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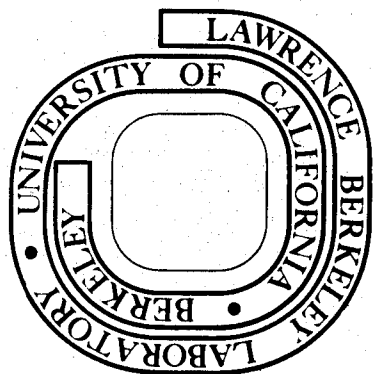# CURRENT DISTRIBUTION ON A DISK ELECTRODE FOR
REDOX REACTIONS

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February 1975

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Current Distribution on a Disk Electrode for Redox Reactions

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Abstract

Current and concentration distributions on a rotating disk electrode are computed for general electrode reactions where the product concentrations must be included. The effect of migration on the surface concentration of the supporting electrolyte is also demonstrated.

Newman[1] introduced a method for the calculation of current
and concentration profiles over the surface of a rotating disk
electrode operated below the limiting current. The problem is
complex, since the concentration variations near the electrode, the
surface overpotential associated with the electrode reaction,
and the ohmic potential drop in the bulk of the solution must be
included in the analysis. The diffusion layer on a rotating disk electrode
is thin compared with the characteristic dimensions of the electro-
chemical cells used in most experimental applications. This physical
situation, in which the concentration changes rapidly in a region
much smaller than the bulk of the solution where the potential
continues to vary, was naturally formulated as a singular perturbation.[6]
Thus the potential in a large portion can be considered to satisfy
Laplace's equation with the current density distribution on the
boundaries matched to the mass flux entering the diffusion boundary
layer. In the diffusion layer, the concentrations are determined
from the appropriate mass transport equations with a mass flux at the
electrode surface related by Faraday's law to the current density
distribution on the electrodes, and with the concentrations approaching
the bulk concentrations far from the electrode. The current
distribution and concentrations at the electrode surface are further
specified by the overpotential computed as the difference of the
applied voltage, the equilibrium potential, and the ohmic drop in the
solution.[2] Marathe and Newman[3] experimentally proved the soundness
of the theory by plating copper from a cupric-sulfate-sulfuric acid
solution and then measuring the thickness of the deposit. The potential

mapping experiments of Miller and Bellavance[4] also agree quantitatively

with theoretical predictions. Other verification exists in the

work of Miller and Bruckenstein,[11] and Smyrl and Newman.[9,12]

In an attempt to keep the treatment of the problem from being a

quagmire of computational detail, common experimental situations were

evaluated,and assumptions were made that would permit the broadest

application of the theory. The flow was considered fully developed

and laminar. The disk was designed to minimize edge effects. The

mass transfer boundary layer must lie well within the hydrodynamic

boundary layer; thus the Schmidt number must be large. Radial

diffusion was neglected over the entire surface of the electrode,

even at the outer edge. A mathematically convenient cell utilized a

centered disk, embedded in an infinite insulating plane, and placed

the counterelectrode at infinity. Actual cells must be carefully

devised to approximate the condition of infinite dimension,or a

correction to the potential description is necessary. Any electrochemical

reaction may be studied except those evolving gas, but attention was

restricted to metal deposition from a single salt solution and to an

electrode reaction with an excess of supporting electrolyte, having

a zero transference number and no dependence upon the product concentration.

Copper plating from a cupric sulfate solution is an example of

the single salt reaction while the addition of enough sulfuric acid

to suppress migration effects on the reactants illustrates the second

type. Since the product does not remain in solution, it may be validly

ignored. Any electrode reaction that involves only electron transfer

usually requires that the effect of the product concentration be included. Redox couples and organic syntheses are in this class of reactions.

The alternating current response of a disk electrode has been investigated by Newman,[13] but the effect of concentration variation was not included. Variations of double layer effects can be computed only if the concentrations of all the ionic species are known at the electrode surface. The supporting electrolyte does not participate in the surface reaction, but migration causes the surface concentration to deviate from the bulk solution. A future objective to treat the alternating current response more completely requires the knowledge of the local value of each component in solution.

We shall extend here the original perturbation scheme to general electrode reactions depending on both reactant and product concentrations and will develop a procedure for determining the concentration of the supporting electrolyte. (See also Newman,[14] p. 380.)

Overpotential

The major departure from the formulation that omits the product dependence[1] lies in the treatment of the overpotential expressions and the variation of the exchange current density i_o . The necessary reaction parameters are conveniently introduced by the general electrode reaction

$$\sum_i s_i M_i^{z_i} \rightarrow ne^-$$
(1)

where s_i is the stoichiometric coefficient, M_i is the symbol for the chemical species, z_i is the species charge number, and n is the number of electrons participating in the reaction. The total voltage V applied to the cell is decomposed into the equilibrium potential U , ohmic drop Φ_o , the concentration over-potential η_c , and the surface overpotential η_s

$$V = U + \Phi_o + \eta_c + \eta_s \; . \tag{2}$$

The surface overpotential is defined by the Butler-Volmer expression

$$i = i_o \left[\exp \left(\frac{\alpha ZF}{RT} \eta_s \right) - \exp \left(- \frac{\beta ZF}{RT} \eta_s \right) \right] \; . \tag{3}$$

The local value of the exchange current density i_o can be related to the concentrations of the reactants and products at the electrode surface by

$$i_o = i_{o,\infty} \Pi \left(\frac{c_{i,o}}{c_{i,\infty}} \right)^{\gamma_i} \tag{4}$$

where $i_{o,\infty}$ is a constant determined by the reaction properties and the constituents of the bulk solution, and Z is equal to $-n$. The kinetic parameters α , β , and γ_i are associated with the type of reaction occurring. The parameters of Eq. (3) and Eq. (4) may be measured experimentally; Newman[5] suggests rules for the evaluation of the exponents γ_i .

The concentration overpotential depends upon the variation of concentration through the diffusion layer in a complicated way. A

relatively high electric conductivity which can be considered
constant and enough supporting electrolyte to suppress the effect of
migration on the reactants and products allow concentration dependent
potential effects to be adequately represented by[6]

$$\eta_c = \frac{RT}{nF} \sum_i s_i \ln \left(\frac{c_{i,\infty}}{c_{i,o}} \right) . \tag{5}$$

Although no formal arguments about the order of the perturbation
approach have been given, Eq. (5) may be considered a first
approximation which is justified by the small variation in electrical
conductivity through the diffusion layer.

Potential Distribution in the Bulk of the Solution outside the Diffusion Layer

The potential distribution in the bulk of the solution outside
the diffusion layer, where the concentrations are uniform, satisfies
Laplace's equation. Rotational elliptic coordinates have proven
both natural and convenient for the representation of the ohmic
effects of rotating disk electrodes.[7,1] The expression for the
potential at the surface of the electrode is

$$\Phi_o = \frac{RT}{-nF} \sum_{m=0} B_m P_{2m}(\eta) \tag{6}$$

$P_{2m}(\eta)$ is the Legendre polynomial of order $2m$ and $\eta = \sqrt{1 - (r/r_o)^2}$
at the surface. The constants B_m are evaluated by taking the normal
derivative of the potential distribution, then making use of the

orthogonal properties of Legendre polynomials and the current matching condition between the diffusion layer and the bulk solution.

The Diffusion Layer

The mass balance is

$$\underline{v} \cdot \nabla c_i = D_i \nabla^2 c_i + z_i u_i F \nabla \cdot (c_i \nabla \Phi) . \tag{7}$$

Levich[8] advanced the idea of investigating the concentration distribution of all components in the solution by a perturbation technique. The method has been successfully applied to show the effect of ionic migration on the supporting electrolyte at the limiting current.[15] For a solution that contains minor species and a binary indifferent electrolyte, the zero approximation omits the minor species. The potential and concentration profile associated with the supporting ions are then found to be constants, since the major species do not participate in the electrode reaction. Therefore no current is passed, and the solution is the bulk concentration of the supporting ions, $c_1^{(o)} = c_{1,\infty}$ and $c_2^{(o)}$ is specified by electroneutrality. The first order approximation is

$$c_1 = c_1^{(o)} + c_1^{(1)}$$

$$c_2 = c_2^{(o)} + c_2^{(1)}$$

$$c_i = c_i^{(1)} \quad \text{where} \quad i > 2 . \tag{8}$$

Eq. (8) is substituted into Eq. (7), and second order terms are dropped, which gives

$$\underline{v} \cdot \nabla c_i^{(1)} = D_i \nabla^2 c_i^{(1)} \quad \text{for} \quad i > 2 \tag{9}$$

$$\underline{v} \cdot \nabla c_1^{(1)} = D_e \nabla^2 c_1^{(1)} + \sum_i \frac{z_i u_i (D_2 - D_i)}{z_1 u_1 - z_2 u_2} \nabla^2 c_i^{(1)} . \tag{10}$$

The physical parameter D_e is the diffusion coefficient of the binary electrolyte

$$D_e \equiv \frac{z_1 u_1 D_2 - z_2 u_2 D_1}{z_1 u_1 - z_2 u_2} . \tag{11}$$

The potential is removed from Eq. (7) by the binary electrolyte approximation; then the electroneutrality condition is used to eliminate $c_2^{(1)}$.

The minor components are found by solving Eq. (9), the equation of convective diffusion that applies when the effect of migration can be ignored. Smyrl and Newman[9] have worked out a formal solution to Eq. (9) that can be applied to diffusion layers in laminar forced convection at high Schmidt numbers on axisymmetric bodies. The concentration derivative at the electrode surface, as a function of the surface concentration, is

$$\left. \frac{\partial c_i}{\partial \zeta} \right|_{\zeta=0} = \frac{-r}{\Gamma(4/3)} \int_0^r \left. \frac{dc_{i,o}}{dr} \right|_{r=r'} \frac{dr'}{(r^3 - r'^3)^{1/3}} \tag{12}$$

and Eq. (12) can be inverted

$$c_{i,o} - c_{i,\infty} = \frac{-1}{\Gamma(2/3)} \int_0^r \frac{\partial c_{i,o}}{\partial \zeta}\bigg|_{\substack{\zeta=0 \\ r=r'}} \frac{r' dr'}{(r^3 - r'^3)^{2/3}} \qquad (13)$$

where the dimensionless distance from the surface is

$$\zeta = y(a\nu/3D_i)^{1/3}(\Omega/\nu)^{1/2} . \qquad (14)$$

All of the minor ionic species are either a reactant or a product in the general electrode reaction Eq. (1) which combined with Eq. (13) provides the relationship

$$\frac{c_{i,o} - c_{i,\infty}}{c_{j,o} - c_{j,\infty}} = \frac{s_i}{s_j}\left(\frac{D_j}{D_i}\right)^{2/3} . \qquad (15)$$

A great economy in computation can be achieved by using Eq. (15) to find the concentrations of all reaction species except for one, which must be determined from Eq. (12). The reference ion will be taken to be the third species, and this can be conveniently regarded as the limiting reactant.

For the case of two minor species, Eq. (10) is solved subject to the boundary conditions

$$c_1^{(1)} \to 0 \qquad \text{as} \quad \zeta \to \infty \qquad (16)$$

and

$$\frac{dc_1^{(1)}}{d\zeta}\bigg|_{\zeta=0} = \frac{u_1 D_2}{z_2 u_2 D_1 - z_1 u_1 D_2} \left[z_3 \frac{dc_3^{(1)}}{d\zeta}\bigg|_{\zeta=0} + z_4 \frac{dc_4^{(1)}}{d\zeta}\bigg|_{\zeta=0} \right] \quad (17)$$

to give (15)

$$\frac{c_{1,o}^{(1)} - c_{1,\infty}^{(1)}}{c_{3,o}^{(1)} - c_{3,\infty}^{(1)}} = \left\{ \frac{z_3 u_1}{z_1 u_1 - z_2 u_2} \left(\frac{D_2 - D_3}{D_e - D_3} \right) \left[\left(\frac{D_e}{D_3} \right)^{1/3} - 1 \right] - \right.$$

$$\frac{z_3 u_1 D_2}{z_1 u_1 D_2 - z_2 u_2 D_1} \left(\frac{D_e}{D_3} \right)^{1/3} \right\} + \frac{s_4}{s_3} \left(\frac{D_3}{D_4} \right)^{2/3} \left\{ \frac{z_4 u_1}{z_1 u_1 - z_2 u_2} \right.$$

$$\left. \left(\frac{D_2 - D_4}{D_e - D_4} \right) \left[\left(\frac{D_e}{D_4} \right)^{1/3} - 1 \right] - \frac{z_4 u_1 D_2}{z_1 u_1 D_2 - z_2 u_2 D_1} \left(\frac{D_e}{D_4} \right)^{1/3} \right\} . \quad (18)$$

The remaining concentration, $c_2^{(1)}$, is calculated from the electro-neutrality condition.

Numerical Example

For a numerical example, a fast redox reaction equimolar in the bulk concentrations of minor species, such as the ferro-ferricyanide couple with sodium fluoride as the supporting electrolyte, was chosen for a system that would exhibit significant differences between a product dependent and a product independent treatment. Many other systems would serve just as well. The dimensionless groups that characterize the solutions are[1,10]

$$N = -\Gamma(4/3) \frac{nFr_o i_{lim}}{RT\kappa_\infty} \qquad (19)$$

and

$$J = \frac{i_{o\varphi} r_o nF}{RT\kappa_\infty} . \qquad (20)$$

The basic solution procedure for the set of equations is similar to that of Parrish and Newman [10] with the addition of Eq. (15) for the concentration of the product and Eq. (18) for the concentration of the supporting electrolyte.
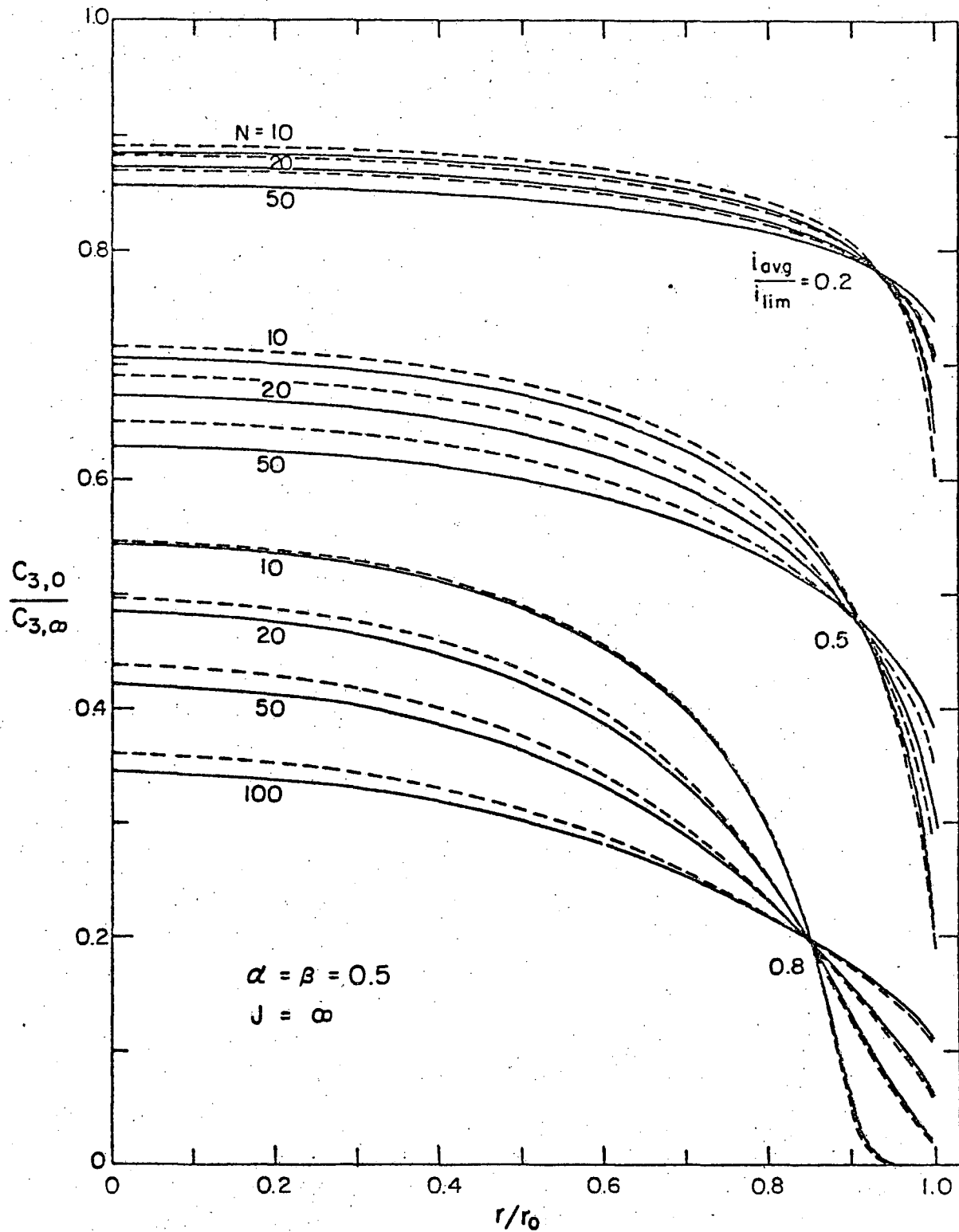
Concentration and current distributions are calculated with a given average current rather than a specified fraction of the limiting current at the center of the disk, by adding an extra loop[3] to the basic iteration[1] The parametric dependence of the computations on the dimensionless stirring rate N is thus clearly emphasized in Figs. 1 and 2. Increasing N produces larger differences between the product dependent and independent approaches. The concentration of the supporting electrolyte cation differs from the bulk value as shown in Fig. 3. The effect is small, but it must be taken into account for alternating current impedance calculations or double layer investigations.

Fig. 2 for the reactant concentration is related to Fig. 1 for the current distribution by means of Eq. (12) or Eq. (13). The product concentration $c_{4,o}$ would be higher than the bulk concentration by an amount proportional to the depletion of the reactant in Fig. 2,
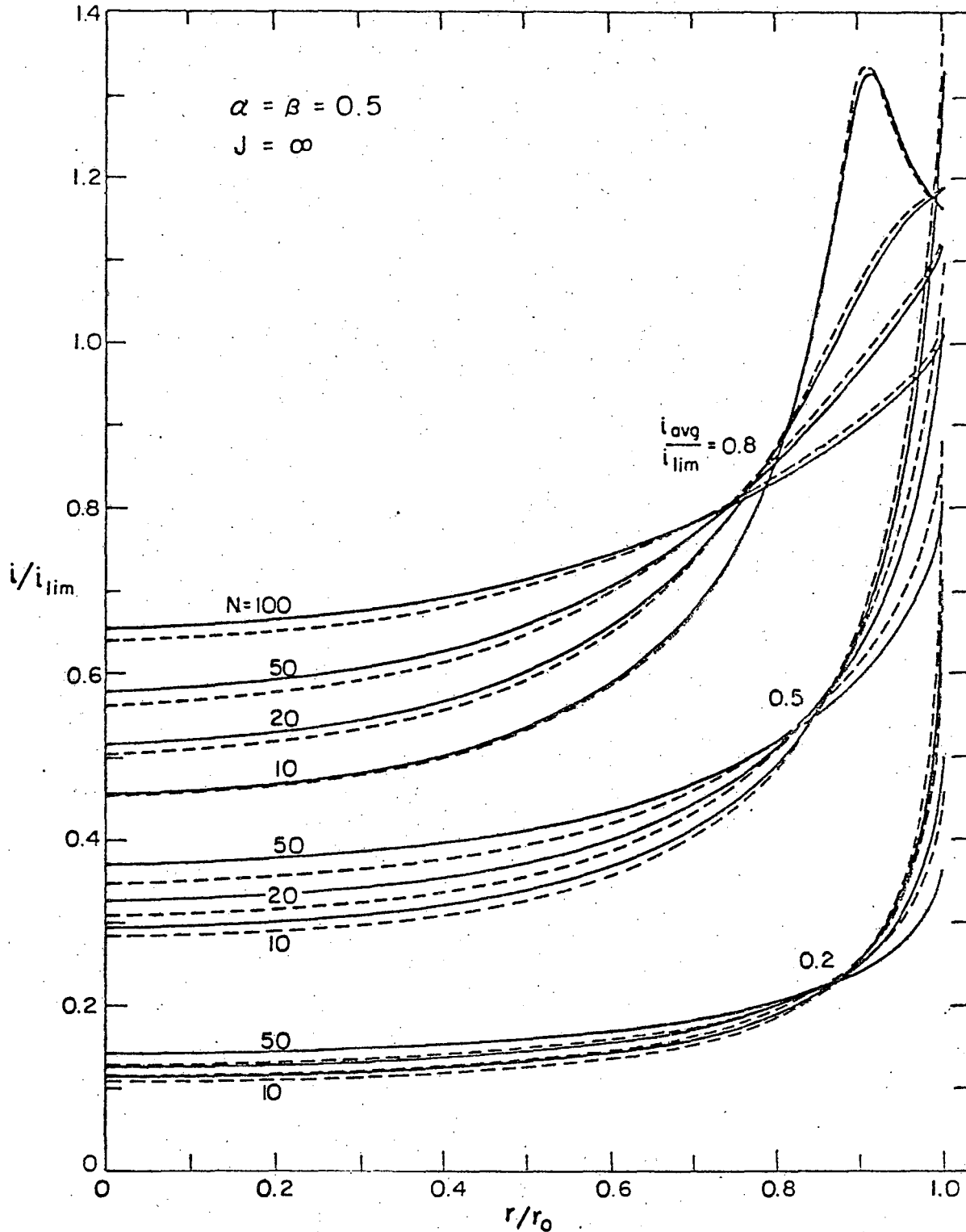
Figure 1. Current distribution; dashed lines represent the product-independent reaction and solid lines are for the product-dependent reaction (reduction of ferricyanide with equal bulk concentrations of ferricyanide and ferrocyanide). $D_4/D_3 = 1.0$; the curves are not appreciably different for $D_4/D_3 = 0.825$, the ratio at infinite dilution.

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Figure 2. Concentration distribution; dashed lines represent the product independent reaction and the solid lines are for the product dependent reaction.

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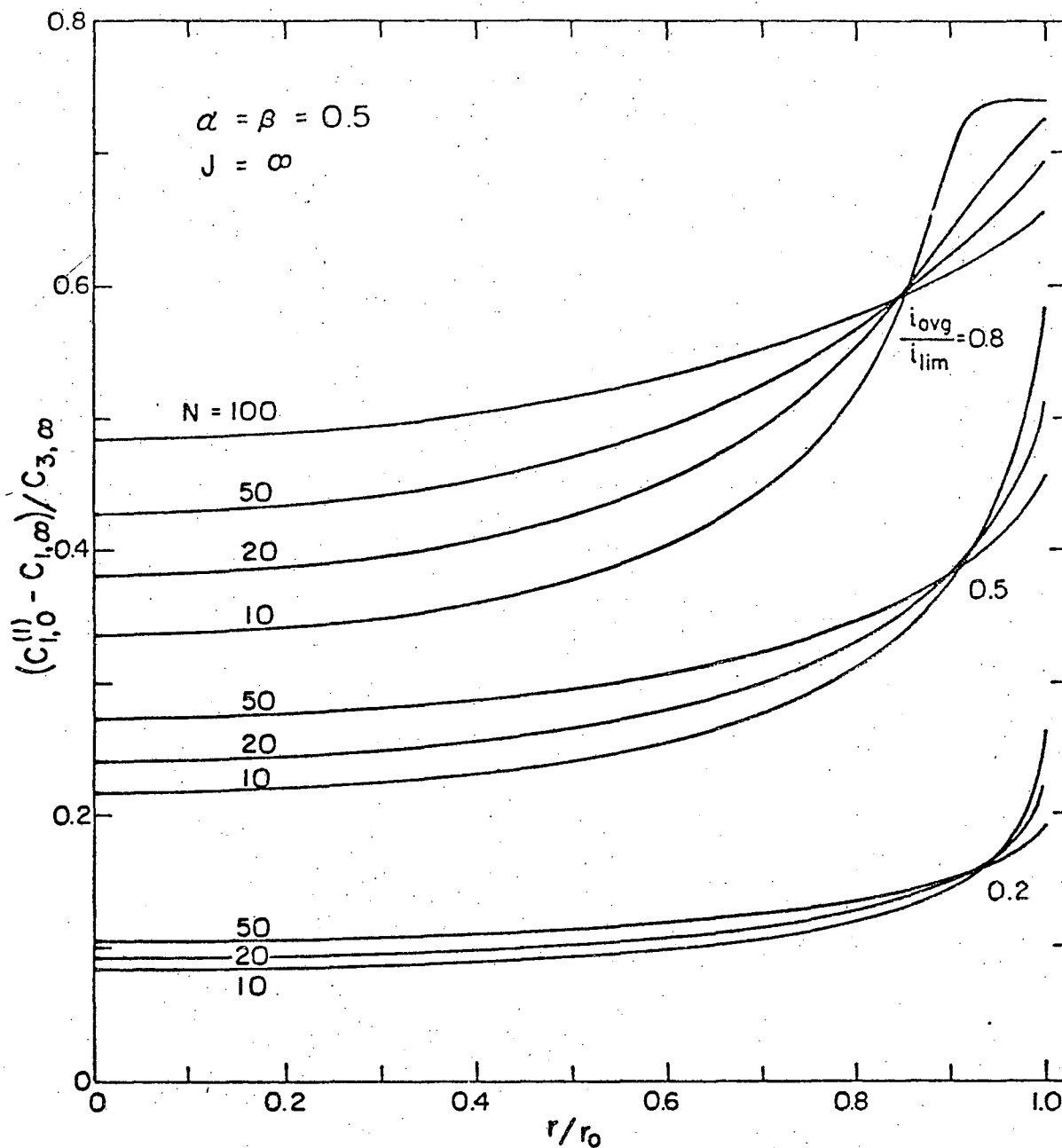
Figure 3. Concentration distribution of the cation of the uni-univalent supporting electrolyte for the product and reactant dependent reaction. (D_e/D_3 = 1.798 and D_4/D_3 = 0.825. Mobilities are obtained from the Nernst-Einstein relation.)

and could be computed through Eq. (15). The supporting cation in Fig. 3 reflects the current distribution also, but this is through the reactant and product concentrations according to Eq. (18).

Acknowledgement

Nomenclature

a	0.51023
B_m	coefficients in series for potential
c_i	concentration of ith species, mole/cm^3
$c_i^{(j)}$	concentration of ith species in the jth perturbation, mole/cm^3
$c_{i,o}$	concentration of the ith species at the electrode surface, mole/cm^3
$c_{i,\infty}$	concentration of the ith species in the bulk solution, mole/cm^3
D_e	diffusion coefficient of the binary electrolyte, cm^2/sec
D_i	diffusion coefficient of the ith species, cm^2/sec
F	Faraday's constant, coulomb/equiv
i	normal current density at electrode surface, amp/cm^2
i_o	exchange current density, amp/cm^2
$i_{o,\infty}$	characteristic exchange current density, amp/cm^2
i_{lim}	current density at the limiting current, amp/cm^2
J	dimensionless exchange current density
M_i	chemical symbol for ith species

N	dimensionless stirring rate
n	number of electrons produced in the reaction
P_{2m}	Legendre polynomial of order 2m
R	universal gas constant, joule/mole-deg
r	radial coordinate, cm
r_o	radius of disk electrode, cm
s_i	stoichiometric coefficient of species i
T	absolute temperature, °K
U	open circuit cell potential, volt
u_i	mobility of species i, cm^2-mole/joule-sec
V	applied potential, volt
y	normal distance from disk, cm
z_i	charge number of species i
Z	negative number of electrons produced in the reaction
α, β	parameter in Butler-Volmer kinetic expression
γ_i	parameter in exchange current relation (see Eq. (4))
ζ	dimensionless normal distance (see Eq. (14))
η	elliptic coordinate
η_c	concentration overpotential, volt
η_s	surface overpotential, volt
κ_∞	electrical conductivity of bulk solution, $ohm^{-1}cm^{-1}$
ν	kinematic viscosity, cm^2/sec
Φ	electrostatic potential, volt
Φ_o	electrostatic potential extrapolated to the electrode surface, volt
Ω	rotation speed, radians/sec

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