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Authors

Smyrl, William H.
Newman, John.

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William H. Smyrl and John Newman

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Limiting Current on a Rotating Disk with Radial Diffusion

William H. Smyrl
Boeing Scientific Research Laboratories,
Seattle, Washington

and

John Newman
Inorganic Materials Research Division,
Lawrence Radiation Laboratory, and
Department of Chemical Engineering,
University of California, Berkeley

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Abstract

The edge effect on limiting currents due to radial diffusion is calculated by a singular-perturbation technique for large Schmidt numbers, and a correction to the Levich formula is thereby obtained.

Key words: Current distribution.

Radial diffusion, which is usually ignored, is included here in an analysis of the limiting current distribution on a rotating disk electrode. This small edge effect has created a controversy over whether it can cancel the correction for a finite Schmidt number. The results of this analysis are also applicable to the trailing edge of other electrodes.

Steady transfer of a solute species obeys the equation of convective diffusion

$$\underline{v} \cdot \nabla c_i = D_i \nabla^2 c_i \quad , \quad (1)$$

if, for one reason or another, electric migration of this species can be ignored. This condition applies to a neutral solute and to a minor ionic solute in a solution with an excess of inert, supporting electrolyte. The equation also applies to a solution of a single electrolyte where the migration terms can be eliminated by means of the electroneutrality condition.^{1,2,3} In this case, D_i is replaced by the diffusion coefficient of the electrolyte.

The appropriate form of this equation for the diffusion layer on a rotating disk, including radial diffusion, is

$$A y \left(r \frac{\partial c_i}{\partial r} - y \frac{\partial c_i}{\partial y} \right) = D_i \left[\frac{\partial^2 c_i}{\partial y^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) \right] \quad , \quad (2)$$

where $A = a\Omega\sqrt{\Omega/\nu}$. For large values of the Schmidt number $Sc = \nu/D_i$, as encountered in electrolytic solutions, the diffusion layer is much thinner than the hydrodynamic boundary layer, and it is appropriate to

approximate the normal and radial components v_y and v_r of the velocity by the first terms of their power-series expansions in the normal distance y from the disk. This introduces the rotation speed Ω , the kinematic viscosity ν , and the dimensionless constant a from the solution of the hydrodynamic problem,^{4,5,6} where it is assumed that the mass-transfer process does not influence the hydrodynamics.

The radial diffusion term is usually neglected on the basis of the thinness of the diffusion layer compared to the radius of the electrode. At the limiting current, this "diffusion-layer solution" is

$$c_i = \frac{c_\infty}{\Gamma(4/3)} \int_0^\zeta e^{-x^3} dx, \quad (3)$$

where

$$\zeta = y(av/3D_i)^{1/3}(\Omega/\nu)^{1/2}, \quad (4)$$

and gives a uniform current density on the disk electrode.

We wish to consider the effect of radial diffusion on the limiting current density distribution at the downstream end of a diffusion layer, still at high Schmidt numbers. The rotating disk electrode is assumed to be embedded in an insulating plane. The region where radial diffusion is important is very small, and the problem can be treated by a singular-perturbation method similar to that used to treat the breakdown of the diffusion-layer method at the rear of a bluff body^{7,8} and at the upstream end of an electrode embedded in an insulator.⁹

In the region of radial diffusion near the edge of the disk,
use stretched coördinates

$$X = (r-r_o)(Ar_o/2D_i)^{1/2} \text{ and } Y = y(Ar_o/2D_i)^{1/2}, \quad (5)$$

so that equation 2 becomes

$$\frac{2r_o}{r_o} Y \frac{\partial c_i}{\partial X} - 2Y^2 \left(\frac{2D_i}{Ar_o^3} \right)^{1/2} \frac{\partial c_i}{\partial Y} = \frac{\partial^2 c_i}{\partial X^2} + \frac{\partial^2 c_i}{\partial Y^2} + \frac{r_o}{r} \left(\frac{2D_i}{Ar_o^3} \right)^{1/2} \frac{\partial c_i}{\partial X}. \quad (6)$$

Neglecting terms of order $(2D_i/Ar_o^3)^{1/2}$, we obtain

$$2Y \frac{\partial c_i}{\partial X} = \frac{\partial^2 c_i}{\partial X^2} + \frac{\partial^2 c_i}{\partial Y^2}. \quad (7)$$

Since $\zeta = Y(8D_i/9Ar_o^3)^{1/6}$, ζ is small in this region, and the concentration must match the diffusion-layer solution for small values of ζ . In other words, the region of radial diffusion is embedded in the diffusion layer and

$$c_i \rightarrow \frac{c_\infty \zeta}{\Gamma(4/3)} = \frac{c_\infty Y}{\Gamma(4/3)} \left(\frac{8D_i}{9Ar_o^3} \right)^{1/6} \text{ as } X \rightarrow -\infty \text{ or } Y \rightarrow \infty. \quad (8)$$

Consequently, let us define Θ as

$$\Theta = \Gamma(4/3) \frac{c_i}{c_\infty} \left(\frac{9Ar_o^3}{8D_i} \right)^{1/6}. \quad (9)$$

Then, Θ satisfies the differential equation

$$2Y \frac{\partial \theta}{\partial X} = \frac{\partial^2 \theta}{\partial X^2} + \frac{\partial^2 \theta}{\partial Y^2} \quad (10)$$

and the boundary conditions

$$\left. \begin{array}{l} 1. \quad \theta \rightarrow Y \text{ as } Y \rightarrow \infty \\ 2. \quad \theta \rightarrow Y \text{ as } X \rightarrow -\infty \\ 3. \quad \theta = 0 \text{ at } Y = 0, X < 0 \\ 4. \quad \partial \theta / \partial Y = 0 \text{ at } Y = 0, X > 0 \\ 5. \quad \partial^2 \theta / \partial X^2 \text{ becomes negligible as } X \rightarrow \infty \end{array} \right\} \quad (11)$$

The coördinate stretching makes the radial and normal diffusion terms appear to be of the same magnitude in equation 10. At the same time, the normal convection term disappears, and the radial convection term assumes a simpler form. From the form of the problem for θ one perceives that by appropriate stretching of distances and concentration the problem for the effect of streamwise diffusion at high Schmidt numbers at the downstream end of any diffusion layer, where the electrode is embedded in an insulating surface, can be reduced to the same problem, and the results obtained here will also apply to those cases.

The ratio of the size of the region where radial diffusion is important to the thickness of the diffusion layer is $(8D_i/9Ar_o^3)^{1/6}$ or of the order of the square root of the ratio of the diffusion layer thickness to the electrode radius. Thus, the size of the region where radial diffusion is important is much smaller than the diffusion-layer thickness, whereas one might at first have assumed them to be of the same order. For a rotation speed of 300 rpm ($\Omega = 31.416$ radian/sec),

$r_0 = 0.25$ cm, $v = 0.01$ cm²/sec, and $D_i = 10^{-5}$ cm²/sec, the value of this ratio is $(8D_i/9Ar_0^3)^{1/6} = 0.093$.

The fifth boundary condition means that radial diffusion again becomes negligible far downstream in the diffusion layer on the insulator. This condition can be stated more explicitly by obtaining the asymptotic solution for large X . Seek a similarity solution of equation 10 with the term $\partial^2\theta/\partial X^2$ neglected and subject to the boundary conditions 1 and 4.

$$\theta \rightarrow (9X/2)^{1/3} f(\xi) \text{ as } X \rightarrow \infty, \quad (12)$$

where

$$\xi = Y(2/9X)^{1/3}. \quad (13)$$

The function f is found to satisfy the ordinary differential equation

$$f'' + 3\xi^2 f' - 3\xi f = 0 \quad (14)$$

with the boundary conditions

$$f' = 0 \text{ at } \xi = 0, \quad f \rightarrow \xi \text{ as } \xi \rightarrow \infty, \quad (15)$$

and the solution

$$f = \xi + \frac{e^{-\xi^3}}{\Gamma(2/3)} - \frac{3\xi}{\Gamma(2/3)} \int_{\xi}^{\infty} x e^{-x^3} dx. \quad (16)$$

To effect a numerical solution of the problem for θ , we used parabolic coördinates in order to avoid infinite derivatives at the

origin. The mass-transfer rate near the edge of the disk is shown in figure 1. Here the normal derivative of Θ is multiplied by $\sqrt{-X}$ in order to give an accurate representation of the results; the limiting current density becomes infinite near the edge of the disk like $\partial\Theta/\partial Y = 0.601/\sqrt{-X}$ at $Y = 0$. The recovery of the concentration on the insulating surface downstream is shown in figure 2; the diffusion-layer solution is given by

$$\Theta_0 = \Theta(X, 0) = (9X/2)^{1/3} f(0) = (9X/2)^{1/3} / \Gamma(2/3) \quad (17)$$

The recovery of the surface concentration is hindered by the back diffusion to the disk and is not so rapid as would be predicted by the diffusion-layer solution in the absence of radial diffusion. This back diffusion results in the infinite current density at the edge of the disk electrode. (This diffusion layer solution for the surface concentration beyond the disk electrode can also be obtained from equation 13 or 14 of reference 10 by letting r approach r_0 .)

The mass-transfer rate shown in figure 1 approaches the diffusion-layer solution rather rapidly for large values of $\sqrt{-X}$ in contrast to the behavior depicted in figure 2 for the recovery of the surface concentration for large values of $\sqrt{X}$. This is because effects are propagated more easily downstream than upstream in a diffusion layer.

The correction to Levich's formula for the limiting current on a rotating disk electrode can now be obtained.

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Figure 1. Mass-transfer rate near the edge of the disk when radial diffusion is considered.

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Figure 2. Recovery of the surface concentration downstream of the disk.

$$\frac{I_{\text{lim}}}{I_{\text{Levich}}} = \frac{1}{\pi r_o^2} \int_0^{r_o} \frac{\partial \theta}{\partial Y} \Big|_{Y=0} 2\pi r dr = 1 + B/Sc^{1/2} Re^{3/4}, \quad (18)$$

where $Re = r_o^2 \Omega/\nu$ and

$$B = 4\sqrt{2/a} \int_0^\infty \sqrt{-X} \left[\frac{\partial \theta}{\partial Y} \Big|_{Y=0} - 1 \right] d\sqrt{-X} = 1.9193. \quad (19)$$

The value of B is obtained from the results plotted in figure 1.

For the same values of the parameters as used in the last example, the correction to Levich's formula amounts to only 0.116 percent. For this system, the Schmidt number correction^{11,12} would be -3.1 percent, and the two effects cannot cancel. This comparison is of some interest since Levich¹³ has discussed data which purport to support his formula rather than the Schmidt number correction. These data have since been repudiated.¹⁴

Figure 3 indicates how a plot of limiting current versus square root of rotation speed might be expected to look. Levich's solution plots as a straight line; equation 18 is represented by a solid curve. Levich's result is the asymptotic solution for large values of $ScRe^{3/2}$. Equation 18 gives the first correction, again valid for large values of $ScRe^{3/2}$. Additional correction terms would become necessary for smaller values of $ScRe^{3/2}$. The dotted curve represents a guess at the true solution; the intercept, $4/\pi$, is known for this curve, but not its initial slope.

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Figure 3. Limiting current versus the square root of rotation speed (in dimensionless form) in the absence of free convection.

Conclusions

A singular-perturbation procedure allows treatment of the edge effect for the rotating disk for large values of $ScRe^{3/2}$. A large value of the Schmidt number was also assumed. The current density at the edge of the disk becomes infinite when radial diffusion is taken into account, and the recovery of the surface concentration is correspondingly less rapid than the diffusion-layer solution predicts. These results allow one to obtain a correction to the classical formula of Levich for the limiting current to a rotating disk electrode. The region near the edge of the disk where radial diffusion is important lies well within the diffusion layer for large values of $ScRe^{3/2}$.

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Nomenclature

$a = 0.51023$.

$A = a\Omega\sqrt{\Omega/\nu}$

B - see equation 19.

c_i - concentration of the species of interest (mole/cm³).

c_∞ - concentration of the species of interest outside the diffusion layer (mole/cm³).

D_i - diffusion coefficient of the species of interest (cm²/sec).

f - see equation 12.

I - total current to disk electrode (A).

N_{avg} - average flux to disk electrode (mole/cm²-sec).

r - radial distance from the axis of the disk (cm).

r_0 - radius of disk electrode (cm).

$Re = r_0^2 \Omega / \nu$, the Reynolds number.

$Sc = \nu / D_i$, the Schmidt number.

$\underline{v}$ - fluid velocity (cm/sec).

v_r, v_y - radial and normal components of the velocity (cm/sec).

X - dimensionless radial distance for the region of radial diffusion.

y - normal distance from the disk surface (cm).

Y - dimensionless normal distance for the region of radial diffusion.

Γ - gamma function.

ζ - dimensionless normal distance for the diffusion layer.

Θ - dimensionless concentration appropriate to the region of radial diffusion.

ν - kinematic viscosity (cm²/sec).

$\xi = Y(2/9X)^{1/3}$.

Ω - rotation speed (radian/sec).

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