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POLAROGRAPHY IN A BINARY SALT SOLUTION

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March, 1966

Polarography in a Binary Salt Solution

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March, 1966

Abstract

The instantaneous current and the average current to a dropping mercury electrode in a binary salt solution are calculated. At very small times the instantaneous current depends only on the ohmic drop and varies as $t^{1/3}$, whereas at sufficiently large times and voltages a limiting current is reached, which varies as $t^{1/6}$. The average current over a drop lifetime is not well represented by the limiting current approximation of the Ilkovič equation if either the drop life or the applied voltage is too small. However, the current is always directly proportional to the bulk concentration of the reactant.

The dropping mercury electrode is used quite widely for the qualitative and quantitative analysis of solutions containing reducible solutes. It is also used occasionally to measure diffusion coefficients when only rough values are required. Ilkovic[1] derived an expression for the limiting current to the drop in a well supported electrolyte, and von Stackelberg[2] determined the effect of migration on the limiting current for the case of a binary electrolyte. In order to apply these theoretical results one integrates the instantaneous current expression over the lifetime of a drop to obtain the average current, the quantity which is measured experimentally. This procedure assumes that the limiting current is attained at all times, which is a good approximation for a well supported electrolyte. With a binary electrolyte, however, the relatively high ohmic drop in the diffusion layer and even in the bulk solution retards the approach to zero of the concentration at the surface of the drop. In this case the expression for limiting current may not be adequate to interpret experimental results correctly. For this purpose it is necessary to investigate the transient behavior of the concentration to determine its effect on the measured average current. Levich[3] has attempted to treat the problem, but unfortunately his analysis contains serious errors.

The Concentration Equation

In our analysis we consider a spherical mercury drop formed at time zero in a binary salt solution of initial concentration c_o. The drop is held at a constant potential V relative to a reversible counter-electrode far from the drop such that the cation is reduced and dissolves in the mercury.

Following Levich[4], we write the equation of convective diffusion for this case in the following form:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial z^2} \tag{1}$$

where
$$z \equiv t^{2/3} y,$$

$$\tau \equiv (\frac{3D}{7}) t^{7/3}, \qquad C \equiv \frac{c - c_0}{c_0},$$

t is time, y is normal distance from the drop surface, $c = c_+/(-z_-) = c_-/z_+$ is the concentration, and D is the diffusion coefficient, the latter two quantities referring to the neutral salt. Two of the boundary conditions are

$$C = 0 \quad \text{at} \quad \tau = 0, \; z > 0$$

and
$$C = 0 \quad \text{as} \quad z \to \infty.$$

The depletion of salt in the diffusion layer causes the electrical conductivity of the solution to decrease in that region and contributes to a large ohmic drop. Since we have specified a particular potential between the electrodes, the surface concentration and the current must adjust themselves to balance the ohmic drop and the concentration polarization with the total applied voltage. Thus the third boundary condition is

$$C = C_1(\tau) \text{ at } z = 0$$

where $C_1(\tau)$ is some function of time which remains to be determined.

Equation (1) may be solved by a Laplace transformation. The result is

$$C(\tau, z) = \frac{2}{\sqrt{\pi}} \int_{z/2\sqrt{\tau}}^{\infty} C_1\left(\tau - \frac{z^2}{4x^2}\right) e^{-x^2} \, dx \; . \tag{2}$$

The problem remains to determine $C_1(\tau)$, the dimensionless concentration at the surface, from a consideration of the polarization.

The Potential Equation

From dilute electrolytic solution theory one can show that the current density i at the mercury drop is

$$\frac{i}{-z_+ z_- F} = \frac{-D}{(1-t_+)} \left. \frac{\partial c}{\partial y} \right|_{y=0} \tag{3}$$

where z_+ and z_- are the valences of the ions, F is Faraday's constant, and t_+ is the cation transference number defined as

$$t_+ = \frac{z_+ D_+}{z_+ D_+ - z_- D_-} . \tag{4}$$

Also the diffusion coefficient of the salt may be written as

$$D = \frac{D_+ D_- (z_+ - z_-)}{z_+ D_+ - z_- D_-} \tag{5}$$

where D_+ and D_- are the individual ionic diffusion coefficients.

In general, the current density in the solution may be written as

$$\frac{i}{-z_+ z_- F} = -(z_+ D_+ - z_- D_-) \frac{F}{RT} c \frac{\partial \phi}{\partial y} - (D_+ - D_-) \frac{\partial c}{\partial y} \tag{6}$$

where ϕ is the potential in the solution. Elimination of the current density from equations (3) and (6) and integration over y from zero to infinity yield the required equation for c_1:

$$V - \frac{Da}{-z_- D_- c_0} \left(\frac{\partial c}{\partial y}\right)_{y=0} = \frac{(z_+ - z_-)}{-z_+ z_-} \ln \frac{c_0}{c_1} + \frac{(z_+ - z_-)}{-z_+ z_-} t_+ \left(\frac{c_1 - c_0}{c_0}\right) \tag{7}$$

where a is the radius of the drop. Specifically the radius is given by

$$a = \gamma t^{1/3} \tag{8}$$

where

$$\gamma = \left(\frac{3d^2 U_0}{16}\right)^{1/3} ,$$

d is the diameter of the capillary tube and U_0 is the average flow velocity of the mercury through the capillary. In this integration the concentration in the diffusion layer was approximated by a linear profile, and the thickness of the diffusion layer was assumed to be small relative to the drop radius. Also we have made use of the Nernst expression for the concentration overvoltage,

$$(\phi_1 - \phi_{met}) = \frac{RT}{z_+ F} \ln \frac{c_0}{c_1} , \tag{9}$$

the difference in potential between the mercury and the solution at the interface.

Nondimensionalization of equation (7) and substitution of $\left(\frac{\partial C}{\partial z}\right)_{z=0}$ from the differentiation of equation (2) give the following integro-differential equation for the determination of the surface concentration:

$$- \Phi - \int_0^1 \frac{dC_1(\eta)}{d\eta}\bigg|_{\eta=\theta\psi} \frac{d\psi}{\sqrt{1 - \psi^{14}}} = \ln (1+C_1) + t_+ C_1 \tag{10}$$

where

$$\Phi \equiv \frac{-z_+ z_-}{z_+ - z_-} \frac{FV}{RT} . \tag{11}$$

The variable θ is a dimensionless time defined as

$$\theta \equiv \left[\frac{(z_+ - z_-) \sqrt{\pi} \left(\frac{3D}{7}\right)^{3/7} D_-}{z_+ D\gamma} \right] \tau^{1/14} . \tag{12}$$

The Current

Let us define a dimensionless current $E(\theta, \Phi, t_+)$ as

$$E(\theta, \Phi, t_+) \equiv - \frac{3}{28} \frac{I\, D_-}{\gamma^3 F c_o z_+^2 D_+} \tag{13}$$

where I is the total current flowing to the drop at the time t to which the variable θ corresponds. From combination of equations (2), (3), (10), and (13) the reduced total current is found to be

$$E(\theta, \Phi, t_+) = \theta^2 [\ln (1+C_1) + \Phi + t_+ C_1] . \tag{14}$$

Thus, from the solution of equation (10) for C_1, the instantaneous current may be calculated.

The Concentration at the Drop Surface

It has been possible to obtain a solution to equation (10) valid at small times by expanding C_1 as a power series in θ.

$$C_1 = a_1 \theta + a_2 \theta^2 + a_3 \theta^3 + \dots . \tag{15}$$

The coefficients a_i are functions of the parameters Φ and t_+. Their values are determined by substituting the series (15) into equation (10) and equating terms of the same power in θ.

The first term of this series corresponds to Ohm's law and leads to

$$i = - \frac{\kappa V}{a} \tag{16}$$

where κ is the conductivity of the solution and is equal to

$$\kappa = \frac{-z_+ z_- F^2 c_+ D_-}{RT\, t_-} \; . \tag{17}$$

That is, at very small times the only contribution to the potential drop is the ohmic resistance of the solution around the sphere. This first term gives the small time asymptote for the reduced current

$$E(\theta, \Phi, t_+) = \Phi\theta^2 \; . \tag{18}$$

At very large times C_1 will be constant, and the third boundary condition for the solution of equation (1) is no longer a function of time. Normally the applied voltage is sufficiently large to produce a limiting current condition, and the solution then corresponds to that of Ilkovič. This result is the large time, large voltage asymptote and may be expressed in dimensionless form as

$$E(\theta, \Phi, t_+) = \theta. \tag{19}$$

Comparison of this expression with the limiting current of a cation with a supporting electrolyte given by the Ilkovič equation yields the result

$$\left(\frac{I_{binary}}{I_{supported}} \right)_{limiting} = \frac{1}{(1-t_+)} \left(\frac{D}{D_+} \right)^{1/2} \tag{20}$$

which is identical with the expression derived by von Stackelberg.

Using the small time expansion introduced in equation (15) we have calculated the reduced instantaneous current to the drop for various values of Φ and for

values of θ up to 1.0. The results are shown in Figure 1. It is seen that the value of the transference number has only a small effect on the current particularly at large voltages; the effect, in fact, vanishes in both the small and large time limits. We note that the current varies with θ^2 or $t^{1/3}$ at small times and then changes over to a θ or $t^{1/6}$ dependence at large times, the transition being earlier, the greater the applied potential.

The Average Current

The significant quantity for comparison with experiment is usually not the instantaneous current but rather the current averaged over the lifetime of a drop. This average current is defined as

$$\overline{I}(\Phi, t_+) \equiv \frac{1}{T} \int_0^T I \, dt \;, \tag{21}$$

where T is the drop life.

The solution for the instantaneous current has been integrated to obtain the average current to the drop. The results are shown in Figure 2 where the dimensionless average current $\overline{E}(\Theta, \Phi, t_+)$, defined analogously to E, is plotted versus dimensionless drop life $\Theta = \theta_{final}$ with the dimensionless voltage and t_+ as parameters. For a typical experiment Θ is on the order of 0.1 to 0.5. Also, for a 1-1 electrolyte an applied potential of one volt corresponds to $\Phi = 19.5$.

The line $\overline{E} = \frac{6}{7} \Theta$ is the Ilkovic - von Staokelberg limiting current result and represents the large time, large voltage asymptote.

Conclusions

In Figure 2 it is seen again that the value of the transference number has little effect on the average current, particularly for reasonably large voltages. Curves for values of t_+ between zero and 1.0 fall between the two curves given for these values.
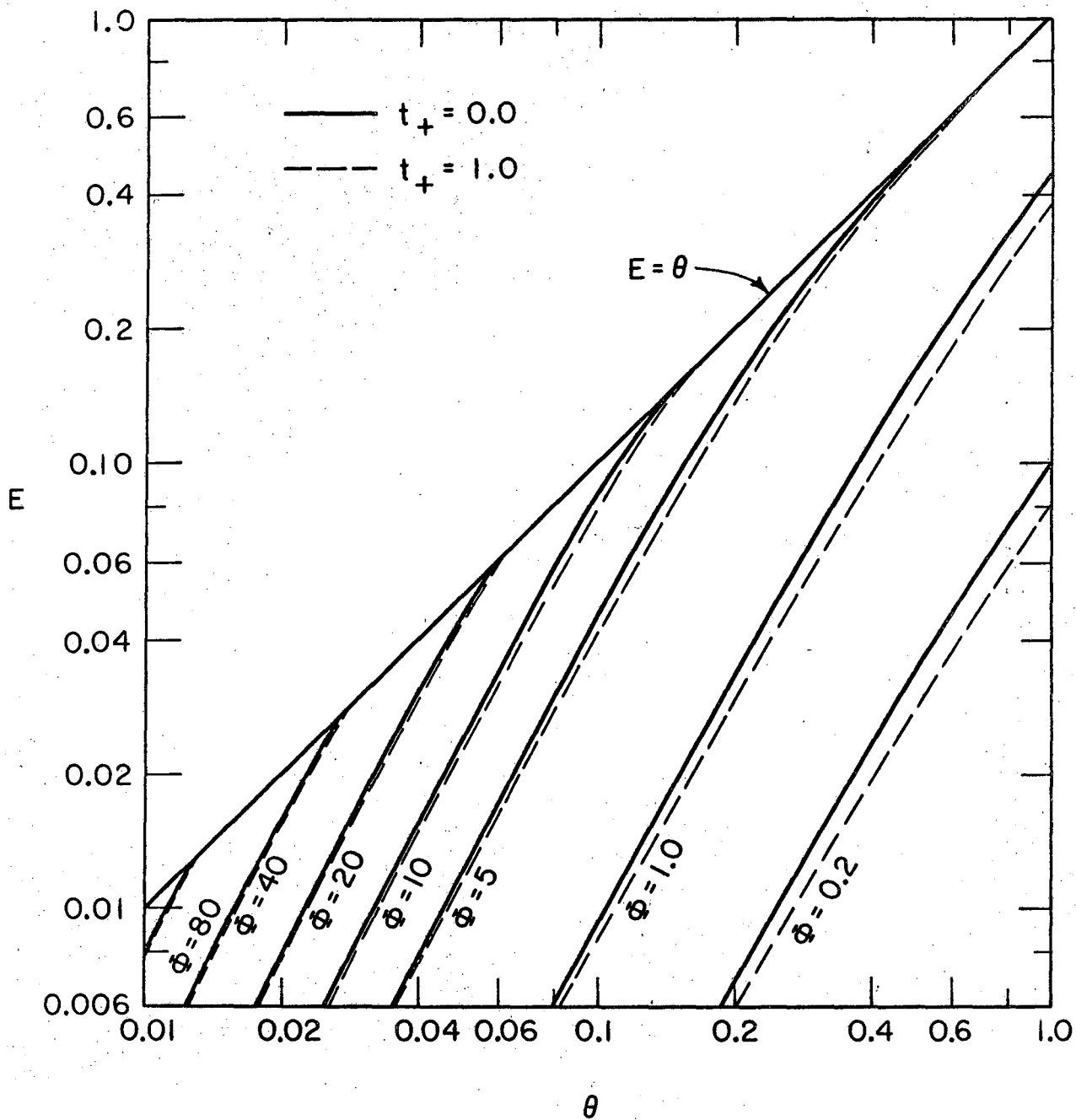
Figure 1. The reduced instantaneous current to the drop as a function of dimensionless time, dimensionless applied voltage, and cation transference number.
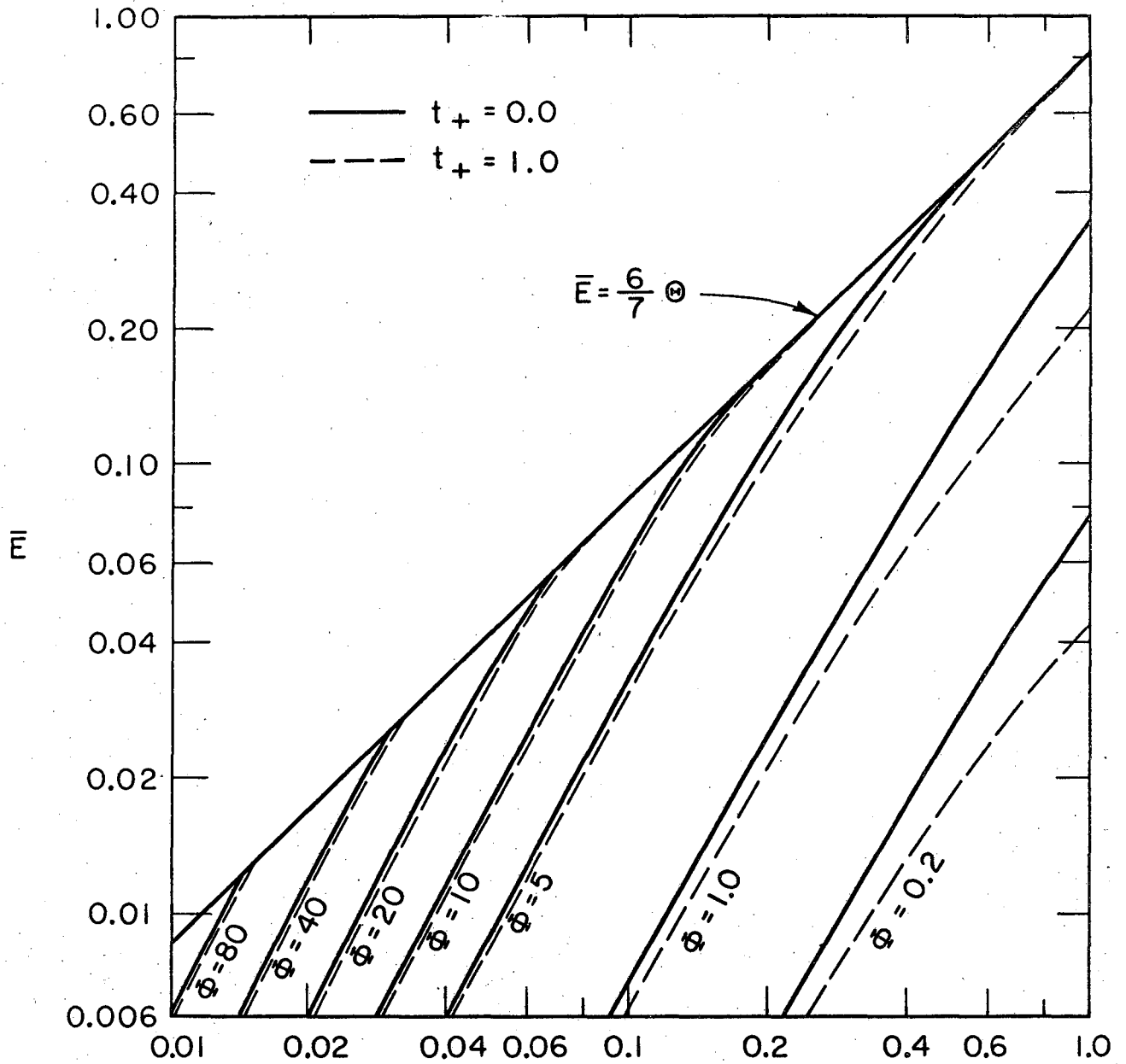
Figure 2. The reduced average current to the drop as a function
of dimensionless drop life, dimensionless applied
voltage, and cation transference number.

For $\Phi > 20$ and $\Theta > 0.07$ it is found that the limiting current approximation provides a good representation of the average current. However, for $\Phi = 10$ the approximation is not very accurate unless $\Theta > 0.20$, and it becomes much less adequate for smaller voltages and shorter times. Therefore, the correct interpretation of experimental data obtained under circumstances where values of drop life or applied voltage may be necessarily small or where instantaneous current is measured directly requires consideration of the detailed results of this analysis.

A further conclusion of this work follows from equations (13) and (14). The right-hand side of equation (14) is dimensionless and independent of c_o. Therefore, even during the transient concentration behavior, the current is always proportional to the bulk concentration of the reactant. This is the characteristic of all polarographic situations which gives the method its great usefulness as a quantitative analytical tool.

The phenomena considered here for a binary electrolyte also occur in a supported electrolyte. However, because of the higher conductivity, the transient effects are of much shorter duration and therefore insignificant in that case.

Acknowledgment

Nomenclature

a   - radius of mercury drop (cm).

a_i - coefficients in expansion of dimensionless concentration at the surface.

c   - electrolyte concentration $(mole/cm^3)$.

c_o - electrolyte concentration in bulk solution $(mole/cm^2)$.

c_1 - electrolyte concentration at the surface of the drop $(mole/cm^3)$.

c_+ - cation concentration $(mole/cm^3)$.

C   - dimensionless electrolyte concentration.

D   - diffusion coefficient of the salt (cm^2/sec).

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

d   - diameter of capillary from which mercury issues (cm).

E   - dimensionless current to the drop.

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

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

I   - total current to the drop (amp).

R   - gas constant (joule/mole-°K).

T   - temperature (°K).

t   - time (sec).

t_+ - cation transference number.

U_o - average velocity of mercury in capillary (cm/sec).

V   - applied voltage (volts).

y   - normal distance from drop surface (cm).

z_i - charge number of species i.

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

κ - electrical conductivity of the solution (mho/cm).

$\emptyset$ - electrostatic potential (volts).

Φ - dimensionless potential.

θ - dimensionless time variable.

Θ - dimensionless drop life.

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