

ESTABLISHING THE PERIODIC DIFFUSION CURRENT OF A SPHERICAL ELECTRODE

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The conclusion of [1], for the case of a planar slit electrode, regarding the relationship between the time required to establish a periodic limiting diffusion current and the thickness of the hydrodynamic (but not diffusion) periodic layer cannot be extended to the general case of hydrodynamic vibrations of the electrolyte solution around an electrode of arbitrary shape. This is due to the fact that the time required to establish the current should depend on the mechanism of transfer of the reacting substance in a direction perpendicular to the electrode surface. Two mechanisms for this transfer are possible and can be illustrated in the case of two simple models. The first mechanism (purely diffusion) is realized in the rather well-studied model of a slit electrode [2-4] which occupies the inner surface of a channel where transfer of the reacting substance in a direction perpendicular to the electrode surface is carried out by transverse or lateral diffusion over the entire volume of the channel. In this case, the hydrodynamic flow carries the reacting substance in only a tangential direction. The second mechanism is realized in the case of the small vibrations of a spherical electrode [5], where convective transfer of the reacting substance in a direction perpendicular to the electrode surface is the dominating factor everywhere except for the diffusion layer. This transfer is produced by the radial component of the hydrodynamic velocity, while molecular diffusion predominates only in the diffusion layer. One can therefore expect that, when an oscillating external signal is switched on, the time required to establish the periodic diffusion current of a spherical electrode will be associated with the thickness of the diffusion periodic layer rather than the hydrodynamic periodic layer.

We bring the origin of the spherical system of coordinates into coincidence with the center of the spherical electrode of radius R which is in an electrolyte solution which fills an infinite volume. The concentration distribution which corresponds to limiting current conditions in the quiescent solution has the form [6]

$$c^{(0)} = c_0 (1 - R/r), \quad (1)$$

where c_0 is the concentration in the solution, and r is the radial coordinate. Suppose that when $t=0$ the electrolyte solution instantaneously comes into motion with frequency ω , during which the hydrodynamic velocity (v) outside of or beyond the region disturbed by the electrode changes according to the $v/r \rightarrow \infty = U \exp[-i(\omega t + \varphi)]$ (U is the velocity amplitude, φ is the signal switching phase, and i is an imaginary number). The establishment of the periodic diffusion processes is described by the equation [7]:

$$\partial c / \partial t + \vec{v} \text{ grad } c = D \Delta c \quad (2)$$

with boundary conditions:

$$c|_{r=0} = c^{(0)}; \quad c|_{r=R} = 0; \quad c|_{r \rightarrow \infty} = c_0, \quad (2')$$

where D is the diffusion coefficient, and Δ is the Laplace operator. If the liquid vibrations are characterized by a small Peclet number, Eq. (2) can then be solved by the method of successive approximations [5]. Distribution (1), disregarding the convective feeding of substance, can be used as a null approximation with respect to the velocity amplitude. To a first approximation we arrive at the following boundary problem:

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$$D \Delta c^{(1)} - \partial c^{(1)} / \partial t = v_r \partial c^{(1)} / \partial r, \quad (3)$$

$$c^{(1)}|_{t=0} = c^{(1)}|_{r=R} = c^{(1)}|_{r \rightarrow \infty} = 0, \quad (3')$$

where $c^{(1)}$ is the change in the concentration distribution of the reacting substance produced by the hydrodynamic motion, and v_r is the radial component of the hydrodynamic velocity.

We will limit ourselves to the case where the thickness of the periodic hydrodynamic layer ($\delta_v \approx \sqrt{\nu/\omega}$) is much larger than the electrode radius ($\delta_v \gg R$). One can then disregard the relaxation of the hydrodynamic process and can consider that the hydrodynamic flow around the electrode is Stokesian. In the process, the radial component of the convective flow velocity has the form [8, 9]

$$v_r = U [1 - (3/2)(R/r) + (1/2)(R/r)^3] \cos \vartheta \exp [-i(\omega t + \varphi)], \quad (4)$$

where ϑ is the angle between the direction of vibrations and the radius vector (r).

We seek a solution of problems (3) and (3') in the form

$$c^{(1)} = (c_0 R U / D) r \psi(r, t) \cos \vartheta, \quad (5)$$

where $\psi(r, t)$ is a solution of the following boundary problem:

$$\partial^2 \psi / \partial r^2 + (4/r) \partial \psi / \partial r - D^{-1} \partial \psi / \partial t = r^{-3} f(r) \exp [-i(\omega t + \varphi)], \quad (6)$$

$$\psi|_{t=0} = \psi|_{r=R} = \psi|_{r \rightarrow \infty} = 0, \quad (6')$$

where $f(r) = 1 - (3/2)(R/r) + (1/2)(R/r)^3$. Satisfying the Laplace transform $\lambda = \int_0^\infty e^{-pt} \psi dt$, we obtain

$$\frac{d^2 \lambda}{dr^2} + \frac{4}{r} \frac{d\lambda}{dr} - \left(\frac{p}{D}\right) \lambda = r^{-3} f(r) (p + i\omega)^{-1} \exp(-i\varphi), \quad (7)$$

$$\lambda|_{r=R} = \lambda|_{r \rightarrow \infty} = 0. \quad (7')$$

The density of the additional diffusion current produced by the hydrodynamic vibrations is

$$j^{(1)} = D \frac{\partial c^{(1)}}{\partial r} \Big|_{r=R} = c_0 R^2 U \cos \vartheta \cdot \frac{\partial \psi}{\partial r} \Big|_{r=R}.$$

The integral of the diffusion current density ($j^{(1)}$) over the entire surface of the spherical electrode is zero. However, assuming the presence of a thin insulating interlayer between the two electrode hemispheres, the plane of which is perpendicular to the direction of vibrations [5], we obtain the other-than-null diffusion current of the hemisphere

$$J_{1/2} = \pi R^2 c_0 U \frac{\partial \psi}{\partial r} \Big|_{r=R}. \quad (8)$$

The boundary problem (7)-(7') enables us to obtain the Laplace transform of the function $\frac{\partial \psi}{\partial r} \Big|_{r=R}$

$$\begin{aligned} \frac{d\lambda}{dr} \Big|_{r=R} &= [16R^2 (\mu \sqrt{p} + 1) (p + i\omega)]^{-1} \{-6 + 10\mu \sqrt{p} + \mu^2 p \\ &+ 12e^{\mu \sqrt{p}} E_1(-\mu \sqrt{p}) \mu^2 p - \mu^3 p^{3/2} - e^{\mu \sqrt{p}} E_1(-\mu \sqrt{p}) \mu^4 p^2\} \exp(-i\varphi), \end{aligned} \quad (9)$$

where $\mu = R/\sqrt{D}$, and $E_1(z)$ is the integral exponential function. The asymptotic expansion of the original, which corresponds to large t , can most simply be constructed from expression (9) in the following manner.

We define $\frac{d\lambda}{dr} \Big|_{r=R} = q(\sqrt{p})$ and formally examine the $q(p)$ function. Of the four singular points of the

$q(p)$ function (poles at the points $p_0 = \sqrt{\omega/2} (1-i)$, $p_1 = -\sqrt{\omega/2} (1-i)$, $p_2 = -\mu^{-1}$, and the logarithmic peculiarity at the point $p_3 = 0$), the asymptotic behavior of the $Q(t)$ function, which is the original for $q(p)$, determines the

singular point with the most real portion, i.e., pole p_0 [10]. We then expand the $q(p)$ function into a Laurent series in the vicinity of point p_0 . Since the right-hand portion of the Laurent expansion of the $q(p)$ function in the vicinity of p_0 is unimportant in the construction of the asymptote of the $Q(t)$ function [10], we need only consider a single term of the major portion which is equal to $K(p_0) (p-p_0)^{-1}$, where $K(p_0) = [(p-p_0)q(p)]_{p=p_0}$ is a function which is analytical at point p_0 . The asymptote of the $Q(t)$ function for large t has the form

$$Q(t) \approx K(p_0) e^{p_0 t}. \quad (10)$$

The original $\left. \frac{\partial \psi}{\partial r} \right|_{r=R}$ of the $q(\sqrt{p})$ function is related to $Q(t)$ in the following way [11]:

$$\left. \frac{\partial \psi}{\partial r} \right|_{r=R} = (2 \sqrt{\pi t^3})^{-1} \int_0^\infty Q(\tau) \tau e^{-\tau^2/(4t)} d\tau. \quad (11)$$

The $Q(t)$ function is unknown over the entire region of integration (11). We know only that the $Q(t)$ function, according to Eq. (10), increases exponentially at large t ($\text{Re } p_0 > 0$), and, in addition, it is easy to establish that $\lim_{t \rightarrow 0} Q(t) = \lim_{p \rightarrow \infty} pq(p) = 0$. However, the form of the core ($\tau \exp[-\tau^2/(4t)]$) of transform (11) is such that

for the asymptotic behavior of the $\left. \frac{\partial \psi}{\partial r} \right|_{r=R}$ function, integration in (11) with respect to small t values is

unimportant. In fact, the greatest contribution to integral (11) is made by integration with respect to the neighborhood of the point $\tau = \tau_{\max}$ at which the integrand reaches a maximum. Due to the exponential increase of the $Q(t)$ function as $t \rightarrow \infty$, the position of the maximum of the integrand satisfies the inequality $\tau_{\max} > \tau^*$, where τ^* is the position of the maximum of the core $\tau \exp[-\tau^2/(4t)]$. The τ^* value and, consequently, $\tau_{\max}$ are shifted to the large t region ($\tau^* = \sqrt{2t}$) with increasing t . In integrating in Eq. (11), it is therefore sufficient to use asymptote (10) of the $Q(t)$ function, and, as a result, we find that for large t

$$\left. \frac{\partial \psi}{\partial r} \right|_{r=R} \approx K(p_0) (\pi t)^{-1/2} \exp(p_0^2 t/2) D_{-2}(-\sqrt{2t} p_0), \quad (12)$$

is asymptotically valid, where $D_\nu(z)$ is a parabolic cylinder function. If $|p_0^2 t| \gg 1$, the asymptotic series follows from (12):

$$J_{1/2}^* \approx (3/8) \pi R^2 c_0 U \exp(-i\varphi) \{ \exp(-i\omega t) + \sqrt{-i/(4\sqrt{\pi})} [(\omega t)^{-3/2} - (3/2) i (\omega t)^{-5/2} + \dots] \}. \quad (13)$$

We will consider two limiting cases:

1) The frequency of the vibrations of the solution is low and the thickness of the periodic diffusion layer ($\delta_D \approx \sqrt{D/\omega}$) is much larger than the electrode radius ($\delta_D \gg R$). In this case, $|\mu p_0| \ll 1$, and, substituting expression (13) into (8), in which we disregard the terms of higher order of smallness with respect to $|\mu p_0|$, we obtain an asymptotic formula for the additional diffusion current which, when $\omega t \gg 1$, has the form

$$\left. \frac{\partial \psi}{\partial r} \right|_{r=R} \approx -K(p_0) p_0 \{ 2 \exp(p_0^2 t) + \pi^{-1/2} [(1/2) (p_0 \sqrt{t})^{-3} - (3/4) (p_0 \sqrt{t})^{-5} + \dots] \}. \quad (14)$$

2) The thickness of the periodic diffusion layer is much less than the electrode radius ($\delta_D \ll R$). In this case, $|\mu p_0| \gg 1$. Performing the asymptotic expansion into $K(p_0)$ of the integral exponential functions for large argument values and omitting the terms of higher order of smallness with respect to $|\mu p_0|^{-1}$, we obtain an asymptotic expression when $\omega t \gg 1$ for the additional diffusion current of the electrode hemisphere:

$$J_{1/2}^b \approx -3\pi c_0 U R^{-1} (D/\omega)^{1/2} \exp(-i\varphi) \{ \sqrt{-i} \exp(-i\omega t) + 1/(4\sqrt{\pi}) \times [i(\omega t)^{-3/2} - (3/2)(\omega t)^{-5/2} + \dots] \} \quad (15)$$

The first term in expressions (14) and (15) is the established alternating diffusion current investigated in [5]. The second term asymptotically describes the nonoscillating attenuation of the transient current component. It is apparent that the characteristic time (τ_D) required to establish the periodic diffusion current of a spherical electrode in Eqs. (14) and (15) is associated with the thickness of the periodic diffusion (but not hydrodynamic) layer (δ_D). In fact, its order of magnitude should be $\tau_D \sim L^2/D$, where L is the characteristic length of the process. But since $\tau_D \sim \omega^{-1}$, $L \sim \sqrt{D/\omega} \approx \delta_D$.

The result obtained ($\tau_D \sim \omega^{-1}$) confirms the validity of disregarding the relaxation of the hydrodynamic process when $\delta_\nu \gg R$. It is well known [8] that $\tau_\nu \sim R^2/\nu$ is valid for the characteristic relaxation time of a hydrodynamic process during Stokesian flow. It therefore follows from the condition $\sqrt{\nu/\omega} \gg R$, that $\tau_\nu \ll \tau_D$. We note that the transient component of the additional diffusion current ($J_{1/2}^b$), in the case of sinusoidal switching in of the vibrations, attenuates as $(\omega t)^{-3/2}$, and, in the case of cosinusoidal switching in, attenuates as $(\omega t)^{-5/2}$ ("sinusoidal" and "cosinusoidal switching in" are used in the sense defined in [1]).

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