Wall-Jet Electrode Linear Sweep Voltammetry

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Theory is presented which predicts the linear sweep voltammetry behavior at the wall-jet electrode for a reversible couple. The scan rate and electrode geometry dependences are established, and hence the requirements for the measurement of true "steady state" hydrodynamic voltammograms are defined. Theory is found to be in good agreement with experiments conducted on the oxidation of the ferrocyanide anion in aqueous solution.

Introduction

The wall-jet electrode (WJE) is a well-characterized hydrodynamic electrode in which the flow is due to a (submerged) fluid jet which strikes a planar electrode at right angles and spreads out radially over that surface, the fluid outside the jet being at rest. The mass transport experienced by the electrode is dependent on its size relative to the impinging jet, and two extremes are recognized. The term "wall jet" is understood to pertain to "wall-tube" geometry. The description "impinging jet" finds occasional usage and is recognized. The term "wall jet" is understood to pertain to "wall-tube" geometry. The description "impinging jet" finds occasional usage and is recognized. The term "wall jet" is understood to pertain to "wall-tube" geometry.

WJEs are finding increasing use in analysis, e.g. ref 11, primarily due to the advantages of on-line detection and fast sample throughput. Moreover, in the context of the mechanistic investigation of electrode processes, the wall-jet geometry has been shown to possess considerable advantages most notably due to its highly nonuniform primary current distribution. Further merits arise first from the flow-through nature of the device which means that the constant supply of fresh solution prevents the buildup of intermediates and products of the electrode reaction which might otherwise alter the course of the electrode process (chemical and electrical conditions) and second from the high sensitivity of the wall jet (as compared to, say, the rotating disc electrode) to variations in the rate of mass transport. The use of wall-jet electrodes in flow analysis has been recently reviewed. In this paper we establish theory which predicts the current/voltage response resulting from a potential sweep, at the wall-jet electrode. The problem is of interest since it effectively defines the "response time" of the electrode and, additionally, such simulations can define the range of scan rates for which an effective steady-state current/voltage curve can be recorded. Experiments are reported which quantitatively confirm the theoretical predictions.

Theory

We examine a simple reversible one electron transfer

\[ A + e^- \rightarrow B \]

and consider the case where the electrode potential is swept from a potential at which no current flows to one that corresponds to the transport limited reduction/oxidation of species A. The convective diffusion equation describing the concentration of A in time (t) and space is

\[ \frac{\partial [A]}{\partial t} = D \frac{\partial^2 [A]}{\partial z^2} - v_r \frac{\partial [A]}{\partial r} - v_z \frac{\partial [A]}{\partial z} \]  

(1)

where D is the diffusion coefficient of A, \( v_r \) is the radial solution velocity (r direction), and \( v_z \) is the velocity in the direction normal to the electrode surface (z direction). Expressions for \( v_r \) and \( v_z \) for wall-jet flow are given in ref 12. Note that in writing eq 1 radial diffusion has been neglected: the basis of this approximation has been developed elsewhere. We also assume the presence of sufficient supporting electrolyte that migration effects are negligible.

The electrode potential \( E_i \) is swept linearly with time at a rate \( v \ V \ s^{-1} \) (where \( v \) is either positive or negative) through the reduction/oxidation wave of A, starting from an initial potential \( E_1 \).

\[ E_i = E_1 - vt \]

The relevant boundary conditions to the problem, as defined above, may be formulated as

\[ \tau = 0, \ z \geq 0, \ 0 < r < R \ [A] = [A]_{bulk} \ [B] = 0 \]  

(2)

\[ \tau > 0, \ z = 0, \ 0 < r < R \ \frac{\partial [A]}{\partial z} = -\frac{\partial [B]}{\partial z} \]  

(3)

\[ \tau > 0, \ z = 0, \ 0 < r < R \ [A] = [A]_{bulk} \ [B] = 0 \]  

(4)

all \( \tau, \ z \rightarrow \infty, \ 0 < r < R \ [A] = [A]_{bulk} \ [B] = 0 \]  

(5)

where \([A]_{bulk}\) is the bulk concentration of A,

\[ \theta = \exp \left[ \left( \frac{e}{k_BT} \right) (E_1 - E^0) \right] \]  

(6)

\[ \tau = \left( \frac{A \sigma D}{R^{1/4} \kappa} \right)^{1/2} \]  

(7)

\[ \sigma = \left( \frac{e \nu}{k_BT} \right) \left( \frac{R^{1/4} \kappa}{A^2 \sigma} \right) \]  

(8)
A = R^{3/2}(9C/8D)^{1/3}, C = [5|M|]/216e, M = k_e V^2/2π^2 a^2, e is the electronic charge, k_e is Boltzmann's constant (e/k_BT) = 38.9 V^2 K^{-1}, v is the kinematic viscosity of the solution, and R is the radius of the electrode. The reason for defining r (normalized time) and \( \sigma \) (dimensionless scan rate) as given is explained in the Appendix. In eq 3 we have made the approximation that A and B have identical diffusion coefficients.

In order to solve eq 1 we approximate the derivatives by their finite-difference equivalents. The r-z plane is thus divided up into a two-dimensional grid such that increments in the r direction are \( \Delta r \) and in the z direction \( \Delta z \). We use the subscripts \( k \) and \( j \) to denote distances in the radial and normal directions:

\[
(radial distance)_k = k \Delta r
\]

\[
(j-1) matrix equation:
\]

\[
\begin{pmatrix}
\mathbf{d}
\end{pmatrix} = [\mathbf{T}]\{\mathbf{u}\}
\]

The matrix elements are given by

\[
d_i = [a_{i,j}] + \lambda_i^{r/s} + \frac{\lambda^\theta \exp(-\sigma(t+1)\Delta r)}{1 + \theta \exp(-\sigma(t+1)\Delta r)}
\]

\[
d_j = [a_{i,j}] + \lambda_i^r, j = 2, 3, ..., J - 2
\]

\[
d_{j+1} = [a_{j+1,j}] + \lambda_j^{r/s} + \lambda_i^{r/s} + (\lambda^r - \lambda_j^r)
\]

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\]

\[
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\]

for all \( k \) and \( j \)

\[
a = -\lambda^r
\]

\[
b_j = 2\lambda^r + \lambda_j^r - \lambda_i^r + 1
\]

\[
c_j = -(\lambda^r - \lambda_j^r)
\]

Equation 20 is analogous to that arising in the procedure we have previously described for the solution of steady-state problems at the WJE and we have adopted here the same notation as that paper. The method of solution below follows the general strategy developed in ref 12. A brief summary is given in the next paragraph.

Notice that the matrix equation (20) shows how the concentrations throughout the cell at time \( t + 1 \) \( \Delta t \) may be calculated if we know those at time \( t \Delta t \). To do this we have to find the set of vectors \( \{\mathbf{u}\} \); each \( k \) value has its own vector \( \{\mathbf{u}\}_k \). The matrix \( [\mathbf{T}] \) being of triadiagonal form allows us to use the Thomas algorithm to give \( \{\mathbf{u}\}_k \) from \( \{\mathbf{d}\}_k \). The boundary condition (2) supplies the vector \( \{\mathbf{d}\}_0 \) from which \( \{\mathbf{u}\}_0 \) is calculated. Then \( \{\mathbf{d}\}_J = \{\mathbf{u}\}_J \), so \( \{\mathbf{u}\}_J \) is calculated from \( \{\mathbf{d}\}_J \), and so on until \( \{\mathbf{u}\}_J \) is obtained. The calculation is then repeated. Note that an expanding grid, which increases in size in proportion to the diffusion layer thickness, is used on account of the electrode being very non-uniformly accessible so as to give accurate results. The protocol for the implementation of this is exactly as in the solution of steady-state WJE problems.

In this way the concentration profile of \( A \) within the WJE may be calculated as a function of time. The current at the electrode may thus be evaluated at any instant from

\[
I = \sum_{k=1}^{J} \int_{-1}^{1} \{A\}_k \{\mathbf{u}\}_k (d\mathbf{x}) \frac{k(\Delta z)^2}{\Delta z}
\]

and thus the form of the current-voltage curve established.

Theoretical Results and Discussion

Using the theory outlined above, potential sweep transients were computed (using a Sun Sparc workstation); copies of the FORTRAN program are available on request from the authors. Convergence was examined by varying \( J, K, \) and \( \Delta t \) values. For a typical electrode of geometry of radius \( R = 0.1637 \) cm, cell constant \( k_e = 0.9 \), and jet diameter \( a = 0.0345 \) cm, for volume solution flow rates in the range \( 0.1 \text{ cm}^3 \text{s}^{-1} \leq V/\text{cm}^3 \text{s}^{-1} \leq 0.001 \) s were found to give satisfactory and rapid convergence (to 3 significant figures) with typical aqueous solution parameters (\( \sigma = 0.0089 \) cm s\(^{-1} \); \( 1 \times 10^{-8} < D/\text{cm}^2 \text{s}^{-1} < 1 \times 10^{-8} \)).

Initial computations were undertaken to test the predictions of the numerical approach at very slow scan rates and compared to the behavior computed directly for steady-state conditions from the appropriate boundary conditions. Figure 1 shows the current (normalized to the steady-state limiting current) response of a steady-state calculation for a reduction wave using a flow rate
of \( V_f = 0.1 \text{ cm}^3 \text{s}^{-1} \), for the electrode geometry specified earlier, with a scan rate of 0.001 V s\(^{-1} \). A diffusion coefficient of \( 5 \times 10^{-4} \text{ cm}^2 \text{s}^{-1} \) was assumed. As can be seen, excellent agreement is observed, supporting our general theoretical approach.

Having established the validity of the method, we then applied the approach to predict the response of a current/voltage scan under increasingly faster scan rates for a reduction process at an electrode with the wall-jet geometry detailed above. Figure 2 shows a typical plot for a flow rate of \( 0.95 \times 10^{-2} \text{ cm}^3 \text{s}^{-1} \), with the varying scan rates detailed. The following parameters were employed in the computations: \( D = 6.5 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \), \([A]_{\text{bulk}} = 2 \times 10^6 \text{ mol cm}^{-3} \). As can be seen, with increasing scan rate finite diffusion in solution causes the concentration profile of \( A \) to "lag behind" that of the steady-state response and a peak appears in the current/voltage curve. At the same time, the wave becomes shifted anodically from that observed under steady-state conditions. As indicated in the Appendix voltammograms such as those in Figure 2 are, if the current is normalized to the steady-state limiting current (as on the right hand \( y \) axis of Figure 2), simply a unique function of \( \sigma \) and \( \theta \). Thus, the four curves shown are general in that they relate to any wall-jet system with the same \( \sigma \) values as specified in the figure legend and to assist the reader in the application of our analysis to his experiments we present numerically the results plotted in Figure 2 in Table I.

Next, the simulations were employed to establish the criteria for the experimental measurement of steady-state voltammograms.
slow scan rate at a particular flow rate for the determination of quantitative agreement. The requirement of using a sufficiently defined.

Appendix

Consider eq 1 and note that with the explicit equations for $v_f$, $v_r$, given in ref 12 the definition of the following dimensionless variables

\[ \xi = \frac{r}{R}^{9/8} \]  
\[ \chi = \frac{Az}{r^{7/8}} \]  

and that of $\tau$ (eq 7) leads to the following normalized equation:

\[ \xi^{14/9} \frac{\delta[A]}{\delta \tau} = \frac{\delta^2[A]}{\delta \xi^2} \chi \frac{\delta[A]}{\delta \xi} \]  

Then on considering eq A3 together with the boundary conditions (2), (3), (4), and (5) it follows that the current transient when normalized to the steady-state limiting current, $i_{\text{lim}}$, and plotted against $\theta$ (or $\ln \theta$, as in Figure 3) should be a unique function of the parameter $\sigma$.

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References and Notes

Permanganate Oscillators with Keto Dicarboxylic Acids

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A new group of chemical oscillators is reported based on the reduction of MnO₄⁻ by ketomalonic, oxalacetic or α-ketoglutaric acid in a continuously stirred tank reactor (CSTR). Conditions are described under which a kinetic bistability between an oxidized steady state and a reduced steady state can be observed and under which sustained oscillations occur.

Introduction

The recently discovered permanganate oscillators⁴⁻⁷ constitute a new family of chemical oscillators based on transition-metal chemistry. All members of the family consist of permanganate as the oxidant, a reducing substrate (H₂O₂, ninhydrin, S₂O₅²⁻, S²⁻, SO₄²⁻, MnO₂, NH₂OH, AsO₄³⁻, thiocyanate, thiourea, L-ascorbic acid), and phosphate ion to stabilize the colloidal form of MnO₂. A manganese oscillator based on the oxidation of Mn²⁺ ions by periodate in a continuously stirred tank reactor (CSTR) revealed only very recently also belongs to this family of transition-metal oscillators and might represent a new branch of this family.⁸⁹

Since the mechanism of permanganate oscillators is not understood so far, further studies are needed on both branches of transition-metal oscillators.

Therefore, we tried to find even more permanganate oscillators, and the following study might start a new subgroup. It deals with permanganate oscillators based on the oxidation of keto dicarboxylic acids, i.e. ketomalonic (a), oxalacetic (b), and α-ketoglutaric acids (c), by MnO₄⁻. We believe that the study of this subgroup should bring a new insight into the mechanism of permanganate-based oscillators.

Experimental Section

Materials. Stock solutions of the components besides ketomalonic acid were prepared from commercially available KMnO₄ (p.a., Lachema, Brno, Czechoslovakia), Na₂PO₄ (p.a., Lachema), α-ketoglutaric acid (p.a., Loba, Switzerland), and oxalacetic acid (p.a., Reanal, Budapest, Hungary). Ketomalonic acid was prepared by oxidation of saccharose by the procedure of Chattaway and Harris⁰ and was isolated as a bisodium salt that was used for the preparation of stock solutions. A stock solution of KMnO₄ was prepared by the procedure of Kolthoff, Belcher, Stenger, and Matsuyama.¹ The concentration of H₃PO₄ was checked alkalimetrically. Dilutions were made with bidistilled water.

Apparatus. We used glass CSTRs (27.6 mL) with a mantle connected to a TB 150 ultrathermostat (Medingen) and monitored the oscillatory reaction voltamperometrically (Polargraph LP 7, Laboratorní Přístroje, Prague, Czechoslovakia) by means of a static platinum electrode in a flowing, well-stirred solution. The reaction systems were stirred by a mixing propeller driven by a motor connected to a stabilized voltage supply. Our reactors were equipped with propellers with a stirring frequency of 2250 min⁻¹.

In a closed system the reaction was followed spectrophotometrically using a spectrophotometer (SPECORD M 40 Zeiss, Jena, Germany) with a thermostated 1-cm quartz cuvette with a magnetic stirrer.

The experimental procedure was the same as that in earlier work.¹⁻³,⁶,⁹