MASS TRANSPORT WITH AN ALTERNATING CONCENTRATION IN THE BOUNDARY LAYER OF THE FLOW OF AN ELECTROLYTIC SOLUTION

V. A. Lopatin, B. M. Grafov,
and V. G. Levich

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The method of rotating disc electrodes with rings [1, 2] is used widely to study the kinetics of electrode processes. The theoretical and experimental data in the literature [3-8] refer to the case in which the measurements are carried out with a direct current. Use of an alternating current expands the capabilities of the method, since an additional adjustable parameter, the ac frequency, becomes available.

We are concerned in this paper with the passage of a sinusoidal alternating current through an electrochemical cell consisting of two isolated electrodes machined flush with a solid surface and placed at successive points in a hydrodynamic flow. An alternating current $Ie^{i\omega t}$ is supplied to the first (working electrode) $(0, x_1)$, causing a periodic evolution of an electrochemically active substance, which is analyzed at the second (indicator) electrode (x_2, x_3) in either the limiting-current or potential regime (x is the tangential coordinate, and the electrode width is assumed equal to unity). In addition, there is a common electrode having a large surface area; ion migration is suppressed by an excess of indifferent electrolyte. The disc electrode with a ring is a particular case of this electrode system.

This type of electrochemical cell can be used to study the Faradaic component of the alternating current in impedance measurements. This capability is particularly important in the case in which the Faradaic current and the charging current affect each other.

Matsuda [9] treated the steady-state problem in this geometry for an arbitrary dependence $\tau(x)$ surface tension on the tangential coordinate. The case in which the concentration c is a periodic function of the time t,

$$c(x,\ y,\ t) = c^0(x,\ y) + \Phi(x,\ y)\, e^{i\omega t}, \tag{1}$$

is a much more difficult problem to analyze, so we will make the following assumptions: 1) The size x_3 of the electrode system is small in comparison with the dimension L characteristic of an important change in the surface tension, so that in the zeroth approximation in x_3L we have $\tau(x) = \tau_0$; 2) the velocity profile is linear ($v_x = \omega_\tau \cdot y$, $v_y = 0$, where $\omega_\tau = \tau_0/\mu$, y is the normal coordinate, and μ is the dynamic viscosity coefficient). 3) The electrode dimensions $(0, x_1)$ and (x_2, x_3) are small in comparison with the length of the insulating zone, so that with $x \gg x_1$ the surface-concentration amplitude does not depend on the current-density distribution at the working electrode.

Using assumptions 1)-3), we can write the boundary-value problem $\Phi(z, u)$ in the following manner:
$\varepsilon_1\Phi + u\Phi_z' = \Phi_{uu}''(2)\ u \to \infty\ (z > 0) : \Phi \to 0$

$$z = 0\ (u > 0) : \Phi = 0 \tag{3}$$

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$$\text{a) } u = 0 \begin{cases} 0 < z < z_2 : \Phi_u' = -b\theta(1-z) \\ z_2 < z < z_3 : \Phi = 0 \end{cases} \qquad \text{(current regime)} \tag{4}$$

$$\text{b) } u = 0\ (z > 0) : \Phi_u' = -b\theta\ (1-z) \quad \text{(potential regime),} \tag{5}$$

where

$$\varepsilon_1 = i\omega L_D^2(x_1)/D, \qquad L_D(x_1) = (Dx_1/\omega_\tau)^{1/3}, \quad b = J_1 L_D(x_1)/DS$$

$$u = y/L_D(x_1), z = x/x_1,\ z_2 = x_2/x_1,\ z_3 = x_3/x_1, \theta(z)$$

is the unit step function, S is the area of the electrode at $(0, x_1)$, a prime denotes differentiation with the variable indicated by the subscript, and J_1 is the total diffusive flux at the working electrode, which corresponds to the Faradaic component of alternating current I_1. The quantity J_1 must be determined by measuring the limiting current or the surface concentration at the indicator electrode.

The governing parameter in this problem is the ratio of the dimension $L_D(x) = (Dx/\omega_T)^{1/3}$ of the steady-state diffusion layer at point x to the dimension $\delta_D = (D/\omega)^{1/2}$ of the periodic layer: $\varepsilon = L_D^2(x)/\delta_D^2$. With $\varepsilon \ll 1$, molecular diffusion follows the temporal changes in the concentration over distances on the order of x. This is a particularly simple case for which to carry out calculations if the boundary conditions is specified in form (5) (potential regime). Using boundary condition (5), we can write the solution of (2), (3) as

$$\Phi(z,\ u) = -b\,[G_0(z,\ u) - \theta\,(1-z)\ G_0\,(z-1,\ u)], \tag{6}$$

where $G_0(z, u)$ is the solution in the region $0 < z < 1$.

Using Laplace transforms, we find

$$g_0(p,\ u) = L\ \{G_0\ (z,\ u)\} = \text{Ai}\ (p^{1/3}\ u + w)/p^{4/3}\ \text{Ai}'\ (w), \tag{7}$$

where $w = \varepsilon_1 p^{-2/3}$ and Ai(z) is the Airy function [10]. The problem of finding the surface concentration thus reduces to one of inverting the Laplace transform:

$$g_0\ (p,\ 0) = \text{Ai}\ (w)/p^{4/3}\ \text{Ai}'\ (w).$$

Expanding $g_0(p, 0)$ in a series in powers of $p^{-2/3}$ [10], and using a theorem regarding term-by-term inversion of the functions specified as a power series $p^{-\nu}$ $(\nu > 0)$ [11], we find

$$\Phi(z,\ 0) = b\frac{3^{2/3}}{\Gamma(2/3)}\Big[\sigma^{1/3}(z) - 3^{-2/3}\,\Gamma(2/3)\,\varepsilon_1 + \frac{3^{4/3}}{20a^2}\,\sigma^{(4/3)}(z)\cdot\varepsilon_1^2 - \frac{3}{14}\,\sigma^{(7/3)}(z)\,\varepsilon_1^3 + \frac{3^{1/3}}{72}\,\Gamma(2/3)(1 + a^{-3})\,\sigma^{(3)}(z)\,\varepsilon_1^4 + 0\,(\varepsilon_1^5)\Big], \tag{8}$$

where $a = 3^{1/3}\Gamma(2/3)\Gamma(1/3)$ and $\sigma^{(\nu)}(z) = z^\nu - (z-1)^\nu$.

In carrying out calculations for the current regime, i.e., using (4) with (2), (3), we will make use of the method proposed by Matsuda for the steady-state case [9]. According to this method we first find the relation between the Laplace transforms of the surface concentration $\varphi(p, 0)$ and its derivative $\varphi'_{u=0}| = \bar{f}(p)$, treating $\Phi(z, 0)$ and $\Phi'_u|_{u=0}$ as arbitrary functions of z. Then, using the convolution equation, and satisfying the boundary conditions at u = 0, we find an integral equation with a difference kernel or

$$f(z) \text{ for } z_2 < z < z_3: \tag{9}$$

$$\int_{z_2}^{z} dt\, f(t)\cdot G_{0z}'(z-t,\ 0) + b\int_0^1 dt\, G_{0z}'(z-t,\ 0) = 0. \tag{10}$$

We seek a solution of Eq. (10) as a series in terms of the small parameter ε_1

$$f(z) = f_0(z) + \varepsilon_1 f_1(z) + \varepsilon_1^2 f_2(z) + 0\,(z_1^3). \tag{11}$$

Equating terms having equal powers of ε_1, we find a system of integral Abel equations for the functions $f_0(z)$, $f_1(z)$, and $f_2(z)$, which we solve by standard methods [11]:

$$(3b)^{-1}\int_{z_2}^{z} dt f_0(t) = -[\Gamma(1/3)\Gamma(2/3)]^{-1}\int_{z_2}^{z} dt\,(z-t)^{-1/3}\sigma^{(1/3)}(t);$$

$$(3b)^{-1}\int_{z_2}^{z} dt f_1(t) = a(z-z_2)^{2/3}\,2\Gamma(2/3) - 3\Gamma^{-2}(4/3)\int_{z_2}^{z} dt\,(z-t)^{1/3}\sigma^{1/3}(t);$$

$$(3b)^{-1}\int_{z_2}^{z} [dt f_2(t) = 3a^2(z-z_2)^{4/3}/4\Gamma(1/3) - 3^{4/3}\sqrt{3}/16\pi a^2\int_{z_2}^{z} dt\,(z-t)^{-1/3}$$

$$\times\,\sigma^{(5/3)}(t) - (\Gamma(2/3)/\Gamma^2(1/3) - 1/2a^2\Gamma(1/3))\int_{z_2}^{z} dt\,(z-t)^{1/3}\sigma^{(7/3)}(t). \tag{12}$$

It is interesting to compare the functional dependences on z in (8) and (12) for $z \gg 1$. We can use (8) to write the following approximate equations for $z \gg 1$ for the damping of the magnitude $|B|$ of the periodic concentration and for the phase shift arg B with an account of terms up to the order of ε^4 inclusively:

$$|B| = 1 - 0{,}13\varepsilon^2 + 0{,}010\varepsilon^4 + 0(\varepsilon^6) + 0(z^{-1}) - \arg B = 1{,}95\varepsilon - 0{,}005\varepsilon^3 + 0(\varepsilon^5) + 0(z^{-1}), \tag{13}$$

where $B = \Phi(z, 0)/[\Phi(z, 0)]_{\omega=0}$. Equations (11) and (12) with $z \gg 1$ lead to the same result, within terms on the order of ε^2 inclusively, but the corrections are on the order of $z^{-2/3}$, rather than z^{-1}. Accordingly, with $x_2 \gg x_1$ the transfer coefficient B does not depend on the operation of the indicator electrode (x_2, x_3). This is almost an obvious result, since with $x_2 \gg x_1$ the amplitude damping of the periodic concentration occurs primarily in the insulation zone (x_1, x_2), rather than in the electrode zone.

This calculation has dealt with the case of a constant surface tension $\tau(x) = \tau_0$. To determine the applicability of these equations for a quite arbitrary geometry of the surface in the flow, we consider the problem for the potential regime in the case in which the surface tension is specified to be a linear function of the tangential coordinate

$$\tau(L+x) = \tau_0(L) + \tau_x'(L)\cdot x + 0(x^2/L^2). \tag{14}$$

The problem reduces to one of solving the equation

$$\varepsilon_1\Phi + u\Phi_z' + \lambda_1 u(z\Phi_z' - 0{,}5u\,\Phi_u') = \Phi_{uu}'' \tag{15}$$

with boundary conditions (3), (5), where $\lambda_1 = x_1\tau_x'(L)/\tau(L)$ or $\lambda_1 \sim x_1/L$.

We seek the solution of Eq. (15) for the region $0 < z < 1$ as a series in terms of the small parameter λ_1

$$G(z, u) = G_0(z, u) + \lambda_1 G_1(z, u) + 0(\lambda_1^2). \tag{16}$$

The Laplace transform $g_1(p, u) = L_p\{G_1(z, u)\}$ is a solution of the inhomogeneous Airy equation:

$$g_{1uu}'' - (\varepsilon_1 + up)g_1 = u(pg_0)_p' + 0{,}5\,u^2 g_{0u}'. \tag{17}$$

To find $g_1(p, 0)$ we multiply (17) by $\mathrm{Ai}(p^{1/3}u + w)$ and integrate both parts of the equation over u from 0 to ∞, finding

$$g_1(p, 0) = \frac{1}{9p^{7/3}}\left[\left(\frac{7}{2} - 4w^3\right)\frac{\mathrm{Ai}(w)}{\mathrm{Ai}'(w)} + 4w^4\,\frac{\mathrm{Ai}^3(w)}{\mathrm{Ai}'^3(w)} - 12w^3\,\frac{\mathrm{Ai}^2(w)}{\mathrm{Ai}'^2(w)} + 10\,w\right] \tag{18}$$

Expanding (18) in a series in powers of $w = \varepsilon_1 p^{-2/3}$, carrying out a term-by-term inverse transformation, and using (6), we find

$$\Phi_1(z, 0) = \frac{3b}{8\Gamma(3/3)}\left[\frac{7}{3^{4/3}}\sigma^{(4/3)}(z) - 4\Gamma\left(\frac{2}{3}\right)\left(z - \frac{1}{2}\right)\varepsilon_1 + \frac{11}{8a^3}\sigma^{(7/3)}(z)\,\varepsilon_1^2 + O(\varepsilon_1^3)\right]. \tag{19}$$

We can use Eqs. (8) and (19) to write expressions for $|B|$ and arg B, taking into account terms of first order in $\lambda = x\tau_x'(L)/\tau(L)$ and x_1/x and of second order in ε:

$$-\arg B = 3^{1/3}\,\Gamma(2/3)\,(1 + \lambda/3 - x_1/3x)\;\varepsilon = 1{,}95\left(1 + \frac{\lambda}{3} - \frac{x_1}{3x}\right)\varepsilon, \tag{20}$$

$$|B| = 1 - \frac{1}{4}\left[(\Gamma^2(1/3)/2\Gamma^4(2/3)) - 1\right](\arg B)^2 = 1 - 0{,}031\,(\arg B)^2, \tag{21}$$

where

$$[\Phi(x, 0)]_{\omega=0} = (3\sqrt{3}/4\pi\cdot(J_1/J)\,(x_1/x)^{2/3}\,(1 + 7\,\lambda/6 + x_1/3x), \tag{22}$$

and

$$J = (3^{4/3}/2\Gamma(1/3))\,DS/L_D\,(x_1).$$

According to Eq. (21), $|B|$ depends explicitly on only arg B. The functional dependence of arg B on ε can be found on the basis of the following considerations. We assume that with $x \gg x_1$ the phase shift can be written as the sum of two terms, a diffusive term $\arg B_y = \omega t_D$ and a convective term $\arg B_x = \omega t_v$, where $t_D = y^2/D$ is the characteristic time for diffusive mass transport from the wall over a distance y, and $t_v = x/v_x(y)$ is the characteristic time for convective mass transport along the wall over a distance x at a velocity $v_x(y) = \omega_T y$. The substance evolved at the working electrode is carried by the hydrodynamic flow over a distance y^* from the wall such that the phase shift is minimal. Finding the minimum of the function $\arg B(y) = (\omega y^2/D) + (\omega x/\omega_T y)$, we then find

$$\begin{gathered} y^* \sim (Dx/\omega_\tau)^{1/3} \sim L_D(x) \\ \arg B \sim \omega L_D^2\,(x)/D \sim \varepsilon. \end{gathered} \tag{23}$$

At low frequencies, therefore, transport of an alternating concentration occurs primarily over a distance from the wall which is on the order of the thickness of the steady-state diffusion layer.

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