Title
THE EFFECT OF IONIC MIGRATION ON LIMITING CURRENTS

Author
Newman, John.

Publication Date
1966

UCRL-16586

University of California

Ernest O. Lawrence Radiation Laboratory

THE EFFECT OF IONIC MIGRATION ON LIMITING CURRENTS

DISCLAIMER

Submitted to Industrial and
Engineering Chemistry
Fundamentals

UCRL-16586

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE EFFECT OF IONIC MIGRATION ON LIMITING CURRENTS

John Newman

January, 1966

The Effect of Ionic Migration on Limiting Currents

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

January, 1966

Abstract

The effect of migration on limiting currents is calculated for four hydrodynamic situations: the rotating disk, the growing mercury drop, the semi-infinite, stagnant fluid, and the Nernst diffusion layer and for several electrolytic systems.

The addition of supporting or indifferent electrolyte to a solution tends to change the value of the limiting current for an electrode reaction. This may be because (1) the viscosity and diffusion coefficients are changed, (2) the activity coefficients and driving forces for diffusion are changed or (3) the conductivity and the driving force for migration are changed. We are concerned here with the last of these effects. For sufficiently dilute solutions the first two can be ignored.

If the ratio of the supporting electrolyte concentration to the concentration of the reactant is very large, the high conductivity suppresses the electric field, and the resulting limiting current, denoted by I_D, is due solely to diffusion. If the supporting electrolyte concentration is reduced, the electric field becomes larger and may enhance or depress the limiting current depending upon the sign of the charge of the limiting reactant and the direction of the current. The ratio I_L/I_D of the limiting current to the limiting diffusion current is a convenient measure of the effect of migration. The mechanism of this effect has been discussed qualitatively by Heyrovský.[5]

We have calculated this effect of migration for four geometries of the diffusion layer. The reader may wish to skip the mathematical formulation and go directly to the results, which are presented in the form of the ratio I_L/I_D as a function of the ratio of the concentration of the supporting ion to that of the counter ion.

Mathematical Formulation

In dilute electrolytic solutions, transport processes can be described by the following four equations:

$$\underline{N}_i = - z_i u_i F c_i \nabla\Phi - D_i \nabla c_i + \underline{v} c_i \ , \tag{1}$$

$$\frac{\partial c_i}{\partial t} = - \nabla \cdot \underline{N}_i , \quad \underline{i} = F \sum_i z_i \underline{N}_i , \quad \sum_i z_i c_i = 0 \ . \qquad (2,3,4)$$

We wish to apply these equations to analyze the effect of migration on the limiting current in four situations of interest in electrochemistry; (1) steady mass transfer to a rotating disk, (2) unsteady mass transfer to a growing mercury drop, (3) unsteady mass transfer to a plane electrode in a stagnant fluid, and (4) steady mass transfer in a stagnant Nernst diffusion layer. The condition of electroneutrality is the same, and the boundary conditions at the electrode are similar in all these cases, so let us first treat the conservation equations to see how they can be made similar in the four cases.

Rotating Disk

In this case, the normal component of the velocity depends only on y, the distance from the disk. Consequently, c_i and Φ also depend only on y in the diffusion layer, and the current density is uniform over the surface of the disk. Equations (1) and (2) can be combined to yield

$$D_i \frac{d^2c_i}{dy^2} - v_y \frac{dc_i}{dy} + z_iu_iF\left(c_i \frac{d^2\Phi}{dy^2} + \frac{dc_i}{dy}\frac{d\Phi}{dy}\right) = 0 . \qquad (5)$$

For a numerical solution there would be no fundamental difficulty in attacking the problem in this form, with the use of the velocity profile calculated by Cochran.[1] Instead we shall make the same approximation as Levich[2] and use only the first term in the power-series expansion of v_y:

$$v_y = - a(\Omega^3/\nu)^{\frac{1}{2}}y^2 + \ldots , \qquad (6)$$

where a = 0.51023. This approximation is valid for high Schmidt numbers $Sc = \nu/D$, the error in the calculated limiting current being about 3 percent at Sc = 1000. The error in the ratio of the limiting current to the limiting diffusion current should be much smaller.

If we accept the approximation represented in equation (6) and introduce a new variable

$$\eta = y\ (a\nu/3D_R)^{1/3}\sqrt{\Omega/\nu}\ , \tag{7}$$

where D_R is the diffusion coefficient of the limiting reactant, then equation (5) becomes

$$(D_i/D_R)c_i'' + 3\eta^2 c_i' + (z_i u_i F/D_R)(c_i\Phi'' + c_i'\Phi') = 0\ . \tag{8}$$

Growing Mercury Drop

Consider a mercury drop growing in a solution which initially had a uniform composition, and let the current always have its limiting value. Let the radius of the drop be denoted by $R(t)$ where R is zero at $t=0$. If the drop is growing in a radial regime, that is, there are no tangential motions of the drop surface, radial symmetry can be assumed, and equations (1) and (2) can be combined to yield

$$\frac{\partial c_i}{\partial t} + v_r\frac{\partial c_i}{\partial r} = D_i\left[\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r}\frac{\partial c_i}{\partial r}\right] + z_i u_i F c_i\left[\frac{\partial^2\Phi}{\partial r^2} + \frac{2}{r}\frac{\partial\Phi}{\partial r}\right] + z_i u_i F\frac{\partial c_i}{\partial r}\frac{\partial\Phi}{\partial r}\ , \tag{9}$$

where the radial velocity component v_r is related to the rate of growth of the drop

$$v_r = \frac{R^2}{r^2}\frac{dR}{dt}\ . \tag{10}$$

It is convenient to introduce a new variable y

$$y = r - R(t)\ , \tag{11}$$

the distance from the surface of the drop.

In treating the growing drop we make the same approximations as are made in the derivation of the Ilkovič equation[3,4,5]. These are valid when the thickness of the diffusion layer is small compared to the size of the drop:

1. Neglect first derivatives compared to second derivatives

$$\frac{2}{r}\frac{\partial c_i}{\partial r} \ll \frac{\partial^2 c_i}{\partial r^2} \quad \text{and} \quad \frac{2}{r}\frac{\partial\Phi}{\partial r} \ll \frac{\partial^2\Phi}{\partial r^2}\ .$$

2. Approximate the radial velocity by the first two terms in an expansion in powers of y

$$v_r = \frac{dR}{dt}\left[1 - \frac{2y}{R} + \ldots\right] .$$

If we make the coördinate transformation (11) and introduce these approximations, equation (9) becomes

$$\frac{\partial c_i}{\partial t} - \frac{2y}{R}\frac{dR}{dt}\frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} + z_i u_i F\left[c_i \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_i}{\partial y}\frac{\partial \Phi}{\partial y}\right] . \tag{12}$$

Next we introduce a similarity variable

$$\eta = R^2 y/\left[4D_R \int_0^t R^4 dt\right]^{1/2} , \tag{13}$$

and assume that c_i and Φ depend only on this variable. Equation (12) then reduces to

$$(D_i/D_R)c_i'' + 2\eta c_i' + (z_i u_i F/D_R)(c_i \Phi'' + c_i' \Phi') = 0 . \tag{14}$$

For a constant rate of increase of the volume of the drop

$$R = \gamma t^{1/3} , \tag{15}$$

and equation (13) reduces to $\eta = y/2\sqrt{3D_R t/7}$. (16)

Unsteady Diffusion into a Stagnant Fluid

Diffusion from a plane into a semi-infinite, stagnant medium should obey the equation

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial y^2} + z_i u_i F\left[c_i \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_i}{\partial y}\frac{\partial \Phi}{\partial y}\right] . \tag{17}$$

The similarity transformation

$$\eta = y/2\sqrt{D_R t} \tag{18}$$

reduces equation (17) to equation (14), that is, the same as for a growing mercury drop.

Nernst Diffusion Layer

Steady diffusion in a stagnant layer of thickness δ obeys the equation

$$0 = D_i \frac{d^2c_i}{dy^2} + z_iu_iF\left[c_i\frac{d^2\Phi}{dy^2} + \frac{dc_i}{dy}\frac{d\Phi}{dy}\right] . \tag{19}$$

Let
$$\eta = y/\delta \tag{20}$$

so that equation (19) becomes

$$(D_i/D_R)c_i'' + (z_iu_iF/D_R)(c_i\Phi'' + c_i'\Phi') = 0. \tag{21}$$

One should note the similarity of equations (8), (14), and (21).

Conditions at the Electrode

Let the electrode reaction be denoted by

$$\sum_i s_iM_i^{z_i} \rightarrow ne^- , \tag{22}$$

where the s's are stoichiometric coefficients of the species. Then at the electrode surface we have

$$N_i = -\frac{s_i i}{nF} = -z_iu_iFc_i\frac{\partial\Phi}{\partial y} - D_i\frac{\partial c_i}{\partial y} , \tag{23}$$

and the fluid velocity relative to the surface is zero. Since we do not know the current in advance, we can relate instead the flux of a species to the flux of the limiting reactant

$$z_iu_iFc_i\frac{\partial\Phi}{\partial y} + D_i\frac{\partial c_i}{\partial y} = \frac{s_i}{s_R}\left(z_Ru_RFc_R\frac{\partial\Phi}{\partial y} + D_R\frac{\partial c_R}{\partial y}\right) , \tag{24}$$

while the boundary condition for the limiting reactant becomes

$$c_R = 0 \quad \text{at} \quad y = 0 . \tag{25}$$

It is very convenient that condition (24) can be written in terms of the variable η as

$$z_iu_iFc_i\Phi' + D_ic_i' = (s_i/s_R)(z_Ru_RFc_R\Phi' + D_Rc_R') \quad \text{at } \eta = 0 , \tag{26}$$

for each of the four cases studied. Condition (25) becomes

$$c_R = 0 \quad \text{at} \quad \eta = 0 . \tag{27}$$

Conditions in the Bulk

For the first three cases we have

$$c_i = c_{i\infty} \text{ at } \eta = \infty, \quad \Phi = 0 \text{ at } \eta = \eta_{max} , \tag{28}$$

where η_{max}, the zero of potential, can be chosen arbitrarily. In the fourth case, the stagnant diffusion layer, we have

$$c_i = c_{i\infty}, \ \Phi = 0 \quad \text{at } \eta = 1 . \tag{29}$$

The Current Density

Let us define a dimensionless current density at the electrode as

$$I = [c_R'(0) + (z_R u_R F c_R / D_R) \ \Phi'(0)]/c_{R\infty} . \tag{30}$$

Then this is related to the actual current density as follows:

for the rotating disk

$$I = \frac{is_R}{nF \ c_{R\infty}} \ \frac{3^{1/3} \nu^{1/6}}{a^{1/3} \Omega^{1/2} D_R^{2/3}} . \tag{31}$$

for the growing mercury drop

$$I = \frac{is_R}{nF \ c_{R\infty}} \ \frac{2}{R^2 D_R^{1/2}} \sqrt{\int_0^t R^4 dt} . \tag{32}$$

for the mercury drop growing at a constant rate

$$I = \frac{is_R}{nF \ c_{R\infty}} \ 2\sqrt{\frac{3t}{7D_R}} . \tag{33}$$

for the semi-infinite, stagnant medium

$$I = \frac{is_R}{nF \ c_{R\infty}} \ 2\sqrt{\frac{t}{D_R}} . \tag{34}$$

for the stagnant diffusion layer

$$I = \frac{is_R}{nF \ c_{R\infty}} \ \frac{\delta}{D_R} . \tag{35}$$

The limiting "diffusion current" corresponds to the absence of migration and hence to the presence of an excess of supporting electrolyte or to a neutral reactant. One finds that the limiting diffusion current is expressed by

$$\left.\begin{array}{l} I_D = 1/\Gamma(4/3) = 1.1198 \text{ for the rotating disk} \\ I_D = 2/\sqrt{\pi} = 1.12838 \text{ for mercury drops.} \\ I_D = 1 \text{ for the Nernst diffusion layer.} \end{array}\right\} \quad (36)$$

Numerical Solution Method

In these four cases the problem consists of a group of coupled, non-linear differential equations with boundary conditions at zero and infinity or at zero and one. These equations can be linearized about a trial solution producing a series of coupled, linear differential equations. In finite difference form these give coupled, tri-diagonal matrices which can be solved readily on a high-speed, digital computer. The non-linear problem can then be solved by iteration. A total of one hundred mesh points was used. This method failed to converge to a solution when the conductivity near the electrode was very small, for example, for discharge of cations from a solution with very little supporting electrolyte.

Results

In the calculations reported here, limiting ionic conductances at 25° were taken from Conway's tabulation[6], and it was assumed that the Nernst-Einstein relation

$$D_i = RT\, u_i \quad (37)$$

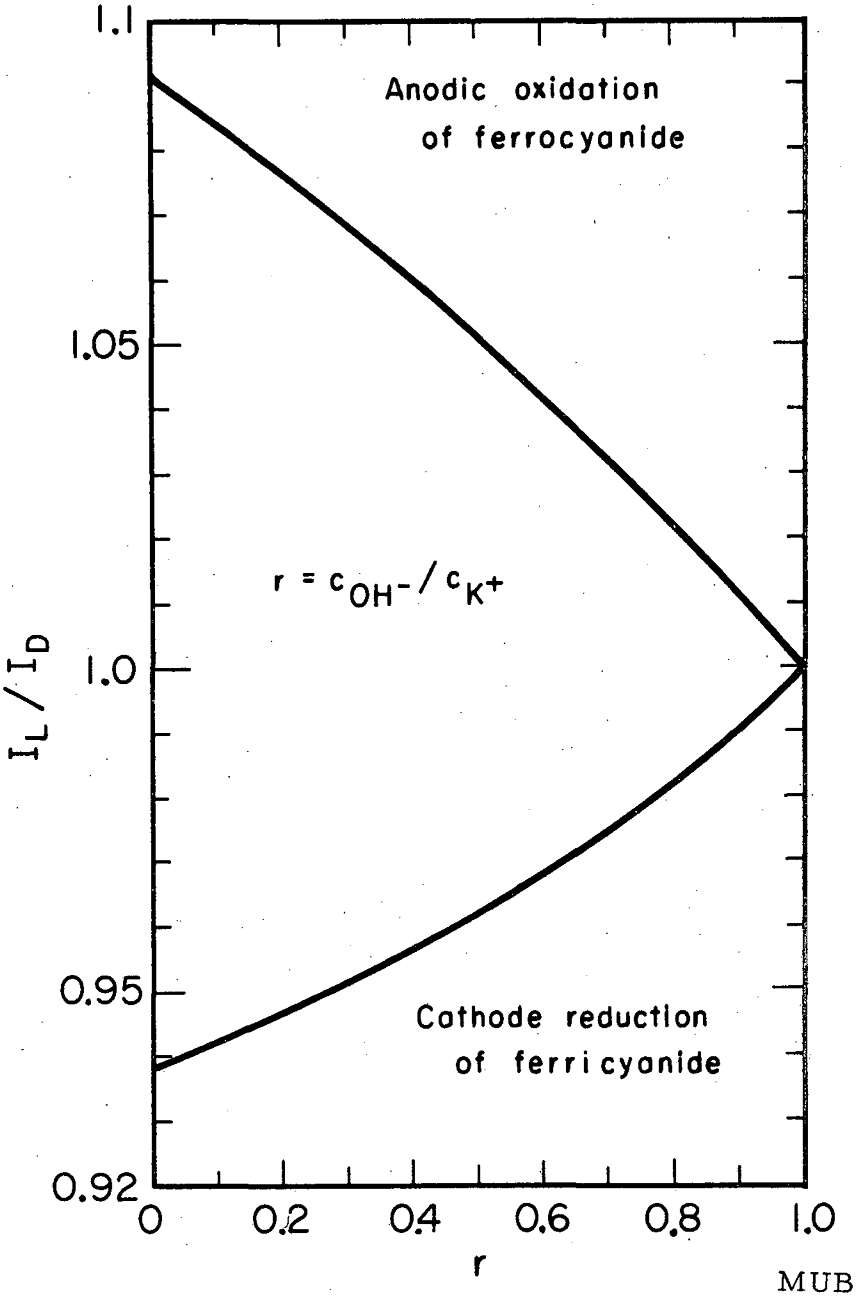
is valid.

The effect of migration on limiting currents is shown in figure 1 and table I for a redox reaction. The effect is small and does not amount to more than ten percent unless the supporting electrolyte and the product of the redox reaction are eliminated from the bulk of the solution (see last entries in Table I). It makes very little difference whether the electrode is a rotating disk or a growing drop or whether the supporting electrolyte is NaOH or KOH; therefore, only one set of curves is plotted in figure 1.

Table II shows the effect of migration for the discharge of cations. Here the effect can be very large, easily a factor of two, since the electric field becomes very large in a solution of a single salt at limiting current.

The effect is perhaps most dramatic for discharge of hydrogen ions from acidified KCl as shown in figure 2. The abscissa is $r^{1/2} = (c_{K^+}/c_{Cl^-})^{1/2}$, that is, the square root, since only a small amount of supporting electrolyte (or ionic impurity) greatly reduces the limiting current by greatly reducing the electric field at the electrode surface. This case of discharge of hydrogen ions shows considerable differences between the rotating disk, the growing drop, and the Nernst diffusion layer because the cation transference number for HCl is much different from 0.5. The effective diffusion layer thickness is proportional to the effective diffusion coefficient to the one-third power in the case of the disk and to the one-half power in the case of the drop, while it is arbitrarily taken to be δ for the Nernst diffusion layer. It is this variation of the effective diffusion layer thickness which is responsible for the deviation of I_L/I_D from 2 at r=0.

Experimental polarographic data of Šlendyk[7] are also plotted on figure 2; the agreement with the present results is very good for 0.001 N HCl. The experimental points were normalized to the theoretical value, 3.3412, at r=0 since this corresponds to the most dilute solution. Deviations from the calculated results can be expected in concentrated solutions because migration is not the only causal force acting. However, this would not be an adequate explanation



MUB-9135

Figure 1. Effect of Migration on Limiting Currents for a Redox Reaction. Equimolar potassium ferrocyanide and ferricyanide in KOH, for a disk electrode.

Table I. Ratio of limiting current to limiting diffusion current for a redox reaction.

Cathodic reduction of ferricyanide (equimolar ferro-ferri except as noted)

r	I_L/I_D			
	disk		drop	
	in KOH	in NaOH^A	in KOH	in NaOH^A
1.0	1.0	1.0	1.0	1.0
0.9050	0.9906	0.9901	0.9923	0.9918
0.8264	0.9838	0.9832	0.9865	0.9857
0.7042	0.9746	0.9738	0.9781	0.9771
0.5435	0.9644	0.9635	0.9681	0.9670
0.3731	0.9551	0.9543	0.9583	0.9573
0.1923	0.9464	0.9460	0.9486	0.9480
0	0.9382	0.9382	0.9390	0.9390
B	0.8658	----	0.8670	----

Cathodic oxidation of ferrocyanide (equimolar ferro-ferri except as noted)

r	I_L/I_D			
	disk		drop	
	in KOH	in NaOH^A	in KOH	in NaOH^A
1.0	1.0	1.0	1.0	1.0
0.9050	1.0107	1.0128	1.0086	1.0106
0.8264	1.0199	1.0216	1.0163	1.0180
0.7042	1.0328	1.0344	1.0275	1.0293
0.5435	1.0481	1.0495	1.0415	1.0433
0.3731	1.0627	1.0637	1.0559	1.0573
0.1923	1.0770	1.0776	1.0710	1.0719
0	1.0911	1.0911	1.0868	1.0868
C	1.1688	----	1.1605	----

$r = c_{OH^-}/(c_{K^+} + c_{Na^+})$

A - equimolar $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ plus added NaOH.

B - no KOH or NaOH and no $Fe(CN)_6^{4-}$ in the bulk solution.

C - no KOH or NaOH and no $Fe(CN)_6^{3-}$ in the bulk solution.

Table II. Ratio of limiting current to limiting diffusion current for discharge of cations.

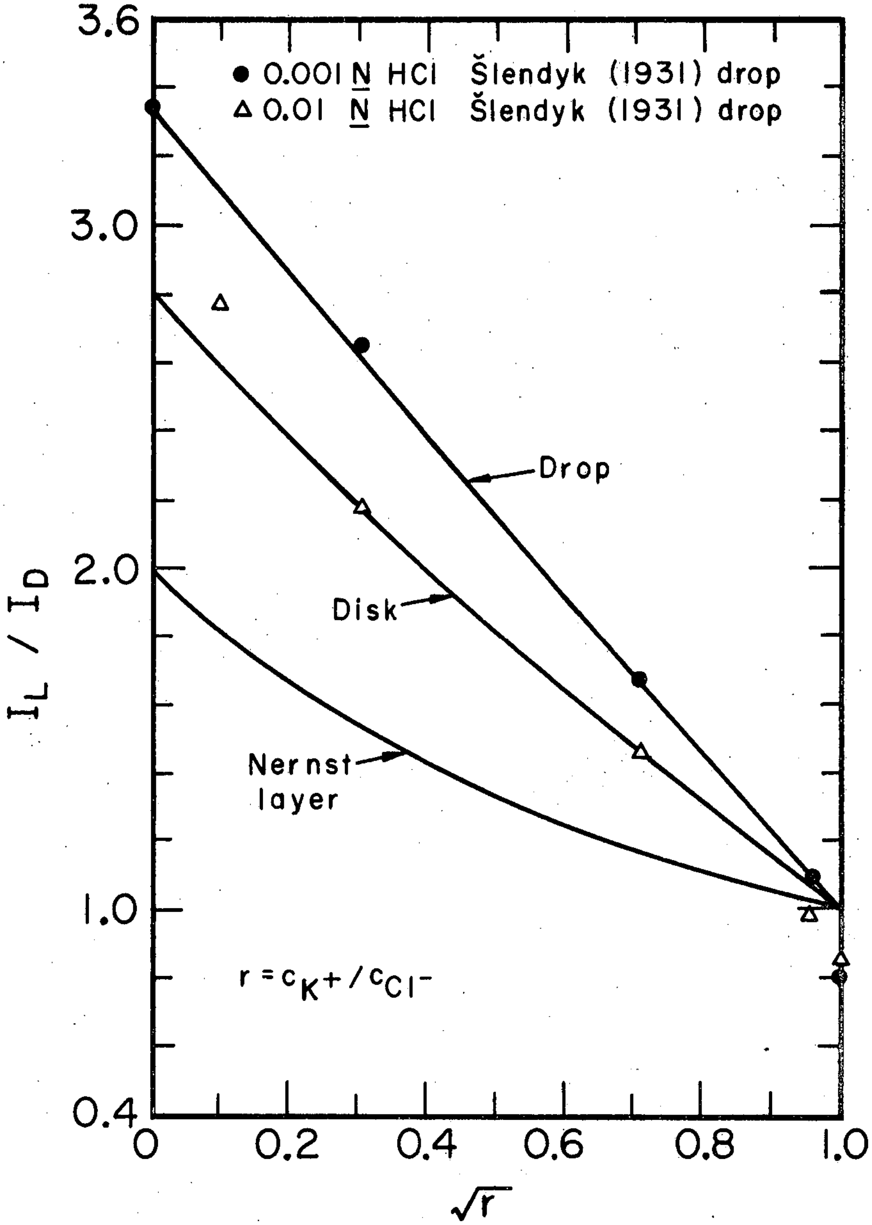
r	I_L/I_D								
	HCl in KCl^A			$CuSO_4$ in $H_2SO_4^B$		$CuSO_4$ in $MgSO_4^C$		$AgNO_3$ in HNO_3^D	
	disk	drop	Nernst	disk	drop	disk	drop	disk	drop
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
0.8	1.1711	1.2381	1.0558	1.0534	1.0467	1.0567	1.0611	1.0425	1.0389
0.6667	1.2933	1.4108	1.1011	1.0961	1.0841	1.1020	1.1095	1.0774	1.0714
0.5	1.4650	1.6548	1.1716	1.1621	1.1424	1.1716	1.1829	1.1331	1.1237
0.3333	1.6753	1.9527	1.2680	1.2520	1.2239	1.2645	1.2792	1.2120	1.1996
0.2	1.9006	2.2684	1.3821	1.3607	1.3278	1.3718	1.3881	1.3116	1.2977
0.1	2.1522	2.6280	1.5200	1.5043	1.5047	1.4991	1.5170	1.4458	1.4322
0.04	2.4597	----	1.6695	----	----	1.6506	----	1.6017	1.6605
0	2.8160	3.3405	2.0001	1.8852	1.8304	1.8852	1.8303	1.9545	1.9322
0(theory)	2.8159	3.3412	2.0	1.8852	1.8303	1.8852	1.8303	1.9546	1.9322

A $r = c_{K^+}/c_{Cl^-}$

B $r = c_{H^+}/2c_{SO_4^=}$

C $r = c_{Mg^{++}}/c_{SO_4^=}$

D $r = c_{H^+}/c_{NO_3^-}$



MUB-9136

Figure 2. Effect of Migration on Limiting Currents in Discharge of Hydrogen from KCl Solutions. Lines represent values calculated with the present theory.

for the deviation of the first three points for 0.01 N HCl.

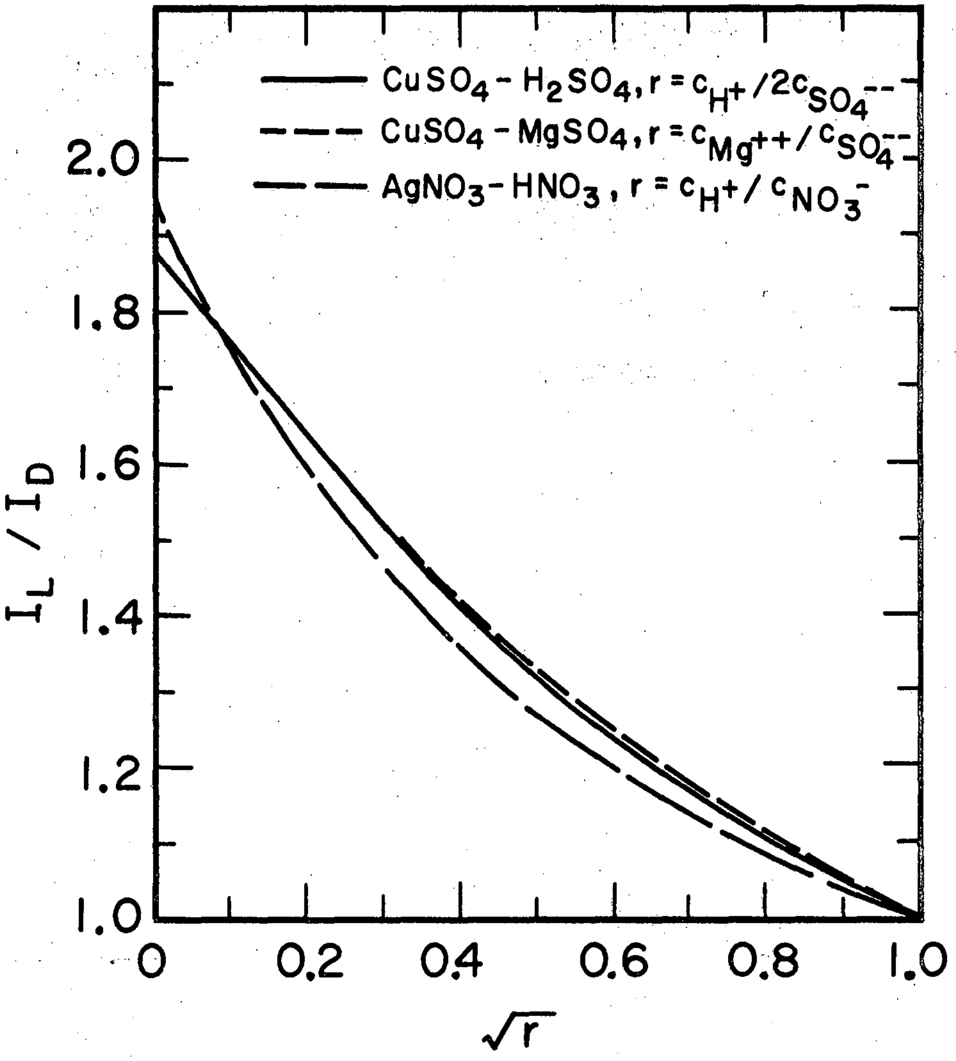
Figure 3 is a similar plot for metal deposition on a rotating disk.

It should be recalled that results for I_L/I_D for growing mercury drops also apply to unsteady diffusion into an infinite, stagnant fluid.

Except for the hydrogen ion discharge, the results are not so very different between the disk and the drop, and the ratio I_L/I_D probably could be approximately applicable to other electrochemical problems which are more difficult to analyze.

Acknowledgment

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



MUB-9137

Figure 3. Effect of Migration on Limiting Currents for Metal Deposition on a Disk Electrode.

Nomenclature

a = 0.51023.

c_i - concentration of species i (mole/cm^3).

D_i - diffusion coefficient of species i (cm^2/sec).

e^- - symbol for the electron.

F - Faraday's constant (coulomb/equiv.).

i - current density (amp/cm^2).

I - dimensionless current density.

M_i - symbol for species i.

n - number of electrons transferred in electrode reaction.

$\underline{N}_i$ - flux of species i (mole/cm^2-sec).

r - radial distance in spherical coördinates (cm).

r - concentration ratio.

R - radius of mercury drop (cm).

R - gas constant (joule/mole-deg K).

s_i - stoichiometric coefficient in electrode reaction.

t - time (sec).

T - temperature (deg K).

u_i - mobility of species i (cm^2-mole/joule-sec).

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

y - distance from electrode surface (cm).

z_i - charge number of species i.

γ - constant in rate of growth of mercury drops (cm/sec$^{1/3}$).

$\Gamma(4/3)$ = 0.89298.

δ - thickness of Nernst diffusion layer (cm).

η - dimensionless independent variable [see equations (7),(13),(16),(18), and (20)].

ν - kinematic viscosity (cm^2/sec).

Φ - electrostatic potential (volts).

Ω - rotation speed of disk (radians/sec).

References

1. W. G. Cochran. "The flow due to a rotating disc." Proceedings of the Cambridge Philosophical Society, 30, 365-375 (1934).

2. B. Levich. "The Theory of Concentration Polarization." Acta Physicochimica U.R.S.S., 17, 257-307 (1942).

3. D. Ilkovič. "Polarigraphic Studies with the Dropping Mercury Kathode. - Part XLIV. - The Dependence of Limiting Currents on the Diffusion Constant, on the Rate of Dropping and on the Size of the Drops." Collection of Czechoslovak Chemical Communications, 6, 498-513 (1934).

4. D. MacGillavry and E. K. Rideal. "On the Theory of Limiting Currents. I. Polarographic limiting currents." Recueil des Travaux Chimiques des Pays-Bas, 56, 1013-1021 (1937).

5. D. Ilkovič. "Sur la valeur des courants de diffusion observés dans l'électrolyse a l'aide de l'électrode a gouttes des mercure. Étude polarographique." Journal de Chimie Physique, 35, 129-135 (1938).

6. B. E. Conway. Electrochemical Data. Amsterdam: Elsevier Publishing Company, 1952.

7. I. Šlendyk. "Polarographic Studies with the Dropping Mercury Kathode. - Part XXI. - Limiting Currents of Electrodeposition of Metals and of Hydrogen." Collection of Czechoslovak Chemical Communications, 3, 385-395 (1931).