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# The Koutecký Correction to the Ilkovič Equation

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## Abstract

The Ilkovič equation for diffusion limiting currents to a dropping mercury electrode was modified by Koutecký in order to account for the fact that the thickness of the diffusion layer increases faster than the radius of the mercury drop. It is found that the correction of Koutecký can be expressed in terms of tabulated gamma functions.

## Introduction

An equation describing the limiting diffusion current at a dropping mercury electrode was obtained by Ilkovič[1,2] and also by Mac Gillavry and Rideal[3]. In the derivation the diffusion layer was taken to be thin compared to the size of the drop. Koutecký[4] calculated a first order correction for the fact that the diffusion layer (thickness proportional to $t^{1/2}$) grows faster than the mercury drop (radius proportional to $t^{1/3}$). Earlier derivations[5,6] of the correction were either erroneus[7] or inexact. Koutecký and Stackelberg[8] have discussed this correction and the difficulties in its experimental verification. Levich[9] gives a derivation which is largely correct, but the final result is misstated.

The result for the total current to the drop, averaged over the life time T of the drop, is

$$I_{avg} = 3.5723 \ nF \ c_{\infty} \ D_i^{1/2} Q^{2/3} T^{1/6} \ [1 + K \ (D_i^3 T/Q^2)^{1/6}] \ , \qquad (1)$$

and coincides with Ilkovič's equation when K = 0. In the present work it is shown that the coefficient K of the correction has the value

$$K = \frac{14\Gamma(15/14)}{11\Gamma(11/7)} \sqrt{\frac{3}{7}} \left(\frac{4\pi}{3}\right)^{1/3} = 1.4530 \ . \qquad (2)$$

In equation (1), Q is the volumetric flow rate of the mercury ($cm^3/sec$). If one insists on using the mass flow rate of mercury m(g/sec), then the correction factor for Ilkovič's equation is

$$1 + K' \ (D_i^3 T/m^2)^{1/6} \qquad (3)$$

where $K' = 3.4626 \ g^{1/3}/cm$, in good agreement with the value 3.4 of Koutecký[4]. The density of mercury at 25°C was taken to be 13.5336 $g/cm^3$. (Koutecký and Stackelberg[8] give $K' = 3.47 \ g^{1/3}/cm$.)

The rather modest contribution of the present work is the expression (2) for the coefficient of the correction.

## Analysis

The analysis of Levich appears to be simpler than that of Koutecký and will therefore be followed here. For radial growth of the mercury drop without any tangential surface motion, the concentration of the reactant obeys the equation of convective diffusion in the form

$$\frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} = D_i \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} \right) . \tag{4}$$

The radius $r_o$ of the drop grows with the cube root of time:

$$r_o = \gamma \, t^{1/3} , \tag{5}$$

where $Q = 4\pi\gamma^3/3$ is the constant volumetric flow rate of mercury through the capillary, and the convective velocity in the solution is due to the radial growth of the drop:

$$v_r = \frac{r_o^2}{r^2} \frac{dr_o}{dt} = \frac{\gamma^3}{3r^2} . \tag{6}$$

Let us use the dimensionless variables

$$\tau = \left( \frac{3D_i}{7\gamma^2} \right)^7 t^{7/3}, \qquad z = \left( \frac{3D_i}{7\gamma^2} \right)^3 \frac{r-r_o}{\gamma} \, t^{2/3} . \tag{7}$$

Equation (4) then becomes

$$\frac{\partial c_i}{\partial \tau} - \frac{\partial^2 c_i}{\partial z^2} = \frac{1}{7\tau^{4/7}} \left[ 1 - \frac{1}{(1+z/\tau^{3/7})^2} - \frac{2z}{\tau^{3/7}} \right] \frac{\partial c_i}{\partial z} + \frac{2/\tau^{3/7}}{1+z/\tau^{3/7}} \frac{\partial c_i}{\partial z} . \tag{8}$$

The result of Ilkovič is obtained by neglecting the right side of this equation. The corresponding concentration, denoted $c_1$, satisfies the equation

$$\frac{\partial^2 c_i}{\partial \tau} = \frac{\partial^2 c_1}{\partial z^2} . \tag{9}$$

subject to the boundary and initial conditions

$$c_1 = c_\infty \text{ at } \tau = 0, \quad c_1 = c_\infty \text{ at } z = \infty, \quad c_1 = 0 \text{ at } z = 0. \tag{10}$$

The result is

$$c_1 = \frac{2c_\infty}{\sqrt{\pi}} \int_0^{z/2\sqrt{\tau}} e^{-x^2}\, dx . \tag{11}$$

Equation (11) shows that z is of order $\sqrt{\tau}$ in the diffusion layer. The terms on the left side of equation (8) are of order $\tau^{-1}$ while the neglected terms on the right are of order $\tau^{-13/14}$. Thus the approximation of Ilkovič appears to be justified, and a correction can be calculated by letting

$$c_i = c_1(z,\tau) + c_2(z,\tau) , \tag{12}$$

where $c_2$ takes care of the lowest order terms neglected on the right side of equation (8). Thus $c_2$ satisfies the equation

$$\frac{\partial c_2}{\partial \tau} - \frac{\partial^2 c_2}{\partial z^2} = \left(\frac{-3z^2}{7\tau^{10/7}} + \frac{2}{\tau^{3/7}}\right)\frac{\partial c_1}{\partial z} = \frac{c_\infty}{\sqrt{\pi}}\left(\frac{-3z^2}{7\tau^{27/14}} + \frac{2}{\tau^{13/14}}\right) e^{-z^2/4\tau}, \tag{13}$$

subject to the boundary and initial conditions

$$c_2 = 0 \text{ at } \tau = 0, \quad c_2 = 0 \text{ at } z = \infty, \quad c_2 = 0 \text{ at } z = 0. \tag{14}$$

As suggested by Levich, the solution $c_2$ can be expressed as the sum of a particular solution $c_{2P}$ and a homogeneous solution $c_{2H}$:

$$c_2 = c_{2P} + c_{2H} , \tag{15}$$

and the particular solution is given by

$$c_{2P} = \left[ - \frac{3c_\infty}{11\sqrt{\pi}} \frac{z^2}{\tau^{13/14}} + \frac{28c_\infty}{11\sqrt{\pi}} \tau^{1/14} \right] e^{-z^2/4\tau}. \tag{16}$$

Hence the homogeneous solution $c_{2H}$ satisfies the equation

$$\frac{\partial c_{2H}}{\partial \tau} = \frac{\partial^2 c_{2H}}{\partial z^2} \tag{17}$$

subject to the boundary and initial conditions

$$c_{2H} = 0 \text{ at } \tau = 0,\ c_{2H} = 0 \text{ at } z = \infty,\ c_{2H} = -28c_\infty \tau^{1/14}/11\sqrt{\pi} \text{ at } z = 0. \tag{18}$$

At this point we depart from the method of Levich. The desired result can be obtained by using the Laplace transform $C(z,s)$ of the homogeneous solution $c_{2H}(z,\tau)$. The Laplace transform of equation (17) subject to the initial condition is

$$sC = \frac{\partial^2 C}{\partial z^2} \tag{19}$$

with the solution

$$C = B(s)e^{-\sqrt{s}\,z}. \tag{20}$$

Transformation of the boundary condition at $z = 0$ shows that

$$B(s) = -\frac{28c_\infty}{11\sqrt{\pi}} \frac{\Gamma(15/14)}{s^{15/14}}. \tag{21}$$

Inversion of $C(z,s)$ is not necessary since all that is required is the concentration derivative at the surface of the drop, and this can be obtained from

$$\left.\frac{\partial C}{\partial z}\right|_{z=0} = -B(s)\sqrt{s} = \frac{28c_\infty}{11\sqrt{\pi}} \frac{\Gamma(15/14)}{s^{4/7}}. \tag{22}$$

Inversion gives

$$\left.\frac{\partial c_{2H}}{\partial z}\right|_{z=0} = \frac{16c_\infty}{11\sqrt{\pi}} \frac{\Gamma(15/14)}{\Gamma(11/7)} \frac{1}{\tau^{3/7}}. \tag{23}$$

## The Current

The instantaneous current to the surface of the drop is given by

$$I = nFD_i 4\pi r_o^2 \left.\frac{\partial c_i}{\partial r}\right|_{r=r_o} = nFD_i 4\pi\gamma \left(\frac{3D_i}{7\gamma^2}\right)^3 t^{4/3}\left(\left.\frac{\partial c_1}{\partial z}\right|_{z=0} + \left.\frac{\partial c_2}{\partial z}\right|_{z=0}\right)$$

$$= 4\sqrt{\frac{7\pi}{3}}\, nFc_\infty \gamma^2 D_i^{1/2} t^{1/6}\left(1 + a\,\frac{D_i^{1/2} t^{1/6}}{\gamma}\right), \tag{24}$$

where

$$a = \sqrt{\frac{3}{7}}\,\frac{16\Gamma(15/14)}{11\Gamma(11/7)} = 1.0302\ . \tag{25}$$

The term with the coefficient a represents the correction to Ilkovič's equation for the instantaneous current. By averaging equation (24) over the life of the drop and replacing $\gamma$ by the volumetric flow rate of mercury, one obtains equation (1) for the average diffusion limiting current.

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## Nomenclature

$c_i$ - reactant concentration ($mole/cm^3$).

$c_\infty$ - bulk concentration of reactant ($mole/cm^3$).

$C$ - Laplace transform of concentration.

$D_i$ - diffusion coefficient of reactant ($cm^2/sec$).

$F$ - Faraday's constant (coul/equiv).

$I$ - instantaneous current to the drop (amp).

$I_{avg}$ - average diffusion limiting current (amp).

$m$ - mass flow rate of mercury in the capillary (g/sec).

$n$ - number of electrons consumed when one reactant ion or molecule reacts.

$r$ - radial position coördinate (cm).

$r_o$ - radius of the growing drop (cm).

$Q$ - volumetric flow rate of mercury ($cm^3/sec$).

$s$ - Laplace transform variable.

$t$ - time (sec).

$T$ - life time of the drop (sec).

$v_r$ - radial component of velocity (cm/sec).

$z$ - dimensionless variable.

$\gamma$ - constant in rate of growth of mercury drop ($cm/sec^{1/3}$).

$\tau$ - dimensionless variable.

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