THEORY OF STATIONARY CURRENT–POTENTIAL CURVES AT MICRODISK ELECTRODES FOR QUASI-REVERSIBLE AND TOTALLY IRREVERSIBLE ELECTRODE REACTIONS

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ABSTRACT

An analytical equation for stationary current–potential curves at microdisk electrodes was derived by the Wiener–Hopf method when the electrode reaction is quasi-reversible and totally irreversible. The current–potential curve is a function of the kinetic parameter, $\lambda = (a/D)(k + k')$, where $k$ and $k'$ are the forward and backward reaction rate constants, respectively; $a$ is the radius of the electrode and $D$ is the diffusion coefficient. The equation consisted of a set of simultaneous equations and was solved numerically. A technique of evaluating the kinetic parameters from experimental current–potential curves is presented which is similar to the method of a polarographic log-plot. The theoretical current–potential curves were compared with that at a hemispherical electrode.

INTRODUCTION

Microelectrodes such as microsphere and microdisk electrodes subject to three-dimensionally diffusional mass transport exhibit a steady-state current except at a short electrolysis time because three-dimensional diffusion produces a steady-state concentration profile. Thus the steady-state current–potential curve can be obtained simply by cyclic voltammetry at a low potential sweep rate, as is measured at a hydrodynamic electrode. If an electrode reaction is associated with electrode kinetics, it can be deduced from the well-known behaviour at hydrodynamic electrodes that the current–potential curve at a microelectrode shifts by an extent equal to the logarithm of the inverse of the electrode reaction rate constant from the reversible voltammogram. Since three-dimensional diffusion plays a role similar to convection at hydrodynamic electrodes in the sense that mass transport is enhanced, irreversibility of the electrode reaction is reflected more significantly on current–potential curves with a decrease in the electrode size.

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Several investigations have been done on electrode kinetics at microelectrodes. The kinetics of the reduction of mercuric ion at mercury droplets deposited on a vitreous carbon electrode have been investigated under quasi-steady state conditions [1, 2]. It has been demonstrated that a rapid electrode reaction rate can be estimated from even a slow current transient at microdisk electrodes [3]. Exchange currents have been evaluated from a plot of the current against the overpotential at microdisk electrodes by the use of a linearized Tafel relation [4]. A kinetic study employing microdisk electrodes has been made in highly resistive solutions with rapid potential sweep rates [5]. An attempt has been made to apply the kinetic equation at a hemispherical electrode to the simulation of cyclic voltammograms [6]. Potential shifts in cyclic voltammograms due to sluggish electrode reactions have also been observed at microcylinder [7] and microband [8, 9] electrodes. Some quantitative studies have been reported. Gueshi and co-workers [10, 11] determined the kinetic parameters at a partially blocked electrode or an assembly of microdisk electrodes. Amatore and co-workers evaluated the cyclic voltammograms numerically at microcylinder [7] and microband [9] electrodes for a quasi-reversible charge transfer. Aoki et al. [12] derived an analytical expression for pulse voltammetric current-potential curves and presented a technique of the modified log-plot for evaluating the kinetic parameters. It has been reported that microring electrodes are useful for measurements of electrode kinetics [13, 14].

This report focuses on deriving the equations for stationary current-potential curves at microdisk electrodes when an electrode reaction takes place quasi-reversibly and totally irreversibly. A method of determining the kinetic parameters is presented.

DERIVATION

We are concerned with the simple electrode reaction $R \rightleftharpoons O + n e^-$. It is assumed that (i) mass transport is due to three-dimensional diffusion, (ii) only the reduced species is initially present and (iii) the diffusion coefficients of the reduced and the oxidized species have a common value, $D$. Then the steady-state three-dimensional diffusion equation on the axial coordinate is given by

$$\partial \left( r^2 \partial c_i/\partial r \right)/\partial r + (1/\sin \theta) \partial (\sin \theta \partial c_i/\partial \theta)/\partial \theta = 0 \quad (i = O \text{ or } R) \tag{1}$$

where $c_i$ denotes the concentration of the oxidized species (O) or the reduced species (R), $r$ is the radial length from the centre of the microdisk electrode and $\theta$ is the angle measured from the line perpendicular to the electrode surface. Hence the electrode surface and the insulator wall are located on a plane at $\theta = \pi/2$. The boundary conditions are given by

$$\theta = 0, \quad r > 0 \quad : \quad \partial c_i/\partial r = 0 \tag{2}$$

$$\theta \geq 0, \quad r \to \infty \quad : \quad c_o \to 0, \quad c_r \to c^* \tag{3}$$

$$\theta = \pi/2, \quad 0 \leq r \leq a \quad : \quad j/nF = \bar{k}_c R - \bar{k}_o \tag{4}$$

$$j/nF = - (D/r)(\partial c_r/\partial \theta) = (D/r)(\partial c_o/\partial \theta) \tag{5}$$

$$\theta = \pi/2, \quad a < r \quad : \quad \partial c_i/\partial \theta = 0 \tag{6}$$
where \( a \) is the radius of the disk electrode; \( j \) is the current density, which is a function of \( r \); \( n \) is the number of electrons transferred; \( F \) is the Faraday constant; \( c^* \) is the bulk concentration of the reduced species; and \( k \) and \( k' \) are the forward and backward reaction rate constants, respectively. Equation (2) provides the condition that the concentration profiles are symmetrical with respect to the radial line perpendicular to the electrode surface. Adding eqn. (1) for \( c_0 \) to that for \( c_R \) and taking into account conditions (3), (5) and (6) leads immediately to

\[
c_0 + c_R = c^*
\]

(7)

Since \( c_R \) can be replaced by \( c_0 \) by using this equation, only \( c_0 \) (abbreviated by \( c \)) is treated below.

We let the variable \( r \) be \( ax \) and introduce the Mellin transformation [15], defined by

\[
M[c] = \int_0^\infty c x^{s-1} \, dx
\]

(8)

Applying the Mellin transformation to \( \partial (r^2 \partial c / \partial r) / \partial r \) in eqn. (1) and carrying out integration by parts twice taking into consideration that \( c = O(x^{-1}) \) for \( x \to \infty \) and \( c = O(x^0) \) for \( x \to 0 \), we rewrite eqn. (1) as

\[
s(s-1)M[c] + (1/\sin \theta) \, d[\sin \theta \, dM[c]/d\theta] / d\theta = 0
\]

(9)

where \( O(x^\nu) \) indicates that the order of \( x \) is \( \nu \). The solution of this ordinary differential equation is a linear combination of \( P_{s-1}(\cos \theta) \) and \( P_{s-1}(-\cos \theta) \), and \( P_{s-1} \) is the Legendre function of degree \( s-1 \) of the first kind [16]. Since \( P_{s-1}(-\cos \theta) \) diverges for \( \theta \to 0 \), \( M[c] \) is given by

\[
M[c] = CP_{s-1}(\cos \theta)
\]

(10)

where \( C \) is a constant. Eliminating \( C \) from eqn. (10) and its derivative with respect to \( \theta \), which is denoted by \( P' \), and letting \( \theta \) be \( \pi/2 \) yields

\[
P_{s-1}(0)(M[c])_{\theta=\pi/2} + P_{s-1}(0)(dM[c]/d\theta)_{\theta=\pi/2} = 0
\]

(11)

Expressing eqn. (11) as an integral representation by the use of eqn. (8) and inserting boundary condition (6) yields

\[
\int_0^1 c_{\theta'} x^{s-1} \, dx + \int_0^\infty c_{\theta'J} x^{s-1} \, dx = (P_{s-1}(0)/P'_{s-1}(0)) \int_0^1 c_{\theta'} x^{s-1} \, dx
\]

(12)

where \( c_{\theta'} \) and \( c_{\theta'J} \) represent \( c \) and \( \partial c / \partial \theta \) at the electrode surface \( (\theta = \pi/2) \), respectively.

The other relation of \( c_{\theta'} \) with \( c_{\theta'J} \) is the kinetic equation. Substituting eqn. (4) into eqn. (5), eliminating \( c_R \) by the use of eqn. (7), multiplying both sides of the resulting equation by \( x^{s-1} \) and integrating it from 0 to 1 yields

\[
\int_0^1 c_{\theta'} x^{s-1} \, dx = (c^*/s)(1 + e^{-x})^{-1} - (1/\lambda) \int_0^1 c_{\theta'J} x^{s-2} \, dx
\]

(13)

Here, \( \lambda \) is a kinetic parameter defined by

\[
\lambda = (a/D)(\bar{k} + \bar{k})
\]

(14)
and $\xi$ denotes the dimensionless potential given by

$$\xi = (nF/RT)(E - E^o'')$$

(15)

where $E$ and $E^o''$ are the electrode potential and the formal potential, respectively. Inserting eqn. (13) into eqn. (12) and replacing the Legendre functions by combinations of gamma functions through use of the relations [17]

$$P_{s-1}(0) = -2^{-1}e^{-3s/2} \sin[(s-1)\pi] \Gamma(s/2) \Gamma((1-s)/2)$$

(16)

$$P'_{s-1}(0) = -sP_s(0) = 2^{-1}e^{-3s/2} \sin(s\pi) \Gamma((s+1)/2) \Gamma(1-s/2)$$

(17)

we have

$$(c*/s)(1 + e^{-\xi})^{-1} - (1/\lambda) \int_0^1 c_{ij}^* x^{s-2} dx + \int_1^\infty c_{ij}^* x^{s-1} dx$$

$$= \left[ \Gamma(s/2) \Gamma((1-s)/2)/\{2 \Gamma((s+1)/2) \Gamma(1-s/2)\} \right] \int_0^1 c_{ij}^* x^{s-1} dx$$

(18)

Equation (18) contains two unknowns, $c_{ij}$ and $c_{ij}^*$ which are each defined in the different domains of $x$. Such a problem can be solved by the Wiener–Hopf technique [18]. Since this technique is associated with a discussion of the singularity of complex variable functions, it is a mathematical subject rather than an electrochemical one. Hence we have described the derivation in the Appendix.

According to the Appendix, the following dimensionless variable $f_k$:

$$f_k = \left\{ \left( \pi/2 \right)(1 + e^{-\xi})/c^* \right\} \int_0^1 c_{ij}^* x^{2k-2} dx$$

(19)

is expressed implicitly by

$$\left[ \Gamma(k-1/2) / \Gamma(k) \right] f_k + (4/\pi \lambda) \sum_{m=1}^{\infty} \left\{ \Gamma(m+1/2)/((m-1)!(2m-2k+1)) \right\} f_m$$

$$= \sqrt{\pi} / (2k - 1)$$

(20)

for $k = 1, 2, 3, \ldots$.

The total current, $I$, is given by

$$I = \int_0^2 2\pi \eta \, d\eta = 2\pi nFDa \int_0^1 c_{ij}^* \, dx = 4nFe^{-1} (1 + e^{-\xi})^{-1} f_1$$

(21)

When $\xi$ or $\lambda$ is so large that the current is completely controlled by diffusion, $f_1$ becomes unity because of dropping the second and succeeding terms from eqn. (20). Such a current is the diffusion-controlled limiting current, $I_d$, given by

$$I_d = 4nFe^* Da$$

(22)

The ratio of $I$ to $I_d$ becomes

$$I/I_d = (1 + e^{-\xi})^{-1} f_1$$

(23)

Thus it is $f_1$ that we aim to evaluate from eqn. (20). For a time-dependent diffusion problem with a parabolic type of differential equation [19], the problem can be
Fig. 1. Variations of $f_i$ or $I(1 + e^{-i})/I_d$ with $\lambda$ calculated analytically from eqns. (24) (for $N = 1$), (25) (for $N = 2$) and (26) (for $N = 3$) and computed numerically from eqn. (20) for $N = 60$ by the Gauss elimination method.

Fig. 2. Conventional log-plot for $\Lambda = (a) 30$, (b) 3, (c) 1, (d) 0.3, (e) 0.1, (f) 0.03 and (g) 0.01 at $a = 0.5$ and $25^\circ$C.

solved by evaluating successively an increment of a dependent variable corresponding to a small increment of time, as is exemplified by the digital simulation technique [20]. Since the steady-state diffusion equation treated here is, however, of the elliptic form, the problem reduces to solving a set of simultaneous equations. Solving simultaneous equations (20) having infinite dimension might provide $f_i$ or $I(1 + e^{-i})/I_d$ as a function of $\lambda$. Since it is difficult to solve the infinite-dimensional simultaneous equations directly, we replaced infinity in eqn. (20) by a finite number, $N$, and examined variations of the $f_i-\lambda$ curves with $N$. For example, analytical forms of $f_1$ for $N = 1, 2$ and 3 are given by

$$f_1(N=1) = \frac{\pi \lambda}{(\pi \lambda + 2)}$$

$$f_1(N=2) = \frac{\pi \lambda (\pi \lambda + (16/3))}{\{(\pi \lambda)^2 + 8\pi \lambda + 16\}}$$

$$f_1(N=3) = \frac{\pi \lambda \{9(\pi \lambda)^2 + 134.4\pi \lambda + 614.4\}}{\{9(\pi \lambda)^2 + 162(\pi \lambda)^2 + 1024\pi \lambda + 2048\}}$$

For $N \geq 4$, variations of $f_i$ with $\lambda$ were computed numerically by the Gauss elimination method. In Fig. 1, curves of $f_i$ or $I(1 + e^{-i})/I_d$ vs. $\lambda$ are shown for $N = 1, 2, 3$ and 60. With an increase in $N$, the curves approach monotonically a convergent one. Differences in $f_i$ for $N = 3, 10, 20, 40$ and 60 relative to $f_i$ for $N = 100$ are 17.6, 3.6, 1.6, 0.6 and 0.2%, respectively, when $\lambda = 1$. These differences decrease with an increase in $\lambda$. Therefore the solid curve in Fig. 1 can be regarded as a convergent one, i.e. an almost rigorous curve.
We attempted to examine the limiting behaviour of \( f_1 \) for \( \lambda \to 0 \). When the values of \( \lambda \) are so small that the current is controlled only by the electrode reaction rate, the current density is given by \( nF_c* \bar{k} \) with a uniform current distribution. Then the total current is expressed by

\[
I = nF_c* (\pi a^2) \bar{k} = nF_c* Da\lambda/(1 + e^{-1}) \quad (\lambda \to 0)
\]

Thus \( f_1 \) is given by

\[
f_1 = I(1 + e^{-1})/I_0 \sim (\pi/4) \lambda = 0.7854\lambda \quad (\lambda \to 0)
\]

The slope of \( f_1 \) against \( \lambda \) evaluated by the numerical solutions of eqn. (20) was 0.785 ± 0.002, indicating good agreement with eqn. (28).

**DISCUSSION**

According to the conventional classification for an electrode reaction, we classified the current-potential curves into reversible, quasi-reversible and totally irreversible cases on the assumption of the Butler–Volmer equation, i.e., \( \bar{k} = k^{\ast}\exp[(1 - \alpha)\xi] \) and \( \bar{k} = k^{\ast}\exp(-\alpha\xi) \), where \( k^{\ast} \) is the formal electrode reaction rate constant and \( \alpha \) is the cathodic transfer coefficient. It is convenient to introduce a potential-independent kinetic parameter defined by

\[
\Lambda = k^{\ast}\alpha/D\left[\lambda \exp((1 - \alpha)\xi)/(1 + e^{-1})\right]
\]

This is equivalent to a half \( \Lambda \) at \( E = E^{\ast} \). The characteristics of the current-potential curves are specified by a polarographic log-plot, i.e., a plot of \( \log[I/(I_0 - I)] \) vs. \( E \). In Fig. 2, the log-plots calculated from eqns. (20), (23) and (29) are shown for various values of \( \Lambda \) at \( \alpha = 0.5 \) and 25°C. For \( \Lambda \geq 10 \), the plot falls on a straight line of which the inverse slope is 59 mV and the intercept with the \( E \)-axis is at \( E^{\ast} \), indicating that the electrode reaction is reversible. On the contrary, for \( \Lambda \leq 0.2 \), the plot shifts to more positive potentials keeping the shape of a curve as \( \Lambda \) decreases. Hence \( \Lambda \leq 0.2 \) is a totally irreversible domain. In the intermediate domain, \( 0.2 < \Lambda < 10 \), the electrode reaction belongs to the quasi-reversible class.

Some examples at \( \alpha = 0.5 \), \( D = 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) and 25°C are shown below. When \( \Lambda = 5 \), at which the half-wave potential shifts ca. 10 mV from the formal potential, the values of \( k^{\ast} \) are 0.05, 0.5 and 5 cm s\(^{-1} \) at \( \alpha = 10^{-2} \), \( 10^{-3} \) and \( 10^{-4} \) mm, respectively. Thus the microdisk electrode has the possibility of measuring a rapid electrode reaction under the steady-state condition. For the totally irreversible domain, \( \Lambda < 0.2 \), the half-wave potential shifts by an amount equal to \(-[59/(1 - \alpha)] \times \log(\Lambda) \) or \(-118 \times \log(k^{\ast}\alpha/D) \) mV when \( \Lambda \) varies by one decade. If an electrode with a radius of one-tenth is employed, a wave which was overlapped with an ascending background current for decomposition of the supporting electrolytes or solvent may fortunately be discerned from the background current due to the potential shift of \(-118 \) mV.

In order to analyse the current-potential curve obtained experimentally, it is necessary to express the relation between \( f_1 \) and \( \lambda \) as a closed form. We plotted
\[ \ln(\lambda) \text{ against } \ln\left[ f_1/(1 - f_1) \right] \text{ and found that the plot fell on a straight line with a } \\
\text{slope of unity for } f_1 < 0.5 \text{ and on another line with a slope of } 1.11 \text{ for } f_1 > 0.5. \text{ Thus } \\
\lambda \text{ can be expressed approximately by} \\
\lambda = (4\pi)f_1(1 - f_1)^{-1.11} \quad (30) \]

This approximation contains errors that are less than 1.5%. Rearranging eqn. (30) leads to

\[ E = E^* - 2.3\left[ RT/(1 - \alpha)nF \right] \log\left[ \left( 1 - \frac{I/I_d}{(1 + e^{-\lambda})} \right)^{1.11}/(I/I_d) \right] \quad (31) \]

where

\[ E^* = E^{o*} - 2.3\left[ RT/(1 - \alpha)nF \right] \log\left[ \left( \frac{\pi/4}{k^{o*}a/D} \right) \right] \quad (32) \]

Equation (31) is similar to the polarographic log-plot. A plot of the logarithmic term in eqn. (31) against \( E \) falls on a straight line, whose slope provides \( (1 - \alpha)nF/RT \). The intersection of the line and the \( E \)-axis gives \( E^* \), from which \( k^{o*} \) can be evaluated provided that \( E^{o*} \) is known. This kind of modified log-plot has been reported for pulse voltammetric current–potential curves at a planar electrode [21], a microcylinder electrode [12] and a wall–jet electrode [22].

It is interesting to compare the current–potential curves at a microdisk electrode with those at a hemispherical electrode. The expression for the stationary current–potential curve at a hemispherical electrode is given by [6,23]

\[ \frac{I/I_d}{I_0} = (1 + e^{-\lambda})^{-1}\lambda_a/(\lambda_a + 1) \quad (33) \]

where

\[ \lambda_a = \frac{a_a}{D}(k + \bar{k}) \quad (34) \]

and \( a_a \) is the radius of the hemispherical electrode. The curve for eqn. (33) is almost the same as the curve for \( N = 3 \) in Fig. 1 when \( \lambda = \lambda_a \). For the same values of \( I(1 + e^{-\lambda})/I_d \) at a microdisk and a hemispherical electrode, the values of \( \lambda \) are larger than those of \( \lambda_a \). In other words, the current–potential curves at a microdisk electrode are more irreversible than those at a hemispherical electrode with the same radius, i.e. \( a = a_a \). When the area of the microdisk is the same as that of the hemispherical electrode, i.e. \( \pi a^2 = 2\pi a_a^2 \) or \( \lambda = \sqrt{2}\lambda_a \), the current–potential curves corresponding to \( I(1 + e^{-\lambda})/I_d < 0.36 \) are the same at both electrodes within 5% errors. This equivalence can be elucidated by the proportionality of the electrode reaction rate to the electrode area for the case of fully kinetically controlled electrode reactions.

**APPENDIX**

In this Appendix, eqn. (18) is solved with respect to \( c'_f \) by applying the Wiener–Hopf method [18]. Multiplying both sides of eqn. (18) by 

\[ 2\Gamma((1 - s)/2)\Gamma((1 - s)/2) \int_1^\infty c'_f x^{s-1} \, dx \]

\[ = \frac{\Gamma(s/2)}{\Gamma((s + 1)/2)} \int_0^1 c'_f x^{s-1} \, dx \quad (A1) \]
where
\[ R = 2c^*(1 + e^{-i})^{-1}\Gamma(1 - s/2)/(s\Gamma((1 - s)/2)) \]  
(A2)
\[ S = (2/\lambda)(\Gamma(1 - s/2)/(\Gamma((1 - s)/2))\int_0^1 c'_i x^{x-1} \, dx \]  
(A3)

The gamma function, \( \Gamma(z) \), is an integral function [24] for \( \text{Re}(z) > 0 \) while it has poles at negative integers of \( z \). Hence \( S \) has poles at \( s = 2, 4, 6, \ldots \). Since \( c_i \) is the order of \( x^{-1} \) as \( x \to 0 \), \( \int_0^\infty c'_i x^{x-1} \, dx \) in eqn. (A1) converges for \( \text{Re}(s) < 1 \). Thus the third term on the left-hand side of eqn. (A1) is regular for \( \text{Re}(s) < 1 \). The integral, \( \int_0^1 c'_i x^{x-1} \, dx \), is regular for \( \text{Re}(s) > 0 \) because \( c'_i \) becomes constant as \( x \to 0 \). Hence the term on the right-hand side of eqn. (A1) is regular for \( \text{Re}(s) > 0 \). On the other hand, eqns. (A2) and (A3) are not regular for \( \text{Re}(s) > 0 \) because of the presence of \( \Gamma(1 - s/2) \). We separate eqn. (A1) into terms which are regular for \( \text{Re}(s) < 1 \) and those which are regular for \( \text{Re}(s) > 0 \). Then eqn. (A1) is rewritten as
\[ (2\Gamma(1 - s/2)/(\Gamma((1 - s)/2))\int_0^\infty c'_i x^{x-1} \, dx = S_+ + R_- \]  
(A4)

with
\[ S_+ + S_- = S \]  
(A5)
\[ R_+ + R_- = R \]  
(A6)

where the terms on the right- and left-hand sides of eqn. (A4) are regular for \( \text{Re}(s) < 1 \) and for \( \text{Re}(s) > 0 \), respectively. When the Cauchy integral theorem [25] is applied to eqns. (A5) and (A6), \( R_+ \) and \( S_- \) are given by
\[ R_+ = \left\{ e^*(1 + e^{-i})^{-1}/\pi i \right\} \int_{L_2} \Gamma(1 - z/2)/(z\Gamma((1 - z)/2)(z - s)) \, dz \]  
(A7)
\[ S_- = (1/\pi i)\int_{L_1} \Gamma(1 - z/2)\int_0^1 c'_i x^{x-2} \, dx/(\lambda\Gamma((1 - z)/2)(z - s)) \, dz \]  
(A8)

respectively, where \( L_1 \) and \( L_2 \) are integral contours parallel to the imaginary axis, as shown in Fig. A1. Since the integrand in eqn. (A7) is \( O(z^{-3/2}) \) for \( z \to -\infty \), \( L_2 \) can be shifted to the left keeping the residue at \( z = 0 \). Then \( R_+ \) is given by
\[ R_+ = 2c^*/[\sqrt{\pi s}(1 + e^{-i})] \]  
(A9)

The integrand in eqn. (A8) has poles at \( z = 2m \) \( (m = 1, 2, 3, \ldots) \). Shifting \( L_1 \) to the right and calculating the residues at \( z = 2m \) yields
\[ S_- = -4/\pi \lambda \sum_{m=1}^{\infty} \left\{ \Gamma(m + 1/2)/[(m - 1)!(2m - s)] \right\} \int_0^1 c'_i x^{2m-2} \, dx \]  
(A10)

where the following relation has been employed:
\[ \left\{ \Gamma(1 - z/2)/(\Gamma((1 - z)/2)) \right\}_{z=2m} = (2/\pi)\Gamma(m + 1/2)/(m - 1)! \]  
(A11)
From eqns. (A3), (A5) and (A10), it follows that

$$S_s = \left[ 2 \Gamma((1-s)/2)/(\lambda \Gamma((1-s)/2)) \right] \int_0^1 \frac{c_i^* x^{s-2}}{\sqrt{1 - x^2}} \, dx$$

$$+ \left( \frac{4}{\pi} \lambda x \right) \sum_{m=1}^{\infty} \left[ \frac{\Gamma(m+1/2)}{(m-1)!2m-1} \right] \int_0^1 \frac{c_i^* x^{2m-2}}{\sqrt{1 - x^2}} \, dx$$

$$= \frac{2c^* \left[ \sqrt{\pi} (2k-1) \right]}{\Gamma(k-1)}$$

$$- \left( \frac{4}{\pi} \lambda x \right) \sum_{m=1}^{\infty} \left[ \frac{\Gamma(m+1/2)}{(m-1)!2m+1} \right] \int_0^1 \frac{c_i^* x^{2m-2}}{\sqrt{1 - x^2}} \, dx$$

because $1/\Gamma(1-s/2)$ vanishes at $s = 2k - 1$. Multiplying both sides of eqn. (A13) by $(\pi/2)(1 + e^{-1})/c^*$ results in eqn. (20).

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