INFLUENCE OF PERIODIC PRESSURE-GRADIENT COMPONENT ON MAXIMUM ELECTRIC CURRENT

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The mathematical aspect of the process of internal diffusion in a flat channel in the presence of an oscillating pressure gradient has been treated by Siegel and Perlmutter [1] (see also [2]), who considered internal heat exchange. However, their expression for the stream density at a wall took the form of two infinite series; in order to find the terms of these series, it is necessary to know the solution of a transcendental equation. The result obtained by these authors [1] is therefore very inconvenient for applied problems.

We will derive below an analytic expression for the maximum electric current at a flat or cylindrical electrode in the presence of a constant pressure drop on which a periodic component with the frequency ω is superimposed. The current density is related by a simple formula (using Faraday's law) to the diffusion flow at the electrode. We will therefore limit ourselves to analysis of the diffusion process.

Let us first consider the case of a flat channel formed by two parallel planes separated by a distance $2r_0$. We choose a coordinate system such that the z axis is directed parallel to the flow, the x axis is perpendicular to the electrode plates, and the origin is in the center of the channel cross section passing through the start of the electrode. The periodic pressure-gradient component $\nabla P = F_0 \exp(-i\omega t)$ causes development of the following velocity field [3]:

$$v = -(iF_0/\omega\rho)[1 - \operatorname{ch} kx / \operatorname{ch} kr_0] \exp(-i\omega t), \tag{1}$$

where $k = \sqrt{\omega/2\nu}(1-i)$; ρ is the density of the liquid; ν is the kinematic viscosity, i is an imaginary unit, and t is the time. Let us assume that the electrode length is greater than the complete-absorption length, so that we can consider an electrode of infinite length. The constant Poiseuille flow therefore sets up a steady-state complete-absorption diffusion flow equal to the amount of electrically active material introduced into the channel by the hydrodynamic flow, $I_s = 2r_0bc_0\bar{v}$ (where b is the cross section of the electrode plate and $\bar{v}$ is the average velocity over the channel cross section). Oscillations produced by the periodic fluctuations ∇P are superimposed on the constant flow. Since diffusion in the flow direction does not have a perceptible influence on transport of the electrically active material at high Peclet numbers, we obtain the following boundary problem for the diffusion process at the maximum current:

$$\partial c/\partial t + (v + v_p)\partial c/\partial z = D\partial^2 c/\partial x^2, \tag{2}$$

$$c|_{x=\pm r_0} = 0; \qquad c|_{z=0} = c_0, \tag{2'}$$

where c is the concentration of the electrically active material, D is the diffusion constant, c_0 is the initial concentration of the electrically active material introduced into the channel, and v is determined from Eq. (1). The boundary condition at c = 0 can be written in the form of Eq. (2') if the amplitude of the velocity oscillations in Eq. (1) is not comparable to the velocity v_p of the Poiseuille flow produced by the constant pressure-gradient component. Integrating Eq. (2) with respect to z from zero to infinity, taking into account the boundary conditions ($c|_{z=0} = c_0$; $c|_{z\to\infty} \to 0$) and using the notation $Q(x, t) + Q_n(x) = \int_0^{\infty} c\,dz$, we obtain the following expression for Q(x, t):

$$\partial^2 Q/\partial x^2 - D^{-1}\partial Q/\partial t = f(x)\exp(-i\omega t), \tag{3}$$

$$Q|_{x=\pm r_0} = 0, \tag{3'}$$

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where $f(x) = (iF_0c_0/D\omega\rho)\,[1-\mathrm{ch}\,kx/\mathrm{ch}\,kr_0]$. Since we are considering a steady-state oscillatory process, the solution must be sought in the form $Q(x, t) = Q_0(x)\exp(-i\omega t)$. We then obtain,

$$d^2Q_0/dx^2 + i\omega Q_0/D = f(x), \tag{4}$$

$$Q_0|_{x=\pm r_0} = 0, \tag{4'}$$

for $Q_0(x)$. Equations (4) and (4') can be written in the form

$$Q_0 = (iF_0c_0/D\omega\rho)[(k^2-p^2)^{-1}(\mathrm{ch}\,px/\mathrm{ch}\,pr_0 - \mathrm{ch}\,kx/\mathrm{ch}\,kr_0) - p^{-2}(1-\mathrm{ch}\,px/\mathrm{ch}\,pr_0). \tag{5}$$

where $p = \sqrt{\omega/2D}\,(1-i)$. The diffusive flow at both electrode plates is $I = 2b\int_0^\infty j\,dz = -2bD\partial Q/\partial x|_{x=r_0}$, where $j = -D\partial c/\partial x|_{x=r_0}$ is the ion-flux density at the electrode. Consequently,

$$I = -(2iF_0c_0b/\omega\rho)\,\{[p^{-1} + p/(k^2-p^2)]\mathrm{th}\,pr_0 + [k/(k^2-p^2)]\,\mathrm{th}\,kr_0\}\exp(-i\omega t), \tag{6}$$

whence, assuming $D/\nu \ll 1$, we arrive at the following expression for the diffusive flow:

$$I = (2F_0c_0bD/\omega^2\rho)[k\,\mathrm{th}\,kr_0 - (D/\nu)p\,\mathrm{th}\,pr_0]\exp(-i\omega t). \tag{7}$$

Let us consider the three limiting cases: a) the thicknesses of the periodic hydrodynamic and diffusive layers are much greater than the channel width $r_0^2/\nu \ll \omega^{-1}$, $r_0^2/D \ll \omega^{-1}$; b) the thickness of the periodic diffusive layer is much less than the channel cross section, which in turn is much less than the thickness of the periodic hydrodynamic layer $r_0^2/\nu \ll \omega^{-1}$, $r_0^2/D \gg \omega^{-1}$; c) the thickness of the periodic hydrodynamic and diffusive layers are much less than the channel width $r_0^2/\nu \gg \omega^{-1}$, $r_0^2/D \gg \omega^{-1}$.

In case (a), $|kr_0| \ll 1$ and $|pr_0| \ll 1$, i.e., the hydrodynamic and diffusive processes can follow the external-perturbation oscillations. Expanding the hyperbolic tangents in Eq. (7) into power series of small arguments and limiting ourselves to the first two terms in each expansion, we obtain

$$I^a = -(2F_0c_0br_0^3/3\rho\nu)\exp(-i\omega t). \tag{8}$$

Hence it can be seen that, at sufficiently small frequencies (i.e., $\omega \ll D/r_0^2$), the diffusive flow at the electrode varies antiphasically with respect to ∇P [the minus sign in Eq. (8) is due to the fact that the hydrodynamic viscosity is opposite in direction to ∇P], while its amplitude is independent of the frequency and numerically equal to the steady-state diffusive flow under the action of the constant pressure gradient F_0. The conversion function K_p, which relates the varying diffusive flow to the oscillating pressure-gradient component, has the form

$$K_P^a = -(2c_0br_0^3/3\rho\nu).$$

In order to write the conversion function K_v, which relates the varying diffusive flow to the average viscosity of the hydrodynamic flow $\bar{v}$, we average Eq. (1) over the channel cross section:

$$\bar{v} = -(iF_0/\omega\rho)\,[1 - \mathrm{th}\,kr_0/kr_0]\exp(-i\omega t). \tag{9}$$

When $|kr_0| \ll 1$, we obtain $\bar{v} \simeq r_0^2\nabla P/3\rho\nu$, whence we find $K_v^a = -3\rho\nu K_p^a/r_0^2 = 2c_0br_0$.

The diffusion process in case (b) cannot follow the external-perturbation oscillations, while the hydrodynamic process can do so. In this case $|kr_0| \ll 1$ and we can, as above, expand $\mathrm{th}\,kr_0$ in Eq. (7) into a power series for kr_0 limiting ourselves to the linear term; the condition $|pr_0| \gg 1$ enables us to utilize an asymptotic expansion of $\mathrm{th}\,pr_0$ for large pr_0. This yields

$$I^b = -(2iF_0c_0r_0bD/\rho\omega\nu)\exp(-i\omega t), \tag{10}$$

whence it can be seen that the phase of the varying diffusive flow leads that of the pressure gradient by the angle $\vartheta = \pi/2$. For the conversion function K_v, we obtain $K_v^b = -3\rho\nu K_p^b/r_0^2 = 6ic_0bD/\omega r_0$. The amplitude-frequency characteristic is therefore $|K_v^b| = 6c_0bD/\omega r_0$.

In case (c), neither the diffusive nor the hydrodynamic process can follow the external-perturbation oscillations: $|kr_0| \gg 1$ and $|pr_0| \gg 1$. Using the asymptotic expansions for large arguments, Eq. (7) yields

$$I^c = -F_0 c_0 bD\sqrt{2/\nu\omega^3}(i-1)\exp(-i\omega t)/\rho, \tag{11}$$

in first approximation, whence it follows that, with the assumptions made, the phase of the varying diffusive flow lags behind that of the pressure gradient by an angle $\vartheta = 7\pi/4$. When $|kr_0| \gg 1$, we obtain $\bar{v} \simeq -(iF_0/\omega\rho)\exp(-i\omega t) = -i\nabla P/\omega\rho$ from Eq. (9), which gives $K_v^c = i\omega\rho K_p^c = c_0 bD\sqrt{2/\nu\omega}\,(1+i)$ for the conversion function K_v; the amplitude-frequency characteristic therefore has the form

$$|K_v^c| = 2c_0 bD/\sqrt{\nu\omega}.$$

2. For a cylindrical channel of radius r_0, we use a cylindrical coordinate system with the z axis and the origin located in the same positions as for a flat channel. Various authors [4, 5] have obtained the steady-state equation

$$v = -(iF_0/\omega\rho)\{1 - J_0(kr)/J_0(kr_0)\}\exp(-i\omega t), \tag{12}$$

for the hydrodynamic process at $\nabla P = F_0 \exp(-i\omega t)$, where $k = \sqrt{\omega/2\nu}\,(1+i)$ and J_β is a type I Bessel function of order β. The diffusive process at the maximum current is described by the boundary equation

$$\begin{gathered}\partial c/\partial t + (v + v_{\text{п}})\partial c/\partial z = D(r^{-1}\partial c/\partial r + \partial^2 c/\partial r^2),\\ c|_{r=r_0} = 0; \quad c|_{z=0} = c_0\end{gathered} \tag{13}$$

where v is determined from Eq. (12). Converting to $Q + Q_p \int_0^\infty c\,dz$, we find

$$\begin{gathered}\partial^2 Q/\partial r^2 + r^{-1}\partial Q/\partial r - D^{-1}\partial Q/\partial t = \varphi(x)\exp(-i\omega t),\\ Q|_{r=r_0} = 0,\end{gathered} \tag{14}$$

where $\varphi(r) = (iF_0c_0/\omega\rho D)[1 - J_0(kr)/J_0(kr_0)$. Assuming $Q(r, t) = Q_0(r)\exp(-i\omega t)$, we obtain

$$\begin{gathered}d^2Q_0/dr^2 + r^{-1}dQ_0/dr + i\omega Q_0/D = \varphi(x),\\ Q_0|_{r=r_0} = 0.\end{gathered} \tag{15}$$

The solution of this problem has the form

$$\begin{gathered}Q_0 = (iF_0c_0/\omega\rho D)\{(p^2-k^2)^{-1}[J_0(pr)/J_0(pr_0) - J_0(kr)/J_0(kr_0)]\\ + p^{-2}[1 - J_0(pr)/J_0(pr_0)]\},\end{gathered} \tag{16}$$

where $p = \sqrt{\omega/2D}\,(1+i)$. The diffusive flow at the electrode is

$$\begin{aligned}I &= -2\pi r_0 D\partial Q/\partial r|_{r=r_0}\\ &= -\frac{2\pi i F_0 c_0 r_0}{\omega\rho}\left\{\frac{1}{p}\frac{J_1(pr_0)}{J_0(pr_0)} + \frac{1}{p^2-k^2}\left[k\frac{J_1(kr_0)}{J_0(kr_0)} - p\frac{J_1(pr_0)}{J_0(pr_0)}\right]\right\}\exp(-i\omega t),\end{aligned} \tag{17}$$

whence, assuming $D/\nu \ll 1$, we find

$$I = (2\pi F_0c_0r_0D/\omega^2\rho)[(D/\nu)pJ_1(pr_0)/J_0(pr_0) - kJ_1(kr_0)/J_0(kr_0)]\exp(-i\omega t). \tag{18}$$

As in the case of a flat channel, we can consider the three limiting cases. Using the power-series expansion of the Bessel function for small arguments and their asymptotes for large arguments, cases (a), (b), and (c) can be characterized in the following manner:

a) $|kr_0| \ll 1$, $|pr_0| \ll 1$. For the diffusive current I and the conversion function K_p we find,

$$\begin{gathered}I^a = -(\pi F_0c_0r_0^4/8\rho\nu)\exp(-i\omega t),\\ K_P^a = -\pi c_0 r_0^4/8\rho\nu.\end{gathered} \tag{19}$$

From Eq. (12), we obtain the average velocity over the channel cross section $\bar{v} = -r_0^2 \nabla P/8\rho\nu$, whence

$$K_v{}^a = -8\rho\nu K_P{}^a / r_0^2 = \pi r_0^2 c_0.$$

b) $|kr_0| \ll 1$, $|pr_0| \gg 1$.

$$I^b = -(i\pi F_0 c_0 r_0^2 D / \omega\rho\nu)\exp(-i\omega t), \qquad (20)$$

$$K_v{}^b = -8\rho\nu K_P{}^b / r_0^2 = 8i\pi c_0 D / \omega, \text{ i.e., } |K_v{}^b| = 8\pi c_0 D / \omega.$$

c) $|kr_0| \gg 1$, $|pr_0| \gg 1$.

$$I^c = -\pi F_0 c_0 r_0 D \sqrt{2/\nu\omega^3}(i-1)\exp(-i\omega t)/\rho. \qquad (21)$$

From Eq. (12), we find the average velocity over the channel $\bar{v} = -i\nabla P/\omega\rho$, which yields $K_v{}^c = i\omega\rho K_P{}^c$ $\pi c_0 r_0 D\sqrt{2/\nu\omega}(1+i)$; hence we obtain $|K_v{}^c| = 2\pi c_0 r_0 D/\sqrt{\nu\omega}$. for the amplitude-frequency characteristic.

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