05	0.11	0.13	0.15	0.15	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	
	$n\Delta E^{o\prime}$	17.3	31.4	44.7	57.6	70.3	83.0	95.9	109	122	136	151	168	187	213	279	
200.0	λ	2.98	1.79	1.37	1.14	1.00	0.89	0.81	0.74	0.67	0.62	0.57	0.52	0.47	0.42	0.35	0.22
	α	0.05	0.10	0.13	0.14	0.14	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
	$n\Delta E^{o\prime}$	17.3	31.2	44.4	57.2	69.7	82.2	94.8	108	120	134	148	163	180	199	225	303

Table II (Continued)

$n\Delta E_{1/4}$,mV / $n\Delta E_{3/4}$,mV	Parameter	50	70	90	110	130	150	170	190	210	230	250	270
	λ	1.81	1.17	0.92	0.77	0.65	0.55	0.46	0.35				
210.0	α	0.10	0.13	0.14	0.14	0.15	0.15	0.15	0.15				
	$n\Delta E^{o\prime}$	31.1	56.8	81.5	106	132	159	191	237				
	λ	1.83	1.18	0.94	0.79	0.68	0.58	0.50	0.41				
220.0	α	0.09	0.12	0.13	0.14	0.14	0.14	0.14	0.14				
	$n\Delta E^{o\prime}$	31.0	56.5	80.9	105	130	157	186	222				
	λ	1.84	1.20	0.96	0.82	0.71	0.61	0.53	0.45	0.35			
230.0	α	0.09	0.12	0.13	0.13	0.13	0.13	0.13	0.13	0.13			
	$n\Delta E^{o\prime}$	30.9	56.2	80.4	104	129	154	182	214	262			
	λ	1.85	1.22	0.98	0.84	0.73	0.64	0.56	0.48	0.40			
240.0	α	0.09	0.11	0.12	0.13	0.13	0.13	0.13	0.13	0.13			
	$n\Delta E^{o\prime}$	30.8	55.9	79.9	104	128	153	179	208	246			
	λ	1.86	1.24	1.00	0.86	0.75	0.67	0.59	0.51	0.44	0.35		
250.0	α	0.08	0.11	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12		
	$n\Delta E^{o\prime}$	30.7	55.7	79.5	103	127	151	177	204	237	287		
	λ	1.87	1.25	1.02	0.88	0.77	0.69	0.61	0.54	0.47	0.40		
260.0	α	0.08	0.11	0.11	0.12	0.12	0.12	0.12	0.12	0.12	0.12		
	$n\Delta E^{o\prime}$	30.7	55.5	79.1	102	126	150	175	201	231	269		
	λ	1.88	1.26	1.03	0.89	0.79	0.71	0.64	0.57	0.50	0.43	0.34	
270.0	α	0.08	0.10	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	
	$n\Delta E^{o\prime}$	30.6	55.3	78.8	102	125	149	173	199	227	260	312	
	λ	1.89	1.27	1.05	0.91	0.81	0.73	0.66	0.59	0.53	0.46	0.39	
280.0	α	0.07	0.10	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	
	$n\Delta E^{o\prime}$	30.5	55.2	78.5	101	124	148	172	197	223	253	294	
	λ	1.90	1.29	1.06	0.93	0.83	0.75	0.68	0.61	0.55	0.49	0.43	0.33
290.0	α	0.07	0.09	0.10	0.10	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
	$n\Delta E^{o\prime}$	30.5	55.0	78.2	101	124	147	170	195	220	249	282	341
	λ	1.91	1.30	1.07	0.94	0.85	0.77	0.70	0.63	0.57	0.51	0.45	0.39
300.0	α	0.07	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
	$n\Delta E^{o\prime}$	30.4	54.9	78.0	101	123	146	169	193	218	245	276	316

the value of a parameter $P(\Delta E_{1/4},\Delta E_{3/4})$:

$$P(\Delta E_{1/4},\Delta E_{3/4}) = P(E_I,E_{III}) + (P(E_{II},E_{III}) - P(E_I,E_{III}))\frac{\Delta E_{1/4} - E_I}{E_{II} - E_I} + \left[P(E_I,E_{IV}) - P(E_I,E_{III}) + (P(E_{II},E_{IV}) + P(E_I,E_{III}) - P(E_{II},E_{III}) - P(E_I,E_{IV}))\frac{\Delta E_{1/4} - E_I}{E_{II} - E_I}\right]\frac{\Delta E_{3/4} - E_{III}}{E_{IV} - E_{III}} \quad (42)$$

For example, if $\Delta E_{1/4}$ = 42 mV and $\Delta E_{3/4}$ = 104 mV, find the corresponding λ value from Table I. Substituting E_I = 39 mV, E_{II} = 49 mV, E_{III} = 100 mV, E_{IV} = 110 mV, $\lambda(E_I,E_{III})$ = 2.05, $\lambda(E_{II},E_{III})$ = 1.10, $\lambda(E_I,E_{IV})$ = 2.08, and $\lambda(E_{II},E_{IV})$ = 1.15 into eq 42, one finds λ = 2.05 + 0.3(1.10 − 2.05) + 0.4[2.08 − 2.05 + 0.3(1.15 + 2.05 − 1.10 − 2.08)] = 1.78. This somewhat cumbersome procedure is also necessary to extract precise values of kinetic parameters from graphs such as those presented in ref 17. Note that in most cases the differences between the nearest tabulated values are small enough to suggest determination of parameters by inspection rather than using eqs 41 or 42.

Other Microelectrode Geometries. The growing interest in using microelectrodes shaped as a spherical segment[10,11] or a cone[11,24,25] is due to the relative simplicity of their preparation. While it is difficult to construct very small (nanometer) insulated electrodes with a true disk or hemispherical shape, the preparation and characterization of spherically or conically shaped ultramicroelectrodes is easier.[11,24] The theory for steady-state voltammetry at a spherical segment (smaller than a hemisphere) or conical electrode has not been reported, and only expressions for the diffusion-controlled plateau current have been proposed.[10,26] Obviously, the voltammograms at a disk and at a hemisphere represent two limiting cases for spherical segment geometry (Figure 1a). Since the Nernstian steady-state voltammograms are identical for a disk and an equivalent hemisphere,[18] they should possess the same shape for any electrode shaped as a spherical segment (smaller than a hemisphere). It seems reasonable to determine the equivalent size of the segment (or, in turn, the equivalent mass-transfer coefficient) through the superficial diameter,[18] $d = \beta R$ (Figure 1a). It was shown in Figure 3 of ref 18 that the difference between the quasi-reversible voltammogram obtained at a hemisphere and at a disk is quite small. For a sufficiently fast electrochemical reaction it is definitely within the range of experimental error. Correspondingly, the differences between the values of kinetic parameters presented

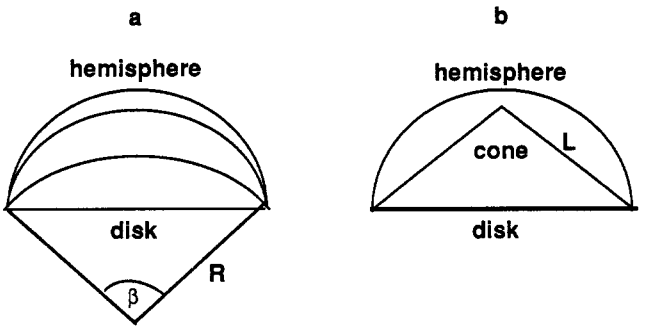

Figure 1. Geometry of an electrode shaped as a spherical segment or a cone considered as intermediate between a disk and a hemisphere: (a) continuous transition from disk to hemispherical geometry; (b) a cone enclosed between a disk and a hemisphere.

(24) Mirkin, M. V.; Fan, F.-R. F.; Bard, A. J. *Science* **1992**, *257*, 369.
(25) Aoki, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *281*, 29.
(26) Myland, J. C.; Oldham, K. B. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *288*, 1.

in Tables I and II are often negligible. Therefore, one can use these tables and eq 35 to analyze quasi-reversible steady-state CV obtained at a spherical segment without the risk of significant error. For better accuracy, Table I should be used when β is close to π, and Table II when β is closer to 0.

The situation with a conical electrode is less clear. However, a blunt cone apparently displays steady-state behavior[11,24] (although a long and sharp cone,[25] whose geometry approaches that of a cylinder, will not). From geometrical considerations (Figure 1b), the steady-state current should intuitively have a value intermediate between those for a disk and a hemisphere. The superficial diameter of such an electrode seems to be equal to $2L$. Probably, steady-state measurements with this type of electrode should also provide a good estimate of the electrochemical kinetic parameters.

In general, when the exact geometry of an electrochemical system is unknown, but the surface of the working electrode is evaluated and its uniform accessibility can be assumed, one can calculate m_O as

$$m_O = i_d/(nFAc_O^*) \quad (43)$$

and then use Table I to determine $E^{\circ\prime}$ and kinetic parameters.

Scanning Electrochemical Microscope. SECM theory is sufficiently complicated to allow only a rigorous approach to the determination of the kinetic parameters, i.e., curve fitting,[16] because of nonuniform accessibility of the disk-shaped tip electrode. Clearly, when the tip and the conductive substrate are sufficiently far from each other, the tip behaves as a normal microdisk electrode. When the tip/substrate separation, d, becomes smaller, the tip current increases due to positive feedback and one can observe a gradual transition from a microdisk- to a thin-layer-type behavior. When d is significantly smaller than the tip radius, a, the SECM current is essentially the same as in a thin-layer cell;[12] i.e., the surface concentration is apparently uniform. Therefore, the assumption of a uniform tip surface concentration should lead to the largest possible error at an infinite tip/substrate separation. One can estimate this error by taking the effective mass-transfer coefficient for a microdisk to be[18]

$$m_O = \pi D/2a \quad (44)$$

A comparison between the kinetic parameters found in Table I with m_O expressed by eq 44 and those obtained from Table II showed that the differences are always fairly small, and they decrease with the increase of λ, i.e., the faster the electrode reaction, the more uniform the concentration distribution at a microdisk surface. Thus the analysis of SECM results by using Table I should be quite accurate, when the tip/substrate separation is small and the reaction is fast.

The effective mass-transfer coefficient for SECM with a conductive substrate can be found using the analytical approximation for a diffusion-limited steady-state current:[11]

$$i_T(L) = 4nFac_O^*D_O(0.68 + 0.78377/L + 0.3315\exp(-1.0672/L)) \quad (45)$$

where $L = d/a$ is the normalized distance between the conductive substrate and the tip. Thus the effective mass-transfer coefficient

$$m_O = 4D_O(0.68 + 0.78377/L + 0.3315\exp(-1.0672/L))/(\pi a) \quad (46)$$

is a function of both tip radius and tip/substrate separation. The analysis of the steady-state SECM tip current as a function of tip potential (with a diffusion-controlled substrate process and fairly small d/a, e.g., 0.1) should yield the kinetics at the tip electrode. Analogously, the kinetics at the substrate can be evaluated from the dependence of the tip current vs substrate potential (while the tip process is diffusion controlled) by using Table I. This procedure is simpler than the curve fitting described in ref 16 and yields the α and $E^{\circ\prime}$ values in addition to k°.

CONCLUSIONS

A new methodology has been proposed to extract kinetic information from different types of quasi-reversible steady-state voltammograms. The following advantages can be noted.

(i) The method is very easy to use. Only one steady-state voltammogram is needed, and the kinetic parameters can be found immediately from a table without any numerical or graphical analysis of the data. The same table is suitable for any steady-state electrochemical technique with a uniformly accessible working electrode. An analogous table is constructed for a microdisk electrode. Although the accuracy of measurements of k° and α is probably more affected by systematic, than by random, errors, more precise values of these parameters can be obtained after the initial estimation from the tables by fitting the whole voltammogram, eq 6.

(ii) Only three easily accessible experimental values, $E_{1/4}$, $E_{1/2}$, and $E_{3/4}$ are required. This procedure also yields the formal potential, $E^{\circ\prime}$, and does not require knowledge of the concentration of the electroactive species. Thus the proposed method can be employed when the above values are unknown, for example, in studies of the electrochemical kinetics in ion-conductive polymers.[24]

(iii) The microelectrode steady-state measurements are free from the influence of charging current and largely from ohmic potential drop.[6] Therefore, the values of quartile potentials can be found with high accuracy. The results are also independent of the values of the electrode surface area and the concentration of the electroactive species, which are usually an additional source of error.

(iv) The steady-state response of a microelectrode shaped as a spherical segment or blunt cone can be approximated by that of a hemispherical or microdisk electrode of equivalent size. The above analysis can be applied to data obtained with these electrodes. A similar approximation has been proposed for the SECM.

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SUPPLEMENTARY MATERIAL AVAILABLE

More extensive tables of kinetic parameters for uniformly accessible electrodes and microdisks (12 pages). Ordering information is given on any current masthead page.

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