



Higher corrections of the Ilkovich equation

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ABSTRACT

A short-time asymptotic analysis is performed to establish corrections of the Ilkovich equation, which describes the polarographic response of a dropping mercury electrode. The convective diffusion equation governing diffusion limited reactant flux for small drop times is solved by a regular perturbation based on powers of the sixth root of time. This produces a framework within which higher terms of the Ilkovich equation can be derived systematically. As well as reproducing Ilkovich's original formula and verifying Newman's correction of Koutecky's first-order term, we calculate the second-order term for the first time. The calculation is compared to the Newman–Levich procedure and tested against numerical simulations with finite-element software.

1. Introduction

The Ilkovich equation quantifies the limiting diffusion current at a dropping mercury electrode, an experimental apparatus first deployed for electrochemical measurements by Heyrovsky [1]. Ilkovich originally developed a formula for the current in the limit where the diffusion boundary layer is negligibly small compared to the mercury drop's radius. He showed that the total current flow, averaged over the droplet lifetime, is proportional to the sixth root of time [2,3]. The model was formulated as a convective-diffusion problem by MacGillavry and Rideal [4]. A first-order correction, with an additional term up to the cube root of time, was developed by Koutecky [5], although Levich noted that the reported formula was incorrect [6]. An accurate calculation of the first-order term was presented by Newman in this journal [7]. More recently, Samec gave a compelling history of the Ilkovich problem, although it omits the later corrections of Koutecky's results by Levich and Newman [8].

The purpose of this paper is to develop a second-order correction to the Ilkovich equation. We show that the instantaneous molar flowrate $N(t)$ of a solute with bulk concentration c_∞ and diffusivity D at the surface of a dropping mercury electrode supplied at volumetric flowrate Q depends on time t as¹

$$N(t) = K_0 c_\infty Q^{2/3} D^{1/2} t^{1/6} \left[1 + K_1 \left(\frac{D^3 t}{Q^2} \right)^{1/6} + K_2 \left(\frac{D^3 t}{Q^2} \right)^{1/3} + \dots \right], \quad (1)$$

in which K_0 , K_1 , and K_2 are numerical constants given by

$$\begin{aligned} K_0 &= \left(\frac{16464}{\pi} \right)^{1/6} = 4.16771085 \dots \\ K_1 &= \frac{16 \cdot 48^{1/6} \Gamma(\frac{15}{14}) \pi^{1/3}}{11 \Gamma(\frac{11}{7}) \sqrt{7}} = 1.66060563 \dots \\ K_2 &= \frac{162^{1/3} \pi^{2/3}}{1694} \left(\frac{480 \Gamma(\frac{15}{14}) \Gamma(\frac{8}{7})}{\Gamma(\frac{11}{7}) \Gamma(\frac{23}{14})} - 469 \right) = 0.49216295 \dots, \end{aligned} \quad (2)$$

and Γ represents the gamma function. Time averaging $N(t)$ over the drop time t_d produces the Ilkovich formula in its standard form, discussed further in Section 5 below.

In the course of identifying the constants in Eq. 1 we introduce an asymptotic perturbation analysis that systematically produces equation systems governing terms of higher order, clarifying the earlier Newman–Levich calculation of K_1 . Finally, we test our analytical results against a numerical solution of the governing system, showing that the second-order correction increases the timescale across which the asymptotic model is valid.

2. Problem statement and nondimensionalization

Consider a spherical droplet of mercury with time-dependent radius, which grows at constant volumetric flowrate from a volume

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¹ Note that the expression in Eq. 1 is given in terms of time t after the droplet begins to fall. Ilkovich reported an equation averaged over the drop time t_d . The averaged form of the flux is developed in Section 5.

Nomenclature

List of Symbols

$\{A', B', \dots, Y', Z'\}$	Arbitrary constants, see Eqs. 47, 62, and 65. [unitless]
c	Molar concentration of solute. [mol m ⁻³]
c_∞	Bulk solute concentration, see Eq. 1. [mol m ⁻³].
C	Dimensionless solute concentration, defined in Eq. 8. [unitless]
$\{C_0, C_1, C_2\}$	Nought, first, and second order terms in perturbation expansion of C , defined in Eq. 36. [unitless]
D	Solute diffusivity, see Eq. 1. [m ² s ⁻¹].
$f_i^j(\xi)$	Function describing the particular ($j = p$) or homogeneous ($j = h$) case of a solution to the governing system at perturbation order i . Related to $C_i(\xi)$ through transformation 45. [unitless]
$H_\lambda(x)$	Hermite polynomial of order λ , dependent on x . [unitless]
$\{K_0, K_1, K_2\}$	Constants in the expansion of $N(t)$ from Eq. 1; values summarized in Eq. 2. [unitless]
$M(a, b, x)$	Kummer's confluent hypergeometric function of the first kind, dependent on x and parametrized by constants a and b . [unitless]
$N(t)$	Instantaneous molar flowrate of solute into the droplet surface, defined by Eq. 68 or 69. Eq. 1 gives its short-time asymptotic expansion. [mol s ⁻¹]
$\langle N \rangle_\tau$	Dimensionless total solute flowrate, averaged over time τ , described by Eq. 87. [unitless]
Q	Volumetric flowrate of droplet, see Eq. 1. [m ³ s ⁻¹].
r	Radial position originating at droplet center, see Eq. 5. [m]
r_0	Radius of the growing droplet, defined as a function of t in Eq. 3. [m]
r	Dimensionless radial position originating at droplet surface, defined in Eq. 12. [unitless]

R	Dimensionless radial position originating at droplet center, defined in Eq. 8. [unitless]
t	Time, see Eq. 1. [s]
t_d	Drop time, see text preceding Eq. 18. [s]
τ	Dimensionless time, defined in Eq. 12. [unitless]
τ_d	Dimensionless drop time, defined in Eq. 18. [unitless]
T	Dimensionless time, defined in Eq. 8. [unitless]
T	Dimensionless time, defined in Eq. 19. [unitless]
$v_r(r)$	Velocity of fluid in radial direction, defined in Eq. 4. [m s ⁻¹]
z	Newman's similarity variable, defined in Eq. 74. [unitless]

Greek Letters

α	Constant determining the scale of transient boundary-layer thickness, introduced in Eq. 27. [unitless]
γ	Newman's parameter expressing the droplet growth rate, defined in Eq. 73. [m s ^{-1/3}]
$\Gamma(x)$	Gamma function, dependent on x . [unitless]
η	Dimensionless similarity variable, defined in Eq. 19. [unitless]
θ_1	Newman's first-order perturbation of concentration, a function of τ' and z introduced in Eq. 80. [unitless]
ξ	Rescaled dimensionless similarity variable, defined in Eq. 31. [unitless]
τ	Transformed dimensionless time, defined in Eq. 31. [unitless]
τ'	Newman's transformed dimensionless time, defined in Eq. 74. [unitless]

of zero at time zero. This droplet is immersed in an incompressible liquid solution containing a solute with constant diffusivity at a dilute constant bulk concentration. Also at time zero, a voltage is applied between the mercury and the bulk solution, inducing an electrochemical surface reaction that consumes the solute. The Ilkovich problem asks: given an applied voltage large enough to make the solute concentration vanish completely and immediately at the droplet boundary, how does the total molar flowrate of solute to the surface vary with time after the voltage is applied? A solution valid at times sufficiently short is given by Eq. 1 above, which we proceed to derive now.

Since the volumetric flowrate of the mercury is constant, the droplet volume at time t is

$$\frac{4}{3}\pi r_0^3 = Qt, \text{ so that } r_0(t) = \left(\frac{3Q}{4\pi}\right)^{1/3} t^{1/3}, \quad (3)$$

i.e., the droplet's radius r_0 grows with the cube root of time. The only nonzero component of the fluid velocity is radial, v_r , and the flow satisfies $v_r(t, r_0) = dr_0/dt$ at the droplet surface. Thus, since the dilute condition ensures that the fluid's density is constant, mass continuity requires that the flow field for all $r \geq r_0$ is

$$v_r(r) = \frac{Q}{4\pi r^2}. \quad (4)$$

Conveniently, the constancy of Q guarantees that this relationship is independent of time. To illustrate the solute's transient behavior, we seek a concentration distribution $c(t, r)$ that satisfies the radial spherical convective diffusion governing equation (GE)

$$\text{GE: } \frac{\partial c}{\partial t} + v_r(r) \frac{\partial c}{\partial r} = D \left(\frac{2}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right), \quad (5)$$

subject to an initial condition (IC)

$$\text{IC: } c(0, r) = c_\infty, \quad (6)$$

as well as inner and outer boundary conditions (BCi and BCii, respectively)

$$\text{BCi: } c(t, r_0(t)) = 0 \text{ and } \text{BCii: } c(t, \infty) = c_\infty. \quad (7)$$

Solving the system of Eqs. (5)–(7) will enable computation of the excess molar flux, which is proportional to the concentration gradient at the droplet surface.

First nondimensionalize the problem to simplify the system of equations. Observe that different powers of parameters D and Q can be combined to identify characteristic length and time scales; inspection of the dimensional matrix for this system shows that it affords three dimensionless degrees of freedom. By changing variables to

$$C = \frac{c - c_\infty}{c_\infty}, \quad T = \frac{16\pi^2 D^3 t}{Q^2}, \quad \text{and} \quad R = \frac{4\pi D r}{Q}, \quad (8)$$

the equation system can be cast dimensionlessly as

$$\text{GE: } \frac{\partial C}{\partial T} + \frac{1}{R^2} \frac{\partial C}{\partial R} = \frac{2}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial R^2} \quad (9)$$

$$\text{IC: } C(0, R) = 0 \quad (10)$$

$$\text{BCi: } C(T, (3T)^{1/3}) = -1 \quad \text{BCii: } C(T, \infty) = 0. \quad (11)$$

Here we see why the Ilkovich problem is particularly interesting: it yields a model of the system response with no free parameters. Hence it should be possible to establish a universal solution applicable to many different experimental situations.

Analytical approaches to solving Eqs. (9)–(11) are impeded by the fact that BCi sits on a moving boundary, a difficulty resolved by changing coordinates. The moving boundary can be made stationary by

introducing a new position descriptor that puts the radial coordinate in units of the droplet radius. Also, since the concentration distribution close to the droplet is of primary interest, it is prudent to translate this position such that BCi moves to the origin. To establish new coordinates take

$$t(T, R) = T \quad \text{and} \quad r(T, R) = \frac{R}{(3T)^{1/3}} - 1. \quad (12)$$

The Jacobian of this coordinate transformation is

$$\begin{aligned} \frac{\partial t}{\partial T} &= 1 & \frac{\partial t}{\partial R} &= 0, \\ \frac{\partial r}{\partial T} &= -\frac{R}{(3T)^{4/3}} = -\frac{r+1}{3t} & \frac{\partial r}{\partial R} &= \frac{1}{(3T)^{1/3}} = \frac{1}{(3t)^{1/3}}. \end{aligned} \quad (13)$$

Thus, according to the chain rule, the derivatives of C in the original laboratory frame $\{T, R\}$ and the new coordinates $\{t, r\}$, in which the inner boundary is fixed to the droplet surface and the radial coordinate is normalized by the droplet radius, relate:

$$\begin{aligned} \frac{\partial C}{\partial T} &= \frac{\partial C}{\partial t} \frac{\partial t}{\partial T} + \frac{\partial C}{\partial r} \frac{\partial r}{\partial T} = \frac{\partial C}{\partial t} - \frac{(r+1)}{3t} \frac{\partial C}{\partial r}, \\ \frac{\partial C}{\partial R} &= \frac{\partial C}{\partial t} \frac{\partial t}{\partial R} + \frac{\partial C}{\partial r} \frac{\partial r}{\partial R} = \frac{1}{(3t)^{1/3}} \frac{\partial C}{\partial r}, \quad \text{and} \\ \frac{\partial^2 C}{\partial R^2} &= \left[\frac{\partial}{\partial t} \left(\frac{\partial C}{\partial R} \right) \right] \frac{\partial t}{\partial R} + \left[\frac{\partial}{\partial r} \left(\frac{\partial C}{\partial R} \right) \right] \frac{\partial r}{\partial R} = \frac{1}{(3t)^{2/3}} \frac{\partial^2 C}{\partial r^2}. \end{aligned} \quad (14)$$

Incorporation of relations 12 and 14 transforms the Ilkovich problem to

$$\text{GE} : \frac{\partial C}{\partial t} + \frac{1}{3t} \left[\frac{1}{(1+r)^2} - 1 - r \right] \frac{\partial C}{\partial r} = \frac{1}{(3t)^{2/3}} \left(\frac{2}{1+r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \right) \quad (15)$$

$$\text{IC} : C(0, r) = 0 \quad (16)$$

$$\text{BCi} : C(t, 0) = -1 \quad \text{BCii} : C(t, \infty) = 0. \quad (17)$$

The new independent variables simplify BCi and BCii at the expense of complicating GE. Nevertheless, the formulation is a useful starting point for asymptotics.

3. Asymptotic analysis and regular perturbation

Since the Ilkovich problem is phrased over a semi-infinite spatial domain, one might expect the system of Eqs. (15)–(17) to be amenable to a similarity transformation. Because it affords three dimensionless degrees of freedom, however, this system is not a self-similar problem of the first kind. The key difficulty is that the convective part of the response (described by the left side of Eq. 15) scales differently with time than the diffusional part (the right side of Eq. 15). One typically expects diffusion boundary layers to grow with the square root of time, but the simultaneous growth of the droplet radius confounds this intuition.

Some practical considerations help to guide the next steps. In a typical experimental apparatus for falling-drop experiments, mercury droplets grow to a maximum diameter of approximately 0.1 cm. A reasonable estimate of the drop time—the time taken for the droplet to grow to its maximum size before falling off the capillary tube that supplies it—is $t_d = 10$ s. The fastest diffusivities that solutes exhibit in water are around $5 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Taking all of this into account, the typical time scale that concerns us is a dimensionless drop time, t_d , of order

$$t_d = \frac{16\pi^2 D^3 t_d}{Q^2} \approx 10^{-1}. \quad (18)$$

Thus analysis of system (15)–(17) can be limited to small times. We assume that $t \ll 1$ moving forward.

One also expects that the concentration distribution varies transiently within a diffusion boundary layer, whose penetration depth should grow with time. Therefore renormalize coordinates again, to amplify the scale of radial positions near the boundary at small times:

$$T(t, r) = t \quad \text{and} \quad \eta(t, r) = \frac{r}{t^\alpha}. \quad (19)$$

For this transformation, the Jacobian is

$$\begin{aligned} \frac{\partial T}{\partial t} &= 1 & \frac{\partial T}{\partial r} &= 0, \\ \frac{\partial \eta}{\partial t} &= -\frac{\alpha t}{t^{\alpha+1}} = -\frac{\alpha \eta}{T} & \frac{\partial \eta}{\partial r} &= \frac{1}{t^\alpha} = \frac{1}{T^\alpha}. \end{aligned} \quad (20)$$

In terms of time T and the similarity variable η , the concentration derivatives with t and r become

$$\begin{aligned} \frac{\partial C}{\partial t} &= \frac{\partial C}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial t} = \frac{\partial C}{\partial T} - \frac{\alpha \eta}{T} \frac{\partial C}{\partial \eta}, \\ \frac{\partial C}{\partial r} &= \frac{\partial C}{\partial T} \frac{\partial T}{\partial r} + \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial r} = \frac{1}{T^\alpha} \frac{\partial C}{\partial \eta}, \quad \text{and} \end{aligned} \quad (21)$$

$$\frac{\partial^2 C}{\partial r^2} = \left[\frac{\partial}{\partial T} \left(\frac{\partial C}{\partial r} \right) \right] \frac{\partial T}{\partial r} + \left[\frac{\partial}{\partial \eta} \left(\frac{\partial C}{\partial r} \right) \right] \frac{\partial \eta}{\partial r} = \frac{1}{T^{2\alpha}} \frac{\partial^2 C}{\partial \eta^2}$$

via the chain rule. With the relationships from Eqs. 19 and 21, the governing system transforms to

$$\begin{aligned} \text{GE} : \frac{\partial C}{\partial T} + \frac{1}{3T^{\alpha+1}} \left[\frac{1}{(1+\eta T^\alpha)^2} - 1 - (3\alpha+1)\eta T^\alpha \right] \frac{\partial C}{\partial \eta} \\ = \frac{1}{3^{2/3} T^{2/3+2\alpha}} \left(\frac{\partial^2 C}{\partial \eta^2} + \frac{2T^\alpha}{1+\eta T^\alpha} \frac{\partial C}{\partial \eta} \right) \end{aligned} \quad (22)$$

$$\text{IC} : \lim_{\eta \rightarrow \infty} C(0, \eta) = 0 \quad (23)$$

$$\text{BCi} : C(T, 0) = -1 \quad \text{BCii} : C(T, \infty) = 0. \quad (24)$$

As mentioned before, one does not expect $\alpha = 1/2$ because of the radial convection. Instead, some other positive power of time will balance the scale of the convective term on the left of GE 22 with that of the diffusional term on the right.

To perform the balancing of GE 22, exploit the conclusion illustrated by Eq. 18, that the dimensionless time is small. Since $T(t, r) = t$, it follows that $T \ll 1$ if t is. Consequently, one can replace the following functions of ηT^α with their Maclaurin expansions:

$$\frac{1}{1+\eta T^\alpha} = \sum_{k=0}^{\infty} (-1)^k (\eta T^\alpha)^k \quad \text{and} \quad \frac{1}{(1+\eta T^\alpha)^2} = \sum_{k=0}^{\infty} (k+1) (-1)^k (\eta T^\alpha)^k. \quad (25)$$

Thus GE 22 can be rewritten for small T when $\eta = O(1)$ as

$$\begin{aligned} \text{GE} : \frac{\partial C}{\partial T} - \frac{\eta}{T} \left[1 + \alpha - \eta T^\alpha \sum_{k=0}^{\infty} \left(1 + \frac{1}{3}k \right) (-1)^k (\eta T^\alpha)^k \right] \frac{\partial C}{\partial \eta} \\ = \frac{1}{3^{2/3} T^{2/3+2\alpha}} \left[\frac{\partial^2 C}{\partial \eta^2} + 2T^\alpha \frac{\partial C}{\partial \eta} \sum_{k=1}^{\infty} (-1)^k (\eta T^\alpha)^k \right]. \end{aligned} \quad (26)$$

In the limit of small T , the sums in Eq. 26 are negligible compared to the other terms in the square brackets containing them. To ensure that diffusion and convection within the boundary layer are of equal importance in the small- T limit, choose α to balance the exponent of T in the steady convective terms on the left with the exponent on the leading diffusional term on the right. That is, take

$$1 = \frac{2}{3} + 2\alpha \Rightarrow \alpha = \frac{1}{6}. \quad (27)$$

After choosing $\alpha = 1/6$, the Ilkovich problem becomes

$$\text{GE} : \frac{1}{3^{2/3}} \frac{\partial^2 C}{\partial \eta^2} + \frac{7}{6} \eta \frac{\partial C}{\partial \eta} = T \frac{\partial C}{\partial T} + T^{1/6} \frac{\partial C}{\partial \eta} \sum_{k=0}^{\infty} \left[\left(1 + \frac{k}{3} \right) \eta^2 - \frac{2}{3^{2/3}} \right] (-\eta)^k T^{k/6} \quad (28)$$

$$\text{IC} : \lim_{\eta \rightarrow \infty} C(0, \eta) = 0 \quad (29)$$

$$\text{BCi} : C(T, 0) = -1 \quad \text{BCii} : C(T, \infty) = 0. \quad (30)$$

The left side of GE 28 relates to the standard Cartesian diffusion-layer penetration problem, whose solution can be used to derive Ilkovich's original equation.

To simplify notation and introduce a new time scaling that will help in subsequent analysis, it is convenient to rescale the position variable such that the left side of Eq. 28 becomes the error-function differential equation, as well as introducing a new time variable proportional to $T^{1/6}$ that makes the right side of GE 28 depend on integer powers of time. The choices

$$\tau(T, \eta) = \frac{2}{\sqrt{7}}(3T)^{1/6} \quad \text{and} \quad \xi(T, \eta) = \frac{\eta\sqrt{7}}{2 \cdot 3^{1/6}} \quad (31)$$

simplify the governing system to

$$\text{GE} : \frac{\partial^2 C}{\partial \xi^2} + 2\xi \frac{\partial C}{\partial \xi} = \frac{2\tau}{7} \frac{\partial C}{\partial \tau} + 2\tau \frac{\partial C}{\partial \xi} \sum_{k=0}^{\infty} (-1)^k \left[\frac{6}{7} \left(1 + \frac{k}{3} \right) \xi^2 - 1 \right] \xi^k \tau^k \quad (32)$$

$$\text{IC} : \lim_{\xi \rightarrow \infty} C(0, \xi) = 0 \quad (33)$$

$$\text{BCi} : C(\tau, 0) = -1 \quad \text{BCii} : C(\tau, \infty) = 0. \quad (34)$$

This restatement clarifies that all the terms on the right are of order τ or higher. By neglecting these terms, one obtains the problem Ilkovich originally solved.

Observe that the transformed independent variables τ and ξ relate to the original, dimensional quantities r and t through

$$\tau(r, t) = \frac{2}{\sqrt{7}} \left(\frac{48\pi^2 D^3 t}{Q^2} \right)^{1/6} \quad \text{and} \quad \xi(r, t) = [r - r_0(t)] \sqrt{\frac{7}{12Dt}}, \quad (35)$$

where $r_0(t)$ is defined in Eq. 3. These differ slightly from transformations used in the past, although they relate in a straightforward way. For example, Newman used a time variable that can be identified as $(\tau/2)^{14}$, and a similarity variable equal to $2\xi(\tau/2)^7$ [7].

Corrections to the Ilkovich equation can be obtained by perturbation expansion of the system of Eqs. (32)–(34) with respect to time. To implement this assume that concentration has the form

$$C(\tau, \xi) = C_0(\xi) + \tau C_1(\xi) + \tau^2 C_2(\xi) + \dots \quad (36)$$

and equate terms with similar powers of τ to formulate a sequence of systems that govern approximations to C of increasing order. Observe that at every order, IC and BCii from Eqs. 33 and 34 collapse to a single condition at $\xi \rightarrow \infty$. At noughth order, one finds that

$$\text{GE}_0 : \frac{d^2 C_0}{d\xi^2} + 2\xi \frac{dC_0}{d\xi} = 0 \quad (37)$$

$$\text{BCi}_0 : C_0(0) = -1 \quad \text{BCii}_0 : C_0(\infty) = 0; \quad (38)$$

at integer orders $n \geq 1$ one finds

$$\text{GE}_n : \frac{d^2 C_n}{d\xi^2} + 2\xi \frac{dC_n}{d\xi} - \frac{2n}{7} C_n = 2 \sum_{k=1}^n (-1)^k \left[1 - \frac{2}{7} (2+k) \xi^2 \right] \xi^{k-1} \frac{dC_{n-k}}{d\xi} \quad (39)$$

$$\text{BCi}_n : C_n(0) = 0 \quad \text{BCii}_n : C_n(\infty) = 0. \quad (40)$$

Every positive order of the problem presents an inhomogeneous, linear second-order ordinary differential equation involving the operator that appears in the error-function differential equation (albeit of negative fractional degree). This sequence provides the systematic route by which higher-order corrections to the Ilkovich equation can be calculated.

4. Solution

The noughth-order problem (Eqs. 37 and 38) is solved by

$$C_0(\xi) = -\text{erfc}(\xi), \quad (41)$$

which is plotted in Fig. 1. Bear in mind that

$$\frac{dC_0}{d\xi} = \frac{2e^{-\xi^2}}{\sqrt{\pi}}, \quad (42)$$

a result needed to write the first-order problem. At first order

$$\text{GE}_1 : \frac{d^2 C_1}{d\xi^2} + 2\xi \frac{dC_1}{d\xi} - \frac{2}{7} C_1 = \frac{4}{\sqrt{\pi}} \left(\frac{6\xi^2}{7} - 1 \right) e^{-\xi^2} \quad (43)$$

$$\text{BCi}_1 : C_1(0) = 0 \quad \text{BCii}_1 : C_1(\infty) = 0. \quad (44)$$

Simplify by letting

$$C_1(\xi) = e^{-\xi^2} f_1(\xi), \quad (45)$$

in which case GE_1 from Eq. 43 becomes

$$\text{GE}'_1 : \frac{d^2 f_1}{d\xi^2} - 2\xi \frac{df_1}{d\xi} - \frac{16}{7} f_1 = \frac{4}{\sqrt{\pi}} \left(\frac{6\xi^2}{7} - 1 \right). \quad (46)$$

The solution to this can be broken up as $f_1 = f_1^h + f_1^p$. To identify a particular solution, guess that it takes the form of a second-order polynomial,

$$f_1^p(\xi) = Z' + Y'\xi + X'\xi^2, \quad (47)$$

in which X' , Y' , and Z' are unknown constants. Substituting Eq. 47 into Eq. 46 and balancing its coefficients with those of the inhomogeneous polynomial in Eq. 46 yields

$$\frac{2}{7} \left(7X' - 8Z' + \frac{14}{\sqrt{\pi}} \right) - \frac{30Y'}{7} \xi + \frac{2}{7} \left(-22X' - \frac{12}{\sqrt{\pi}} \right) \xi^2 = 0. \quad (48)$$

Linear independence of the terms in this expression requires that the coefficients of each power of ξ vanish. The values of X' , Y' , and Z' that satisfy this criterion show that

$$f_1^p(\xi) = \frac{14}{11\sqrt{\pi}} - \frac{6\xi^2}{11\sqrt{\pi}} \quad (49)$$

is a particular solution of GE'_1 . One can recognize the remaining homogeneous problem satisfied by $f_1^h(\xi)$,

$$\text{GE}''_1 : \frac{d^2 f_1^h}{d\xi^2} - 2\xi \frac{df_1^h}{d\xi} - \frac{16}{7} f_1^h = 0, \quad (50)$$

as the (physicist's) Hermite differential equation of order $-8/7$. A closed-form solution in terms of two linearly independent functions is given by [9]

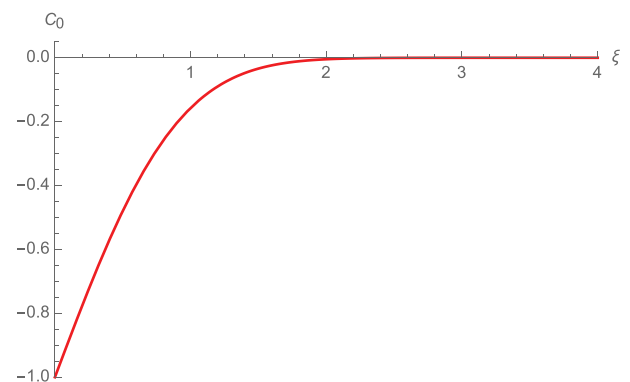


Fig. 1. Solution for the concentration distribution C_0 from Eq. 41, which satisfies the zero-order Ilkovich model, Eqs. 37 and 38.

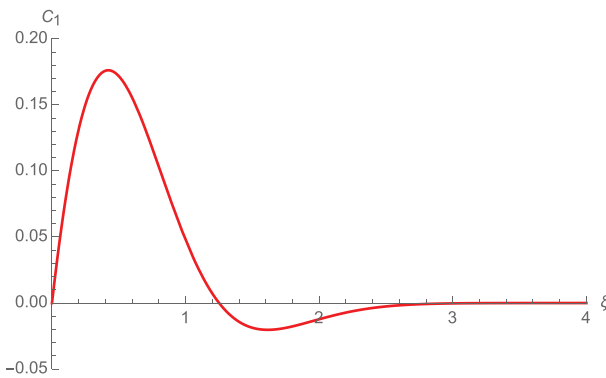


Fig. 2. Solution for the concentration distribution C_1 from Eq. 55, which satisfies the first-order correction of the Ilkovich model, Eqs. 43 and 44. Note the difference in vertical scale from Fig. 1.

$$f_1^h(\xi) = W'M\left(\frac{4}{7}, \frac{1}{2}, \xi^2\right) + V'H_{-8/7}(\xi). \quad (51)$$

Here $M(a, b, \xi)$ is Kummer's confluent hypergeometric function of the first kind and $H_\lambda(\xi)$ is the Hermite polynomial of order λ .² Because $M(a, b, \xi)$ diverges faster than $\exp(\xi^2)$ as ξ approaches infinity, condition BCii₁ requires that $W' = 0$. Condition BCi₁ then requires that $f_1^h(0) = -f_1^p(0)$, leaving

$$V'H_{-8/7}(0) = -\frac{14}{11\sqrt{\pi}}, \quad (52)$$

so that

$$V' = -\frac{28 \cdot 2^{1/7} \Gamma(\frac{15}{14})}{11\pi}. \quad (53)$$

Thus the choice of particular solution demands that the homogeneous solution takes the form

$$f_1^h(\xi) = -\frac{28 \cdot 2^{1/7} \Gamma(\frac{15}{14})}{11\pi} H_{-8/7}(\xi). \quad (54)$$

Adding the functions f_1^h and f_1^p from Eqs. 54 and 49 together to form f_1 in Eq. 45, the first-order correction of the solute concentration is found to be

$$C_1(\xi) = \frac{2e^{-\xi^2}}{11\sqrt{\pi}} \left[7 - 3\xi^2 - \frac{7 \cdot 2^{8/7} \Gamma(\frac{15}{14})}{\sqrt{\pi}} H_{-8/7}(\xi) \right], \quad (55)$$

which is depicted in Fig. 2. The first derivative of this function at the boundary is

$$\frac{dC_1}{d\xi} \Big|_{\xi=0} = \frac{16\Gamma(\frac{15}{14})}{11\Gamma(\frac{11}{7})\sqrt{\pi}} = 0.88780399\dots, \quad (56)$$

a form very similar to Newman's Eq. 25 [7].

Solving the second-order problem is more of a grind, but an essentially similar approach can be taken. Eq. 39 shows that

$$\begin{aligned} \text{GE}_2 : \quad & \frac{d^2 C_2}{d\xi^2} + 2\xi \frac{dC_2}{d\xi} - \frac{4}{7} C_2 \\ & = 2 \left(1 - \frac{8}{7} \xi^2 \right) \xi \frac{dC_0}{d\xi} - 2 \left(1 - \frac{6}{7} \xi^2 \right) \frac{dC_1}{d\xi}. \end{aligned} \quad (57)$$

Apply the transformation in Eq. 45 to C_2 and C_1 , then insert Eq. 42 to show that

$$\begin{aligned} \text{GE}_2' : \quad & \frac{d^2 f_2}{d\xi^2} - 2\xi \frac{df_2}{d\xi} - \frac{18}{7} f_2 \\ & = -\frac{4}{\sqrt{\pi}} \left(1 - \frac{8}{7} \xi^2 \right) \xi - 2 \left(1 - \frac{6}{7} \xi^2 \right) \left(\frac{df_1}{d\xi} - 2\xi f_1 \right). \end{aligned} \quad (58)$$

Eqs. 49 and 54 combine to establish the function $f_1(\xi)$ that appears here:

$$f_1(\xi) = \frac{14}{11\sqrt{\pi}} - \frac{6\xi^2}{11\sqrt{\pi}} - \frac{28 \cdot 2^{1/7} \Gamma(\frac{15}{14})}{11\pi} H_{-8/7}(\xi). \quad (59)$$

After substitution of $f_1(\xi)$, the right side of Eq. 58 is observed to comprise two parts, one of which is a simple polynomial of ξ ; because $dH_\lambda/d\xi = 2\lambda H_{\lambda-1}(\xi)$, the other part is a linear combination of $H_{-8/7}(\xi)$ and $H_{-15/7}(\xi)$, with coefficients that are polynomials of ξ . Exploiting the linearity of GE_2' , the particular solution can be broken into two parts,

$$f_2^p(\xi) = f_2^{p1}(\xi) + f_2^{p2}(\xi), \quad (60)$$

where f_2^{p1} accounts for the simple-polynomial dependence and f_2^{p2} accounts for the Hermite-polynomial dependence. Guessing an arbitrary fifth-order polynomial shows that the simple polynomial part of the inhomogeneous term in Eq. 58 is balanced by a particular solution

$$f_2^{p1}(\xi) = -\frac{1}{121\sqrt{\pi}} \left(18\xi^5 - \frac{424}{3}\xi^3 + \frac{903}{8}\xi \right). \quad (61)$$

The inhomogeneous terms dependent on Hermite polynomials can also be balanced by the method of trial functions, although the procedure is more convoluted. Guess the form

$$\begin{aligned} f_2^{p2}(\xi) = & (A'\xi^3 + B'\xi^2 + C'\xi + D')f_1^h(\xi) \\ & + (E'\xi^3 + F'\xi^2 + G'\xi + H') \frac{df_1^h}{d\xi}, \end{aligned} \quad (62)$$

where $f_1^h(\xi)$ is given by Eq. 54 and A', B', \dots, H' are arbitrary parameters. Observe that since f_1^h satisfies the homogeneous version of GE_1' from Eq. 46 (that is, Hermite's equation of order $-8/7$) by definition, higher derivatives can be eliminated in favor of first and second derivatives:

$$\frac{d^2 f_1^h}{d\xi^2} = 2\xi \frac{df_1^h}{d\xi} + \frac{16}{7} f_1^h \quad \text{and} \quad \frac{d^3 f_1^h}{d\xi^3} = \left(4\xi^2 + \frac{30}{7} \right) \frac{df_1^h}{d\xi} + \frac{32}{7} \xi f_1^h. \quad (63)$$

Thus, upon substitution of Eq. 62 into the form of Eq. 58 obtained after discarding the polynomial part of the inhomogeneous term, and after using Eqs. 63 to limit the Hermite polynomials involved to $H_{-8/7}(\xi)$ and $H_{-15/7}(\xi)$, one obtains an equation that can be balanced by choosing appropriate values of the constants A', B', \dots, H' . This balancing yields

$$f_2^{p2}(\xi) = \frac{\xi}{11} \left(6\xi^2 - \frac{31}{2} \right) f_1^h(\xi) - \frac{1}{11} \left(3\xi^2 - \frac{35}{4} \right) \frac{df_1^h}{d\xi}. \quad (64)$$

With both parts of the particular solution identified, the homogeneous problem can be solved. Boundary condition BCii₂ is satisfied by a solution of the form

$$f_2^h(\xi) = K'H_{-9/7}(\xi), \quad (65)$$

in which the constant K' is chosen to satisfy BCi₂: $f_2^h(0) + f_2^{p1}(0) + f_2^{p2}(0) = 0$. Ultimately, after returning to the original variable $C_2(\xi)$, one finds that

$$\begin{aligned} C_2(\xi) = & \frac{8e^{-\xi^2}}{121\sqrt{\pi}} \left[-\frac{35 \cdot 2^{2/7} \Gamma(\frac{15}{14}) \Gamma(\frac{9}{7})}{\sqrt{\pi} \Gamma(\frac{11}{7})} H_{-9/7}(\xi) - \frac{9}{4} \xi^5 + \frac{53}{3} \xi^3 - \frac{903}{64} \xi \right. \\ & + \frac{7 \cdot 2^{1/7} \Gamma(\frac{15}{14})}{\sqrt{\pi}} \left(\frac{31}{4} - 3\xi^2 \right) \xi H_{-8/7}(\xi) \\ & \left. + \frac{2^{8/7} \Gamma(\frac{15}{14})}{\sqrt{\pi}} (35 - 12\xi^2) H_{-15/7}(\xi) \right]. \end{aligned} \quad (66)$$

² Hermite polynomials are continued over orders that are not whole numbers through the definition $H_\lambda(z) = 2^\lambda \sqrt{\pi} \left[\frac{M(-\frac{1}{2}, \frac{1}{2}, z^2)}{\Gamma(\frac{1}{2})} - \frac{2zM(\frac{1}{2}, \frac{3}{2}, z^2)}{\Gamma(-\frac{1}{2})} \right]$. Generally $\lim_{z \rightarrow \infty} \exp(-z^2) H_\lambda(z) = 0$, $dH_\lambda(z)/dz = 2\lambda H_{\lambda-1}(z)$, and $H_\lambda(0) = 2^\lambda \sqrt{\pi} / \Gamma(\frac{1}{2} - \frac{1}{2}\lambda)$.

Fig. 3 provides a plot of this function. Finally, the derivative of the second-order correction is

$$\left. \frac{dC_2}{d\xi} \right|_0 = \frac{3}{121\sqrt{\pi}} \left(\frac{60\Gamma(\frac{15}{14})\Gamma(\frac{8}{7})}{\Gamma(\frac{11}{7})\Gamma(\frac{23}{14})} - \frac{469}{8} \right) = 0.12466801 \dots \quad (67)$$

at the inner boundary.

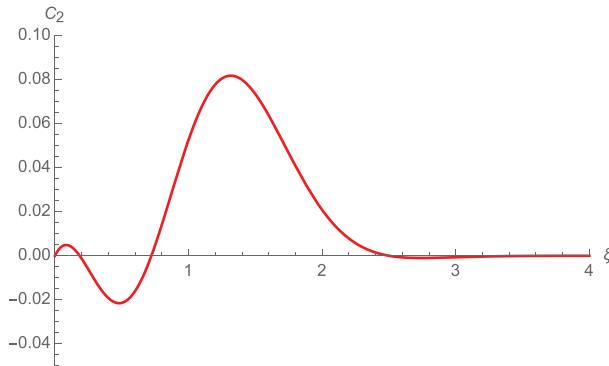


Fig. 3. Solution for the concentration distribution C_2 from Eq. 66, which satisfies the second-order correction of the Ilkovich model, Eq. 57, with homogeneous boundary conditions at $\xi = 0$ and $\xi \rightarrow \infty$. The vertical scale again differs from Figs. 1 and 2.

5. Derivation of the Ilkovich equation

Recall that the Ilkovich problem originally asked for the total diffusion-limited molar flowrate to the droplet surface during the drop time. The instantaneous molar flowrate $N(t)$ can be derived from the concentration distribution through Fick's law,

$$N(t) = 4\pi r_0^2 D \left. \frac{\partial c}{\partial r} \right|_{r=r_0}, \quad (68)$$

where a positive concentration gradient is used to make the equation describe flux out of the fluid phase, and a convection term has been excluded because the solute concentration vanishes at the boundary of the droplet. Bringing in C from Eq. 8 and $r_0(t)$ from Eq. 3, and then using Eq. 35 to replace t and r with the dimensionless variables τ and ξ , puts Eq. 68 in the form

$$N(\tau) = \frac{7c_\infty Q \tau}{4} \left. \frac{\partial C}{\partial \xi} \right|_{\xi=0}. \quad (69)$$

Insertion of the perturbation expansion from Eq. 36, along with the expressions of the derivatives at various orders from Eqs. 42, 56, and 67, shows that the instantaneous flux is given up to the third power of $t^{1/6}$ by Eq. 1, with the constants K_0, K_1 , and K_2 given by Eq. 2.

In closing, this solution can be connected to prior results. Ilkovich originally reported an equation for flux that was averaged over the drop time t_d , i.e.

$$\frac{1}{t_d} \int_0^{t_d} N(t) dt = \frac{6K_0}{7} c_\infty Q^{2/3} D^{1/2} t_d^{1/6} \times \left[1 + \frac{7K_1}{8} \left(\frac{D^3 t_d}{Q^2} \right)^{1/6} + \frac{7K_2}{9} \left(\frac{D^3 t_d}{Q^2} \right)^{1/3} + \dots \right]. \quad (70)$$

With the constants from Eq. 2, one can compute

$$\frac{6K_0}{7} = 3.57232359 \dots \text{ and } \frac{7K_1}{8} = 1.45302993 \dots; \quad (71)$$

the expression with K_0 is the constant originally stated by Ilkovich, and that with K_1 is the first-order correction reported by Newman [7]. The third constant,

$$\frac{7K_2}{9} = 0.38279341 \dots \quad (72)$$

is computed for the first time here. Higher-order terms could be obtained by following the general procedure laid out in Section 4.

6. Connection to the Newman–Levich expansion

Newman and Levich performed more intuitively based analyses of the Ilkovich problem. Although the procedure is more artistic, their method can be shown to produce zeroth, first, and second order corrections consistent with the functions C_0, C_1 , and C_2 identified above. Note that Newman introduces a parameter γ , defined as

$$\gamma = \left(\frac{3Q}{4\pi} \right)^{1/3}, \text{ or } Q = \frac{4}{3} \pi \gamma^3, \quad (73)$$

in place of the flowrate Q . The Newman–Levich form of the Ilkovich problem uses independent variables

$$\tau' = \left(\frac{\tau}{2} \right)^{14} = \left(\frac{3D}{7\gamma^2} \right)^7 t^{7/3} \text{ and } z = 2\xi \left(\frac{\tau}{2} \right)^7 = \frac{r - \gamma t^{1/3}}{\gamma} \left(\frac{3D}{7\gamma^2} \right)^3 t^{2/3}, \quad (74)$$

which were presumably identified by the method of undetermined scales. After introducing C in place of c and substituting τ' and z for t and r , governing Eq. 5 takes the form

$$\frac{\partial C}{\partial \tau'} - \frac{\partial^2 C}{\partial z^2} = \left\{ \frac{1}{7\tau'^{4/7}} \left[1 - \frac{1}{\left(1 + \frac{z}{\tau'^{3/7}} \right)^2} - \frac{2z}{\tau'^{3/7}} \right] + \frac{\frac{z}{\tau'^{3/7}}}{1 + \frac{z}{\tau'^{3/7}}} \right\} \frac{\partial C}{\partial z}, \quad (75)$$

matching Eq. 8 of Newman's paper [7]. Terms on the left describe accumulation and diffusion; terms on the right account for convection and the derivative of the scale factor in the radial part of the spherical Laplacian.

The Newman–Levich asymptotics explores a time regime in which the accumulation and diffusion terms of the governing equation are of similar order, and the convection and geometric terms are of higher order. Assuming that C is of order unity, then $\partial C / \partial \tau' = O(\tau'^{-1})$. Since diffusion is expected to be of comparable importance as accumulation, $\partial^2 C / \partial z^2 = O(\tau'^{-1})$ too; because $C = O(1)$ this requires that $z = O(\tau'^{1/2})$. Indeed, Newman comments that “ z is of order $\sqrt{\tau'}$ in the boundary layer” [7], although he says it after solving the zero-order problem—presumably because his zero-order result makes this scaling of z clearer. Furthermore, since $z = O(\tau'^{1/2})$, it follows that

$$\frac{z}{\tau'^{3/7}} = \tau'^{1/14} \cdot \frac{z}{\tau'} = \tau'^{1/14} \cdot O(1) = O(\tau'^{1/14}), \quad (76)$$

a relationship that helps to identify the orders of all the terms involving z on the right of Eq. 75. Using the forms $\tau'(\tau, \xi)$ and $z(\tau, \xi)$ from Eq. 74 to replace z with ξ and τ' , and subsequently performing a Maclaurin expansion in τ' under the assumption that $\xi = O(1)$, one finds that

$$\left\{ \frac{1}{7\tau'^{4/7}} \left[1 - \frac{1}{\left(1 + \frac{z}{\tau'^{3/7}} \right)^2} - \frac{2z}{\tau'^{3/7}} \right] + \frac{\frac{z}{\tau'^{3/7}}}{1 + \frac{z}{\tau'^{3/7}}} \right\} = \frac{2}{\tau'^{3/7}} \sum_{k=0}^{\infty} (-1)^k \left[1 - \frac{(3+k)z^2}{14\tau'} \right] \left(\frac{z}{\tau'^{3/7}} \right)^k \quad (77)$$

after some algebraic simplification. Remembering that the k th term of the sum on the right is $O(\tau'^{k/14})$, one can insert this sum into Eq. 75 to show that

$$\frac{\partial C}{\partial \tau'} - \frac{\partial^2 C}{\partial z^2} = \tau'^{-13/14} \left[\left(2 - \frac{3z^2}{z\tau'} \right) - \left(4 - \frac{8z^2}{7\tau'} \right) \frac{z}{2\sqrt{\tau'}} \tau'^{1/14} + O(\tau'^{2/14}) \right] \tau'^{1/2} \frac{\partial C}{\partial z}. \quad (78)$$

This explains Newman's statement that the terms neglected by Ilkovich, i.e., the right side of Eq. 78, "are of order $\tau'^{-13/14}$ and higher" [7], because the square-bracketed term and $\tau'^{1/2} \partial C / \partial z$ are both $O(1)$. From a formal perspective, it may be clearer to consider the form of this equation obtained after multiplying it through by τ' , which yields a result in which the terms on the left of the equals sign are $O(1)$, whereas those on the right are $O(\tau'^{1/14})$.

Following Levich, one can identify a zero-order solution C_0 as the solution of Eq. 78 obtained when its right side is set equal to zero. This problem can be solved by standard methods (Laplace transformation, similarity transformation, etc.), to show that

$$C_0(\tau', z) = -\operatorname{erfc}\left(\frac{z}{2\sqrt{\tau'}}\right) = -1 + \frac{2}{\sqrt{\pi}} \int_0^{\frac{z}{2\sqrt{\tau'}}} e^{-x^2} dx, \quad (79)$$

which matches Eq. 41 above, as well as Newman's Eq. 11 [7].

To get Newman's correction of the Levich–Ilkovich solution, one can perturb C around C_0 to first order (i.e., up to order $\tau'^{1/14}$) and require that the perturbation solve the governing equation obtained by keeping only the first term in square brackets on the right of Eq. 78. One can implement this by supposing that

$$C = C_0 + \theta_1 + O(\tau'^{2/14}). \quad (80)$$

Here $C_0 = O(1)$, and we assume that $\theta_1(\tau', z) = O(\tau'^{1/14})$. Noting that $\partial \theta_1 / \partial z = O(\tau'^{-3/7})$, and inserting the result for C_0 , one finds that θ_1 satisfies

$$\frac{\partial \theta_1}{\partial \tau'} - \frac{\partial^2 \theta_1}{\partial z^2} = \frac{1}{\sqrt{\pi}} \left(\frac{2}{\tau'^{13/14}} - \frac{3z^2}{7\tau'^{27/14}} \right) \exp\left(-\frac{z^2}{4\tau'}\right), \quad (81)$$

which is Newman's Eq. 13 [7]. After letting

$$\theta_1 = 2\tau'^{1/14} C_1\left(\frac{z}{2\sqrt{\tau'}}\right), \quad (82)$$

and after replacing τ' and z with the variables ξ and τ via Eq. 74, one discovers Eq. 43. Thus θ_1 relates directly to the function C_1 reported earlier, in Eq. 55.

The Newman–Levich expansion can be continued to second order by keeping a second term on the right of Eq. 78 and incorporating the results for C_0 and θ_1 . Through a similar process this yields the function C_2 given in Eq. 66. Thus the Newman–Levich method produces results that match those developed in Section 4 above, although it follows a more circuitous route.

7. Numerical approach

A key advantage of the perturbation method developed in Section 3 over the Newman–Levich method is that it produces a sequence of systems of linear ordinary differential equations, which readily carries up to arbitrarily high orders. Although the analytical techniques from Section 4 are easily extended in principle, the process of solving these systems of equations becomes increasingly arduous as the order of the perturbation increases. It will be worthwhile to check the solutions of the regularly perturbed problem against numerical results, to see when higher-order corrections beyond those of Ilkovich and Newman are needed.

Another motivation for a numerical approach is that some assumptions underpinning our analysis do not always hold. In Section 3, the regular perturbation in time hinges on Maclaurin expansions of the coefficients in governing Eq. 22. Such expansions require that $\eta T^{1/6} < 1$ (or $\xi \tau < 1$) so that the two series in Eq. 25 lie within their radii of convergence. Recalling that we are interested in a concentration boundary layer, where η (or ξ) is of order unity, use of these series restricts the analysis to situations where $T < 1$ (or $\tau < 1$). The reader should be aware that dimensionless drop times of order unity can be accessed by perfectly reasonable experimental polarography systems: for example, if $D = 5 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $t_d = 15 \text{ s}$, and the droplet diameter

at t_d is 0.075 cm , Eq. 18 yields a dimensionless drop time of ~ 1.4 . In this regime of τ , one must be wary of using a short-time asymptotic expansion.

Because the Ilkovich problem contains no free parameters, an accurate numerical solution is worth pursuing regardless, because any numerical calculation of how flux depends on time will be universal, and can be applied within any regime of τ . From this philosophical perspective, asymptotic formulas valid at small τ simply serve to verify numerical results. Once short-time data have been verified up to the desired precision, a numerical computation can readily be extended into the regime where the regular perturbation discussed above no longer works. One might attempt a matched asymptotic expansion to get analytical traction on the large-time problem, but it is debatable whether this would yield insight or precision superior to a purely numerical plan of attack.

Numerics is not a panacea, however. The ostensible simplicity of the dimensionless problem posed by Eqs. (9)–(11) belies some serious barriers to the accurate computation of solutions. First, the time-varying radial boundary in BCi makes spatial meshing difficult. Second, the involvement of a growing concentration boundary layer, which is extremely thin at small times, necessitates a relationship between the durations of time steps and the fineness of the spatial mesh. A coordinate transformation that makes BCi stationary yields the system of Eqs. (15)–(17). Unfortunately, this formulation does not alleviate the numerical challenge, but instead moves it to another part of the equation system. The time dependence on the right in Eq. 15 makes GE ill conditioned, and consequently highly error prone, at short times.

The asymptotics and perturbation analysis in Section 3 suggest a route to circumvent the numerical difficulties posed by equation systems (9)–(11) and (15)–(17), however. Instead of solving either of these equation systems, we instead solve a transformed version of the Ilkovich problem that includes information gained from short-time asymptotics, but does not employ the Maclaurin expansion used for the perturbation.

A numerically amenable transformed governing equation is found by letting $\alpha = 1/6$ in Eq. 22, exchanging the independent variables η and T for ξ and τ through the definitions in Eq. 31, and then rearranging terms so that the differential operator from Eq. 37 appears on the left side of the equality. Next, a more stable initial condition is identified by recognizing that the expression of $C_0(\xi)$ from Eq. 41 satisfies the requirements of the IC from Eq. 33, while also satisfying GE, BCi, and BCii at $\tau = 0$. Thus one arrives at the equation system

$$\text{GE: } \frac{\partial^2 C}{\partial \xi^2} + 2\xi \frac{\partial C}{\partial \xi} = \frac{2\tau}{7} \left\{ \frac{\partial C}{\partial \tau} + \frac{[2\xi^2 + (1 + \xi\tau)(4\xi^2 - 7)]}{(1 + \xi\tau)^2} \frac{\partial C}{\partial \xi} \right\} \quad (83)$$

$$\text{IC: } C(0, \xi) = -\operatorname{erfc}(\xi) \quad (84)$$

$$\text{BCi: } C(\tau, 0) = -1 \quad \text{BCii: } C(\tau, \infty) = 0, \quad (85)$$

which can be used to find accurate numerical solutions. The terms on the right of GE are of order τ or higher in the neighborhood of $\tau = 0$, as can be verified by observing that Maclaurin expanding the right side of GE with respect to τ produces Eq. 32.

To solve equation system (83)–(85), a finite-element numerical simulation was performed with Firedrake software [10], using the MUMPS direct linear solver [11,12] via PETSc [13,14]. The spatial discretization consisted of continuous piecewise second-order polynomials on 10,000 equispaced grid points across the interval $\xi \in [0, 5]$ and the time discretization used the implicit midpoint method with 20,000 timesteps in the interval $\tau \in [0, 1]$. Exploiting piecewise polynomial functions in the discretization of the problem allows for a straightforward computation of the derivative $\partial C / \partial \xi$ at $\xi = 0$ at each time step.

The instantaneous flux to the droplet surface depends on concentration derivatives at the droplet surface through Eq. 69. Taking the perturbation analysis up to n th order yields an approximate expression for these derivatives,

$$\left. \frac{\partial C}{\partial \xi} \right|_{\tau,0} \approx \sum_{k=0}^n \frac{dC_k}{d\xi} \Big|_0 \tau^k, \quad (86)$$

with the coefficients at noughtth, first, and second order on the right given respectively by Eqs. 42, 56, and 67. Fig. 4 compares the derivative at the surface computed numerically via Firedrake with the approximations yielded by the analyses of Ilkovich ($n = 0$ in Eq. 86) and Newman ($n = 1$), as well as the results developed in Sections 3 and 4 ($n = 2$). Ilkovich's approximate solution deviates rapidly from the numerical solution; the two only match at $\tau = 0$. Newman's solution broadly captures the time dependence of $(\partial C/\partial \xi)|_{\tau,0}$ at short times, matching the numerical result within 0.1% for $\tau < 0.05$, then deviating increasingly from it. The second-order correction extends this domain of agreement, matching the numerical result within 0.1% for $\tau < 0.15$.

Higher corrections impact values of the concentration derivative differently than they affect Ilkovich's equation, because Ilkovich's equation quantifies the average flux over the drop time, rather than the instantaneous flux. By defining a drop-time averaged flux, $\langle N \rangle_{t_d}$, as

$$\langle N \rangle_{t_d} = \frac{1}{t_d} \int_0^{t_d} N(t) dt = \frac{21Qc_\infty}{2\tau_d^6} \int_0^{\tau_d} \tau^6 \left. \frac{\partial C}{\partial \xi} \right|_{\tau,0} d\tau, \quad (87)$$

the essential content of the Ilkovich equation can be cast dimensionlessly by plotting $\langle N \rangle_{t_d}/Qc_\infty$ versus τ_d . The sixth power to which τ is raised in the integral at right makes the error of asymptotic formulas for the average flux behave somewhat differently than the error in the concentration derivative.

To get a numerical expression of $\langle N \rangle_{t_d}$, the integral on the right of Eq. 87 was calculated by applying an explicit second-order backward difference formula to the integrand, which was calculated at each τ using the numerical results for $(\partial C/\partial \xi)|_{\tau,0}$. Fig. 5 compares the numerically computed time functionality of $\langle N \rangle_{t_d}/(Qc_\infty)$ to the original (zero-order) Ilkovich equation, as well as the first-order correction developed by Newman and the second-order correction from Sections 3 and 4. Both the first- and second-order corrections approximate the true solution of the problem much more accurately than the Ilkovich formula, which deviates rapidly from the numerical solution. Newman's approximation deviates by less than 0.1% from Firedrake up to $\tau = 0.12$. The second-order correction of Ilkovich's equation improves on this, agreeing with the Firedrake result within 0.1% up to dimensionless times of $\tau = 0.27$. Still, the averaging approach makes the impact of higher-order corrections relatively marginal. At $\tau = 1$, Newman's first-order result underpredicts the numerical calculation by 2.5%, whereas the present, second-order, result overpredicts the numerics by 2.4%.

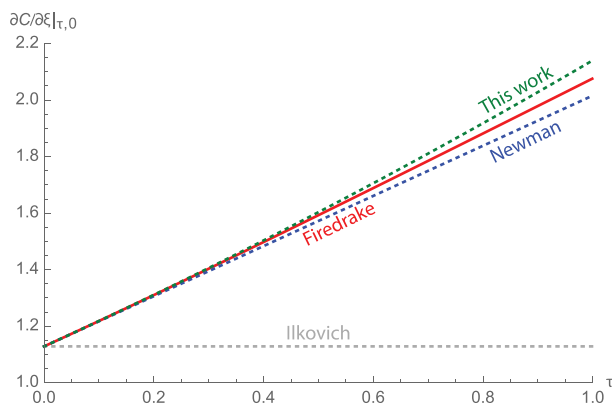


Fig. 4. Dimensionless spatial concentration gradients at the droplet surface, $\partial C/\partial \xi|_{\tau,0}$, computed numerically by solving Eqs. (83)–(85) with the Firedrake finite-element software (solid red) alongside the analytical approximations from Ilkovich (gray dashed), Newman (blue dashed), and this work (green dashed). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

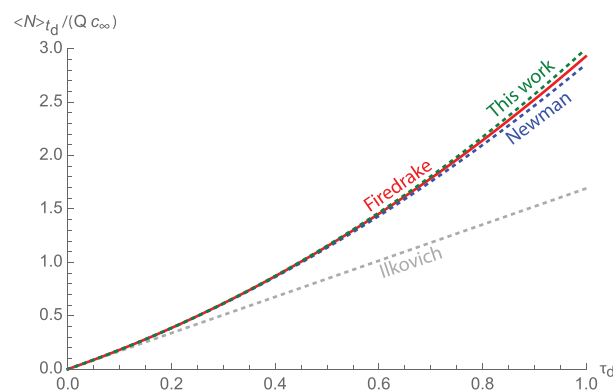


Fig. 5. Dimensionless net flux averaged over the drop time, $\langle N \rangle_{t_d}/(Qc_\infty)$, computed using the Firedrake finite-element software (solid red), compared to the classical Ilkovich result (gray dashed), the first-order correction by Newman (blue dashed), and the second-order correction from this work (green dashed).

8. Conclusion

The classical Ilkovich equation works robustly to describe the polarographic response of relatively slow-diffusing solutes when drop times are short and falling droplets are relatively large. In cases where these conditions are not met — diffusion is fast, drop times are long, or terminal drop sizes are smaller — our analysis showed that higher-order corrections may be needed. We found that Newman's first-order correction and our second-order correction of the Ilkovich equation both track an ostensibly exact numerical solution of the Ilkovich problem within a few percent. The second-order correction we developed in Section 4 matches the numerical solution computed with Firedrake software in Section 7 within 0.1% when the dimensionless drop time τ_d , related to the true drop time t_d through Eq. 35, is less than 0.27 — about twice the range where Newman's approximation is similarly accurate. Whereas the classical Ilkovich equation becomes inaccurate at extremely small dimensionless drop times, Newman's correction and our correction both predict the numerically calculated true solution of the Ilkovich problem within 2–3% across a wide range of dimensionless drop times (up to at least $\tau_d = 1$). The error in both the first-order correction by Newman and our second-order correction is probably comparable to or smaller than the intrinsic error of most polarography experiments. Thus Newman's correction suffices for most applications. Nevertheless, the asymptotic approaches presented here can be usefully applied to develop robust approaches to various physical extensions of the original Ilkovich problem. Possible model extensions include the determination of surface flux in response to potential sweeps rather than potential steps, or accounting for interfacial capacitance and reaction overpotential in the system response.

CRediT authorship contribution statement

S. Jon Chapman: Methodology, Formal analysis. **Charles W. Monroe:** Methodology, Formal analysis, Investigation, Writing – original draft, Supervision. **Shiv Krishna Madi Reddy:** Methodology, Investigation, Writing – review & editing. **Alexander Van-Brunst:** Investigation, Formal analysis, Software. **Ralph E. White:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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