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RADIALLY DEPENDENT CONVECTIVE WARBURG PROBLEM FOR A ROTATING DISK

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Radially Dependent Convective Warburg Problem for a Rotating Disk

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February, 1977

Abstract

The oscillating concentration distribution of a reacting species in excess supporting electrolyte is calculated for a rotating-disk system where a step change in the amplitude of the concentration fluctuation at the surface of the disk occurs at an arbitrary distance from the center of the disk. The response of a product species and of the supporting electrolyte to this step change is presented also.

Introduction

Analysis of the current response of an electrochemical cell to an applied oscillating potential requires knowledge of the interplay between the current distribution in the bulk of the solution, the concentration variations near the electrode, the double-layer response to changes in composition and potential, and reaction kinetics. Our aim is to solve this problem for the rotating-disk system, but in this paper we show the influence of concentration variations only at the surface of the disk on the cell response in terms of the concentration gradients normal to the surface of the disk. It has been shown by Parrish and Newman[1] that if one can calculate the concentration gradients at the surface of an electrode, caused by a step change in the concentration at said surface, one can calculate said gradients for arbitrary surface concentration by superposition.[2] This information can then be used to solve the steady-state problem for the electrode being studied, but by the same reasoning we can apply our knowledge of the response of an electrode to a step change in the amplitude of the concentration variations to solve the alternating problem described above. This seems particularly important for the rotating disk, since there is no reason to assume that the oscillating current distribution on the surface of the disk will be uniform; in fact, the complete analysis shows that this is not the case.[3]

Earlier calculations of the concentration impedance of a rotating disk -- assuming a radially independent concentration distribution

have been made by Levart and Schuhmann[4] and were later extended to include homogeneous, first-order chemical reactions by means of a series expansion in $Sc^{-1/3}$ and a dimensionless parameter involving reaction kinetics and oscillation frequency.[5] This expansion, valid for high frequencies and any practical Schmidt number is shown by these authors[6] to include as a special case the expansion of Homsy and Newman,[7] valid for large Schmidt numbers and high frequencies. Deslouis et al.[8] investigated experimentally the frequency dispersion of a rotating disk, operated below the limiting current. The reaction used was the reduction of ferricyanide in excess supporting electrolyte. Their results are in surprisingly good agreement with the theoretical results of Levart and Schuhmann in view of our finding that both the oscillating current distribution and the time average current distribution for this reaction[9] below the limiting current are nonuniform on the surface of the disk. Also, the concentration fluctuations of the produced species (ferrocyanide) influence the concentration overpotential to the same extent as the reacting species (see Newman,[10] Chapter 20).

Finally, the change in the double-layer capacity is caused by the fluctuations in the potential and the fluctuations of all ionic species in the solution just outside the double layer -- including the supporting electrolyte. The latter fluctuations are caused by the influence of migration on the supporting electrolyte and the condition of electroneutrality outside the double layer. Therefore, we have included the effect of the supporting electrolyte in our calculations.

Mathematical Formulation

In our treatment we assume constant transport properties of the ionic species and neglect the influence of migration on the minor, reacting species. In addition, the cation of the supporting electrolyte is also the cation of the reacting species. This situation arises, for instance, if we reduce sodium ferricyanide to sodium ferrocyanide in excess sodium fluoride.

Since all transport equations used are linear, we may separate the equations into a time dependent and a time independent part. The time independent part has been treated before, and since all time dependent quantities fluctuate with a frequency ω, we may write:

$$\Delta c_i = \mathrm{Re}\{\tilde{c}_i \exp(j\omega t)\} , \qquad [1]$$

where

$$\tilde{c}_i = |\Delta c_i(r,y)| \exp[j\phi(r,y)] . \qquad [2]$$

Radial diffusion is small compared to radial convection, so that the conservation equation in cylindrical coordinates for the minor species becomes:

$$jw\tilde{c}_i + v_r \frac{\partial \tilde{c}_i}{\partial r} + v_y \frac{\partial \tilde{c}_i}{\partial y} = D_i \frac{\partial^2 \tilde{c}_i}{\partial y^2} \qquad [3]$$

with the boundary conditions:

$$\tilde{c}_i = 0 \quad \text{at} \quad y = 0 , \; r < r' , \qquad [4]$$

$$\tilde{c}_i = 1 \quad \text{at} \quad y = 0 , \; r \geq r' , \qquad [5]$$

$$\tilde{c}_i \to 0 \quad \text{as} \quad y \to \infty . \qquad [6]$$

For high Schmidt numbers we may use the expression for the velocity distribution close to the disk surface. If we introduce subsequently the dimensionless variables:

$$x = \left(\frac{r^3 - r'^3}{r^3}\right)^{1/3} , \qquad [7]$$

$$\eta_i = y\left(\frac{a\nu}{3D_i}\right)^{1/3} \left(\frac{\Omega}{\nu}\right)^{1/2} \Big/ x \qquad [8]$$

the conservation equation becomes:

$$\frac{\partial^2 \tilde{c}_i}{\partial \eta_i^2} + 3\eta_i^2 \frac{\partial \tilde{c}_i}{\partial \eta_i} = jK_i x^2 \tilde{c}_i + 3\eta_i x(1 - x^3) \frac{\partial \tilde{c}_i}{\partial x} , \qquad [9]$$

where K_i is a dimensionless frequency, given by:

$$K_i = \frac{\omega}{\Omega} Sc_i^{1/3} \left(\frac{3}{a}\right)^{2/3} . \qquad [10]$$

In this new coordinate system, the boundary conditions given by equations 4 - 6 are transformed into:

$$\tilde{c}_i = 1 \quad \text{at} \quad \eta_i = 0 , \qquad [11]$$

$$c_i \to 0 \quad \text{as} \quad \eta_i \to \infty , \qquad [12]$$

$$\tilde{c}_i = F_o(\eta_i) \quad \text{at} \quad x = 0 . \qquad [13]$$

The function $F_o(\eta_i)$ is obtained by solving equation 9 at $x = 0$ with boundary conditions 11 and 12. The result is:

$$F_o(\eta_i) = \frac{1}{\Gamma(4/3)} \int_{\eta_i}^{\infty} e^{-z^3} dz \ . \qquad [14]$$

The finite-difference form of equation 9 has to take into account the behavior of $\tilde{c}_i$ near $x = 0$ since this is a singular point of this equation. Therefore, an asymptotic solution was sought for small values of x. This solution also serves as a check on the values obtained numerically. For this purpose, we expand $\tilde{c}_i$ in a power series in x:

$$\tilde{c}_i(\eta_i, x) = F_o(\eta_i) + F_1(\eta_i)x^m + F_2(\eta_i)x^n + O(x^p) \ . \qquad [15]$$

Substitution of this expression into equation 9 gives a set of coupled ordinary differential equations, and in addition we find that $m = 2$, $n = 4$, and $p = 5$. All these equations for $F_k(\eta_i)$, where $k > 0$, are subject to the boundary conditions:

$$F_k = 0 \quad \text{at} \quad \eta_i = 0 \ , \ F_k \to 0 \quad \text{as} \quad \eta_i \to \infty \ , \qquad [16]$$

since $\tilde{c}_i$ evaluated from the series expansion must also satisfy boundary conditions 11 - 13. The equation for F_1 is:

$$\frac{d^2F_1}{d\eta_i^2} + 3\eta_i^2 \frac{dF_1}{d\eta_i} - \eta_i F_1 = jK_i F_o \ . \qquad [17]$$

The solution to above equation satisfying boundary conditions 16 is:

$$F_1 = \frac{jK_i}{2\Gamma(4/3)}\,\eta_i^2 \int_{\eta_i}^{\infty} e^{-z^3}dz - \frac{jK_i}{6\Gamma(4/3)}\,e^{-\eta_i^3} +$$

$$\frac{2jK_i}{6(\Gamma(4/3))^2}\int_0^1 X \int_{\eta_i/(1-X^3)^{1/3}}^{\infty} e^{-z^3}dz\,dX \;. \qquad [18]$$

The differential equation for F_2 is:

$$\frac{d^2F_2}{d\eta_i^2} + 3\eta_i^2\frac{dF_2}{d\eta_i} - 12\eta_i F_2 = jK_i F_1 \;, \qquad [19]$$

which has been solved numerically since no analytic solution could be obtained. As mentioned before, we are interested in the flux at the surface of the disk as a function of x, the dimensionless distance from the step change at $r = r'$. Using the analytic solution for F_o and F_1, and the numerical solution for F_2, we obtain the following expression, valid for small values of x:

$$\left.\frac{\partial\tilde{c}_i}{\partial\eta_i}\right|_{\eta_i=0} = -\frac{1}{\Gamma(4/3)} - \frac{jK_i}{4\Gamma(4/3)}\left[\frac{\Gamma(5/3)}{\Gamma(4/3)}\right]^2 x^2 -$$

$$0.01250457\,K_i^2x^4 + O(x^5) \;. \qquad [20]$$

Another singular point of equation 9 occurs at $x = 1$ (infinitely far away from the step change at $r = r'$). Proceeding in the same manner as before, we can show that the asymptotic expansion of $\tilde{c}_i$ valid for values of x close to 1 is:

$$\tilde{c}_i = G_o + G_1(1 - x) + G_2(1 - x)^2 + O[(1 - x)^3] \ . \qquad [21]$$

The equation for G_o is identical to the equation describing the uniform distribution and has been calculated by Levart and Schuhmann[4] and by Mohr (as reported by Homsy):[7]

$$\frac{d^2G_o}{d\eta_i^2} + 3\eta_i^2 \frac{dG_o}{d\eta_i} = jK_1G_o \qquad [22]$$

with boundary conditions 11 and 12. Since the equations for G_o , G_1 , and G_2 do not permit us to obtain an explicit dependence of K_i similar to equation 20, we have solved G_1 and G_2 only for $K_i = 50$. The solution of equation 22 has been obtained for all values of K_i investigated.

The linearization procedure for the convective diffusion equation for the supporting electrolyte, including the effect of migration, has been described elsewhere.[3,10] Basically, it involves the elimination of the migration term by applying the electroneutrality condition, resulting in the appearance of terms in the equation accounting for the interaction of each major component with all minor components in the solution. The analysis will be given for the cation of the supporting electrolyte. Using the same notation as in equation 9 with the effective diffusion coefficient D_e for the supporting electrolyte, where

$$D_e = \frac{z_+u_+D_- - z_-u_-D_+}{z_+u_+ - z_-u_-} , \qquad [23]$$

we arrive at the following equation:

$$\frac{\partial^2 c_+}{\partial \eta_e^2} + 3\eta_e^2 \frac{\partial \tilde{c}_+}{\partial \eta_e} = jK_e x^2 \tilde{c}_+ + 3\eta_e x(1 - x^3) \frac{\partial \tilde{c}_+}{\partial x}$$

$$- \frac{z_R u_+ (D_- - D_R)}{z_+u_+D_- - z_-u_-D_+} \frac{\partial^2 \tilde{c}_R}{\partial \eta_e^2} - \frac{z_P u_+ (D_- - D_P)}{z_+u_+D_- - z_-u_-D_+} \frac{\partial^2 \tilde{c}_P}{\partial \eta_e^2} . \qquad [24]$$

In order to take separately into account the concentration changes of supporting electrolyte, reactant and product species, we first solve the above equation with neglect of the last two terms with boundary conditions 11 - 13, and let its solution be denoted by $\tilde{\alpha}$. This solution is identical to the solution of equation 9 with D_e instead of D_i . Similarly, we solve equation 24, neglecting the interaction with the product species, but with $\partial^2\tilde{c}_R/\partial\eta_e^2$ evaluated from the solution to equation 9, with the boundary conditions:

$$\tilde{c}_+ = 0 \quad \text{at} \quad \eta_e = 0 \ , \ \tilde{c}_+ \to 0 \quad \text{as} \quad \eta_e \to \infty \ . \qquad [25]$$

Let the solution be given by $\tilde{\beta}$; the solution to equation 24 due to interaction with the product species only is given by $\tilde{\delta}$. It is evident that both solutions are identical, except that $\tilde{\beta}$ involves the diffusion coefficient of the reactant and $\tilde{\delta}$ that of the product.

The asymptotic expansion of $\tilde{\beta}$ (and of $\tilde{\delta}$) near $x = 0$ proceeds along the same lines as before. Because the resulting equations are

all linear, it is easy to show that

$$\tilde{\beta} = \tilde{\beta}_o(\eta_e) + jK_e\tilde{\beta}_1(\eta_e)x^2 + K_e^2\tilde{\beta}_2(\eta_e)x^4 + O(x^5) \ , \qquad [26]$$

where $\tilde{\beta}_o$, $\tilde{\beta}_1$, and $\tilde{\beta}_2$ are independent of K_e and real. It is possible to obtain an analytic expression for $\tilde{\beta}_o$, but not for $\tilde{\beta}_1$ and $\tilde{\beta}_2$:

$$\tilde{\beta}_o = \frac{z_R u_+ D_e}{\Gamma(4/3)(z_+ u_+ D_- - z_- u_- D_+)} \left(\frac{D_- - D_R}{D_e - D_R}\right) \int_{\left(\frac{D_e}{D_R}\right)^{1/3} \eta_e}^{\eta_e} e^{-z^3} dz \ . \qquad [27]$$

Numerical solutions for $\tilde{\beta}_1$ and $\tilde{\beta}_2$ were not attempted; with the results obtained so far we are able to check the numberical solution of $\tilde{\beta}$ by evaluating both $\tilde{\beta}(0)$ and $\partial\tilde{\beta}/\partial\eta_e$ (at $\eta_e = 0$ and $x = 0$) and compare these values with the values obtained by using equation 26 at $x = 0$:

$$\tilde{\beta}(0) = 0 \ ; \ \left.\frac{\partial\tilde{\beta}}{\partial\eta_e}\right|_{\eta_e=0} = \frac{z_R u_+ D_e}{\Gamma(4/3)(z_+ u_+ D_- - z_- u_- D_+)} \left(\frac{D_- - D_R}{D_e - D_R}\right)\left[\left(\frac{D_e}{D_R}\right)^{1/3} - 1\right]. \qquad [28]$$

Results and Discussion

A comparison between the asymptotic solutions (equations 15 and 21) and the numerical solution of equation 9 near $x = 0$ and $x = 1$ shows that the values and certain derivatives are identical within 0.1 percent.

Figures 1 and 2 show the derivatives of the real part and the imaginary part of the reactant concentration respectively, evaluated at $\eta_i = 0$. The real part is plotted against x^4 , the imaginary part against x^2 . This choice, as well as the form of the respective expressions on the ordinates, is suggested by the asymptotic solution for small values of x . Figures 3 and 4 show the concentration derivative of the cation of the supporting electrolyte due to a step change in the reactant concentration at the surface of the disk $(\partial\tilde{\beta}/\partial\eta_e(\eta_e = 0))$. Here again, the difference between the values of $\tilde{\beta}(0)$ and $\partial\tilde{\beta}/\partial\eta_e(\eta_e = 0)$ at $x = 0$ calculated from the numerical evaluation of $\tilde{\beta}$ and these values as obtained from equation 28 was less than 0.1 percent. The Nernst-Einstein relation was assumed to be applicable.

We shall now proceed to show how one can obtain the oscillating flux distribution at the disk surface for all ionic species from the results obtained so far once the concentration distribution of these species at the surface of the disk is known. The dimensionless flux is defined as:[7]

$$\left.\frac{\partial\tilde{c}_i}{\partial\zeta_i}\right|_{\zeta_i=0} = \frac{1}{x}\left.\frac{\partial\tilde{c}_i}{\partial\eta_i}\right|_{\eta_i=0} , \qquad [29]$$

since

$$\zeta_i = x\eta_i . \qquad [30]$$

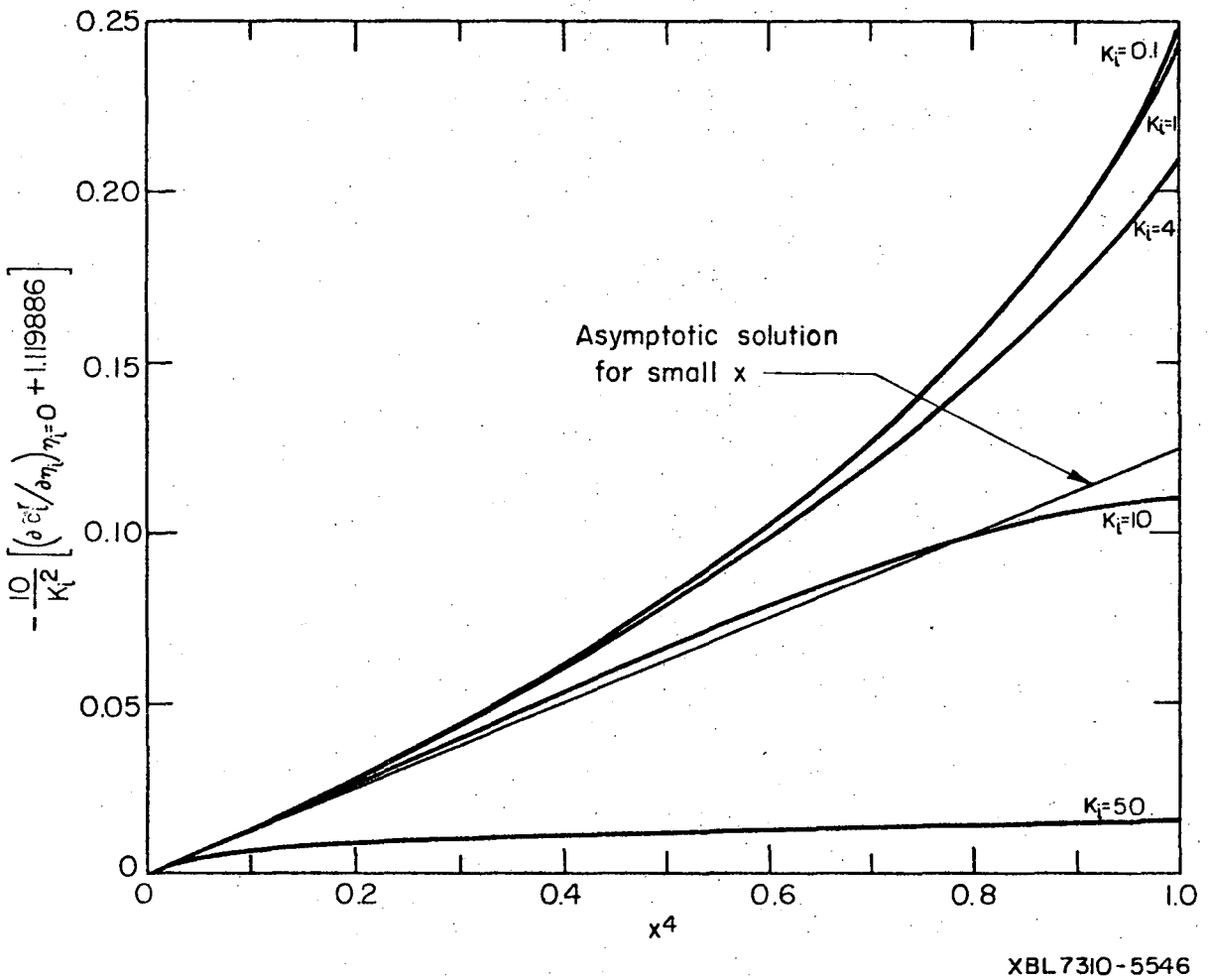

Fig. 1. Derivative of the real part of the concentration at $\eta_i = 0$, as a function of x^4.

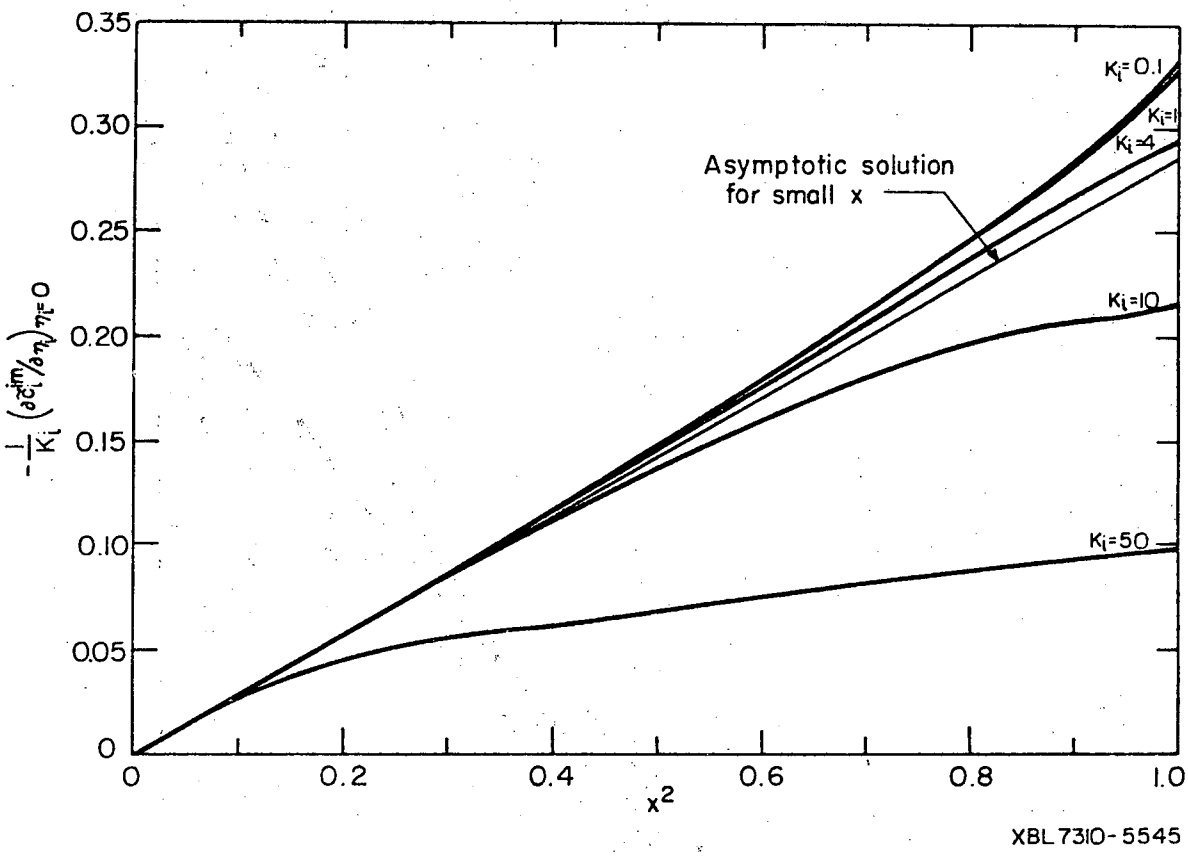

Fig. 2. Derivative of the imaginary part of the concentration at $\eta_i = 0$, as a function of x^2.

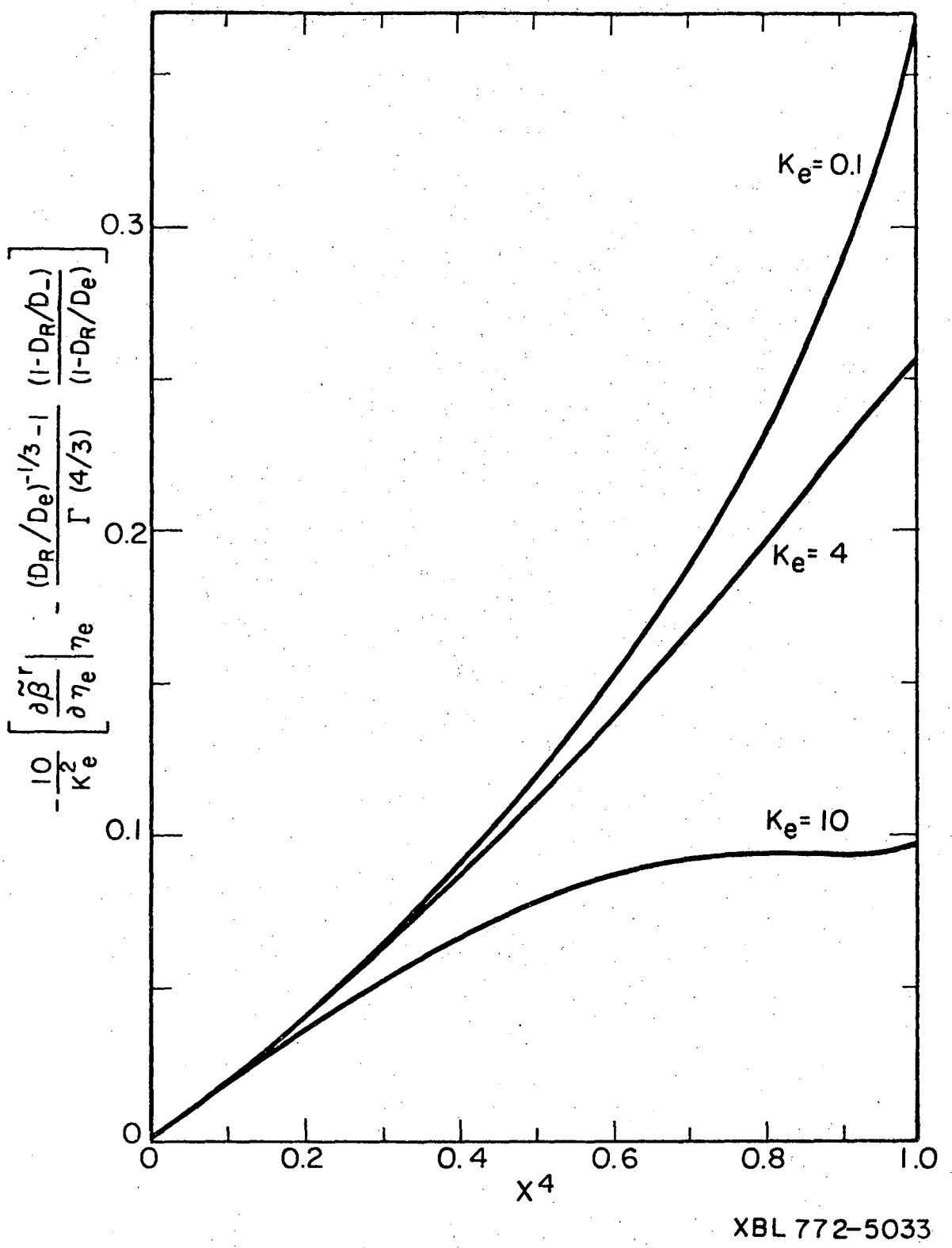

Fig. 3. Derivative of the real part of the concentration fluctuations at the disk surface of the cation of the supporting electrolyte due to a step change in the amplitude of reactant fluctuation.

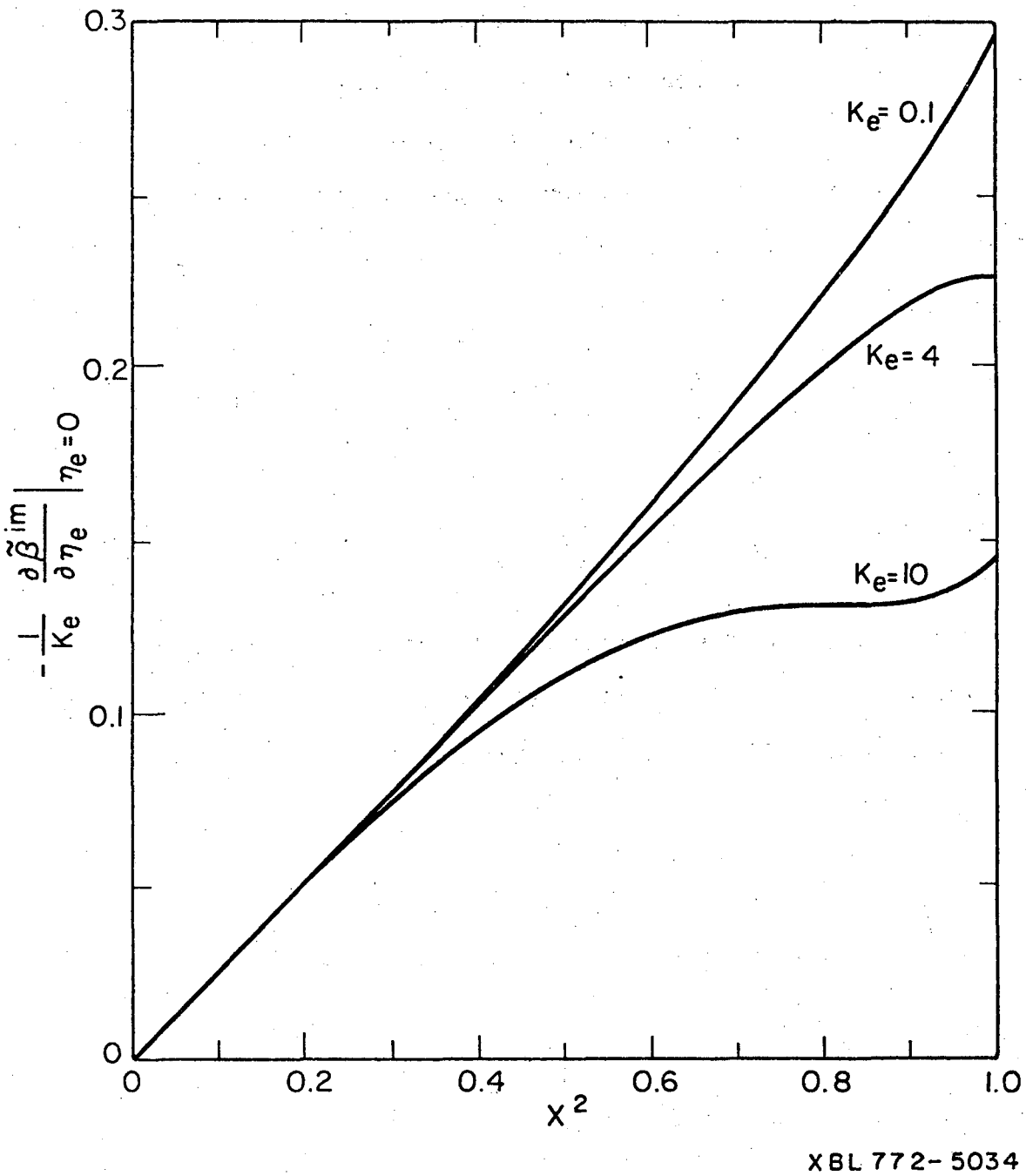

Fig. 4. Derivative of the imaginary part of the concentration fluctuations at the surface of the disk of the cation of the supporting electrolyte due to a stepchange in the amplitude of reactant fluctuation.

The right side of equation 29 has been calculated as a function of x for a step change at $r = r'$. Therefore, for arbitrary surface concentration $\tilde{c}_{i,o}$, we obtain the corresponding flux distribution by superposition, which for the reactant becomes

$$\left.\frac{\partial \tilde{c}_R}{\partial \zeta_i}\right|_{\zeta_i=0} = \int_0^r \left.\frac{d\tilde{c}_{R,o}}{dr}\right|_{r=r'} \left.\frac{\partial \tilde{c}_i}{\partial \eta_i}\right|_{\eta_i=0} \left(\frac{r^3}{r^3 - r'^3}\right)^{1/3} dr' \ . \qquad [31]$$

The same expression holds for the product species, but the subscript R will then be replaced by P. For the cation of the supporting electrolyte we have shown how to take separately into account the contribution of reactant and product species. Because of the linearity of equation 24 we may add these contributions in the expression under the integral sign:

$$\left.\frac{\partial \tilde{c}_+}{\partial \zeta_e}\right|_{\eta_e=0} = \int_0^r \left(\left.\frac{d\tilde{c}_{+,o}}{dr}\right|_{r=r'} \left.\frac{\partial \tilde{\alpha}}{\partial \eta_e}\right|_{\eta_e=0} + \left.\frac{d\tilde{c}_{R,o}}{dr}\right|_{r=r'} \left.\frac{\partial \tilde{\beta}}{\partial \eta_e}\right|_{\eta_e=0} + \right.$$

$$\left. \left.\frac{dc_{P,o}}{dr}\right|_{r=r'} \left.\frac{\partial \tilde{\delta}}{\partial \eta_e}\right|_{\eta_e=0} \right) \left(\frac{r^3}{r^3 - r'^3}\right)^{1/3} dr' \ . \qquad [32]$$

Finally, the anion concentration can be calculated from the electroneutrality equation

$$\sum_i z_i \tilde{c}_i = 0 \ , \qquad [33]$$

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and the anion flux by taking the first derivative of this equation.

Summary

The conservation equations of minor and major species have been solved for a rotating-disk system where a step change in the amplitude of the concentration fluctuations at the surface of the disk occurs at an arbitrary distance from the center of the disk. The effect of migration on the supporting electrolyte was included in the analysis. Results were presented in the form of the flux of each species at the surface of the disk as a function of distance from the place where the step change occurs. The results obtained by the numerical solution of the complete equations were compared with asymptotic solutions valid for short or for very large distances from the step change. The differences were less than 0.1 percent.

It was shown that through the use of superposition integrals these results can be applied to the calculation of the oscillating flux distribution of each ionic species for arbitrary concentration distributions of these species at the surface of the disk.

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List of Symbols

a	0.51023
c_i	concentration of species i, mole/cm^3
Δc_i	deviation of species i from its time average concentration, mole/cm^3
$\tilde{c}_i$	complex alternating concentration of species i, mole/cm^3 (see equation 2)
D_e	diffusion coefficient of supporting electrolyte, cm^2/s (see equation 23)
D_i	diffusion coefficient of species i, cm^2/s
F_o, F_1, F_2	functions in series expansion for the complex concentration near the step change (see equation 15)
G_o, G_1, G_2	functions in series expansion for the complex concentration far from the step change (see equation 21)
j	$\sqrt{-1}$
K_i	dimensionless oscillating frequency based on species i
r	radial distance, cm
r'	distance from the center of the disk were a step change occurs in the complex concentration at the disk surface, cm
$Sc_i = \nu/D_i$	Schmidt number of species i
t	time, s
u_i	mobility of species i, cm^2-mole/J-s
v_r	radial velocity, cm/s
v_y	normal velocity, cm/s
x	dimensionless radial distance (see equation 7)

X	dummy variable in equation 18
y	distance from the surface of the disk, cm
z	dummy variable in equations 14 and 18
z_i	charge number of species i
$\tilde{\alpha}$	complex concentration of the cation of the supporting electrolyte due to a step change in its concentration at the disk surface, mole/cm^3
$\tilde{\beta}$	complex concentration of the cation of the supporting electrolyte due to a step change of reactant concentration at the disk surface, mole/cm^3
$\tilde{\beta}_o, \tilde{\beta}_1, \tilde{\beta}_2$	functions in series expansion of $\tilde{\beta}$ near the step change (see equation 26)
$\Gamma(p)$	the gamma function of the number p
$\tilde{\delta}$	complex concentration of the cation of the supporting electrolyte due to a step change in product concentration, mole/cm^3
ζ_i	dimensionless distance from the disk surface, based on the diffusivity of species i (see equation 30)
η_i	dimensionless distance (see equation 8)
ν	kinematic viscosity, cm^2/s
ϕ	phase shift in alternating concentration, rad (see equation 2)
ω	oscillation frequency of concentrations, rad/s
Ω	rotation speed of disk, rad/s

subscripts

e	supporting electrolyte
P	produced species
R	reacting species
+	cation of the supporting electrolyte
-	anion of the supporting electrolyte

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