DIAGNOSTICS OF ANOMALOUS RHEODYNAMICAL WALL EFFECTS FROM OBSERVATION OF ELECTROCHEMICALLY DRIVEN TRANSIENT CONVECTIVE DIFFUSION

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The time dependence of mean current densities after a step change in the concentration of a depolarizer on the surface of a working electrode was found by solving the equations of the convective diffusion in the Couette flow with anomalous wall effects. The theory is used for determining the velocity profile in the vicinity of the electrode surface.

Significant changes in flow properties of polymer melts[1], polymer solutions[2], suspensions[3] and other rheologically complex fluids in an immediate vicinity of the wall – the so called wall, resp. slip effects – belong to well-known manifestations of the microdispersion structure of these liquid materials. These effects may exhibit a strong influence on results of viscometric measurements[1-4] as well as on the intensity of mass or heat transfer[5,6].

Slip effects can be characterized by the velocity of the apparent (positive or negative) slip along the wall[1,3,4] or by the apparent thickness of the wall layer[2,5,6] (which contains pure solvent or the adsorbed polymer layer). Existing experimental data whether obtained by viscometric techniques[1-4] or by measuring the mass transfer intensity[5,6], do not enable to distinguish between the two model representations of the velocity profile at distances from the wall surface smaller than 10–100 μm.

A detailed study of the velocity field in an immediate vicinity of the wall is made possible by employing methods developed in the electrochemical diagnostics of flow which have been described generally, *e.g.*, in a survey[7]. Their main advantage in comparison with other techniques for investigating the mass transfer intensity[5,6] is in the precise measurement of instantaneous local mass transfer coefficients. The relation between the observed instantaneous local intensity of the electric current, I, and the corresponding diffusion flux J of the active component, the so called depolarizer, is given by Faraday's law

$$I = \nu F J \,. \tag{1}$$

Since, at conditions of the so called limiting diffusion current, the intensity of transfer of the depolarizer is controlled solely by the convective diffusion and the boundary conditions are expressed through concentrations of the depolarizer, the theory of convective diffusion forms the exhaustive theoretical basis for the electrochemical diagnostics of flow.

We can employ these methods for investigating the velocity profile in an immediate vicinity of the wall essentially in two ways. The first possibility consists in determining the longitudinal profile of transfer coefficients at conditions of a steady convective diffusion; see, *e.g.*, Eq. (*3.12*) in the survey[7]. In the second case, we can determine the time dependence of mean transfer coefficients after the step change in the depolarizer concentration on the surface of the measuring electrode due to a step change in the polarizing voltage. This second possibility has been demonstrated experimentally by determining slip velocities in the flow of bentonite suspensions in a rotational viscometer with coaxial cylinders[8]. In this work we formulate the necessary theory for the simplest form of the working electrode.

THEORETICAL

THE MATHEMATICAL MODEL OF THE PROCESS

Let us consider a non-steady mass transfer between a planar wall, $z = 0$, and a liquid flowing paralelly to this wall in the direction of axis x. This steady flow is fully determined by the velocity profile $v_x = u(z)$, where z is the distance from the wall. The part of the wall which is active in the transfer, *i.e.*, the electrode, is an infinite band of width L and oriented perpendicularly to the direction of the flow, $y \in \in (-\infty; \infty)$, $x \in (0, L)$.

At time $t < 0$, the concentration c of the active component (depolarizer) on the electrode surface is identical with the constant concentration, c_0, of the depolarizer in the surrounding liquid. No mass transfer occurs between the electrode and the liquid. The reason for the unsteady mass transfer is the step change in the concentration on the electrode surface at $t = 0$ from the value of $c = c_0$ to, let us say, $c = 0$.

If we neglect the effect of the longitudinal diffusion (which is a reasonable approximation for all really possible cases of forced convective diffusion in liquids at values of the diffusion coefficient D below 10^{-9} m^2/s), the mathematical model of the process considered is described by the following 3-dimensional linear boundary-value problem of the parabolic type for the concentration field $c = c(z, x, t)$

$$D\,\partial^2_{zz}c - u(z)\,\partial_x c - \partial_t c = 0 \quad (z > 0,\ t > 0,\ 0 < x < L) \qquad (2)$$

with the boundary conditions

$$c = c_0 \quad \text{for} \quad t < 0 \quad \text{or} \quad z \to \infty \quad \text{or} \quad x < 0 \tag{3a}$$

$$c = 0 \quad \text{for} \quad t > 0 \quad \text{and} \quad z = 0 \quad \text{and} \quad x > 0 \tag{3b}$$

This boundary-value problem admits the two following asymptotic solutions, analogically to the case of the simple shear flow, $u(z) = Az$ (the Léveque configuration), which has been studied earlier[9].

At $t \to 0$, the initial asymptotic solution can be found by a simplification of problem (*2*), (*3a,b*) if we assume that $\partial_x c = 0$. The corresponding asymptote $c \approx c_i(z, t)$ is the solution of the 2-dimensional problem

$$D\, \partial^2_{zz} c_i - \partial_t c_i = 0 \tag{4}$$

$$c_i = c_0 \quad \text{for} \quad t < 0 \quad \text{or} \quad z \to \infty \tag{5a}$$

$$c_i = 0 \quad \text{for} \quad t > 0 \quad \text{and} \quad z = 0\,. \tag{5b}$$

At $t \to \infty$, a steady asymptotic solution can be found by a simplification of problem (*2*), (*3a,b*) if we assume that $\partial_t c = 0$. The corresponding asymptote $c \approx c_s(z, x)$ is the solution to the 2-dimensional problem

$$D\, \partial^2_{zz} c_s - u(z)\, \partial_x c_s = 0 \tag{6}$$

$$c_s = c_0 \quad \text{for} \quad x < 0 \quad \text{or} \quad z \to \infty \tag{7a}$$

$$c_s = 0 \quad \text{for} \quad x > 0 \quad \text{and} \quad z = 0 \tag{7b}$$

Somewhat surprisingly, nevertheless quite obviously, the complete solution to the original 3-dimensional problem can be expressed in the form of

$$c(z, x, t) = \begin{cases} c_i(z, t)\,; & t < \Theta(z, x) \\ c_s(z, x)\,; & t > \Theta(z, x) \end{cases} \tag{8a,b}$$

in all cases when, for each $z > 0$, $x > 0$, the equation

$$c_i(z, \Theta) - c_s(z, x) = 0 \tag{9}$$

possesses only one root $\Theta = \Theta(z, x)$. The parameter Θ then gives the time of the stabilization of the concentration at given point (z, x). The corresponding expression for the instantaneous local diffusion fluxes, $J = J(x, t)$, is

$$J = D\,\partial_z c|_{z=0} = \begin{cases} D\,\partial_z c_i|_{z=0} = J_i(t)\,; & t < \Theta_w \\ D\,\partial_z c_s|_{z=0} = J_s(x)\,; & t > \Theta_w \end{cases}, \qquad (10a,b)$$

where $\Theta_w = \lim_{z \to 0} \Theta(z, x)$ can be determined either as the corresponding limit from (9) or, more simply, as the root Θ_w of the equation

$$J_i(\Theta_w) - J_s(x) = 0 \qquad (11)$$

which follows from (9) by using L'Hospital's rule.

SIMILARITY CASES

A simple solution to the 2-dimensional problem (6), (7a,b) of steady-state convective diffusion can be constructed for velocity profiles represented by the power-law function

$$u(z) = Az^p\,. \qquad (12)$$

Here it holds[7]

$$c_s(z, x) = c_0\, f_p(\xi)/f_p(\infty)\,, \qquad (13)$$

$$\xi = z\left(\frac{Aq}{Dx}\right)^q \qquad (14)$$

the function f_p is the integral of the differential equation $f_p''(y) + y^{1+p} f_p'(y) = 0$ with the initial conditions $f_p(0) = 0, f_p'(0) = 1$ and it can be expressed explicitly as

$$f_p(y) = \int_0^y \exp\left(-qs^{1/q}\right) \mathrm{d}s = q^{1-q} \int_0^{qy^{1/q}} \exp\left(-t\right) t^{q-1}\, \mathrm{d}t \qquad (15)$$

with

$$q = 1/(2 + p)\,. \qquad (16)$$

Obviously it holds $f_p(\infty) = \Gamma(q + 1)/q^q$.

According to Eqs (10b), (13), steady local diffusion fluxes can be expressed through the relation

$$J_s(x) = \left(q^{2q}/\Gamma(q + 1)\right) c_0 D^{1-q}(A/x)^q = c_0 D^{1-q} \pi^{-1/2}(\beta A/x)^q\,, \qquad (17)$$

where for $\beta = \beta(p)$, it holds

$$\beta = q^2(\pi^{1/2}/\Gamma(q + 1))^{1/q} . \qquad (18)$$

Similarly, the well-known[7] solution to the 2-dimensional problem (*4*), (*5a,b*) yields the following expression for the instantaneous diffusion fluxes during the initial phase of the transient process:

$$J_i(t) = c_0(\pi t/D)^{-1/2} . \qquad (19)$$

By inserting (*17*) and (*19*) into (*11*), we arrive at the following relation for the time Θ_w after which diffusion fluxes at point x become steady:

$$\Theta = \Theta_w(x) = D^{-pq}(\beta A/x)^{-2q} . \qquad (20)$$

It is obvious that relations (*17*), (*19*), (*20*) form the full explicit representation of local instantaneous diffusion fluxes according to (*10a,b*).

MEAN DIFFUSION FLUXES

In our case, when the electrode is a straight band of width L oriented perpendicularly to the flow direction, the instantaneous diffusion fluxes $\bar{J}(t)$ are given by the relation

$$\bar{J}(t) = L^{-1} \int_0^L J(x, t) \, dx . \qquad (21)$$

Since local stabilization times of diffusion fluxes, $\Theta_w(x)$, are, according to (*20*), finite for finite values of x, the total stabilization time of mean fluxes is also finite

$$t_\infty(L) = D^{-pq}(\beta A/L)^{-2q} . \qquad (22a)$$

Now let us introduce $x_\infty = x_\infty(t)$, $0 < x_\infty < L$ as the length of that part of our electrode, where, at given time t, the diffusion fluxes have already become steady

$$x_\infty(t) = \beta A t^{1+p/2} D^{p/2} . \qquad (22b)$$

Then, Eqs (*10a,b*) can assume the alternate form

$$J(x, t) = \begin{cases} J_s(x) \, ; & x < x_\infty(t) \\ J_i(t) \, ; & x > x_\infty(t) . \end{cases} \qquad (23a,b)$$

Obviously it holds

$$\bar{J}(t) = \begin{cases} L^{-1} \int_0^L J_s(x)\,\mathrm{d}x\,; & t > t_\infty \\ L^{-1} \int_0^{x_\infty(t)} J_s(x)\,\mathrm{d}x + [1 - x_\infty(t)/L]\, J_0(t)\,; & t < t_\infty \end{cases} \,. \tag{24a,b}$$

After performing the operations outlined in (*24a,b*) and further appropriate rearrangements, the final result is

$$\bar{J}(t) = \begin{cases} J_i(t)\left[1 + \dfrac{1}{1+p}\left(\dfrac{t}{t_\infty}\right)^{1+p/2}\right]; & t < t_\infty \\ \dfrac{2+p}{1+p}\, J_s(L)\,; & t > t_\infty \end{cases} \,, \tag{25a,b}$$

where $J_s(x)$ and $J_i(t)$ are defined in Eqs (*17*), (*19*). Because of the equality $J_i(t_\infty) = J_s(L)$, $\bar{J}(t)$ is continuous also at point $t = t_\infty$.

DISCUSSION

Relation (*25c*) can serve as a 3-parameter regression formula for a statistical processing of experimental data on the transient limiting diffusion currents from a potentiostatic experiment. The most suitable starting form of the regression formula for the data processing is represented by the following modification of (*25a*)

$$Y \equiv t^{1/2}\bar{J} = a(1 + bt^{2+p/2}) \tag{26}$$

with the parameters a, b, p. For a given liquid and an electrode, the parameter a can be determined from an independent experiment, *e.g.*, by measuring the transient $I - t$ characteristics in the unmoving liquid

$$a = \lim_{t\to 0} Y(t) = c_0(D/\pi)^{1/2}\,. \tag{27}$$

With known a, the parameters b, p can be found, *e.g.*, graphically or by the linear regression in the $\log(Y/a - 1)$ *vs* $\log(t)$ coordinates.

The internal consistency of the $Y - t$ data can be verified in several ways:

1) All experiments with a common liquid should yield the same value of the parameter a if the data are processed according to (*27*).

2) Formula (*26*) should approximate without any systematic deviations the $Y - t$ dependence in the whole transient phase of the process, *i.e.*, in the full range of relevant values of Y,

$$a < Y < \frac{2 + p}{1 + p}\, a\,, \tag{28}$$

3) Actual experimental values of the steady diffusion flux, $\bar{J}_\infty = \lim_{t \to \infty} \bar{J}(t)$ should agree with the extrapolation based on the investigation of the transient phase of the process,

$$\bar{J}_\infty = \frac{2 + p}{1 + p}\, a t_\infty^{-1/2} = \frac{2 + p}{1 + p}\, c_0 D^{1-q} \pi^{-1/2} (\beta A/L)^q \tag{29}$$

in which

$$t_\infty = [(1 + p)\, b]^{-2q} = D^{-pq} (L/\beta A)^{2q} \tag{30}$$

can be determined as the time coordinate of the intersection of curve $Y(t)$ and the straight line $Y = a(2 + p)/(1 + p)$.

It is worth noting that the value of limiting diffusion fluxes depends only on the velocity profile in the immediate vicinity of the electrode surface and that it is quite independent of the velocity field outside the concentration boundary layer. The instantaneous thickness of this layer, $\delta = \delta(t)$, can be estimated approximately from the relations

$$\delta \equiv D c_0 / J = \begin{cases} (\pi D t)^{1/2}\,; & t < t_\infty \\ (DL/A)^q\,; & t > t_\infty \end{cases}\,. \tag{31a,b}$$

For common values of electrode dimensions, liquid diffusivities and rates of flow transient times t_∞ vary from 0·1 to 10 s. This corresponds to the thickness of the steady concentration boundary layer of 10 – 100 μm. A first reliable determination of instantaneous values of $\bar{J}(t)$ can be expected only in the region of values of $\bar{J}$ not exceeding $10\bar{J}_\infty$. This corresponds to the thickness of the developing concentration boundary layer from the range 1 – 10 μm. We can see that the thicknesses of the concentration boundary layer are of the same order as estimated thickness (~10 μm) of the rheologically anomalous wall layer of microheterogeneous dispersions[2]. Thus we may expect that the method[8] proposed for the diagnostics of the apparent slip at the wall can also be used for a more detailed experimental investigation of the kinematics of the flow in the immediate vicinity of the wall.

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