Title
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Publication Date
1970-09-01

Submitted to Journal of
Electrochemical Society

UCRL-20306
Preprint

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September, 1970

AEC Contract No. W-7405-eng-48

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Free-Convection Mass Transfer with a Supporting Electrolyte

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Abstract

Free convection and ionic migration effects are reviewed. Electrolytic free convection is treated theoretically for $CuSO_4$ - H_2SO_4 solutions and for $K_3Fe(CN)_6$ - $K_4Fe(CN)_6$ solutions without added electrolyte and with additions of KOH or NaOH. The effect of ionic migration on limiting currents is investigated. The presence of supporting electrolyte lowers the electric field, as in stagnant or forced convective systems. In addition, the concentration distributions of added electrolytes affect the density distribution, hence the velocity profile in free convection and, indirectly, the value of the calculated limiting currents.

Key words: ionic migration, limiting current, vertical electrode, current distribution

Introduction

Mass transfer to a vertical surface in free convection and the effect of ionic migration on limiting currents have both been studied extensively. Here electrolytic systems are treated where both factors enter simultaneously.

Free convection

Fluid flow along a vertical wall as a result of a density gradient shows a boundary-layer structure. The pressure in horizontal planes is uniform and constant and equal to the hydrostatic pressure. The convection is caused by the difference in density along horizontal planes. By means of a similarity transformation, the fluid-mechanical and mass-transfer equations can be reduced to ordinary differential equations,[1,2] which are relatively much easier to solve than partial differential equations. The quantities of practical interest following from the solution of these equations are the mass transfer to the wall and the shear stress at the wall. For a constant density difference $\Delta\rho$ between the vertical surface and the bulk solution, these results can be expressed in dimensionless form as

$$Nu = C_b(ScGr)^{1/4} \qquad (1)$$

and

$$\tau_o/Lg\Delta\rho = B_b(ScGr)^{-1/4} \quad , \qquad (2)$$

where Nu is the average Nusselt number (defined for our systems in equation 32), τ_0 is the shear stress at the wall averaged over the length L, and g is the magnitude of the gravitational acceleration. Sc is the Schmidt number, Gr is the Grashof number

$$Gr = g\Delta\rho L^3/\rho_\infty \nu^2 \quad , \tag{3}$$

and C_b and B_b are dimensionless coefficients which depend on the Schmidt number. Values of C_b and B_b for free convection in a binary fluid at a vertical surface are given in table 1.

The problem of isothermal mass transfer in a binary fluid is identical, mathematically, to that of heat transfer in a pure fluid, in which case the Prandtl number replaces the Schmidt number as a parameter in the analysis.

For free convection to a vertical surface with a constant density difference $\Delta\rho$, the local rate of mass transfer is inversely proportional to $x^{1/4}$, and the local shear stress is proportional to $x^{1/4}$, where x is the vertical distance along the surface measured from the beginning of the boundary layer.

Table 1. Coefficients expressing the rate of mass transfer and the shear stress for free convection at a vertical plate from a binary fluid with a uniform density difference $\Delta\rho$ between the vertical surface and the bulk solution (from references 1, 3, and 4).

Sc	C_b	B_b	Sc	C_b	B_b
0.003	0.1816	0.2707	1	0.5347	0.7265
0.01	0.2421	0.3528	10	0.6200	0.8434
0.03	0.3049	0.4419	100	0.6532	0.9005
0.72	0.5165	0.7045	1000	0.6649	0.9225
0.733	0.5176	0.7057	∞	0.670327	0.932835

Morgan and Warner[5] have shown how to treat this free-convection problem in the limit of an infinite value of the Schmidt number. This limit is of interest in the present context since for electrolytic solutions the Schmidt number is on the order of 1000. For high Schmidt numbers, the velocity profile extends to much greater distances from the surface than the region of concentration variations, that is, the hydrodynamic boundary layer is much thicker than the diffusion layer, and a singular-perturbation treatment is appropriate. Within the diffusion layer it is permissible to neglect the inertial terms in the equation of motion, and outside the diffusion layer the concentration is uniform and equal to the bulk value. It turns out that it is possible to determine the velocity and concentration distributions within the diffusion layer without carrying out the treatment of the velocity profile outside the diffusion layer.

In this manner, Le Fevre[4] determined the limiting values of C_b and B_b as given in table 1. The singular-perturbation expansions were carried out by Kuiken[6] to obtain three terms in the expansions of

C_b and B_b for large Schmidt numbers. A similar perturbation treatment was given by Roy.[7] Acrivos[8] has shown that this treatment can be applied, in the limit of infinite Schmidt number, to other geometries besides the vertical surface. Then, for two-dimensional geometries, the average Nusselt number is expressed as

$$Nu = C_b(ScGr)^{1/4}\left[\frac{1}{L}\int_0^L (\sin\varepsilon)^{1/3}dx\right]^{3/4} , \qquad (4)$$

where ε is the angle between the normal to the surface and the vertical. For the axisymmetric case, see reference 8 or 23.

The limit of small Schmidt numbers was treated by Le Fevre,[4] and the problem was carried to a higher-order term by Kuiken.[9]

We confine ourselves to the analysis of laminar free convection. The transition to turbulence is discussed in connection with the present results for the ferricyanide-ferrocyanide system with supporting electrolyte.

The effect of ionic migration

The flux of an ionic species contains a contribution due to migration in the electric field as well as those due to diffusion and convection. Frequently in mass-transfer studies, a supporting or inert electrolyte is added to the solution in order to reduce this contribution of migration. In this case, the concentration of the reactant obeys the equation of convective diffusion, applicable in nonelectrolytic mass transfer. This should make the results directly comparable to those of experiments in heat transfer and nonelectrolytic mass transfer. In the case of mass transfer from a solution containing a single electrolyte, the concentration again obeys the equation of convective diffusion,[10] but with the diffusion coefficient of the electrolyte rather than the reactant.

With intermediate amounts of supporting electrolyte, it is necessary to solve a more complicated set of equations. Eucken[11] has carried this out for three univalent ions in the, somewhat artificial, Nernst stagnant diffusion layer. Heyrovský[12] rejected this analysis because it did not agree with polarographic experiments for the discharge of hydrogen ions from HCl-KCl solutions and introduced an approximate correction for migration involving the transference number of the reactant.

Newman[13] solved the relevant equations numerically for a variety of electrolytic systems in the following cases: steady mass transfer to a rotating disk at large Schmidt numbers; unsteady mass transfer to a growing drop (polarography); unsteady mass transfer into a stagnant, semi-infinite fluid; and steady mass transfer in a stagnant, Nernst diffusion layer of finite thickness. Okada, Yoshizawa, Hine, and Asada[14] also solved numerically the problem for a growing mercury drop. Newman[15] showed that the case of steady migration through laminar diffusion layers generally, at high Schmidt numbers, is mathematically identical to that of migration to the rotating disk, solved earlier.[13]

Newman's results[13] showed good agreement with the polarographic experiments on HCl-KCl solutions (see also reference 16), thereby removing Heyrovský's objections to the methods of analysis based on the equations of electrolytic mass transfer.

Attempts to obtain an approximate solution to the problem of migration are also necessarily more restricted. Gordon, Newman, and Tobias[17] treated the rotating disk electrode by assuming a constant potential gradient in the diffusion layer. The rigorous solution by analytic means is hardly tractable,[18,19,20] even if the velocity corresponds to a simple hydrodynamic situation.

Hsueh and Newman[21] treated the $CuSO_4$-H_2SO_4 system with no dissociation of the bisulfate ion and with partial dissociation according to its dissociation constant. The earlier treatment[13] of this system had assumed complete dissociation of bisulfate ions. This source[21] also gives the effect of migration for a stagnant Nernst diffusion layer with ions of arbitrary valence.

The migration effect is most simply expressed as the ratio I_L/I_D of the limiting current to the limiting "diffusion current," corresponding to the absence of migration, that is, with an excess of supporting electrolyte. The ratio I_L/I_D can be expressed as a function of the composition, characterized by the ratio of supporting electrolyte to total electrolyte.

Free convection in electrolytic systems

The addition of supporting electrolyte to a solution does not make the free-convection problem directly comparable to that of heat transfer and nonelectrolytic mass transfer in a binary fluid because, while it does reduce the effect of ionic migration, the concentration variation of the supporting electrolyte affects the density variation to roughly the same extent as the reactant and thus influences the velocity profile. Nevertheless, it has frequently been assumed that the mass-transfer rate is adequately expressed by equation 1. Ibl[22] has reviewed the experimental work on this problem and the applicability of equation 1. (See also reference 23.)

The evaluation of $\Delta\rho$ in the Grashof number (see equation 3) has focused attention on the estimation of the concentration of the supporting electrolyte at the electrode surface, a quantity which is of secondary interest in forced convection. The method traditionally used for this estimation was originally developed by Wilke, Eisenberg, and Tobias[24] for $CuSO_4$-H_2SO_4 solutions. The papers of Wagner,[25] Ibl and Braun,[26] and Asada, Hine, Yoshizawa, and Okada[27] are relevant in this regard. Recently, Ravoo[28] has challenged the method of Wilke, Eisenberg, and Tobias on the basis of a bisulfate model applied to the stagnant Nernst diffusion layer. (See also reference 21.)

Brenner[29] succeeded in quickly freezing the solution surrounding a hollow cathode and cutting slices off the frozen mass in order to analyze them. By measuring the refractive index profile, Hsueh and Newman[21] have obtained values of the sulfuric acid concentration at the electrode for unsteady diffusion into a stagnant medium.

Not all experiments in free convection have involved a supporting electrolyte and a vertical electrode. Ibl and Müller[30] have used aqueous solutions of copper sulfate. Schütz[31] investigated experimentally free-convection mass transfer to spheres and horizontal cylinders. (See also reference 23.)

Analysis

The set of equations which determine free convection as a result of concentration variations in electrolytic solutions near a vertical electrode are the following:

the equation of continuity

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad , \tag{5}$$

the equation of motion

$$\nu \frac{\partial^2 v_x}{\partial y^2} + \frac{\rho - \rho_\infty}{\rho_\infty} g_x = 0 \quad , \tag{6}$$

the mass-transfer equation for each solute species

$$v_x \frac{\partial c_i}{\partial x} + v_y \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} + z_i u_i F \frac{\partial}{\partial y} \left(c_i \frac{\partial \Phi}{\partial y} \right) \quad , \tag{7}$$

and the electroneutrality equation

$$\sum_i z_i c_i = 0 \quad . \tag{8}$$

Equation 6 is the boundary-layer form of the x-component of the equation of motion, and equation 7 is the boundary-layer form of the mass-transfer equation. Here y is the normal distance from the electrode. The inertial terms have been omitted from equation 6. This is a valid approximation within the diffusion layer at high Schmidt numbers, as discussed in the introduction.

The density is supposed to be the only variable physical property of the system, and is represented here by a linear expression in terms of the solute concentrations:

$$(\rho-\rho_\infty)/\rho_\infty = \sum_i \alpha_i (c_i - c_{i\infty}) \quad , \tag{9}$$

where α_i is a (constant) "densification coefficient." The mobility is assumed to be related to the diffusion coefficient by the Nernst-Einstein relation

$$D_i = RTu_i \quad . \tag{10}$$

The boundary conditions for the velocity are

$$v_x = v_y = 0 \text{ at } y = 0 \quad , \tag{11}$$

$$\partial v_x/\partial y = 0 \text{ at } y = \infty \ , \tag{12}$$

$$v_x = 0 \text{ at } x = 0 \quad . \tag{13}$$

The boundary condition at $y = \infty$ corresponds to the matching condition for the inner region (the diffusion layer) in the first term of the singular-perturbation expansion for large Schmidt numbers.[5] The inner region can be solved without treating the outer region.

A general expression for the electrode reaction is

$$\sum_i s_i M_i^{z_i} \rightleftarrows ne^- \quad , \tag{14}$$

where s_i is the stoichiometric coefficient of species i and M_i is a symbol for the chemical formula of species i. The current density is thus proportional to the flux of a reacting species at the electrode:

$$s_i i_y = -nFN_{iy} \text{ at } y = 0 \quad . \tag{15}$$

Since the current density is not known in advance, we express the boundary condition on the species fluxes as

$$D_i \frac{\partial c_i}{\partial y} + z_i u_i F c_i \frac{\partial \Phi}{\partial y} = \frac{s_i}{s_R}\left(D_R \frac{\partial c_R}{\partial y} + z_R u_R F c_R \frac{\partial \Phi}{\partial y}\right) \text{ at } y = 0 \quad , \tag{16}$$

the convective contribution to the fluxes being zero at the solid electrode. Species R is a reactant called the "limiting reactant," whose concentration is taken to be constant at the electrode surface:

$$c_R = c_{RO} \text{ at } y = 0 \quad . \tag{17}$$

At the limiting current, which is of interest here, the concentration of the limiting reactant is zero at the electrode, corresponding to the maximum possible rate of mass transfer. Far from the electrode and at the beginning of the boundary layer, the concentrations have their bulk values:

$$c_i = c_{i\infty} \text{ at } y = \infty \quad , \tag{18}$$

$$c_i = c_{i\infty} \text{ at } x = 0 \quad . \tag{19}$$

We now introduce the similarity transformation

$$\xi = y\left[\frac{3g\alpha_R(c_{R\infty}-c_{RO})}{4\nu D_R x}\right]^{1/4} , \qquad (20)$$

$$\psi = \frac{4}{3} D_R x\left[\frac{3g\alpha_R(c_{R\infty}-c_{RO})}{4\nu D_R x}\right]^{1/4} f(\xi) , \qquad (21)$$

where ψ is the stream function defined so that the equation of continuity 5 is satisfied identically:

$$v_x = \frac{\partial\psi}{\partial y} , \qquad v_y = -\frac{\partial\psi}{\partial x} . \qquad (22)$$

With the dimensionless variables

$$\phi = \frac{F}{RT}\left[\Phi-\Phi_o(x)\right] , \qquad \theta_i = \frac{c_i}{c_{R\infty}-c_{RO}} , \qquad (23)$$

equations 5 to 10 become

$$f''' = \pm\sum_i \frac{\alpha_i}{\alpha_R}(\theta_i-\theta_{i\infty}) , \qquad (24)$$

$$(D_i/D_R)[\theta_i'' + z_i(\theta_i\phi')'] + f\theta_i' = 0 , \qquad (25)$$

$$\sum_i z_i\theta_i = 0 , \qquad (26)$$

where the primes denote differentiation with respect to ξ. In equation 24, the plus sign applies if ρ_o is less than ρ_∞, and _vice versa_.

The boundary conditions 11 to 13 and 16 to 19 become

$$\left.\begin{aligned} &\theta_i' + z_i\theta_i\phi' = (s_iD_R/s_RD_i)(\theta_R' + z_R\theta_R\phi') \quad , \\ &f = f' = 0 \quad , \quad \theta_R = \theta_{RO} \quad \text{at } \xi = 0 \end{aligned}\right\} \tag{27}$$

and

$$f'' = 0, \quad \theta_i = \theta_{i\infty} \text{ at } \xi = \infty \quad . \tag{28}$$

The densification coefficients in equation 9 are not unique for ionic species since the solution must be electrically neutral. The value of α_i can arbitrarily be set equal to zero for one ionic species. As a consequence of this arbitrariness, numerical values of ξ and f are not physically significant, and any results should rather be expressed in terms of the dimensionless distance η and the dimensionless stream function $F(\eta)$ defined according to

$$\eta = y\left[\frac{3g\Delta\rho}{4\nu D_R\rho_\infty x}\right]^{1/4} \tag{29}$$

and

$$\psi = \frac{4}{3}D_R x\left[\frac{3g\Delta\rho}{4\nu D_R\rho_\infty x}\right]^{1/4} F(\eta) \quad . \tag{30}$$

The density difference $\Delta\rho$ is not known at the outset; consequently the calculations must be carried out in terms of ξ and f.

The principal results of interest are the mass-transfer rate or limiting current density and the shear stress at the wall. These are expressed by equations 1 and 2 with the coefficients C_b and B_b

replaced by C and B. Here the Schmidt number is

$$Sc = \nu/D_R \quad , \tag{31}$$

and the average Nusselt number is

$$Nu = \frac{N_{R,Avg}L}{D_R(c_{RO}-c_{R\infty})} = \frac{s_R L\, i_{avg}}{nFD_R(c_{R\infty}-c_{RO})} \quad . \tag{32}$$

Of interest also are the concentrations of the nonreacting ions at the electrode, θ_{iO}. These are necessary to calculate the density difference $\Delta\rho$ used in the correlation of the current density and the shear stress.

Method of Calculation

Equations 24 to 26 form a set of coupled, nonlinear differential equations with boundary conditions at zero and infinity. These equations can be linearized about a trial solution producing a series of coupled, linear differential equations. In finite difference form these give coupled, tridiagonal matrices which can be solved readily on a high-speed digital computer.[32] The nonlinear problem is then solved by iteration. For the principal results 150 mesh points were used. A mesh width on the ξ scale of 0.0611 was used for the $CuSO_4$ - H_2SO_4 system and a mesh width of 0.08 was used in the ferricyanide-ferrocyanide systems.

Ionic diffusion coefficients are calculated from limiting ionic mobilities at infinite dilution.[33,34] The densification coefficients for the various systems are given in table 2. The basis for these values can be found in reference 35. The $CuSO_4$ - H_2SO_4 system will be considered both with complete and with no dissociation of bisulfate ions. For the ferrocyanide-ferricyanide redox system, the OH^- ions or the Na^+ ions may be absent in certain cases treated here.

Table 2. Values of the densification coefficients[35] used in the calculations.

species	α_i (ℓ/mole)
H^+	0.02989
$SO_4^=$	0
Cu^{++}	0.13974
H^+	0.059789
HSO_4^-	0
Cu^{++}	0.19955
OH^-	0.04529
Na^+	-0.00673
$Fe(CN)_6^{4-}$	0.22591
K^+	0
$Fe(CN)_6^{3-}$	0.16727

As a preliminary check on the accuracy of the numerical method, calculations were carried out for a binary fluid at $Sc = 1, 10, 100, 1000$, and ∞ and for metal deposition from a binary electrolytic solution in the limit of large Schmidt number. Comparison of these results with those in table 1 leads to the conclusion that our method is generally accurate to four significant figures. For metal deposition from a binary electrolytic solution, one can show that

$$C = \frac{(D_s/D_R)^{3/4}}{1-t_R} \; C_b(Sc_s) \tag{33}$$

and

$$B = (D_s/D_R)^{1/4} \; B_b(Sc_s) \quad , \tag{34}$$

where Sc_s is based on the diffusion coefficient of the salt

$$D_s = \frac{D_+D_-(z_+-z_-)}{z_+D_+-z_-D_-} \tag{35}$$

and t_R is the transference number of the reacting cation.

Results

$CuSO_4$ - H_2SO_4

The effect of the supporting electrolyte, sulfuric acid, can be expressed in the ratios C/C_b and B/B_b, permitting a comparison with the behavior of a binary fluid. These ratios depend on the relative amount of sulfuric acid, expressed as

$$r = \frac{c^{\infty}_{H_2SO_4}}{c^{\infty}_{H_2SO_4}+c^{\infty}_{CuSO_4}} \quad . \tag{36}$$

One is also interested in the concentration of supporting electrolyte at the electrode, in particular in order to calculate $\Delta\rho$, entering into the Grashof number. This is expressed on the graphs as

$$\frac{\Delta c_{H_2SO_4}}{c_{CuSO_4}} = \frac{c^{o}_{H_2SO_4}-c^{\infty}_{H_2SO_4}}{c^{\infty}_{CuSO_4}} \quad . \tag{37}$$

In view of the low value of the dissociation constant of bisulfate ions, the calculations were carried out for no dissociation of bisulfate ions as well as for complete dissociation to sulfate and hydrogen ions. To obtain an idea of the behavior when partial dissociation is considered, one should consult reference 21.

Results are shown in figure 1 for B/B_b for complete dissociation of bisulfate ions and the ratio C/C_b for both no dissociation and complete dissociation of bisulfate ions. Dashed lines show the corresponding values of I_L/I_D for a rotating disk.[21]

As r approaches unity, one would expect C/C_b and B/B_b to approach unity if the appearance of $\Delta\rho$ in the Grashof number were sufficient to correlate the effect of the supporting electrolyte. The contrary behavior emphasizes the fact that these ratios express not only the effect of ionic migration but also the effect of the density profile not being similar to that for a binary fluid. Where Wilke, Eisenberg, and Tobias's correlation[24] works with $C = C_b$, this may indicate that the errors in assuming $C = C_b$ and in estimating the diffusion coefficients compensate for the error in their method of estimating $\Delta\rho$.

To be specific, the diffuson layer thickness is greater for H_2SO_4 than for $CuSO_4$ on account of the larger value of the diffusion coefficient of hydrogen ions. Thus, the density difference in the outer part of the diffusion layer is positive while it is negative near the electrode. Consequently, the value of $\Delta\rho$ does not, by itself, give sufficient information about the density profile. In fact, with added H_2SO_4, the velocity profile shows a maximum within the diffusion layer. This is shown for

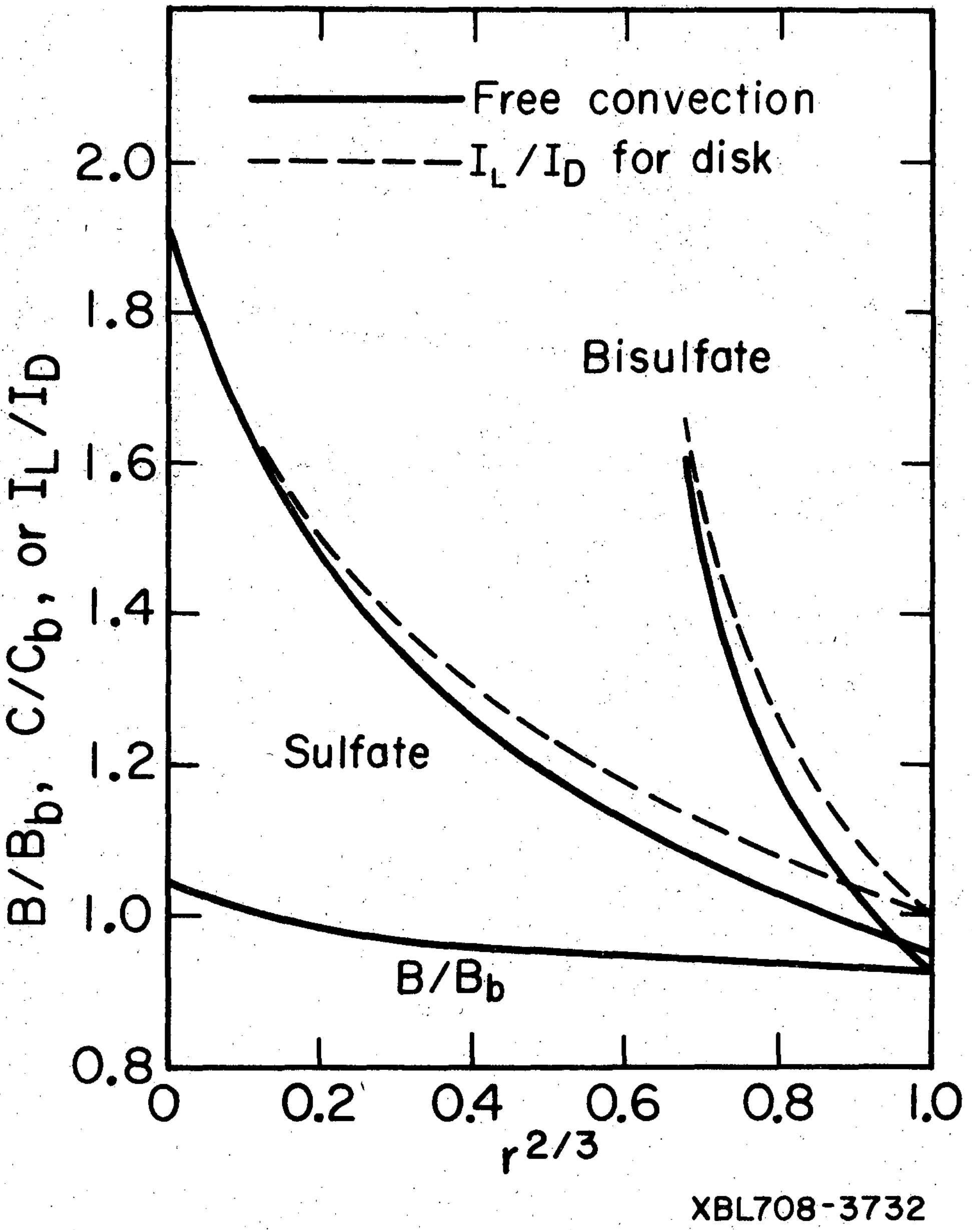

Figure 1. Coefficients for shear stress (complete dissociation only) and mass transfer in the $CuSO_4$ - H_2SO_4 system. Dashed curves show for comparison the values of I_L/I_D for the rotating disk.

excess sulfuric acid in figure 2. The profile for a binary fluid is labeled $CuSO_4$.* Since these phenomena occur in a more drastic fashion in the redox systems, we shall postpone their further discussion.

The ratio B/B_b varies little since it does not involve the dominant effect of ionic migration found in the limiting currents expressed in C/C_b. Values of B/B_b for the bisulfate system are in the same range as those for complete dissociation. They extrapolate to 0.8342 at $r = 1$.

The refractive index profile is shown in figure 3 for complete dissociation of bisulfate ions. A slight maximum occurs when sulfuric acid is present, due again to the larger diffusion-layer thickness of sulfuric acid. These can be compared with figures 7-12 and 7-14 in Hsueh's dissertation.[36] The basis for the refractive index calculation can be found in reference 35.

After the actual velocity profiles have been calculated, one could separate the effect of ionic migration on C/C_b from that due to the dissimilar density profiles. Thus

$$\frac{I_L}{I_D} = (3/4)^{3/4} C \int_0^\infty \exp\left\{- \int_0^\eta F d\eta\right\} d\eta \quad . \tag{38}$$

Here, the "diffusion current" I_D corresponds to the mass transfer by diffusion and convection with the actual velocity profile. Then I_L/I_D approaches unity at $r = 1$. For $r = 0$, I_L/I_D does not coincide with the value of C/C_b given by equation 33 unless $D_s = D_R$. However, this

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*Actually, the profile for a binary fluid would involve D_s instead of D_R in the definitions 29 and 30 of η and F.

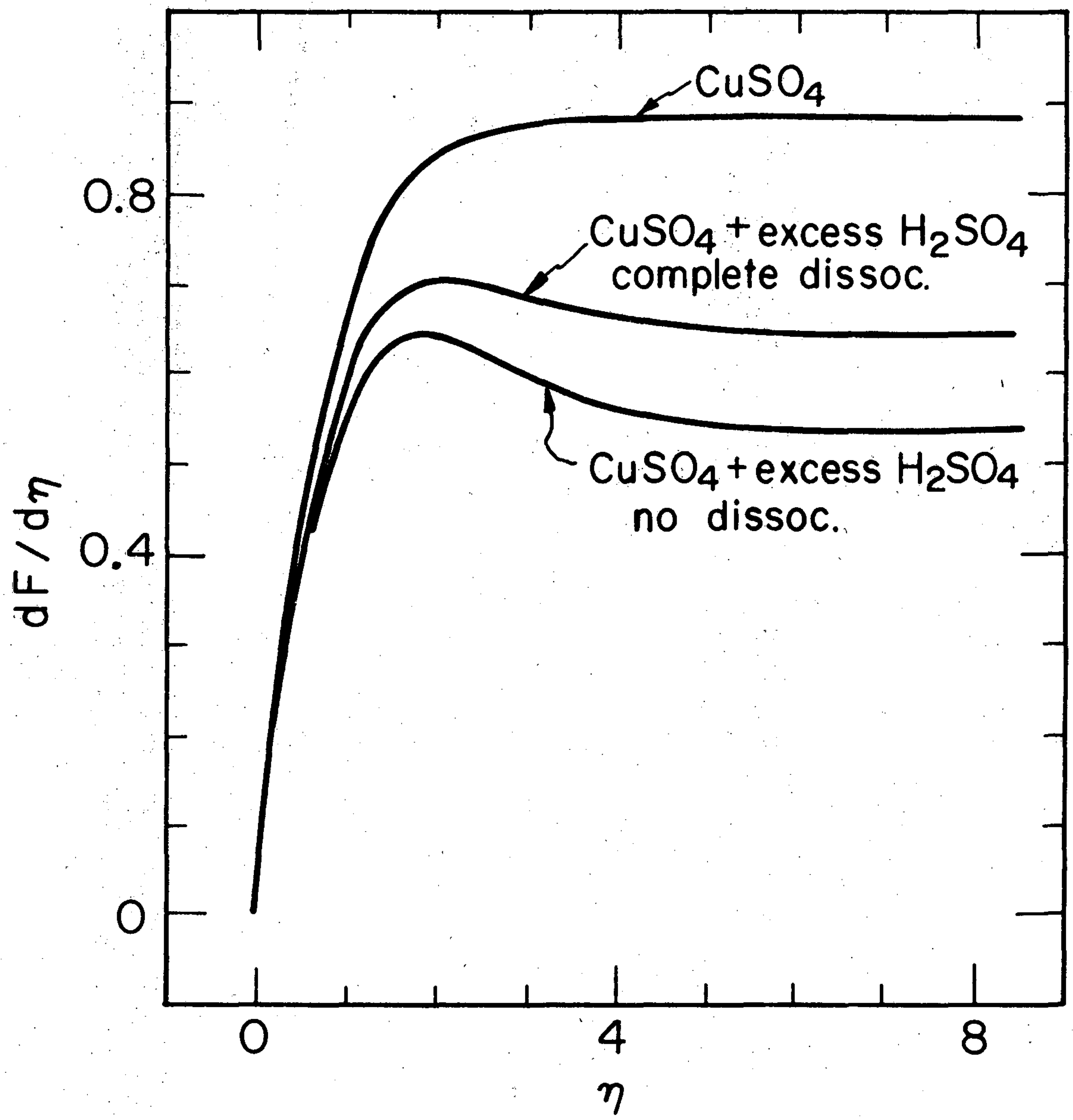

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Figure 2. Velocity profiles for binary salt solution ($CuSO_4$) and for $CuSO_4$ with excess H_2SO_4 (r = 0.99998) completely dissociated and undissociated.

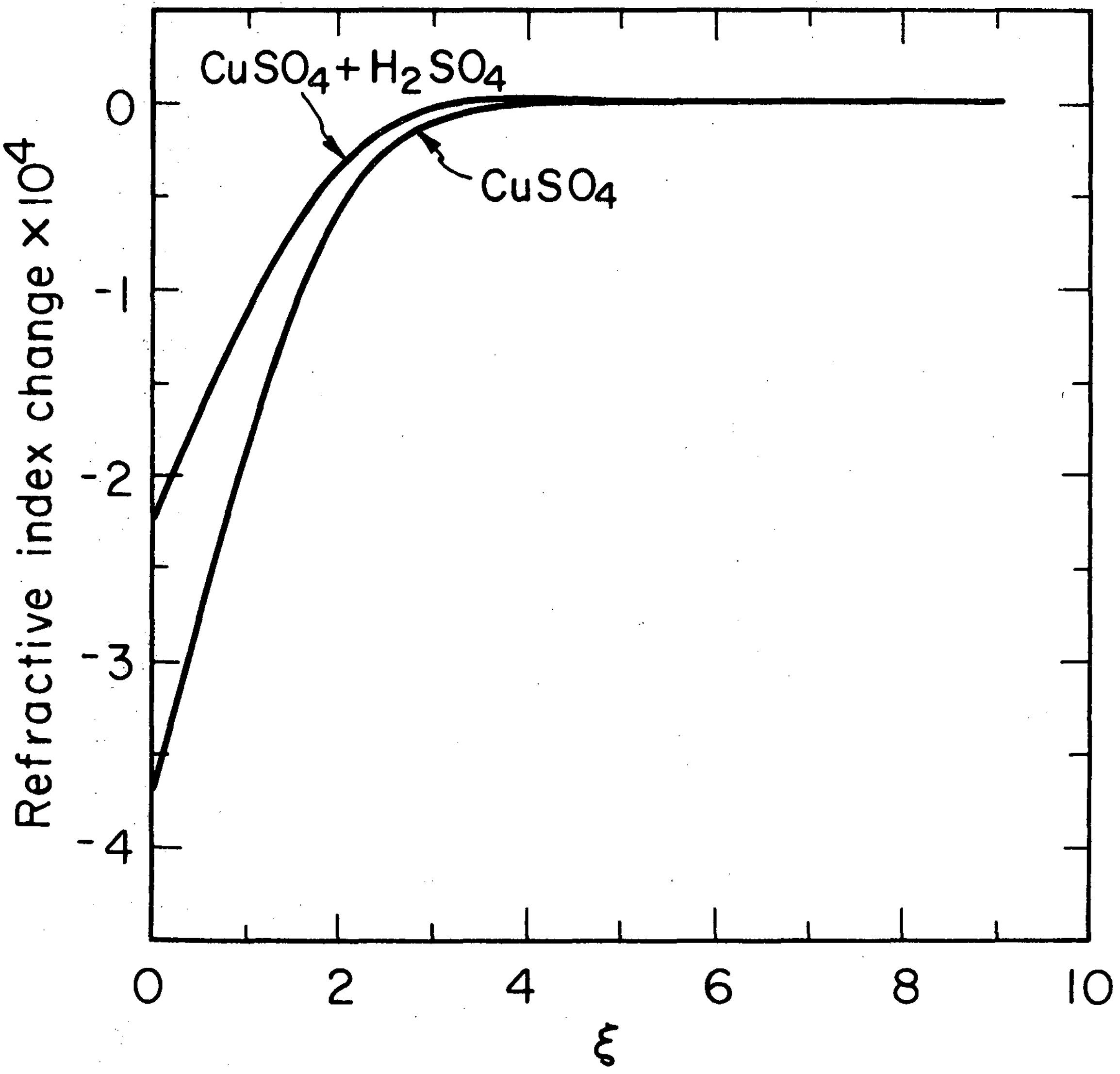

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Figure 3. Refractive index (relative to bulk) in $CuSO_4$ - H_2O (0.02 M bulk, 0.01 M cathode) and in $CuSO_4$ - H_2SO_4 - H_2O (excess H_2SO_4, 0.01 M $CuSO_4$ bulk).

separation has little practical utility since the two effects cannot be separated experimentally. For a system where the diffusion coefficients of the solutes are roughly the same, one could estimate the value of I_L/I_D from calculations for other hydrodynamic situations[13] and then assume that this is equal to the value of C/C_b for free convection with little error. But if detailed calculations for free convection are carried out, one might as well report values of C/C_b, which account for both effects.

The wide range of predictions for the H_2SO_4 concentration at the electrode for the sulfate and bisulfate models and for various hydrodynamic situations is shown in figure 4. Also shown are some values obtained by the method of Wilke, Eisenberg, and Tobias.[24] Ravoo's predictions[28] are based on the bisulfate model for a stagnant Nernst diffusion layer of finite thickness. The value 0.71 is deduced from the results of one of Brenner's experiments.[29] Hsueh and Newman[21] obtained four values in the range from 0.50 to 0.57 and one value of 0.75.

$\underline{K_3Fe(CN)_6}$ - $\underline{K_4Fe(CN)_6}$

The redox reaction

$$Fe(CN)_6^{3-} + e^- \rightleftarrows Fe(CN)_6^{4-} \tag{39}$$

is popular in mass-transfer studies and has been used in free convection, although it is not common. The densification in this system is much weaker than in copper sulfate solutions since the excess of product ion largely compensates for the deficit of the reactant.

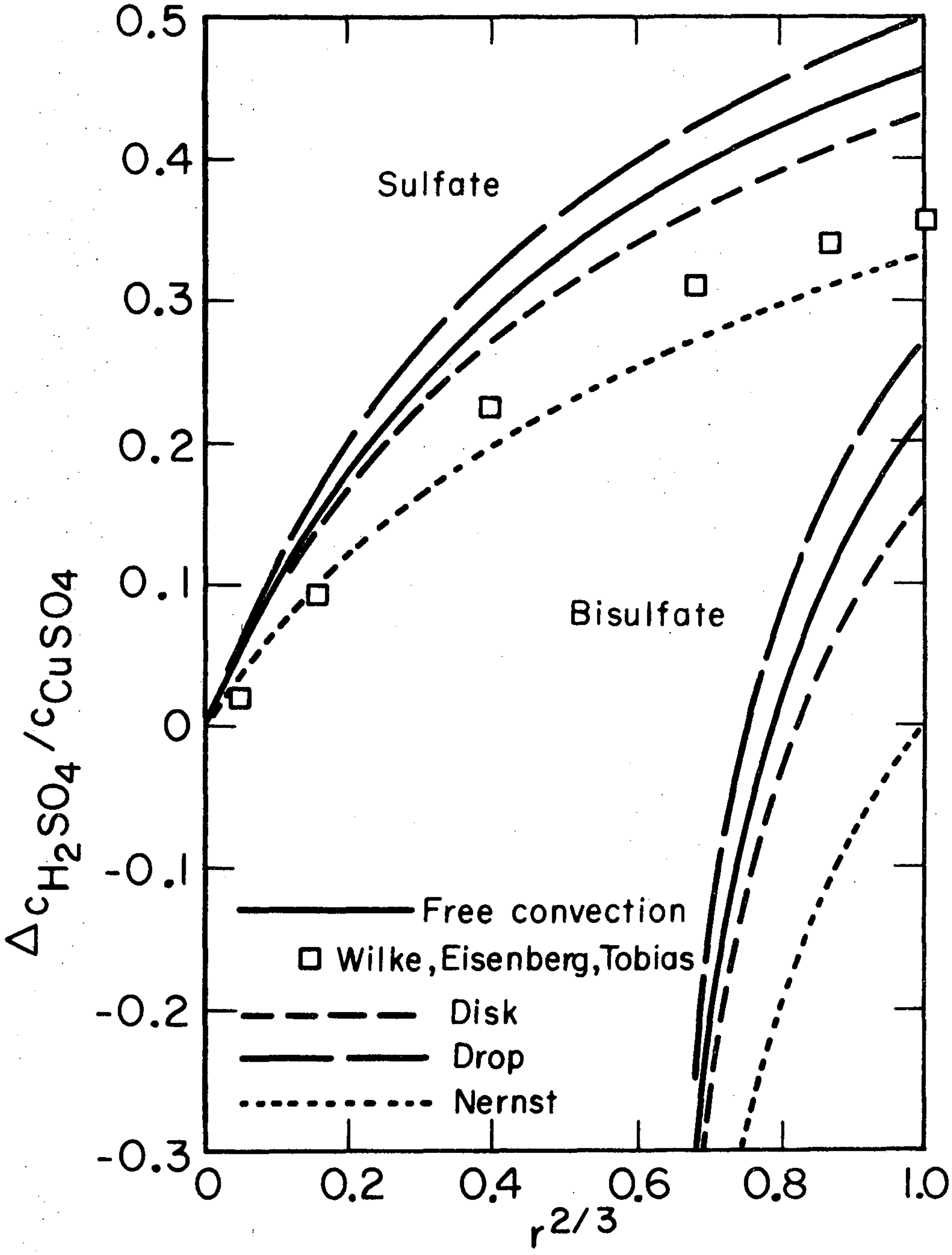

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Figure 4. Excess sulfuric acid at the electrode divided by the bulk copper concentration.

Results for the unsupported ferricyanide-ferrocyanide system are shown in figure 5. Values of I_L/I_D calculated for the rotating disk[13] are also shown. The abscissa is the concentration ratio r_a for the anodic reaction and r_c for the cathodic reaction:

$$r_c = 1 - r_a = \frac{c^{\infty}_{ferro}}{c^{\infty}_{ferro}+c^{\infty}_{ferri}} \quad . \tag{40}$$

The product concentration at the electrode minus that in the bulk, divided by the bulk reactant concentration, is denoted $-\Delta c_p/\Delta c_R$. The effect of ionic migration on limiting currents is relatively small in this system, as observed earlier,[13] since the product ion will always prevent the electric field from becoming infinite at the electrode.

By varying the densification coefficients and diffusion coefficients of the ions, we can study the importance of these factors. The relative unimportance of free convection interacting with migration is evidenced by the fact that it makes little difference for C/C_b or the product concentrations if we assign equal densification coefficients to the reacting and product ions, although the sign of the density difference $\rho_o - \rho_\infty$ reverses and consequently the flow reverses from upward to downward, or vice versa. This emphasizes the fact that the density differences driving the convection in this system are very small. The consequences of this will be seen below when we consider the effect of adding KOH or NaOH as a supporting electrolyte.

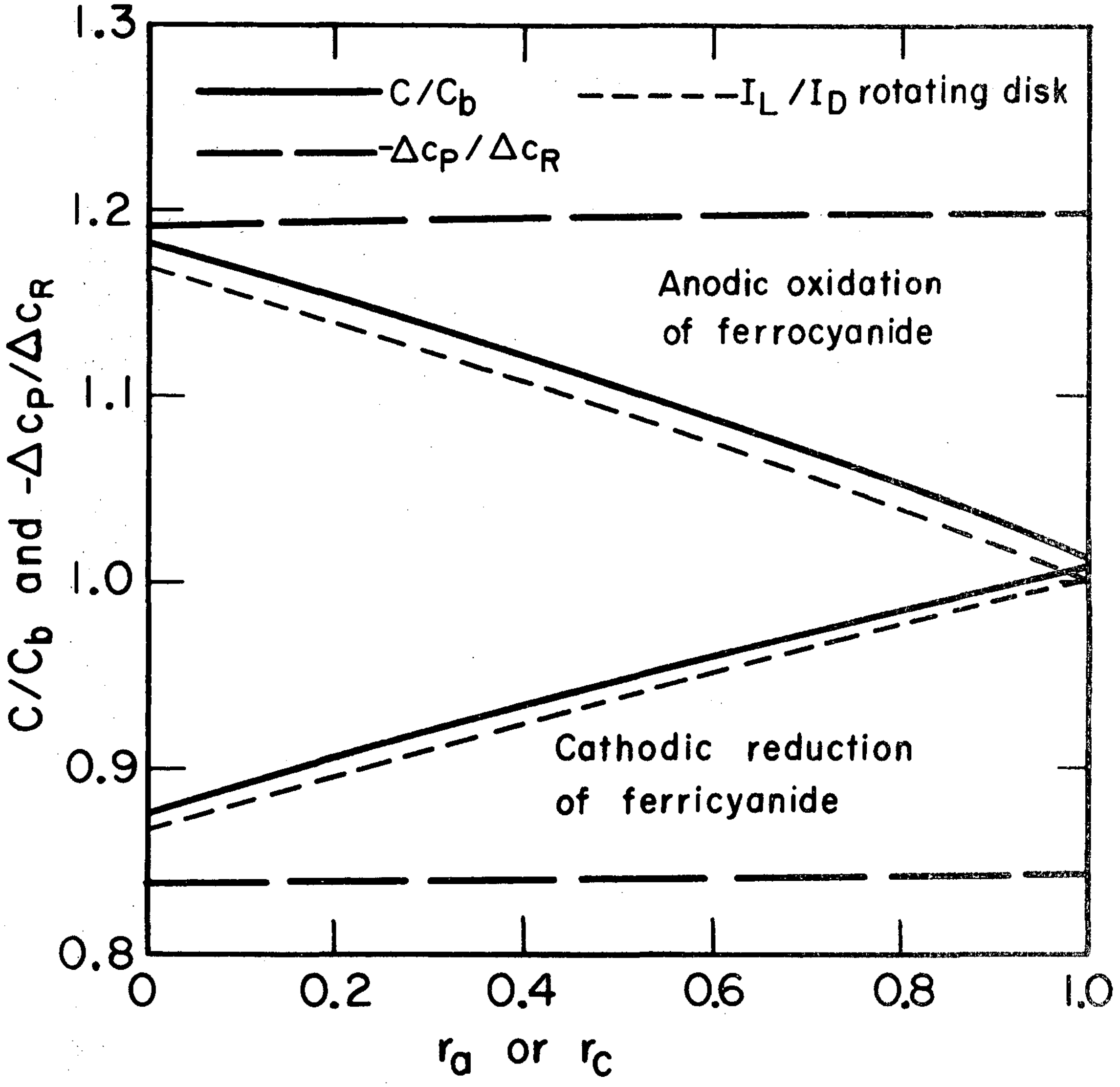

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Figure 5. Product ion concentration at the electrode and the coefficient for the limiting current in the unsupported ferricyanide-ferrocyanide system.

Supported ferricyanide-ferrocyanide

We consider next solutions of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ with KOH or NaOH added as a supporting electrolyte. The latter, although leading to a five-ion system with consequent complications in physical-property estimation, has been used as frequently as the former in reported investigations.[37,38]

In the results, the concentration of supporting electrolyte is expressed in the ratio

$$r = \frac{c^{\infty}_{OH^-}}{c^{\infty}_{K^+}+c^{\infty}_{Na^+}} . \qquad (41)$$

Figures 6 to 8 give the results for these systems for equal bulk concentrations of ferricyanide and ferrocyanide ($r_a = r_c = 0.5$). Additional results for r = 0.5 and various values of r_a or r_c are given in table 3. On figure 6 values of I_L/I_D for the rotating disk with KOH supporting electrolyte[13] are plotted for comparison.

Figure 6 shows a conspicuous deviation of the values of C/C_b from the values of I_L/I_D for the rotating disk, and figure 7 shows a much greater variation of B/B_b than was observed for the $CuSO_4$-H_2SO_4 system. In contrast, the concentration ratios shown in figure 8 are essentially independent of the hydrodynamic situation, almost coinciding with results for the rotating disk (which are not shown).

Figures 6 and 7 reflect the strong dissimilarity of the density profile in the supported solutions compared to that in a binary solution. A dramatic consequence of this is shown in the velocity profiles in

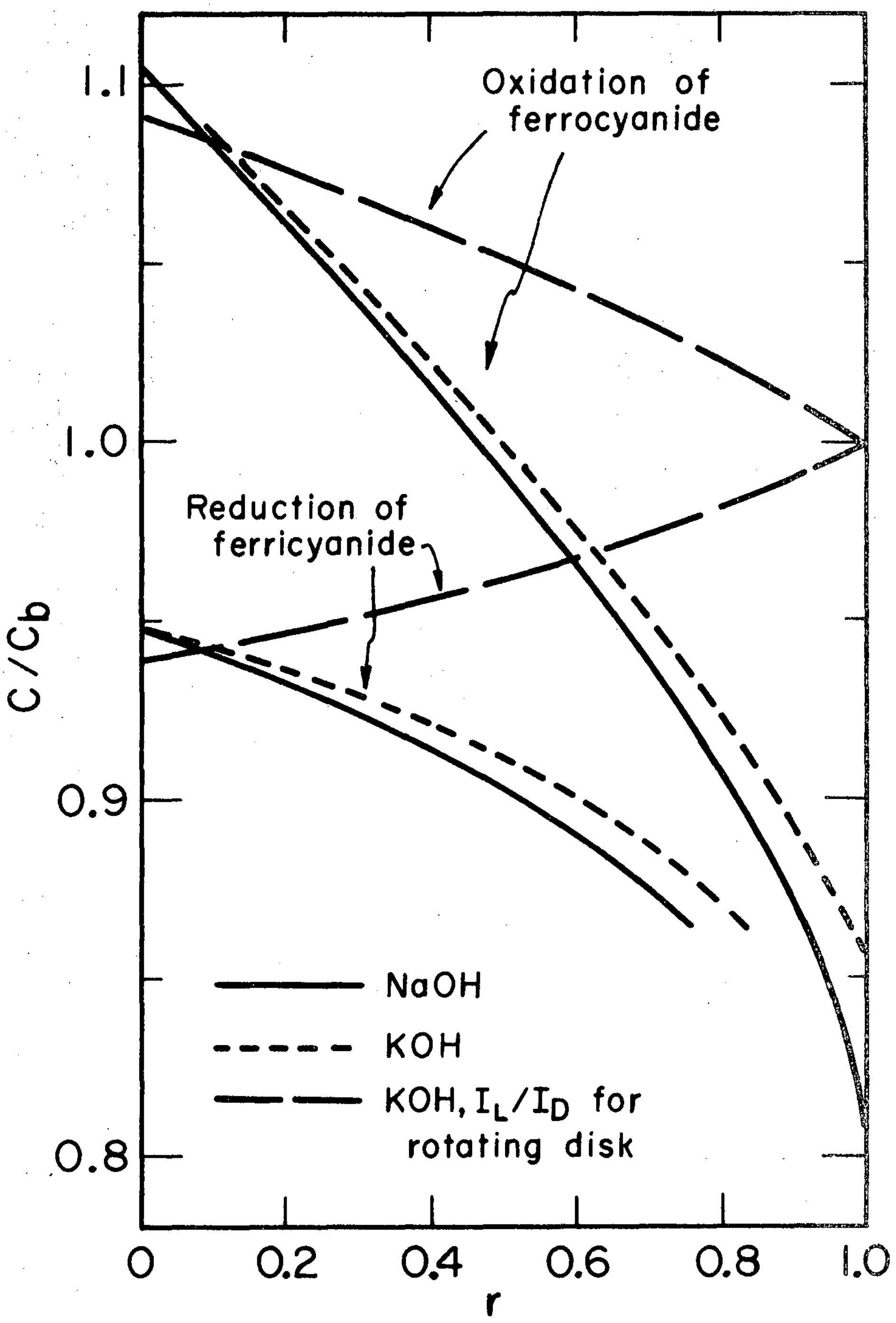

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Figure 6. Coefficient for mass-transfer rate in the supported ferricyanide-ferrocyanide systems, for equal bulk concentrations of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$.

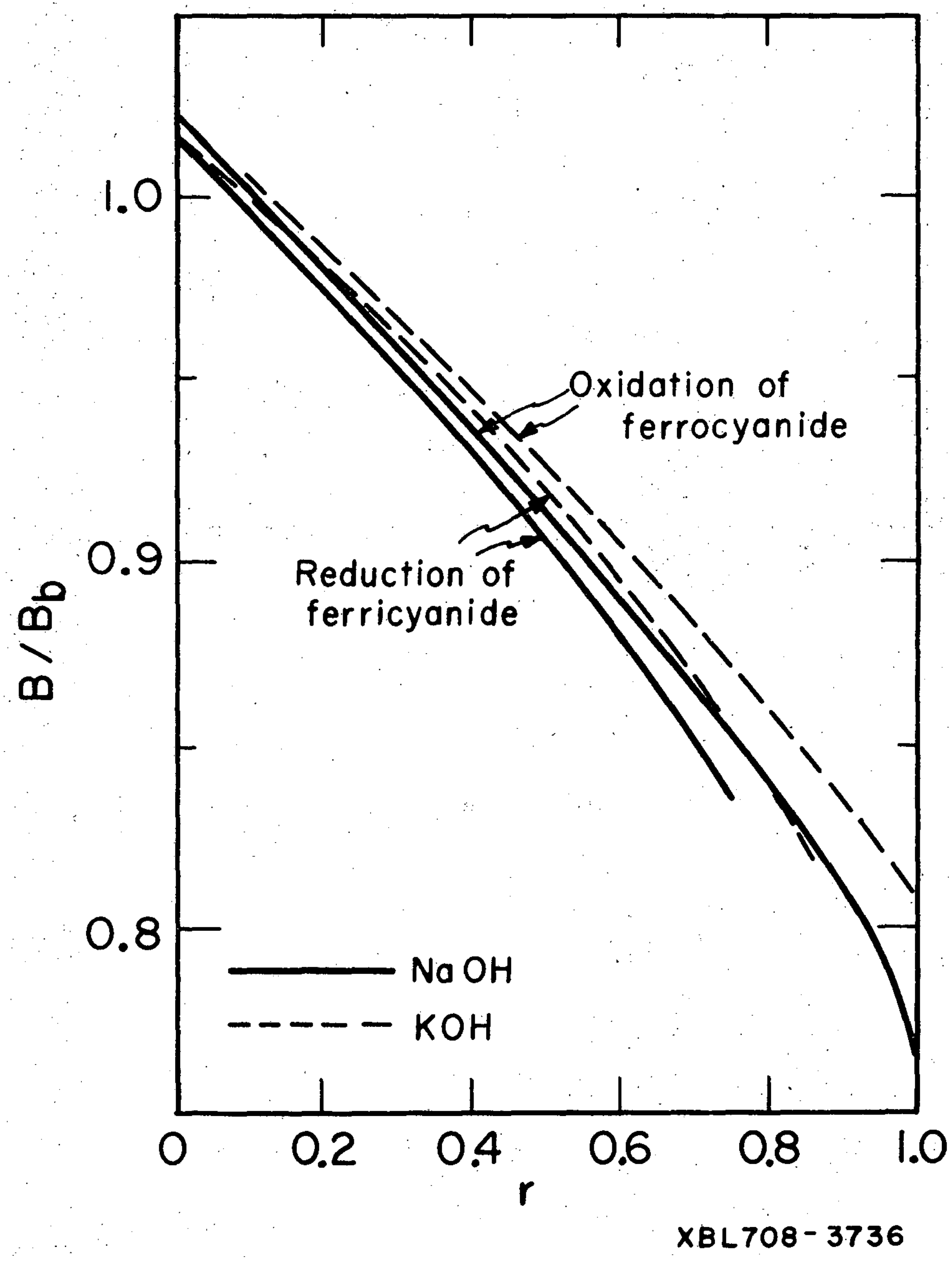

Figure 7. Coefficient for the shear stress in the supported ferricyanide-ferrocyanide systems, for equal bulk concentrations of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$.

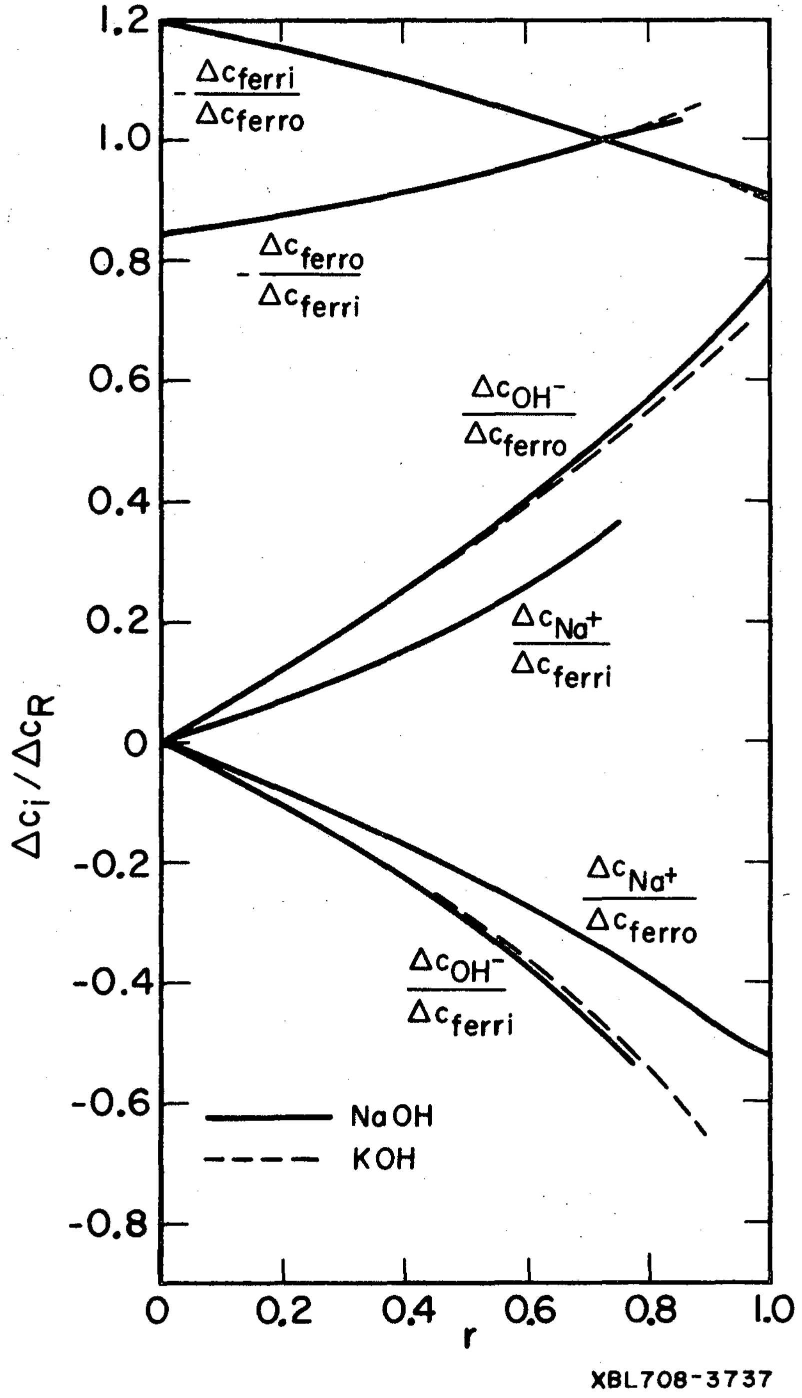

Figure 8. Surface concentrations in the supported ferricyanide-ferrocyanide systems, for equal bulk concentrations of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$.

figure 9. There is a velocity maximum which becomes more pronounced as KOH is added, and the magnitude of the velocities becomes smaller. The profile for r = 0.95 yields a converged but physically unreasonable solution, since the velocity far from the electrode has reversed sign. Reasonable solutions were not obtained in the cathodic case for r greater than 0.85 for KOH, and 0.75 for NaOH, supporting electrolyte. The situation is different only in degree from the one encountered in the case of supported $CuSO_4$. Normalized density profiles for the two cases are compared in figure 10. The ferricyanide-ferrocyanide system has a weaker densification than $CuSO_4$, and consequently the addition of supporting electrolyte can have relatively a much greater effect on the density profile, as we see in figure 10. The velocity far from the electrode (at the outer limit of the diffusion layer) can be expressed as

$$f'(\infty) = -\int_0^\infty \frac{\rho-\rho_\infty}{\rho_\infty \alpha_R c_R^\infty} \xi d\xi \quad . \tag{42}$$

Consequently, in order for there to be a flow reversal, the first moment of the normalized density profile in figure 10 must be negative.

The boundary-layer model clearly breaks down when reversed flow occurs. But even before this happens, the velocity profile may have become unstable. It is known from the theory of hydrodynamic stability[39,40] that boundary layers with an inflection point in the velocity profile are inherently less stable with respect to low perturbation frequencies. It follows that if transition to turbulence takes place in supported solutions, where the supporting ion has a larger diffusion coefficient, it

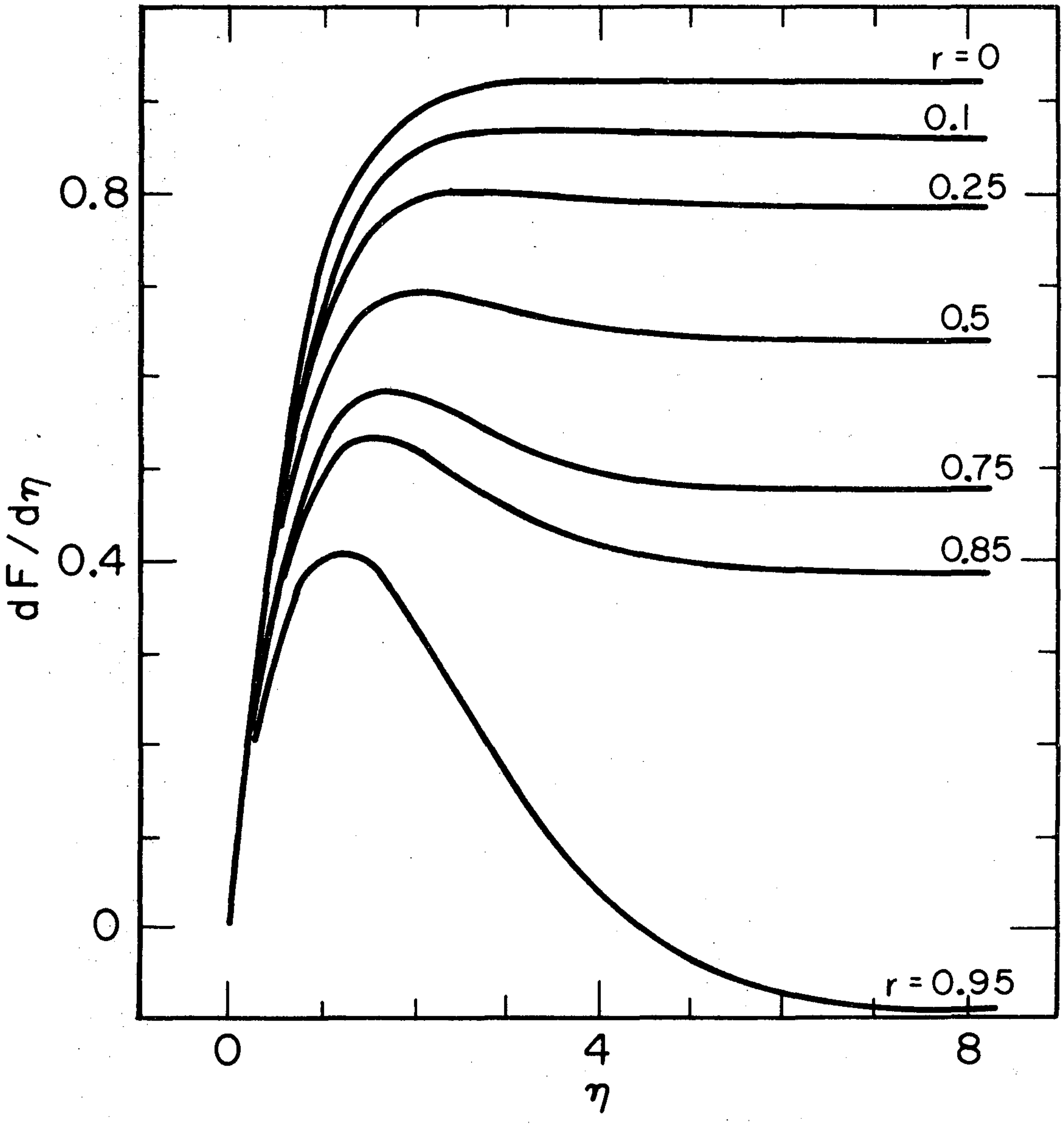

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Figure 9. Velocity profiles for various values of r for cathodic reduction of ferricyanide ions with KOH supporting electrolyte (r_c = 0.5).

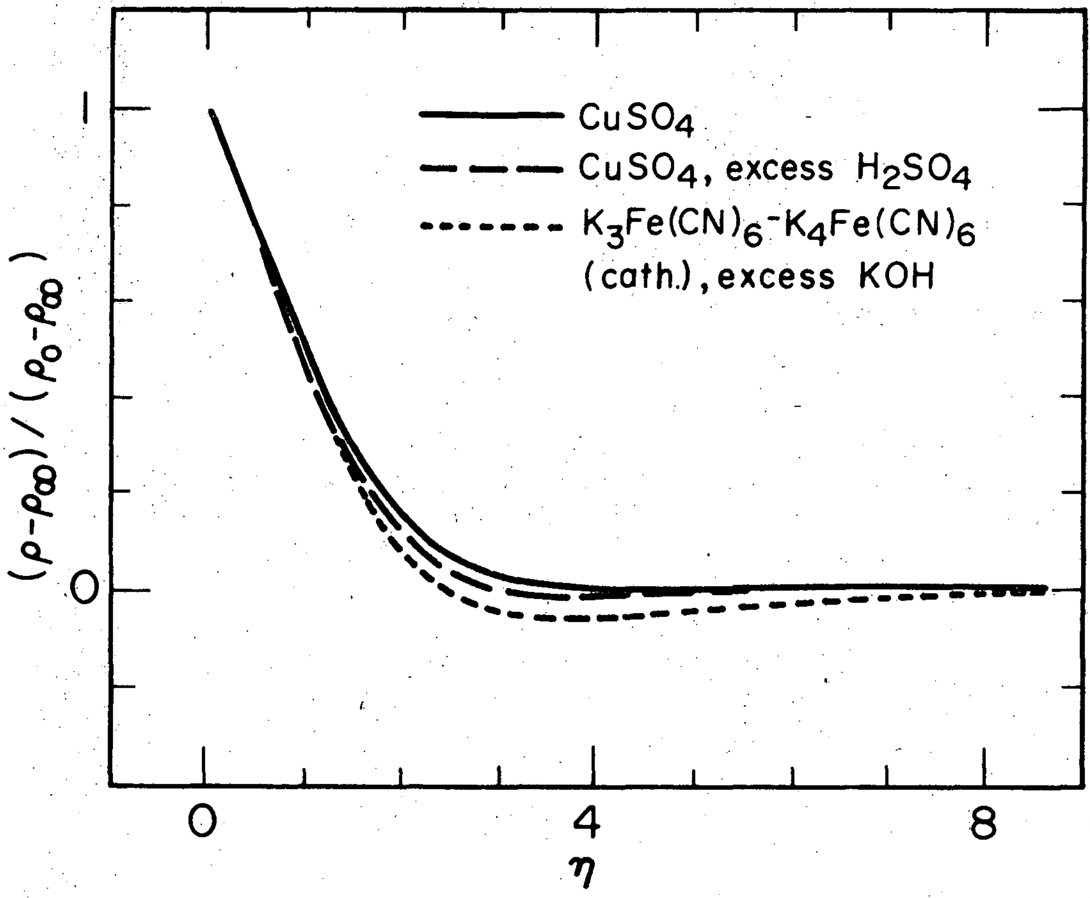

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Figure 10. Normalized density profiles for binary salt solution ($CuSO_4$), for $CuSO_4$ with excess H_2SO_4 ($r = 0.99998$), and for equimolar ferricyanide-ferrocyanide with excess KOH (cathodic reaction, $c_{OH^-}/c_{K^+} = 0.95$).

Table 3. Results for the supported ferricyanide-ferrocyanide systems with $r = 0.5$.

Cathodic reduction of ferricyanide

r_c	C/C_b	B/B_b	$-\frac{\Delta c_{ferro}}{\Delta c_{ferri}}$	$\frac{\Delta c_{OH^-}}{\Delta c_{ferri}}$	$\frac{\Delta c_{Na^+}}{\Delta c_{ferri}}$
KOH supporting electrolyte					
0.1	0.8809	0.9236	0.9278	-0.2731	-
0.25	0.8931	0.9218	0.9306	-0.2792	-
0.5	0.9117	0.9189	0.9352	-0.2890	-
0.75	0.9286	0.9165	0.9394	-0.2981	-
0.9	0.9386	0.9159	0.9419	-0.3032	-
NaOH supporting electrolyte					
0.0003	0.8629	0.9123	0.9235	-0.2756	0.1971
0.1	0.8717	0.9111	0.9255	-0.2799	0.1990
0.25	0.8841	0.9092	0.9284	-0.2861	0.2017
0.5	0.9029	0.9063	0.9330	-0.2961	0.2059
0.75	0.9199	0.9036	0.9372	-0.3054	0.2097
0.9	0.9293	0.9021	0.9397	-0.3107	0.2119
0.9996	0.9353	0.9011	0.9412	-0.3142	0.2133

Anodic oxidation of ferrocyanide

r_a	C/C_b	B/B_b	$-\frac{\Delta c_{ferri}}{\Delta c_{ferro}}$	$\frac{\Delta c_{OH^-}}{\Delta c_{ferro}}$	$\frac{\Delta c_{Na^+}}{\Delta c_{ferro}}$
KOH supporting electrolyte					
0.0004	1.0361	0.9236	1.0583	0.3353	-
0.1	1.0294	0.9241	1.0601	0.3321	-
0.25	1.0188	0.9250	1.0630	0.3271	-
0.5	0.9995	0.9265	1.0682	0.3184	-

Table 3. (Continued)

		KOH supporting electrolyte			
0.75	0.9779	0.9280	1.0737	0.3090	-
0.9	0.9638	0.9289	1.0773	0.3030	-
0.9997	0.9538	0.9296	1.0797	0.2988	-
		NaOH supporting electrolyte			
0.0004	1.0286	0.9102	1.0606	0.3433	-0.2260
0.1	1.0218	0.9108	1.0625	0.3400	-0.2248
0.25	1.0110	0.9117	1.0654	0.3350	-0.2230
0.5	0.9915	0.9133	1.0706	0.3260	-0.2197
0.75	0.9697	0.9149	1.0762	0.3164	-0.2160
0.90	0.9554	0.9160	1.0798	0.3103	-0.2137
0.9997	0.9453	0.9167	1.0822	0.3061	-0.2121

may take place at lower Grashof numbers than for free convection in heat transfer or in binary solutions. This conclusion should be open to experimental verification.

Unfortunately, the experimental evidence on transition in free convection is rather confusing. Only in heat-transfer experiments with air (with a Prandtl number of 0.7) has the transition region been defined by measuring velocity and temperature fluctuations. In air, the lower limit of transition is, by agreement of several experimenters,[41,42] $Gr > 2 \times 10^9$. An upper limit of transition is $Gr < 10^{10}$, above which fully turbulent heat transfer occurs.

In heat-transfer experiments[45] with water and with liquids of Prandtl numbers on the order of 100, the transition criterion was put at

Pr Gr = 4×10^{10}. Wilke, Tobias and Eisenberg[46] report experiments on dissolution of organic acids in water, where laminar mass-transfer relations still hold at Sc Gr = 2×10^{10}. Wagner,[43] in salt dissolution experiments, observed that the flow was still laminar at Sc Gr = 5×10^{11}.

Fouad and Ibl[38] place the transition in acidified $CuSO_4$ solutions, observed optically, between $2 \times 10^{11} <$ Sc Gr $< 4 \times 10^{13}$. They suggest that there is a separate dependence on Sc. Wilke, Eisenberg and Tobias[24] correlate laminar free convection in acidified $CuSO_4$ solutions up to Sc Gr = 5×10^{11}. Fouad and Gouda[44] report transition in ferricyanide reduction with excess NaOH at Sc Gr = 4.6×10^{11}.

One can hardly infer that destabilization had taken place in the supported solutions. However, in such solutions the density has to be estimated (usually by the method of Wilke, Eisenberg and Tobias[24]), which can lead to appreciable errors.

Since the inertial terms in the equation of motion were neglected in this analysis, it follows that a theoretical treatment of instability in electrolytic free convection could also simplify the unsteady equation of motion, retaining only viscous and buoyancy terms. The result would be analogous in form to the so-called viscous solutions in forced flow instability,[40] except for the unknown effect of coupling to the diffusion equation. No solutions are available for high-Pr free-convection instability. Gebhart[47] reports the absence in low-Pr free-convection instability of a critical layer, corresponding in forced flow to the velocity profile inflection, where the disturbance velocity equals the steady velocity. One might conclude, therefore, that the velocity profile inflection obtained in this work does not necessarily indicate instability.

At any rate, the appearance of velocity profiles which exhibit maxima within the diffusion layer can lead to values of C/C_b and B/B_b considerably different from unity so that equations 1 and 2 do not adequately represent the predictions of these calculations for solutions with a supporting electrolyte having a high diffusion coefficient. This is because the density difference $\Delta\rho$ does not, by itself, give sufficient information about the density profile.

Discussion and Conclusions

This investigation concerns the contribution which migration in the electric field makes to the limiting current density in free convection. The effect of migration itself (equation 38 is referred to here) is very similar to that calculated for other hydrodynamic situations. However, the effect of migration also leads to a nonuniform concentration of the supporting electrolyte, and here, in contrast to forced convection, this can change considerably the velocity profile and also affect the limiting current. Because this effect can be partly correlated by using the overall density difference $\Delta\rho$ in the Grashof number, we have reported here the concentration of supporting electrolyte at the electrode.

Frequently used supporting electrolytes, acids and bases, have higher diffusion coefficients than the reacting species. This means that the diffusion layer for the supporting electrolyte extends farther from the electrode than that for the reactants. This leads to a velocity maximum within the diffusion layer if the density difference due to the supporting electrolyte opposes that due to the reacting species, as was the case here.

The analysis applies to large Schmidt numbers. In this limit, the present results can be applied to other geometries by using the transformation of Acrivos. This means that C_b in equation 4 is replaced by C.

Acknowledgment

This work was supported by the United States Atomic Energy Commission.

Nomenclature

B	coefficient for shear stress
B_b	coefficient for shear stress in a binary fluid
c_i	concentration of species i (mole/cm^3)
C	coefficient for mass transfer
C_b	coefficient for mass transfer in a binary fluid
D_i	diffusion coefficient of species i (cm^2/sec)
D_s	diffusion coefficient for a binary electrolyte (cm^2/sec)
f	dimensionless stream function
F	Faraday's constant (96,487 C/equiv)
F	dimensionless stream function
g	magnitude of the gravitational acceleration (cm/sec^2)
Gr	Grashof number
i_y	normal component of the current density (A/cm^2)

I_D	limiting diffusion current
I_L	limiting current
L	height of the vertical electrode (cm)
M_i	symbol for the chemical formula of species i
n	number of electrons transferred in the electrode reaction
N_{iy}	normal component of the flux of species i
Nu	average Nusselt number
r	ratio of supporting electrolyte to total electrolyte
r_a, r_c	ratios of ferricyanide and ferrocyanide concentrations
R	universal gas constant (joule/mole-deg K)
s_i	stoichiometric coefficient of species i
Sc	Schmidt number
t_i	transference number of species i
T	absolute temperature (deg K)
u_i	mobility of species i (cm^2-mole/joule-sec)
v_x	velocity component parallel to the electrode (cm/sec)
v_y	velocity component perpendicular to the electrode (cm/sec)
x	distance along the electrode measured from the beginning of the boundary layer (cm)
y	normal distance from the electrode (cm)
z_i	valence or charge number of species i
α_i	densification coefficient of species i (ℓ/mole)
ε	angle between the normal to the surface and the vertical
η	similarity variable representing dimensionless distance
ξ	similarity variable representing dimensionless distance

θ_i	dimensionless concentration
ν	kinematic viscosity (cm^2/sec)
ρ	fluid density (g/cm^3)
$\Delta\rho$	$\|\rho_\infty - \rho_0\|$
τ_0	shear stress averaged over the electrode ($dyne/cm^2$)
ϕ	dimensionless potential
Φ	electrostatic potential (volt)
ψ	stream function (cm^2/sec)

subscripts and superscripts

o	at the electrode surface
∞	in the bulk solution
R	limiting reactant

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