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CURRENT DISTRIBUTION ON A ROTATING DISK BELOW THE LIMITING CURRENT

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CURRENT DISTRIBUTION ON A ROTATING DISK  
BELOW THE LIMITING CURRENT

John Newman

April, 1966

Current Distribution on a Rotating Disk  
below the Limiting Current

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April, 1966

Abstract

The uniform current density on a rotating disk electrode at the limiting current is not achieved at lower currents because the edge of the disk is more accessible than the center as a result of the ohmic potential drop in the solution. The current distribution is calculated for well-stirred solutions and also for lower rotation speeds where surface overpotential, concentration overpotential, and ohmic drop are all significant. The current density at the center can vary between 50 and 100 per cent of the average current density, and the ohmic potential drop to the center of the disk is 27.3 per cent greater for the uniform current than for the primary current distribution.

## Introduction

The rotating disk electrode is popular for studying both diffusion in electrolytic solutions and the kinetics of moderately fast electrode reactions because the hydrodynamics<sup>1,2</sup> and the mass-transfer characteristics<sup>3</sup> are well understood and because the current density on the disk electrode is supposed to be uniform. However, the current distribution is uniform only at the limiting current where the concentration of the reactant is zero at the electrode surface. In the other extreme, the primary current distribution<sup>7</sup>, applicable in the absence of concentration overpotential and surface overpotential, shows an infinite current density at the edge and a value equal to half the average current density at the center of the disk.

It is of interest to assess the degree of nonuniformity of the current distribution due to the nonuniform ohmic potential drop. Newman<sup>4</sup> has indicated how to treat current distribution in cells where the potential distribution in the bulk of the solution and the concentration distribution in the diffusion layer must be calculated simultaneously. These ideas are applied in the present paper to the specific case of a rotating disk electrode. It is assumed that the disk electrode, of finite size, is embedded in an infinite, insulating ~~place~~ <sup>plane</sup> and that the walls of the cell and the counter electrode are removed to infinity. Dilute-solution theory, with constant diffusion coefficients, mobilities, and activity coefficients, is assumed to be applicable. For simplicity, only two cases are treated, metal deposition from a single-salt solution and electrode reactions with an excess of supporting electrolyte, in which case the transference number of the reactant is zero.

Those readers who wish to skip the mathematical development can go directly to the section on results, keeping in mind that the current

distribution depends on several crucial parameters defined in equations (21), (27), (30), and (37).

#### Concentration Profile in the Diffusion Layer

The concentrations differ from their bulk values only in a thin region near the electrode surface, and in this region the fluid velocity can be approximated by<sup>1,2,3,4</sup>

$$v_r = a r y \Omega \sqrt{\Omega/\nu} \quad \text{and} \quad v_y = - a y^2 \Omega \sqrt{\Omega/\nu}, \quad (1)$$

where  $a = 0.51023$ . This approximation, which is valid for large values of the Schmidt number  $Sc = \nu/D$ , can be expected<sup>5,6</sup> to cause an error of about 3% in calculated rates of mass transfer when  $Sc = 1000$ . The concentration is to be determined from the equation

$$v_r \frac{\partial c}{\partial r} + v_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}, \quad (2)$$

or

$$a y \Omega \sqrt{\Omega/\nu} \left[ r \frac{\partial c}{\partial r} - y \frac{\partial c}{\partial y} \right] = D \frac{\partial^2 c}{\partial y^2}, \quad (3)$$

where only the dominant diffusion term  $D \partial^2 c / \partial y^2$  needs to be included on the right because of the thinness of the diffusion layer. This equation applies to diffusion of a single salt if  $D$  denotes the diffusion coefficient of the salt. The equation also applies to a minor ionic component in a solution with supporting electrolyte where ionic migration can be neglected. Then  $D$  denotes the ionic diffusion coefficient.

Since the diffusion layer is thin, it is appropriate to replace the normal distance  $y$  by the variable

$$\zeta = y (a\nu/3D)^{1/3} \sqrt{\Omega/\nu}. \quad (4)$$

In terms of this variable the concentration in the diffusion layer can be

expressed as a series solution

$$c = c_{\infty} \left[ 1 + \sum_{m=0}^{\infty} A_m (r/r_0)^{2m} \theta_m(\zeta) \right]. \quad (5)$$

This is a power series in  $r$ , but only even powers are included since the concentration must be an even function of  $r$ .

The functions  $\theta_m(\zeta)$  satisfy the differential equation

$$\theta_m'' + 3\zeta^2 \theta_m' - 6m\zeta \theta_m = 0, \quad (6)$$

which can be obtained by substituting the series (5) into equation (3).

The boundary conditions are

$$\theta_m = 1 \text{ at } \zeta = 0 \text{ and } \theta_m = 0 \text{ at } \zeta = \infty.$$

In this way the concentration given by equation (5) equals the bulk value  $c_{\infty}$  far from the disk, and the concentration at the surface of the electrode is

$$c_0 = c_{\infty} \left[ 1 + \sum_{m=0}^{\infty} A_m (r/r_0)^{2m} \right]. \quad (7)$$

The coefficients  $A_m$  are yet to be determined.

The normal current density  $i$  at the electrode surface is related to the derivative of the concentration

$$\frac{i}{nF} = \frac{D}{1-t} \frac{\partial c}{\partial y} \Big|_{y=0} = \frac{Dc_{\infty}}{1-t} \left( \frac{av}{3D} \right)^{1/3} \sqrt{\frac{\Omega}{v}} \sum_{m=0}^{\infty} A_m \left( \frac{r}{r_0} \right)^{2m} \theta_m'(0), \quad (8)$$

where  $t$  is the transference number and  $c$  the concentration of the reactant and  $n$  is the number of electrons produced when one reactant ion or molecule reacts. With excess indifferent electrolyte,  $t = 0$ . The calculation of the current density by this series requires values of  $\theta_m'(0)$ , which are given in table 1.



Table 1. Derivatives at the surface of the functions in the concentration series.

$m$	$\frac{\theta'_m(0)}{m}$	$m$	$\frac{\theta'_m(0)}{m}$
0	-1.11984652	6	-2.47384276
1	-1.53298792	7	-2.59428724
2	-1.80549058	8	-2.70452084
3	-2.01572370	9	-2.80646026
4	-2.18998277	10	-2.90150549
5	-2.34045076		

### Potential Distribution outside the Diffusion Layer

In the region where the concentrations are uniform, the potential satisfies Laplace's equation

$$\nabla^2 \Phi = 0. \quad (9)$$

For this problem we use rotational elliptic coordinates  $\xi$  and  $\eta$  related to the cylindrical coordinates  $r$  and  $y$  by

$$y = r_0 \xi \eta \quad \text{and} \quad r = r_0 \sqrt{(1+\xi^2)(1-\eta^2)}. \quad (10)$$

In this coordinate system Laplace's equation is

$$\frac{\partial}{\partial \xi} \left[ (1+\xi^2) \frac{\partial \Phi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1-\eta^2) \frac{\partial \Phi}{\partial \eta} \right] = 0. \quad (11)$$

Since the ohmic drop for a small disk is concentrated in the solution near the disk, we adopt the following boundary conditions:

$$\left. \begin{aligned} \frac{\partial \Phi}{\partial \eta} &= 0 \text{ at } \eta = 0 \text{ (on the insulating annulus).} \\ \Phi &= 0 \text{ at } \xi = \infty \text{ (far from the disk).} \\ \Phi &\text{ well behaved at } \eta = 1 \text{ (on the axis of the disk).} \end{aligned} \right\} \quad (12)$$

These imply that the disk electrode is embedded in a sufficiently large insulating plane and that the counter electrode is far enough away so that the current distribution is not influenced by its position.

The solution of equation (11) satisfying conditions (12) can be

expressed as a series:

6

$$\Phi = \frac{RT}{ZF} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M_{2n}(\xi), \quad (13)$$

where  $P_{2n}(\eta)$  denotes the Legendre polynomial of order  $2n$  and  $M_{2n}(\xi)$  is a Legendre function of imaginary argument satisfying the differential equation

$$\frac{d}{d\xi} \left[ (1+\xi^2) \frac{dM_{2n}}{d\xi} \right] = 2n(2n+1)M_{2n} \quad (14)$$

and the boundary conditions

$$M_{2n} = 1 \text{ at } \xi = 0 \text{ and } M_{2n} = 0 \text{ at } \xi = \infty. \quad (15)$$

The coefficient  $RT/ZF$  is introduced with regard for the expression to be used later for the concentration overpotential. For the two cases treated in this paper we have

$$\left. \begin{aligned} Z &= -z_+ z_- / (z_+ - z_-) \text{ for the single salt.} \\ Z &= -n \text{ with supporting electrolyte.} \end{aligned} \right\} \quad (16)$$

At  $\xi = 0$ , equation (13) yields

$$\Phi_0 = \frac{RT}{ZF} \sum_{n=0}^{\infty} B_n P_{2n}(\eta), \quad (17)$$

This should be regarded as the potential just "outside" the diffusion layer or as the potential extrapolated to the electrode surface if the actual current distribution prevails but there is no concentration variation near the electrode surface. Effects due to the concentration variation are to be included in the concentration overpotential.

The current density is related to the derivative of the potential just outside the diffusion layer:

$$i = -\kappa_{\infty} \frac{\partial \Phi}{\partial y} \Big|_{y=0} = \frac{-\kappa_{\infty}}{r_0 \eta} \frac{\partial \Phi}{\partial \xi} \Big|_{\xi=0} = \frac{-\kappa_{\infty}}{r_0 \eta} \frac{RT}{ZF} \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M'_{2n}(0), \quad (18)$$

where  $\kappa_{\infty}$  is the conductivity of the bulk solution. From the properties of

Legendre functions one finds that

$$M'_{2n}(0) = -\frac{2}{\pi} \frac{(2^n n!)^4}{[(2n)!]^2} \quad (19)$$

Since the diffusion layer is thin, the current density evaluated from the potential derivative outside the diffusion layer (equation (18)) must equal the current density evaluated from the concentration derivative at the electrode surface (equation (8)). See also reference 4. This provides a relationship between the coefficients  $B_n$  of the potential series and the coefficients  $A_m$  of the concentration series.

$$B_n = \frac{\pi}{4} N \sum_{m=0}^{\infty} Q_{n,m} A_m, \quad (20)$$

where

$$N = -\sqrt{\frac{r_o^2 \Omega}{v}} \left(\frac{av}{3D}\right)^{1/3} \frac{nZF^2 Dc_{\infty}}{RT(1-t)\kappa_{\infty}} \quad (21)$$

and

$$Q_{n,m} = (4n+1) \frac{4\theta'_m(0)}{\pi M'_{2n}(0)} \int_0^1 \eta(1-\eta^2)^m P_{2n}(\eta) d\eta. \quad (22)$$

This relationship is obtained by equating the two expressions for the current density, multiplying by  $\eta P_{2n}(\eta)$ , integrating with respect to  $\eta$  from zero to one, and making use of the orthogonality relation

$$\int_0^1 P_{2n}(\eta) P_{2n'}(\eta) d\eta = \begin{cases} 1/(4n+1) & \text{if } n = n' \\ 0 & \text{if } n \neq n' \end{cases} \quad (23)$$

and the relation

$$(r/r_o)^2 = 1-\eta^2 \text{ at } \xi = 0. \quad (24)$$

Some values  $\lambda$  of  $Q_{n,m}$  are given in table 2.

Table 2. Matrix  $Q_{n,m}$  relating the coefficients of the potential series to the coefficients of the concentration series.

<u>n</u>	<u>m=0</u>	<u>m=1</u>	<u>m=2</u>	<u>m=3</u>	<u>m=4</u>	<u>m=5</u>
0	1.11985	0.76649	0.60183	0.50393	0.43800	0.39008
1	0.34995	-0.0	-0.09404	-0.12598	-0.13687	-0.13931
2	-0.05905	-0.14147	-0.09521	-0.05315	-0.02310	-0.00220
3	0.02221	0.03649	0.06208	0.06398	0.05647	0.04643
4	-0.01112	-0.01675	-0.02237	-0.03138	-0.03666	-0.03818
5	0.00649	0.00943	0.01191	0.01450	0.01812	0.02141
6	-0.00417	-0.00595	-0.00733	-0.00862	-0.00996	-0.01161
7	0.00287	0.00405	0.00492	0.00569	0.00643	0.00719
8	-0.00207	-0.00290	-0.00350	-0.00401	-0.00448	-0.00494
9	0.00155	0.00217	0.00260	0.00296	0.00329	0.00359
10	-0.00120	-0.00167	-0.00200	-0.00226	-0.00250	-0.00272

#### Overpotentials

The potential  $V$  of the metal disk electrode is the sum of the potential drop in the solution  $\Phi_0$ , the concentration overpotential  $\eta_c$ , and the surface overpotential  $\eta_s$ :

$$V = \Phi_0 + \eta_c + \eta_s \quad (25)$$

The three terms on the right will vary with radial position on the disk in such a way that  $V$  is constant. The potential drop in the solution  $\Phi_0$  is evaluated from equation (17).

For the concentration overpotential we adopt the expression (see reference 4)

$$\eta_c = -\frac{RT}{ZF} \left[ \ln \left( \frac{c_\infty}{c_0} \right) - t \left( 1 - \frac{c_0}{c_\infty} \right) \right] \quad (26)$$

This applies approximately to metal deposition from a solution of a single salt. It also applies approximately to the reaction of a minor component from a solution with excess indifferent electrolyte, in which case  $t = 0$ .

The current density and the surface overpotential are assumed to be related by the expression

$$i = i_o \left( \frac{c_o}{c_\infty} \right)^\gamma \left[ \exp \left\{ \frac{\alpha Z F}{RT} \eta_s \right\} - \exp \left\{ - \frac{\beta Z F}{RT} \eta_s \right\} \right], \quad (27)$$

where  $i_o$  is the exchange current density at the bulk concentration and is assumed to be proportional to the concentration to the  $\gamma$  power. Thus the exchange current density at the surface concentration  $c_o$  is expressed as  $i_o \cdot (c_o/c_\infty)^\gamma$  in equation (27). It is convenient to refer the current density to the limiting current density

$$i_{lim} = - \frac{nF D c_\infty}{1-t} \left( \frac{av}{3D} \right)^{1/3} \sqrt{\frac{\Omega}{v}} \theta'_o(0), \quad (28)$$

so that equation (27) becomes

$$\frac{i}{i_{lim}} = \frac{J}{N\theta'_o(0)} \left( \frac{c_o}{c_\infty} \right)^\gamma \left[ \exp \left\{ \frac{\alpha Z F}{RT} \eta_s \right\} - \exp \left\{ - \frac{\beta Z F}{RT} \eta_s \right\} \right], \quad (29)$$

where

$$J = i_o r_o Z F / RT \kappa_\infty. \quad (30)$$

These expressions for the overpotentials have been used so that conclusions of some generality can be drawn without introducing too many parameters. The evaluation of the concentration overpotential requires only the concentration values in the bulk and at the surface, but not a detailed knowledge of the concentration profile. In the case of the solution with supporting electrolyte, there are other species besides the limiting reactant whose concentrations are not being calculated but should perhaps enter into the determination of the overpotential. An example would be the product species in a redox reaction. The present results could be applied approximately to such a case since the product species is not so decisive in the determination of the current distribution, or the calculations could be refined to include the concentration of the product species.

The overpotential relationships cited in this section constitute an additional connection between the coefficients  $A_m$  of the concentration series and the coefficients  $B_n$  of the potential series. The concentration at the surface and the current density must adjust themselves so that the overpotentials add up to the applied voltage  $V$  according to equation (25). However, it is not possible to obtain an explicit expression similar to equation (20).

#### Numerical Calculation Method

In numerical calculations it is necessary to truncate the concentration and potential series. The potential series works very well, but the coefficients  $A_m$  of the concentration series are found to have alternating signs, large absolute values, and considerably different values depending upon how many terms in the series are retained. This can be avoided, to some extent, by re-expressing the concentration on the surface in terms of orthogonal polynomials:

$$c_o = c_\infty \left[ 1 + \sum_{\ell=0}^{\infty} a_\ell P_{2\ell}(r/r_o) \right]. \quad (31)$$

Then the coefficients  $a_\ell$  are small, decrease in magnitude with increasing  $\ell$ , and are roughly independent of the number of terms retained in the series. Furthermore, they can be evaluated by an integration over the surface concentration:

$$a_\ell = (4\ell + 1) \int_0^1 \left( \frac{c_o}{c_\infty} - 1 \right) P_{2\ell}(r/r_o) d(r/r_o). \quad (32)$$

It does become a little more difficult to evaluate the current density according to equation (8), and the problems arising from the fact that the coefficients  $A_m$  are large and of alternating sign are not entirely eliminated.

This can be seen from the expression for the Legendre polynomial of order 20:

$$\begin{aligned}
 P_{20}(x) = & [34,461,632,205 x^{20} - 167,890,003,050 x^{18} \\
 & + 347,123,925,225 x^{16} - 396,713,057,400 x^{14} \\
 & + 273,491,577,450 x^{12} - 116,454,478,140 x^{10} \\
 & + 30,117,537,450 x^8 - 4,461,857,400 x^6 \\
 & + 334,639,305 x^4 - 9,699,690 x^2 \\
 & + 46,189] / 262,144
 \end{aligned} \tag{33}$$

The coefficients become as large as  $1.5 \times 10^6$ ; yet the absolute value of  $P_{20}(x)$  is never greater than one for the range of interest! Consequently the calculation of the contribution to the current density arising from the Legendre polynomial of order 20 in equation (31) requires accurate values for  $\theta'_m(0)$  as given in table 1. Because of these difficulties it was decided to truncate the series (5) and (31) at  $m = 10$  and  $l = 10$ .

The coefficients  $B_n$  and  $A_m$  or  $a_\ell$  were calculated by an iterative procedure:

1. The current density and the surface concentration were specified at the center of the disk. As an initial guess this was taken to apply to the whole disk so that  $a_0 = A_0 = c_0/c_\infty - 1$  and all the other coefficients are zero.

2. The coefficients  $B_n$  were calculated according to equation (20).

3. The potential outside the diffusion layer was calculated at selected values of  $r$  according to equation (17).

4. The potential  $V$  of the electrode was calculated by applying equation (25) to the center of the disk where  $\eta_c$  and  $\eta_s$  could be calculated from the specified current density and surface concentration.

5. The overpotential  $\eta = \eta_c + \eta_s$  was calculated at selected values of  $r$  from equation (25).

6. At these same values of  $r$ , the overpotential  $\eta$  and the assumed current density were used to calculate the surface concentration  $c_0$  by a trial-and-error solution of equations (26) and (27).

7. The coefficients  $a_\ell$  were calculated according to equation (32). In order to achieve convergence it was usually necessary to average these in some way with the previous set of  $a_\ell$ .

8. The current density was calculated from equation (8).

9. The calculations enumerated in items 2 through 8 above were repeated until no significant changes occurred in the values.

This procedure was modified slightly for the well-stirred case ( $N = \infty$ ) where all the concentrations have their bulk values.

## Results

### a) Primary and limiting current distributions

As a point of departure it is worthwhile to examine two limiting cases. The primary current distribution corresponds to a uniform potential  $\Phi_0$  in the solution just outside the diffusion layer and was calculated by Newman<sup>7</sup>. The current density on the disk is

$$i = 0.5 i_{\text{avg}} / \sqrt{1 - (r/r_0)^2}, \quad (34)$$

and the total current to the disk is

$$I = 4\kappa_\infty r_0 \Phi_0. \quad (35)$$

This result is shown in figure 1. In the case of the primary current distribution, the surface overpotential and concentration overpotential are negligible, and the current distribution is completely determined by the ohmic drop in the solution, with the result that the current density is infinite at the edge of the disk and is half of the average value at the center of the disk.



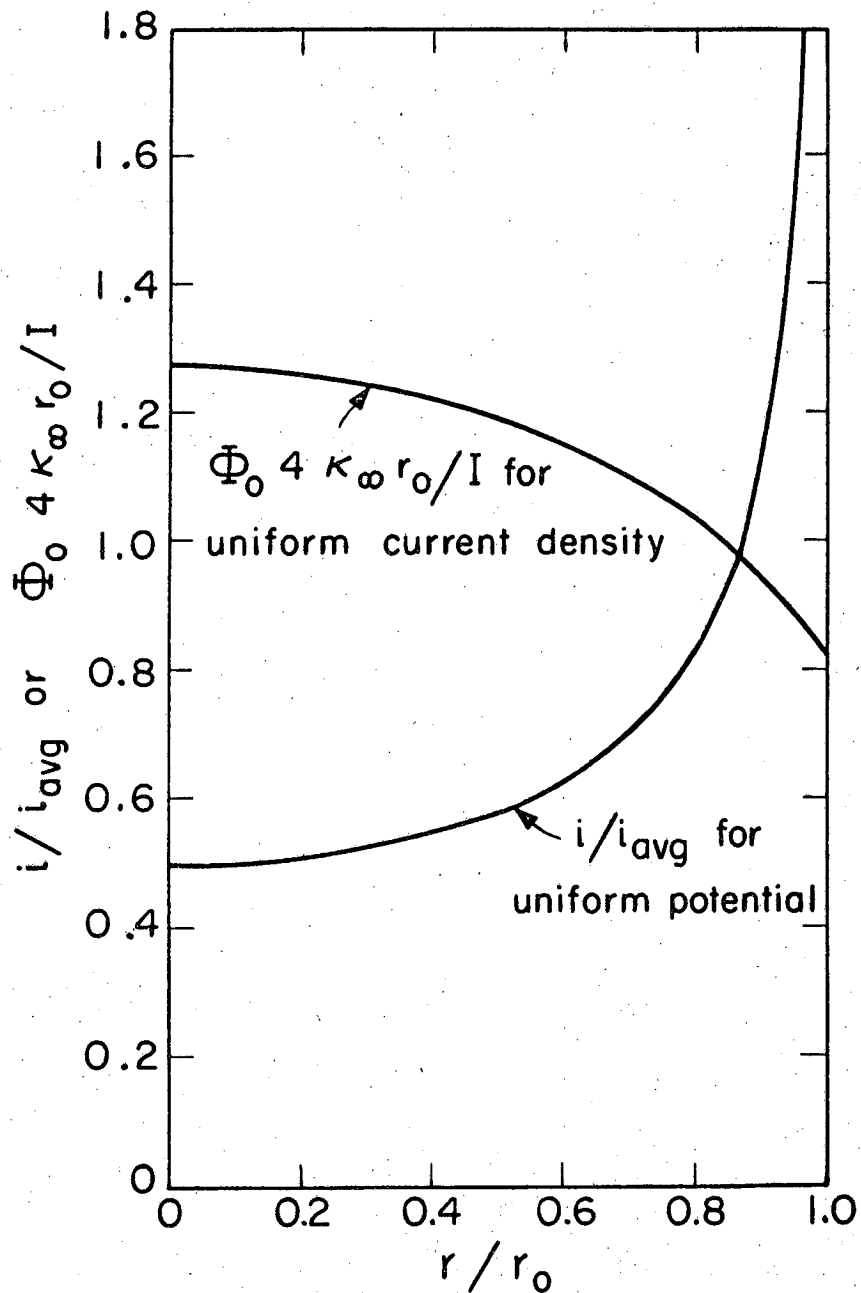


Figure 1. Primary current distribution and potential distribution for a uniform current density.

Levich<sup>3</sup> has shown that the current density is uniform on the disk surface and is given by equation (28) when the current is limited by the rate of mass transfer of a reactant to the disk. The corresponding potential  $\Phi_0$  just outside the diffusion layer can be calculated from equations (17) and (20) with  $A_0 = -1$  and all the other A's set equal to zero. The result is shown in figure 1, normalized in such a way that it can be compared conveniently with the value  $\Phi_0 4\kappa_\infty r_0 / I = 1$  for the primary current distribution. For the same total current, the current density at the center of the disk is twice as high as the primary current, and this requires a potential 27.3% higher in order to force the higher current density to the center of the disk. At the same time the current density at the edge of the disk is finite, and the potential is lower than for the primary distribution.

b) Secondary current distribution

If the rotation speed is high, so that  $|i| \ll |i_{lim}|$ , then the concentration overpotential is negligible, and the so-called secondary current distribution prevails. The current distribution is then determined by the balance between the surface overpotential and the ohmic drop in the solution. The result is shown in figures 2 and 3 for two limiting cases corresponding to linear polarization and to Tafel polarization.

For sufficiently small current densities  $|i| \ll i_0$ , equation (27) becomes linear, and the slope of the polarization curve at zero current is

$$\left. \frac{di}{d\eta_s} \right|_{i=0} = (\alpha + \beta) \frac{ZF}{RT} i_0 \quad (36)$$

The parameter J is thus similar to that identified by Hoar and Agar<sup>8</sup> for the characterization of the influence of electrolytic resistance, polarization, and cell size on current distribution. In the linear range the current distribution depends only on the parameter  $(\alpha + \beta)J$ , as shown in

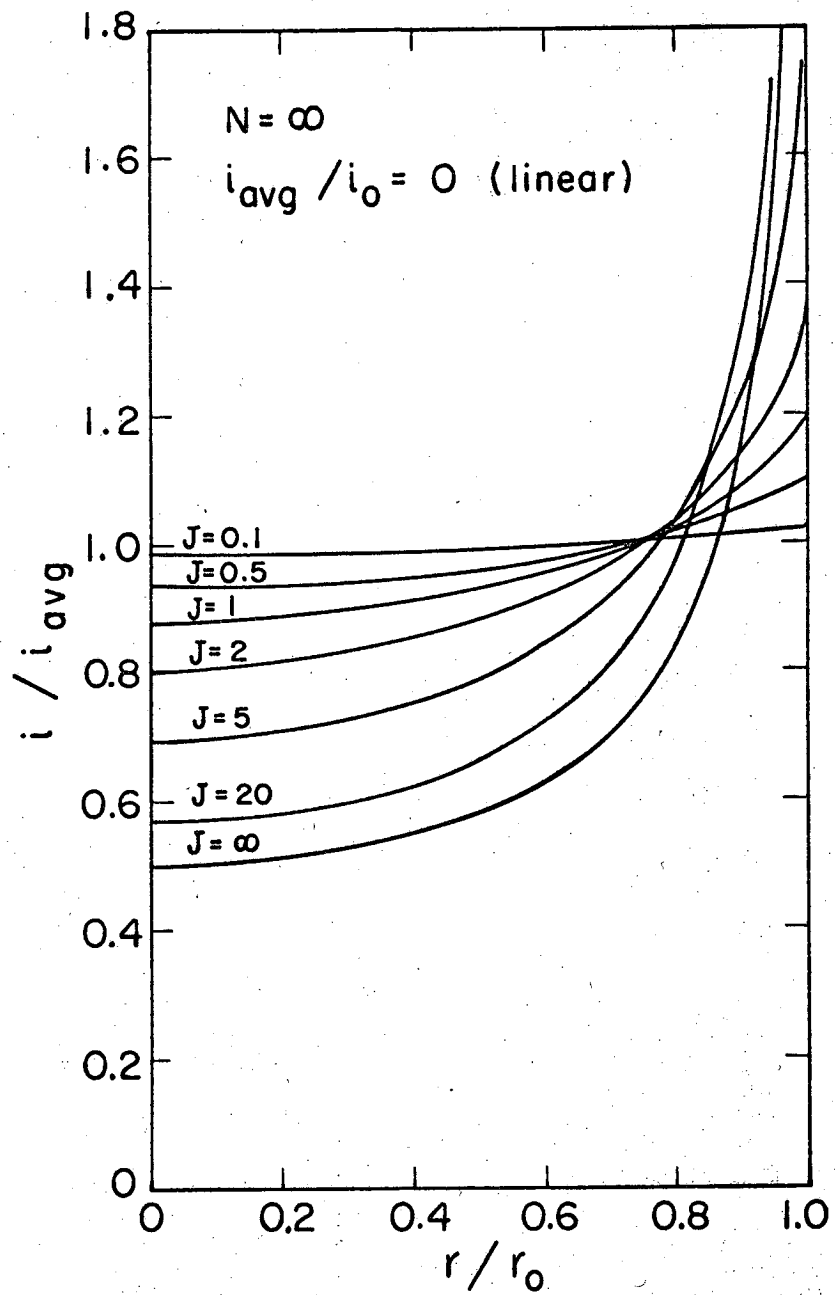


Figure 2. Secondary current distribution for linear polarization.

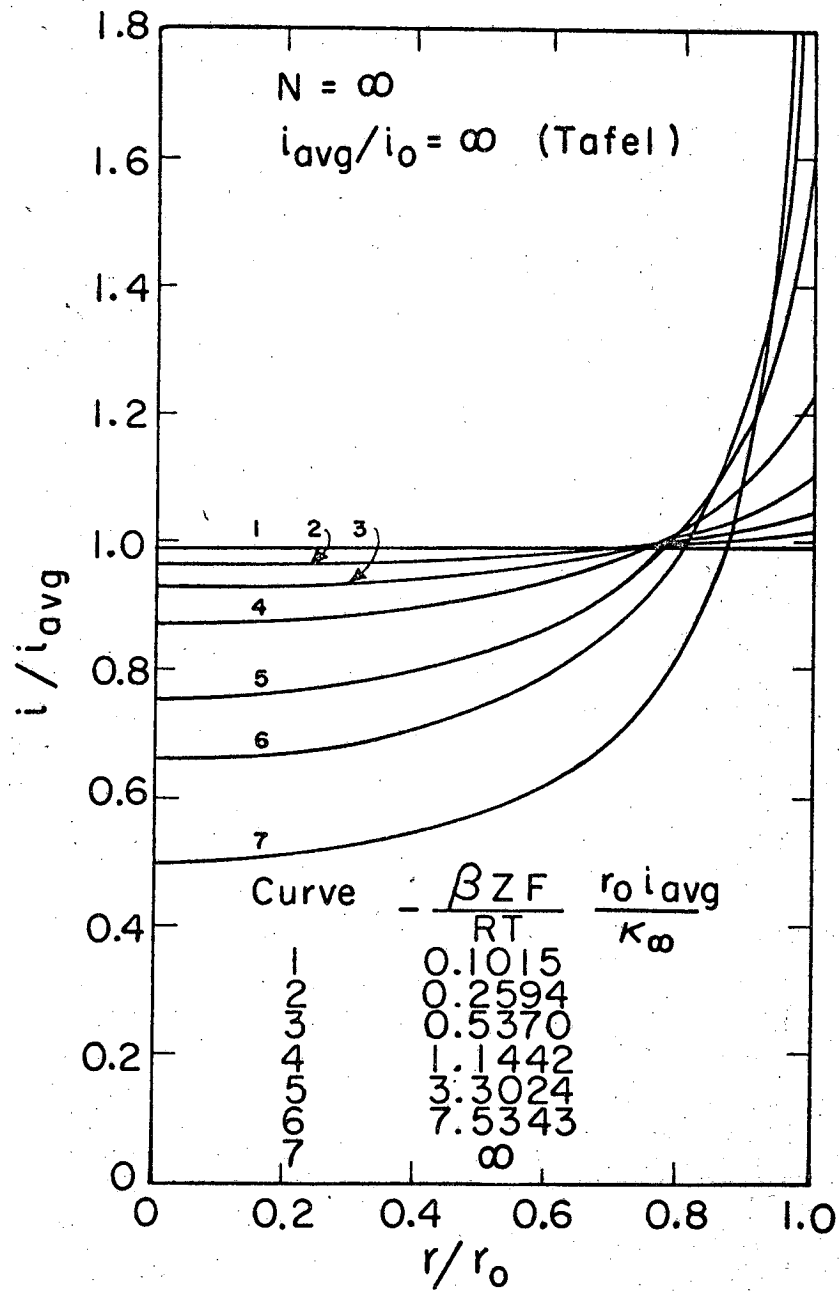


Figure 3. Secondary current distribution for Tafel polarization.

figure 2. In particular, the current distribution  $i/i_{\text{avg}}$  does not depend upon the level of the current. The curve for  $J = \infty$  is the primary current distribution.

At higher currents where the condition  $|i| \ll i_0$  no longer holds, the current level becomes important. This can be characterized by the dimensionless ratio

$$\delta = |i_{\text{avg}}| \frac{ZFr_0}{RT\kappa_\infty} . \quad (37)$$

In the other extreme, when  $|i| \gg i_0$ , one of the exponential terms in equation (27) is negligible, and Tafel polarization is said to apply:

$$\eta_s = - \frac{1}{\beta} \frac{RT}{ZF} (\ln |i| - \ln i_0) . \quad (38)$$

(For current flow in the opposite direction, the term involving  $\alpha$  would be retained.) In the Tafel region the actual value of the exchange current density is no longer important in determining the current distribution since it just contributes an additive constant to the surface overpotential, as shown in equation (38). The current distribution  $i/i_{\text{avg}}$  is completely determined by the parameter  $\beta\delta$  and is shown in figure 3. Curve 7 for  $\beta\delta = \infty$  is the primary current distribution.

It does not seem worthwhile to plot the current distribution for intermediate current levels between the linear and Tafel regions. Instead figures 4 and 5 gives just the values for  $i/i_{\text{avg}}$  and  $\Phi_0$  at the center of the disk. The current ratio can vary between 0.5 and 1.0 in the extreme cases of the primary current distribution and the uniform current distribution. The ohmic drop to the center of the disk is expressed in figure 5 in the form  $\Phi_0 4\kappa_\infty r_0 / I$ , a dimensionless effective resistance which can vary between the values 1.0 for the primary current distribution and 1.273 for the uniform current distribution. For large currents the Tafel results apply.

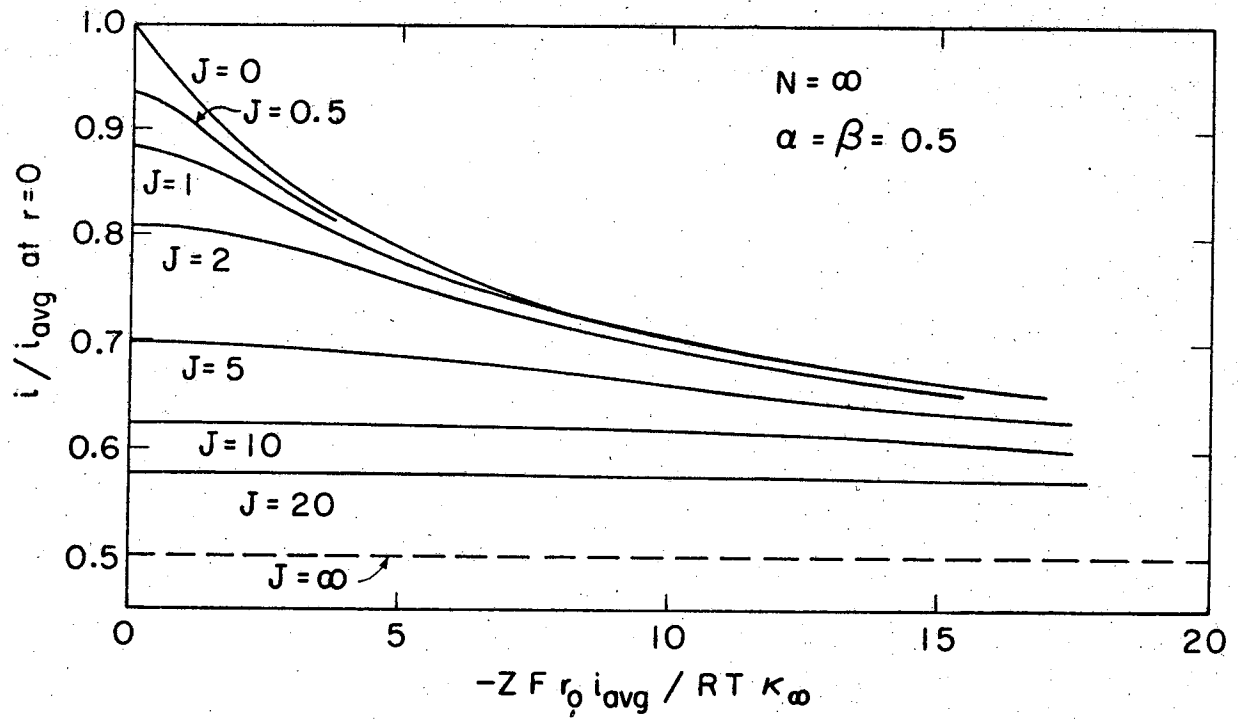


Figure 4. Current density of the center of the disk when concentration polarization is absent.

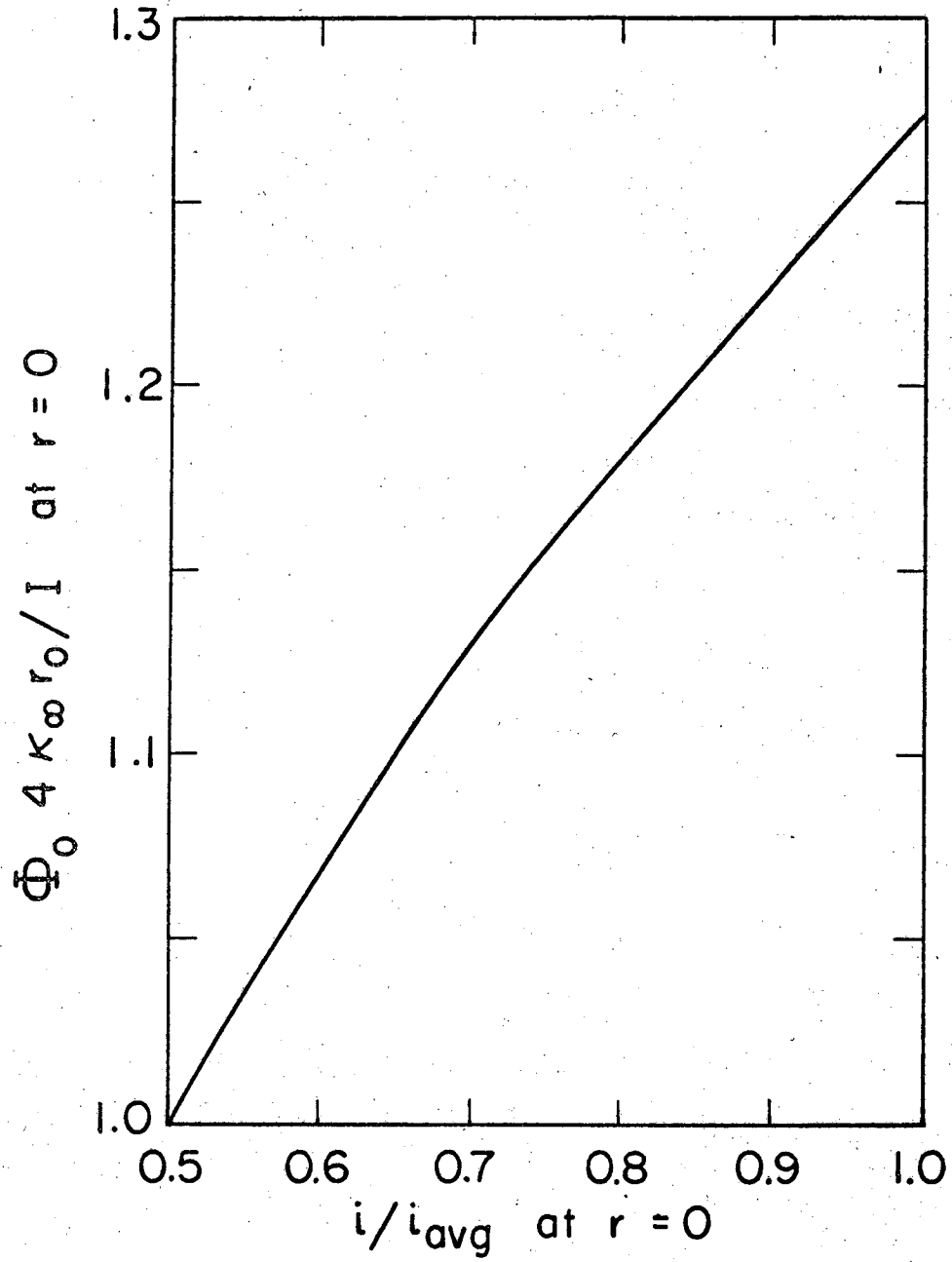


Figure 5. Correction factor for resistance to center of disk.

As the current is decreased, the distribution becomes more uniform but approaches at low currents the linear results for the given value of  $J$  rather than a completely uniform current density. At intermediate current levels, all four parameters  $J$ ,  $\delta$ ,  $\alpha$ , and  $\beta$  can affect the current distribution. Figures 4 and 5 show the effect of  $J$  and  $\delta$  when  $\alpha = \beta = 0.5$ .

c) Effect of concentration polarization

The current density can also be limited by the rate of mass transfer of the reactants to the electrode. An important parameter in this regard is  $N$ , defined in equation (21). This parameter is proportional to the square root of the Reynolds number  $Re = r_0^2 \Omega / \nu$ , the one-third power of the Schmidt number  $Sc = \nu / D$ , and the ratio  $c_\infty / \kappa_\infty$ . It represents the importance of the ohmic potential drop relative to the concentration overpotential at a given fraction of limiting current. An increase in disk size  $r_0$  increases the distance over which current flows and thus increases the magnitude of the variation of the potential  $\Phi_0$ . An increase in rotation speed  $\Omega$  is accompanied by an increase in current at a given fraction of limiting current and thus increases the potential variation due to the ohmic drop. On the other hand, supporting electrolyte can be added so that  $\kappa_\infty$  increases but not  $c_\infty$ . This reduces the importance of the ohmic drop.

Since the limiting current density is given by equation (28), the condition for the concentration overpotential to be negligible and for the secondary current distribution to apply,  $|i_{avg}| \ll |i_{lim}|$ , can be expressed as  $\delta \ll N$ .

Figures 6 and 7 show the concentration and current distributions on the disk for Tafel kinetics and for various levels of current and rotation speed. The corresponding curves on the two graphs can be found by the relationship between the current and the surface concentration at the center of the disk:



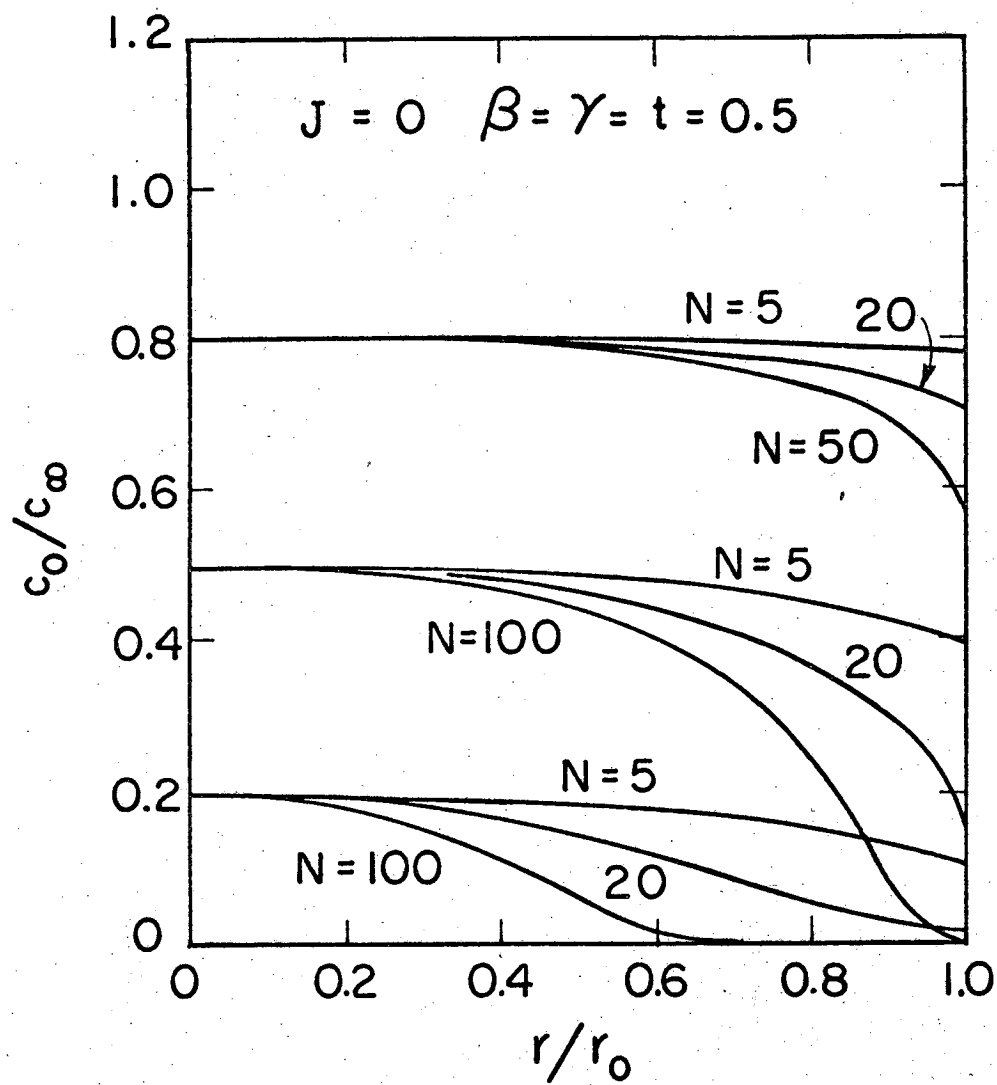


Figure 6. Surface concentration for Tafel kinetics.

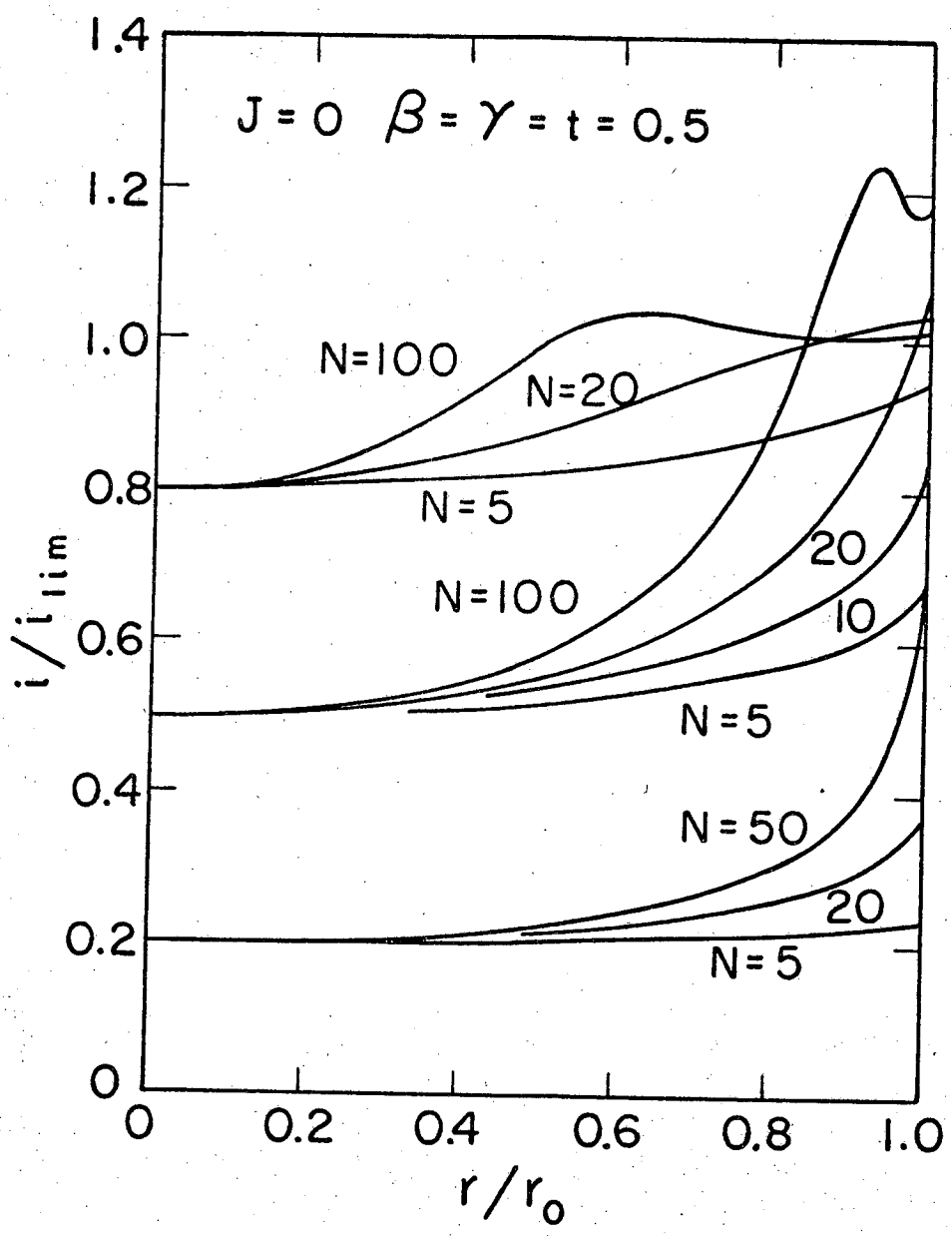


Figure 7. Current distribution for Tafel kinetics with an appreciable fraction of the limiting current.

$i/i_{lim} = 1 - c_0/c_\infty$  at  $r = 0$ . The higher currents correspond to lower surface concentrations.

The distributions of concentration and of current shown on figures 6 and 7 become more nonuniform for larger values of  $N$ , but they still become limited by the rate of mass transfer. The local current density is able to exceed the average limiting current only because the current is less than that value near the center of the disk. This situation can be compared to a disk with an insulator in the center and an annular or ring electrode. For such a system the local limiting current density would be infinite at the inner edge of the ring electrode and would decrease toward the outer edge. Some of the curves on figure 7 show this situation: the current rises as the local overpotential increases with increasing  $r$  but begins again to decrease after the concentration has effectively gone to zero and the increasing overpotential can have no more effect.

Figure 8 shows the correction factor for the current density at the center of the disk. The curve for  $N = \infty$  corresponds to no concentration polarization and was shown on figure 4. The curves for  $N = 5, 10, \text{ and } 20$  depart from the curve for  $N = \infty$  and terminate with a uniform current at their respective limiting currents.

For a sufficiently large value of the exchange current density, the surface overpotential is negligible compared to the ohmic drop in the solution and the concentration overpotential. The electrode is then said to be reversible. The current-density ratios for reversible electrodes are shown as dashed curves on figure 8. The distribution is more nonuniform than for Tafel kinetics, becomes more nonuniform for larger values of  $N$ , and still becomes uniform at the limiting current.

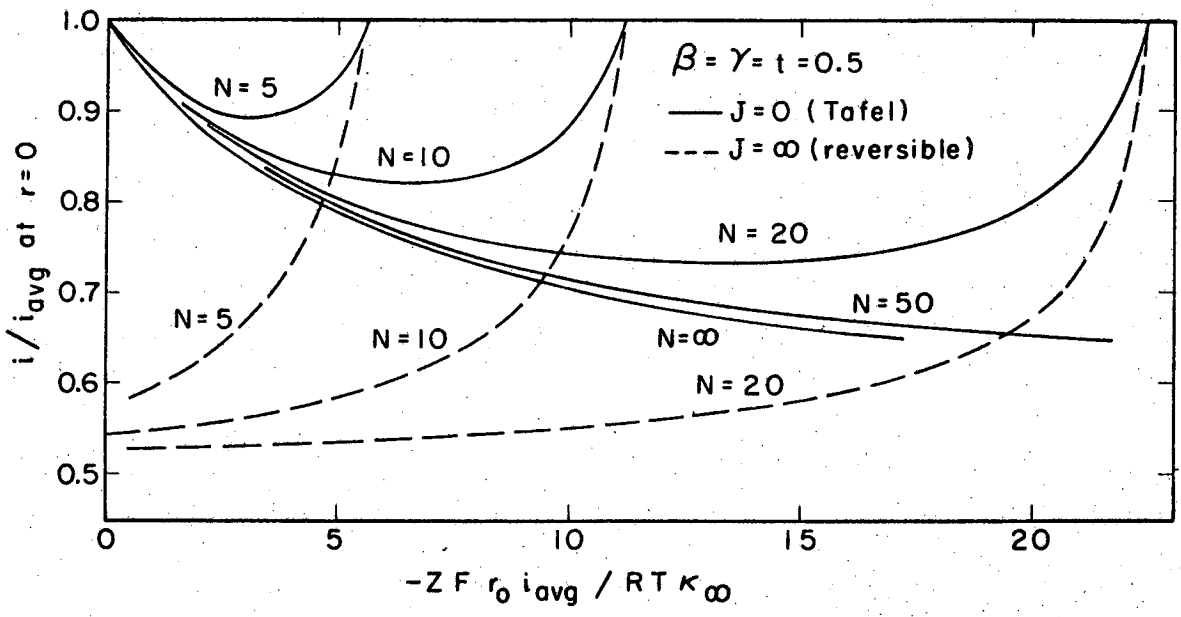


Figure 8. Current density at the center of the disk.

## d) Copper deposition

Figure 9 shows a polarization curve for copper deposition from a solution containing no supporting electrolyte. Measured potentials reported by Hsueh and Newman<sup>9</sup> have been corrected<sup>7</sup> for the fact that the reference electrode was not at infinity. The following parameters were used in the calculation of the surface overpotential, the concentration overpotential, and the ohmic drop at the center of the disk:

$$n = -2, Z = 1, \kappa_{\infty} = 0.00872 \text{ (ohm-cm)}^{-1} \text{ (ref. 10),}$$

$$i_0 = 1 \text{ mA/cm}^2, \alpha = \beta = 2, \gamma = 0.51 \text{ (ref. 11),}$$

$$r_0 = 0.25 \text{ cm}, \Omega = 300 \text{ rpm} = 31.416 \text{ rad/sec}, i_{\text{lim}} = 79.20 \text{ mA/cm}^2,$$

$$D = 0.642 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ (integral value, ref. 12),}$$

$$t = 0.363 \text{ (ref. 13), } \nu = 0.94452 \times 10^{-2} \text{ cm}^2/\text{sec},$$

$$J = 1.116, N = 78.8.$$

Most of the polarization is due to ohmic drop in the solution since the conductivity is so low. The curve shows how the ohmic resistance changes as limiting current is approached due to the current density becoming more uniform. The agreement with the experimental values is considerable better than that obtained with the ohmic drop for the primary current distribution (dashed line). Possible explanations for the discrepancy which remains are uncertainties in the surface overpotential and the fact that the insulating plane of the disk was not infinite, but would allow current to flow in the region above the plane of the disk. The discrepancy is roughly equal to the correction for the fact that the reference electrode is not at infinity.

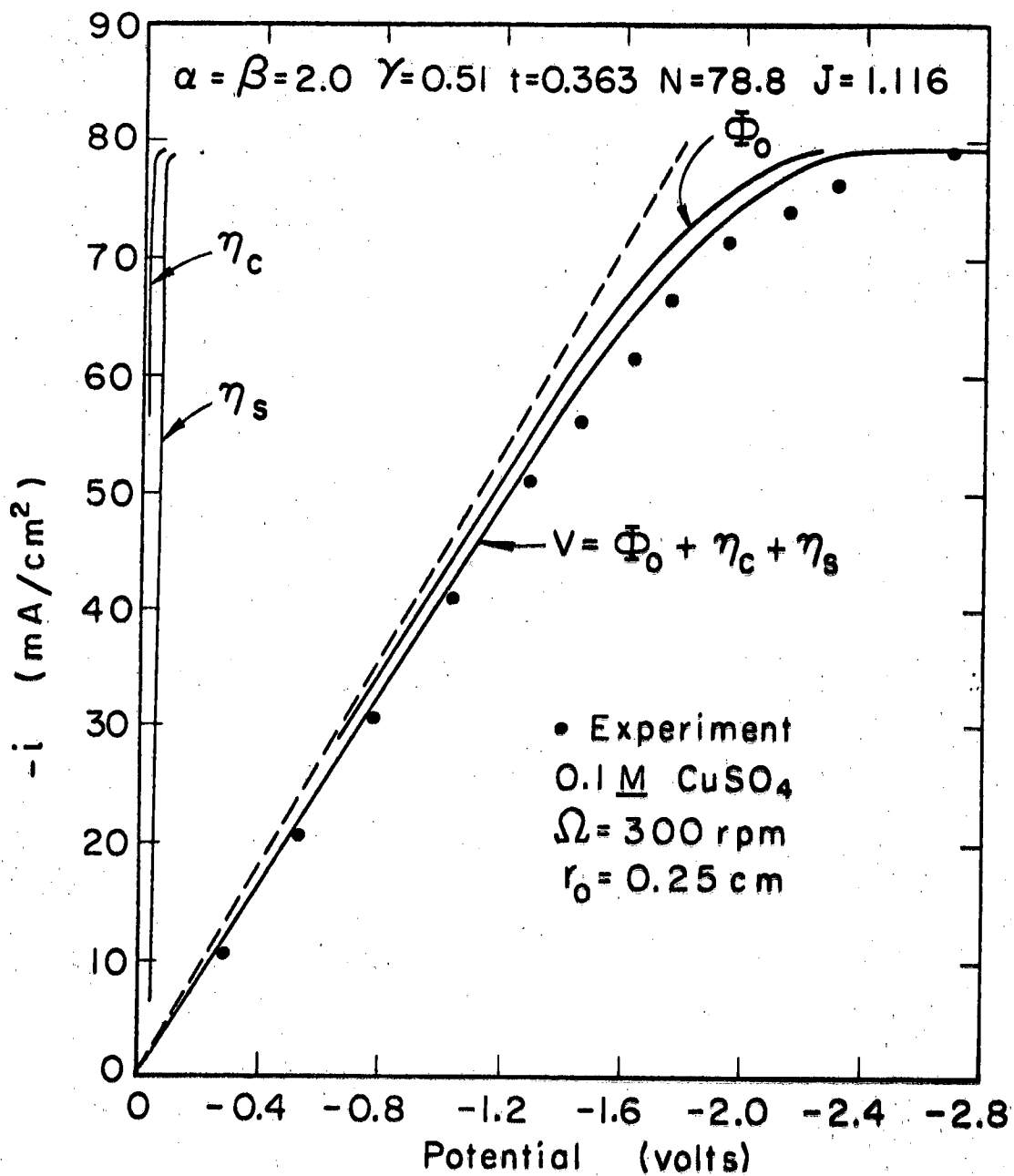


Figure 9. Overpotentials for copper deposition on a rotating disk. Dashed line is ohmic drop for the primary current distribution.

### Conclusions

The present results can be applied most simply to practical problems in studies of electrode kinetics if the actual current density at the center of the disk and the potential drop to the center of the disk can be obtained, perhaps by means of figures 4, 5, and 8, from the measured average current density and the parameters  $N$ ,  $J$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $t$  related to the properties of the solution and the electrode reaction and the size and rotation speed of the disk electrode. Since some of these properties probably are not known in advance, trial-and-error calculations are involved.

The rotating disk is usually used for moderately fast reactions, that is, reactions for which the exchange current density is not too low. The effect of mass transfer can be corrected for (by assuming a uniform current density) or eliminated by extrapolating to infinite rotation speed. However, the effect of a nonuniform current density is not eliminated. To assess the degree of nonuniformity, one should calculate or estimate  $J$ ,  $\delta$ , and  $N$ . Unless  $J$  and  $\delta$  are both small, there will be a significant nonuniformity, and unless  $\delta \ll N$  a correction must be made for the different concentration at the electrode surface.

Suppose that the 0.1 M  $\text{CuSO}_4$  solution studied earlier is made 1.53 M in  $\text{H}_2\text{SO}_4$  for the purpose of suppressing the ohmic potential drop in the solution. For the same current density, say 70 mA/cm<sup>2</sup>, the values of the parameters  $N$ ,  $\delta$ ,  $J$ , and  $t$  would be

$$N = 1.6 \text{ instead of } 78.8,$$

$$\delta = 2.5 \text{ instead of } 78,$$

$$J = 0.037 \text{ instead of } 1.116,$$

$$t = 0 \text{ instead of } 0.363.$$

These changes are primarily results of the increased conductivity (0.548

instead of  $0.00872 \text{ ohm}^{-1}\text{-cm}^{-1}$ ).

It should be noted that with the addition of sulfuric acid the current density is now above the limiting current since the contribution of migration to the mass transfer has now been suppressed by the high electrical conductivity. We might next try to eliminate the mass transfer effect altogether by increasing the rotation speed. If the criterion is taken to be  $N = 20 \delta$ , the rotation speed must now be increased to 290,000 rpm, at which speed the flow becomes turbulent at about  $r = 0.18 \text{ cm}$ . Few people would consider operating even at speeds as high as 30,000 rpm. Nevertheless, let us assume that mass transfer effects can be ignored.

With  $\delta = 2.5$  and  $\beta = 1$  and  $J \approx 0$ , the results presented earlier indicate that the current density at the center of the disk is 79% of the average current density and the ohmic drop is 29.5 mV.

Finally one might note that the a.c. resistance to a disk should be somewhat different from the actual value since the a.c. resistance would correspond more closely to the primary current distribution. For the same reason it would be inconsistent to use current step methods to study electrode kinetics with the rotating disk. In current step methods the initial jump of the potential is taken as a measure of the ohmic drop. This would be proper for a sphere where the initial current distribution is the same as the quasi-steady current distribution (before mass-transfer limitations become important).

#### Acknowledgment

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## Nomenclature

- $a = 0.51023$ .  
 $a_\ell$  - coefficients in series for surface concentration.  
 $A_m$  - coefficients in series for concentration.  
 $B_n$  - coefficients in series for potential.  
 $c$  - concentration of reactant (mole/cm<sup>3</sup>).  
 $c_o$  - concentration at electrode surface (mole/cm<sup>3</sup>).  
 $c_\infty$  - bulk concentration (mole/cm<sup>3</sup>).  
 $D$  - diffusion coefficient (cm<sup>2</sup>/sec).  
 $F$  - Faraday's constant (coulomb/equiv).  
 $i$  - normal current density at electrode surface (amp/cm<sup>2</sup>).  
 $i_o$  - exchange current density (amp/cm<sup>2</sup>).  
 $i_{avg}$  - average current density (amp/cm<sup>2</sup>).  
 $i_{lim}$  - limiting current density (amp/cm<sup>2</sup>).  
 $I$  - total current to the disk (amp).  
 $J$  - dimensionless exchange current density (see equation (30)).  
 $M_{2n}$  - a Legendre function (see equations (14) and (15)).  
 $n$  - number of electrons produced when one reactant ion or molecule reacts.  
 $N$  - parameter related to significance of mass transfer (see equation (21)).  
 $P_n$  - Legendre polynomial of order  $n$ .  
 $Q_{m,n}$  - see equation (22) and table 2.  
 $r$  - radial coordinate (cm).  
 $r_o$  - radius of disk (cm).  
 $R$  - universal gas constant (joule/mole-deg).  
 $Re = r_o^2 \Omega / \nu$ , Reynolds number.  
 $Sc = \nu / D$ , Schmidt number.  
 $t$  - transference number of reactant.

- $T$  - absolute temperature (deg K).
- $v_r, v_y$  - velocity components (cm/sec).
- $V$  - potential of metal disk electrode (volt).
- $y$  - normal distance from disk (cm).
- $z_i$  - charge number of species  $i$ .
- $Z$  - see equation (16).
- $\alpha, \beta, \gamma$  - parameters in kinetic expression (see equation (27)).
- $\delta$  - dimensionless average current density (see equation (37)).
- $\zeta$  - dimensionless normal distance (see equation (4)).
- $\eta$  - elliptic coördinate (see equation (10)).
- $\eta_c$  - concentration overpotential (volt).
- $\eta_s$  - surface overpotential (volt).
- $\theta_m$  - functions in concentration series.
- $\kappa_\infty$  - conductivity of bulk solution ( $\text{ohm}^{-1}\text{-cm}^{-1}$ ).
- $\nu$  - kinematic viscosity ( $\text{cm}^2/\text{sec}$ ).
- $\xi$  - elliptic coördinate (see equation (10)).
- $\Phi$  - electrostatic potential (volt).
- $\Phi_0$  - external potential extrapolated to electrode surface (volt).
- $\Omega$  - rotation speed (radians/sec).

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