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Concentration Profile at the Limiting Current in a Stagnant Diffusion Cell

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Abstract

The limiting current and concentration profile in a stagnant diffusion cell are calculated for a cupric sulfate solution with consideration of the variation of physical properties and nonzero interfacial velocity. The calculated concentration profile is compared with that observed optically. The possibility for obtaining differential diffusion coefficients from limiting current measurements is explored.

Introduction

O'Brien[1] has studied optically the diffusion layers at the anode and the cathode for deposition and dissolution of copper from a stagnant, aqueous solution of cupric sulfate. His experiments at constant current showed deviations from theoretical predictions based on a constant diffusion coefficient.

Under certain conditions, the governing partial differential equations can be reduced to ordinary differential equations. Then it is possible, by means of a rather simple calculation procedure, to account for the variation of the diffusion coefficient and other physical properties as well as the existence of a nonzero interfacial velocity due to the mass transfer process. Results have already been reported for a rotating disk electrode.[2,3] Similar calculations can be carried out for a stagnant diffusion cell if the concentration at the electrode surface, outside the diffuse double layer, is constant in time. This is equivalent to the requirement that the current density should be inversely proportional to the square root of time.

The results of such calculations are reported in the present work for a stagnant diffusion cell. In our experiments, however, it was not possible to maintain a constant concentration of cupric sulfate at the electrode surface. This was due principally to the high ohmic resistance of the cupric sulfate solutions. The work thus fell short of its original goals.

Analysis

For one-dimensional, unsteady diffusion, the concentrated solution theory shows that a binary electrolyte in a solution carrying a current density i_y obeys the equation[4]

$$\rho\left(\frac{\partial\omega_s}{\partial t} + v_y \frac{\partial\omega_s}{\partial y}\right) = \frac{\partial}{\partial y}\left(\rho D \frac{\partial\omega_s}{\partial y}\right) - \frac{M_s i_y}{z_+ \nu_+ F} \frac{\partial t_+}{\partial y} \quad , \tag{1}$$

where y is the distance from the electrode, v_y is the mass-average velocity, ω_s is the mass fraction of the salt, ρ is the density, D is the diffusion coefficient of the salt, M_s is the molecular weight of the salt, t_+ is the cation transference number relative to the mass-average velocity, z_+ is the charge number of the cation, ν_+ is the number of cations per molecule of salt, and F is Faraday's constant. Variations in the mass-average velocity are determined by the equation of continuity,

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial y}(\rho v_y) = 0 \quad . \tag{2}$$

The initial condition is

$$\omega_s = \omega_\infty \text{ at } t = 0 \quad . \tag{3}$$

When the concentration at the surface is assumed to be constant, the boundary conditions become

$$\left.\begin{aligned} &\omega_s = \omega_\infty \text{ as } y \to \infty \quad , \\ &\omega_s = \omega_o, \; v_y = i_y M_+/\rho z_+ F = N_+ M_+/\rho \text{ at } y = 0 \quad . \end{aligned}\right\} \tag{4}$$

For a metal deposition reaction, the fluxes of anions and solvent are zero at the interface; therefore, the current density and the interfacial velocity are directly related to the flux of cations. Furthermore, the flux in a concentrated solution can be expressed in terms of the concentration gradient[4]

$$N_+ = - \nu_+ \frac{D\rho}{M_s} \frac{\partial \omega_s}{\partial y} + \frac{i_y t_+}{z_+ F} + c_+ v_y \quad . \tag{5}$$

A dimensionless distance ξ and a dimensionless velocity H are defined as

$$\xi = y/2\sqrt{D_\infty t} \quad \text{and} \quad H = 2v_y \sqrt{t/D_\infty} \quad , \tag{6}$$

where D_∞ is the value of the diffusion coefficient in the bulk solution. It is assumed that the mass fraction ω_s and the dimensionless velocity H depend only on ξ, that is, depend on the variables y and t only in the combined form $y/\sqrt{t}$. The justification for this assumed similarity transformation follows from the subsequent reduction of the partial differential equations to ordinary differential equations and the statement of the problem for the determination of $\omega_s(\xi)$ and $H(\xi)$ in such a way that the original variables y and t appear only in the combined form ξ

both in the differential equations and in the boundary conditions. It follows from this assumption that the other physical properties, ρ, D, and t_+, also depend only on ξ since variations of temperature and pressure are being ignored.

Substitution of these assumptions into the boundary conditions yields

$$I = \frac{\rho_o}{\rho_\infty} \frac{M_s}{M_+ \nu_+} H(0) = - \frac{\rho_o D_o}{\rho_\infty D_\infty} \frac{1}{(1-t_+-\omega_+)} \frac{d\omega_s}{d\xi}\Big|_{\xi=0} \quad , \tag{7}$$

where

$$I = \frac{2M_s i_y}{\rho_\infty \nu_+ z_+ F} \left(\frac{t}{D_\infty}\right)^{1/2} \tag{8}$$

is a dimensionless constant whose value is yet to be determined. Subscripts o denote properties evaluated at the surface concentration ω_o, and subscripts ∞ denote those evaluated at the bulk concentration ω_∞.

The differential equations 1 and 2 become

$$\left[\frac{\rho}{\rho_\infty} (H-2\xi) + I \frac{dt_+}{d\omega_s}\right] \frac{d\omega_s}{d\xi} = \frac{d}{d\xi}\left(\frac{\rho D}{\rho_\infty D_\infty} \frac{d\omega_s}{d\xi}\right) \quad , \tag{9}$$

$$(H-2\xi)\frac{d\rho}{d\xi} + \rho\frac{dH}{d\xi} = 0 \quad , \tag{10}$$

and the boundary conditions, in addition to equation 7, are

$$\omega_s = \omega_o \text{ at } \xi = 0, \ \omega_s \rightarrow \omega_\infty \text{ as } \xi \rightarrow \infty \quad . \tag{11}$$

These equations can be solved conveniently with a digital computer.[5] The physical properties of aqueous cupric sulfate solutions at 25°C had already[6] been obtained from the literature and correlated as functions of ω_s in connection with the rotating-disk work.[2,3]

The problem stated by equations 7, 9, 10, and 11 is independent of the variables y and t except in the combination ξ, and the similarity transformation satisfies the criteria for success. Since I is a constant, equation 8 shows that the current density is inversely proportional to the square root of time even though the physical properties may depend upon concentration and the interfacial velocity is not zero. A constant concentration at the electrode surface and a current density inversely proportional to the square root of time are equivalent conditions and are necessary for the similarity transformation to work. The constant concentration need not be zero, and the analysis is equally applicable to the anode or the cathode. Such a similarity transformation could also be applied to a multicomponent solution, such as, an aqueous solution of cupric sulfate and sulfuric acid. However, all the relevant physical properties are not known as functions of composition. For such a multicomponent solution, a constant concentration at the electrode surface would imply a current density inversely proportional to the square root of time, and conversely.

Results

A constant concentration at the electrode surface is usually achieved in electrochemical systems by operation at the limiting current; the potential difference across the cell is increased until the surface concentration is forced to approximately zero. For the stagnant diffusion cell, this limiting current density i_L should be inversely proportional to the square root of time. Figure 1 shows calculated values of $i_L\sqrt{t}$ for aqueous solutions of cupric sulfate at 25°C.

The measurement of limiting currents is difficult for solutions without supporting electrolyte. Figure 2 records current as a function of time for a 0.1 M $CuSO_4$ solution where the potential applied to the cell was decreased from 1.0 to 0.8 V during the course of the experiment. (For a description of the experimental cell, see reference 5.) A typical logarithmic plot such as figure 2 should consist of two parts, a horizontal part which corresponds to the ohmic resistance of the solution and a decreasing part with a slope of -1/2 where the concentration of electrolyte near the electrode surface drops to zero. This latter part corresponds to the limiting current density.

For $CuSO_4$ solutions with H_2SO_4 as a supporting electrolyte, an applied potential of 0.3 to 0.4 volt would be satisfactory. However, in the absence of supporting electrolyte, the decreasing part would not show up for several days. If the applied potential is raised, the decreasing part is reached sooner, but eventually hydrogen is evolved, and the current measurements are useless. By decreasing the applied potential as shown in figure 2, a region of slope equal to - 1/2 can be detected.

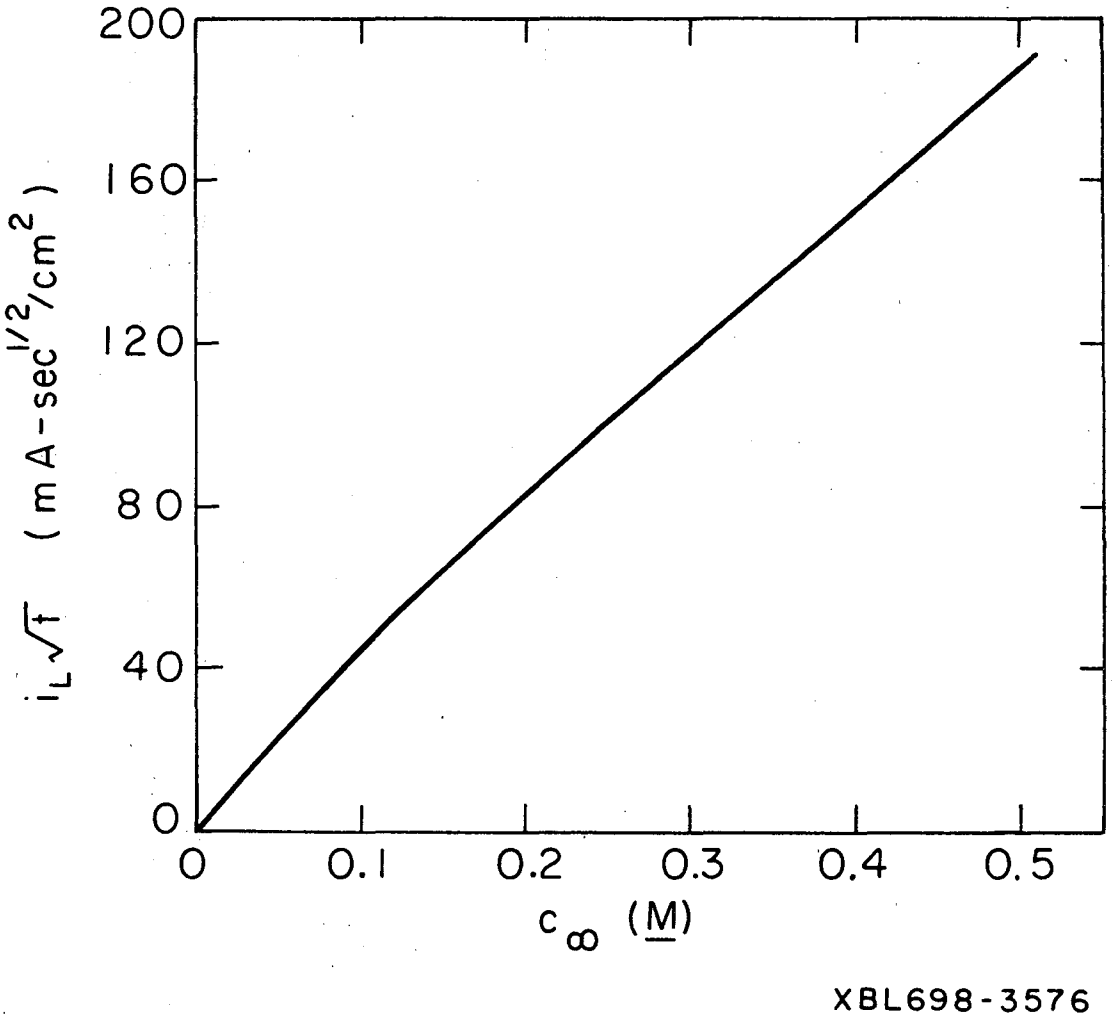

Figure 1. Calculated limiting current densities for aqueous solutions of cupric sulfate at 25°C in a stagnant diffusion cell.

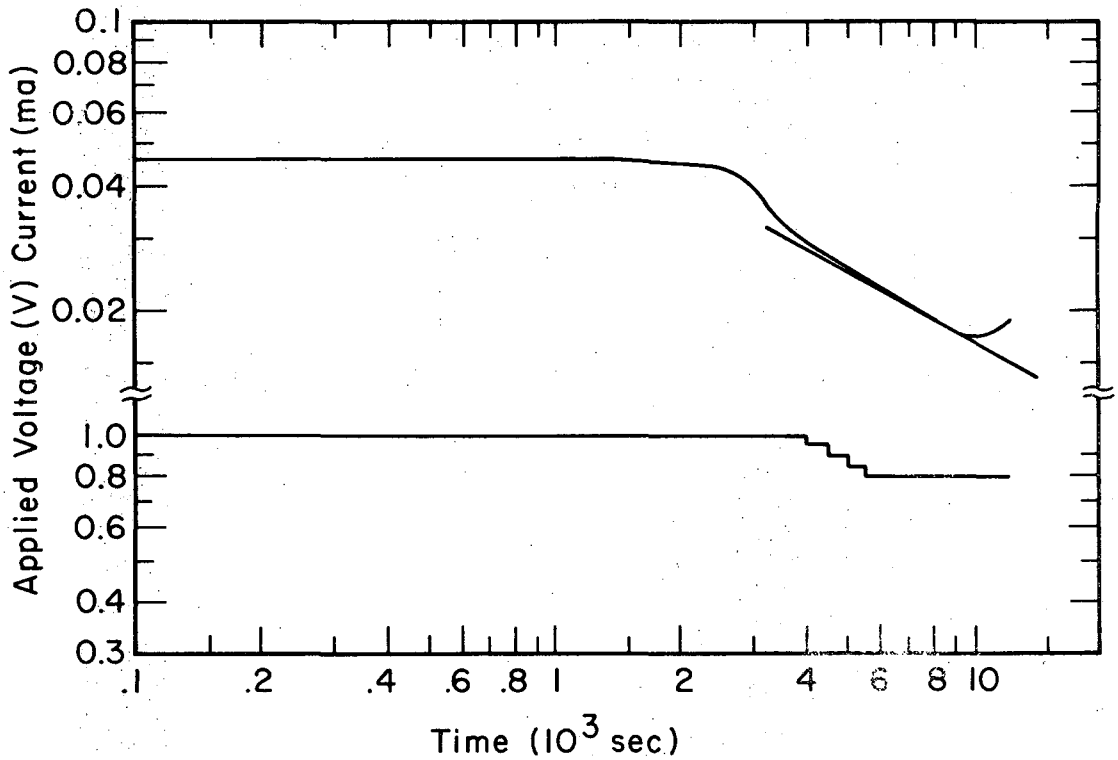

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Figure 2. Current measured in a stagnant diffusion cell for 0.1 M $CuSO_4$ solution with stepwise changes in applied potential. Capillary 2.08 mm in diameter and 4.0 cm long. The straight line of slope - 1/2 corresponds to $i\sqrt{t}$ = 47 mA-$sec^{1/2}/cm^2$, while the calculated value of $i_L\sqrt{t}$ is 44.93 mA-$sec^{1/2}/cm^2$.

Presumably, if the applied potential had been decreased further, hydrogen evolution could have been avoided, and a longer period of limiting current could have been observed.

These experiments lead us to believe that a power source, the output potential of which starts to decrease with respect to the square root of time when the concentration of electrolyte near the electrode has dropped to zero, affords a possible method of measuring $i_L\sqrt{t}$ in a binary electrolyte.

It should be noted that the curve in figure 2 overshoots the line of slope - 1/2, a behavior which is also observed frequently for solutions with supporting electrolyte. The shape of such curves is analyzed in reference 7.

Other experiments involved optical observations of concentration profiles in a Perkin-Elmer Model 238 Electrophoresis Apparatus by means of Rayleigh interference fringes. The optical cell has two channels connected by a U underneath. Each channel has a width of 0.2 cm, a length of 0.9 cm in the direction of the light path, and a depth of 7.9 cm. The light passes twice through the channel, being reflected by a mirror placed behind the cell. A copper anode and cathode were precisely fitted into the upper ends of the channels. Observations were not made at the anode because the adverse density gradient leads to free convection.

Figure 3 shows the concentration at the surface of the cathode as a function of time for a 0.0385 M $CuSO_4$ solution with applied cell potentials of 0.60 and 0.80 V. The curves are calculated according to the analysis in reference 7.

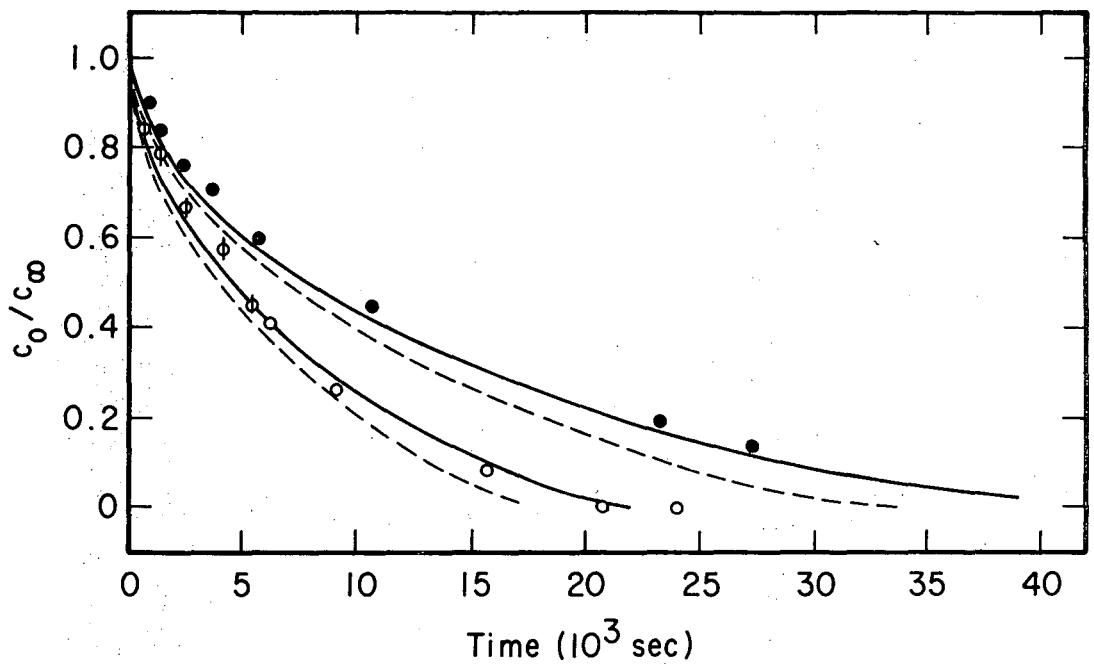

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Figure 3. Transient behavior of surface concentration of copper sulfate (0.0385M) in a stagnant diffusion cell (● 0.60 volt; o 0.80 volt; dashed lines, i_o = 1.0 mA/cm^2; solid lines, i_o = 0.1 mA/cm^2).

The concentration profile in the cathode diffusion layer is plotted in figure 4 with time as a parameter, for a 0.0385 M $CuSO_4$ solution with a cell potential of 0.80 V. The abscissa is the distance from the electrode, stretched by dividing by $\sqrt{t}$. The "theory" curve is calculated according to the above analysis. Comparison indicates that the concentration profile would not reach a steady condition until after a very long time. In other words, the similarity transformation is not a suitable approach to predict concentration profiles although it allows for the variation of physical properties and a nonzero interfacial velocity. The failure is due to the strong transient effect in a binary electrolyte of low conductivity, which makes it difficult to achieve a constant concentration at the electrode. In contrast, for a solution 0.05 M in $CuSO_4$ and 1.0 M in H_2SO_4, the fringe patterns essentially coincide after 10^4 sec when plotted against $y/\sqrt{t}$.[5]

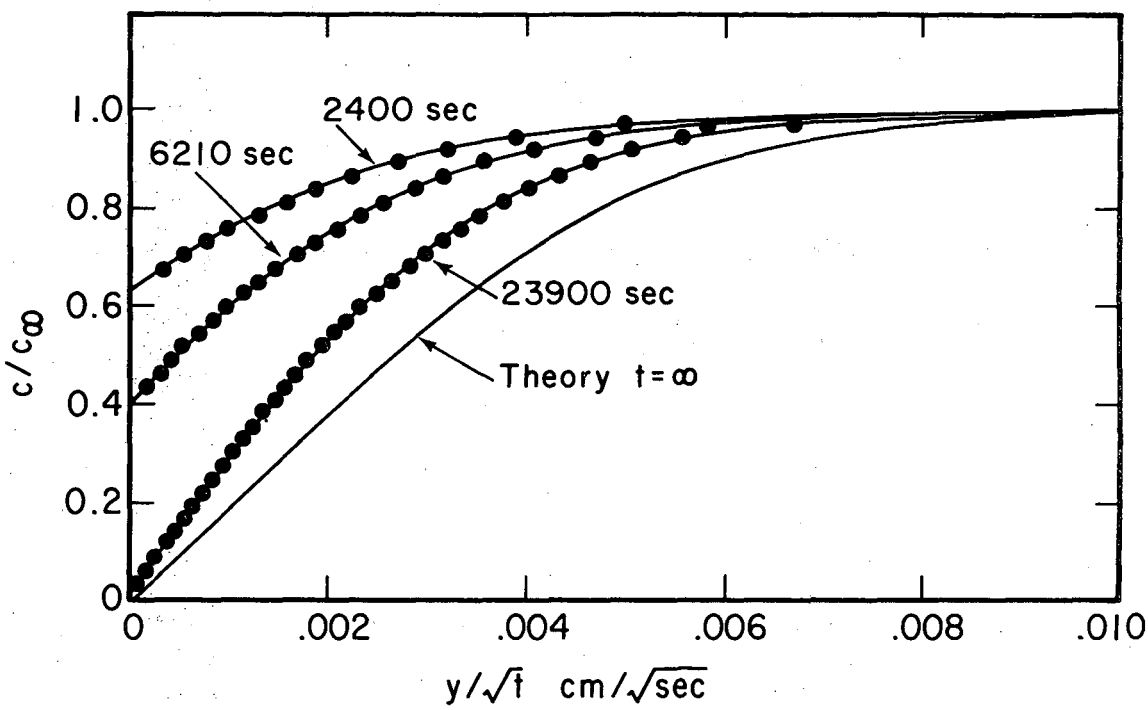

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Figure 4. Concentration profiles for 0.0385 M $CuSO_4$ at 25°C with a cell potential of 0.80 V.

Discussion and Conclusions

The mass transfer rate and concentration profiles in a stagnant diffusion cell have been calculated with consideration of the variation of transport properties and the nonzero interfacial velocity. This work was essentially parallel to that for a rotating disk.[2]

One of the original objectives of the concentration profile measurements was to see whether the variation of physical properties and nonzero interfacial velocity are the causes of the deviation from theory observed in O'Brien's measurements.[1] Unfortunately, a definitive conclusion is not forthcoming because of the strong transient effect in a solution of low conductivity, which makes it difficult to achieve a constant concentration at the electrode surface. The present results do not indicate any additional deviations which cannot be explained by this effect.

The experiments could be made to conform to the conditions under which the similarity transformation is applicable by using a current source whose output is inversely proportional to the square root of time. Alternately, more attention could be devoted to reaching limiting current by using a high applied potential at short times and lowering the potential at later times in order to avoid hydrogen evolution. The experimentally simple arrangement of using a constant current requires numerical integration of partial differential equations in order to account for the variation of physical properties and a nonzero interfacial velocity.

The similarity transformation is also applicable to multicomponent solutions, although the composition dependence of the physical properties is not available at present. Furthermore, simple interference fringes cannot readily be resolved into concentration profiles for the individual components.

Acknowledgment

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Appendix. Differential Diffusion Coefficients

Limiting current measurements in a stagnant diffusion cell lead to values of $i_L\sqrt{t}$ for various compositions of the bulk solution. For a binary solution, these measurements can be inverted to obtain the composition dependence of the differential diffusion coefficient if the transference number and the density are known as functions of concentration. A similar inversion would be possible for values of $i_L/\sqrt{\Omega}$ obtained with a rotating disk electrode, if in addition the viscosities were known.

The procedure consists essentially of the following. A concentration dependence of D is assumed, and values of $i_L\sqrt{t}$ are calculated by the method in the "analysis" section. The assumed dependence of the differential diffusion coefficient is then adjusted until the calculated values of $i_L\sqrt{t}$ agree with the experimental values. Since neither the stagnant diffusion cell nor the rotating disk are likely to become popular for measuring diffusion coefficients in binary solutions, the details will not be reproduced from reference 5.

Nomenclature

c	concentration, mole/cm^3
D	diffusion coefficient, cm^2/sec
F	Faraday's constant, 96,500 coul/equiv
H	dimensionless velocity
i_L	limiting current density, amp/cm^2
i_y	current density, amp/cm^2
I	dimensionless current density
M_s	molecular weight of the salt, g/mole
N_+	flux of cations, mole/cm^2-sec
t	time, sec
t_+	cation transference number relative to the mass-average velocity
v_y	mass-average velocity, cm/sec
y	distance from the electrode, cm
z_+	charge number of the cation
ν_+	number of cations per molecule of electrolyte
ξ	dimensionless distance
ρ	density, g/cm^3
ω_s	mass fraction of salt
Ω	rotation speed of a disk electrode, radian/sec

subscripts

o	at the electrode surface
∞	in the bulk solution
+	cation

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