TRANSIENT CONVECTIVE DIFFUSION TO A UNIFORMLY ACCESSIBLE SURFACE UNDER APPARENT SLIP CONDITIONS

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Analytical solutions are given to a class of unsteady one-dimensional convective-diffusion problems assuming power-law velocity profiles close to the transport-active surface.

The transient currents, observed after a step change of the polarization potential from the initial equilibrium state, provide rather complex information about the electrochemical system under study. The transient behaviour depends on a number of mechanisms, including the double-layer impedance, kinetics of the electrode reaction, migration, convective diffusion to the electrode surface, etc. There is, however, a narrow class of the electrochemical systems whose behaviour is controlled solely by the convective diffusion of a single species. These electrochemical systems (e.g. iodide-triiodide and ferro-ferricyanide) are extensively used[1-3] in the electrodiffusion diagnostics of flow, i.e. under the regime of limiting diffusion currents. The transient potentiostatic experiments in such systems allow ones to determine simultaneously several quantities[3], e.g. the depolarizer concentration (or diffusivity) and a flow parameter (wall shear rate, bulk velocity, etc.).

Recently, potentiostatic transient electrodiffusion measurements have been used to study the flow behaviour of various microdispersion liquids under viscometric flow conditions[4,5]. It has been found for these rheologically complex liquids that the velocity profiles inside the diffusion layer exhibit strong nonlinearity known in the rheology as the apparent slip[3] at the wall. It is highly probable that the same or analogous apparent slip phenomena occur under more complex flow conditions.

It is impossible to detect the apparent slip effects on a single electrode without analyzing transient electrodiffusion data on the base of a proper quantitative theory. Until now, the theory of transient convective diffusion including the apparent slip has been developed only for the unidirectional viscometric flows[6]. Due to the complexity of the theory of transient electrodiffusion processes for general three-dimensional flows, it is reasonable to begin with the simplest transport configurations.

We will limit ourselves in the present paper to developing the theory of transient convective diffusion for the uniformly accessible transport surfaces.

The notion of uniformly accessible mass-transfer configurations, as introduced by Levich[7] in connection with the rotating disk electrode, covers rather broad classes of convective electrodes with the use in electrodiffusion diagnostics of flow[2,3]. The forward fronts of the bodies in a bulk stream and the central parts of the obstacles exposed to an axisymmetric liquid jet are the typical examples of uniformly accessible surfaces[2,3].

THEORETICAL

Transport Equation for Uniformly Accessible Configurations

We call a mass-transfer configuration to be uniformly accessible, if the local diffusion fluxes are the same over the whole transport-active surface.

The uniform accessibility depends both on the mass-transfer conditions and the flow kinematics. The concentration boundary conditions must be uniform both in the bulk of the liquid, $c = c_0$, and on the transport-active surface, $c = c_W$. Under the condition of limiting diffusion currents, assumed exclusively in the electrodiffusion diagnostics of flow, it is $c_W = 0$.

Also the flow conditions must be homogeneous in a specific sense. Let us have the following orthogonal coordinate system (z, x, σ) inside a sufficiently thin diffusion layer[8]. The coordinate z measures the distance to the electrode surface and the coordinate x grows along the surface streamlines. The third coordinate σ is defined implicitly by the orthogonality condition. There are two necessary conditions for achieving the uniform accessibility: (i) The normal velocity component is independent of the coordinates (x, σ), i.e. $v_z = v_z(z)$. (ii) All the surface streamlines have their starting points inside the territory of the electrode surface.

Under these conditions, the x- and σ- components of the concentration gradient are zero and the transport equation can be written in the following simple form:

$$\partial_t c + v_z(z)\, \partial_z c = D \partial_{zz}^2 c \,. \tag{1}$$

The profiles of the longitudinal and normal velocity components are interrelated by the continuity equation

$$\mu \partial_z v_z + \partial_x(\mu v_x) = 0\,, \tag{2}$$

where μ stands for the Lamé metric coefficient of the given coordinate system, $dA = \mu\, d\sigma\, dx$. In particular, for the power-law profiles of the longitudinal velocity component,

$$v_x = b(x, \sigma)\, z^p\,, \tag{3}$$

the corresponding normal velocity component is given by

$$v_z = -a(x, \sigma)\, z^{1+p}\,, \tag{4}$$

where

$$a = -b\partial_x \ln(\mu b)/(1 + p)\,. \tag{5}$$

As a result, we see that the kinematical constraint $\partial_x a = 0$ is sufficient to fulfilling the necessary conditions of the uniform accessibility. The case $p = 1$ corresponds to the no-slip Newtonian flow. Other cases, $0 \leqq p < 1$, correspond to the apparent slip inside the diffusion layer. The theory of the transient convective diffusion for the case $p = 1$ is well-known[9-11]. The theory for the case of apparent slip is developed in the present paper.

The Normalized Boundary-Value Problem

By introducing the normalized variables,

$$C(Z, T) = 1 - c(z, t)/c_0\,,$$

$$Z = z\left[\frac{a}{(2 + p)\, D}\right]^{1/(2+p)}, \quad T = t\left[\frac{a^2 D^p}{(2 + p)^2}\right]^{1/(2+p)}, \tag{6}$$

the problem of the transient convective diffusion to a uniformly accessible surface obtains the following mathematical form:

$$\partial_T C - (2 + p)\, Z^{1+p} \partial_Z C = \partial_{ZZ}^2 C\,, \tag{7}$$

$$C \to 0\,; \quad \text{for} \quad T \to 0 \quad \text{and} \quad Z > 0\,,$$

$$C \to 0\,; \quad \text{for} \quad Z \to \infty\,, \tag{8a,b,c}$$

$$C = 1\,; \quad \text{for} \quad T > 0 \quad \text{and} \quad Z = 0\,.$$

The ultimate aim of solving the problem consists in an explicit expression for the mean diffusion fluxes (identical with the local ones in the case of uniformly accessible surfaces):

$$j(t) = \partial_z c|_{z=0} = c_0[D^{1+p} a/(2 + p)]^{1/(2+p)}\, M(T)\,, \tag{9}$$

where

$$M(T) = (-\partial_Z C|_{Z=0})\,. \tag{10}$$

The asymptotic courses of the function $M = M(T)$ are known from the analogy with other transient problems[3]:

$$M(T)\,T^{1/2} \approx \pi^{-1/2}\,, \quad \text{for} \quad T \to 0\,,$$

$$M(T) \approx 1/\Gamma\left(\frac{3+p}{2+p}\right), \quad \text{for} \quad T \to \infty\,.$$

For the application of the theory in data treating it is suitable to normalize the transient characteristic $j = j(t)$ in the way

$$N = j(t)/j(\infty)\,, \quad \Theta = t/t_0\,, \qquad (11a,b)$$

providing the asymptotic courses with the unity coefficients:

$$N(\Theta)\,\Theta^{1/2} \approx 1\,, \quad \text{for} \quad \Theta \to 0\,,$$

$$N(\Theta) \approx 1\,, \quad \text{for} \quad \Theta \to \infty\,. \qquad (12a,b)$$

This condition is fulfilled with the following definitions of the normalizing parameters

$$t_0 = \left[\frac{(2+p)^2}{a^2 D^p}\right]^{1/(2+p)} \Big/ B\,,$$

$$j(\infty) = \left[\frac{D^{1+p}a}{2+p}\right]^{1/(2+p)} \Big/ \Gamma\left(\frac{3+p}{2+p}\right), \qquad (13a,b)$$

where

$$B = \Theta/T = \pi/\Gamma^2\left(\frac{3+p}{2+p}\right). \qquad (14)$$

Asymptotic Expansion for Short Times

For the case $p = 1$, a formal solution to the problem can be easily found by applying Fourier transform and inverting the result term by term[9,11]. For the fractional values of p, this method becomes unacceptably awkward. We used therefore a direct semi-analytical method which results in a simple algorithm for the final numerical iteration. We start with the following representation:

$$C(Z, T) = \exp\left(-w^2/2\right) \sum_{n=0}^{\infty} T^{(1+p/2)n} F_n(w) / \int_0^\infty \exp\left(-s^2\right) \mathrm{d}s\,, \qquad (15)$$

$$w = Z T^{-1/2}/2\,,$$

which converges to the well-known Cottrell asymptote[3] for $T \to 0$:

$$C(Z, T) \to \int_w^\infty \exp(-s^2)\, ds / \int_0^\infty \exp(-s^2)\, ds\,. \qquad (16)$$

Substituting the representation (*15*) into the definition (*10*) of $M = M(T)$ and making use of the corresponding renormalization (*12*), we obtain the following expansion:

$$N(\Theta) \approx \Theta^{-1/2}\Big(1 + \sum_{n=1}^{\infty} \alpha_n \Theta^{(1+p/2)n}\Big)\,, \qquad (17)$$

where

$$\alpha_n = -F_n'(0)/B^{(1+p/2)n}\,. \qquad (18)$$

For calculating the coefficients α_n, we need to know the values $F_n'(0) = dF_n(w)/dw|_{w=0}$.

The substitution of the starting representation (*15*) into the boundary-value problem (*7, 8*) results in the recurrent system of ordinary differential equations for $F_n = F_n(w)$, $n = 1, 2, \ldots$:

$$F_n'' - [1 + w^2 + 2n(2+p)]\, F_n = 2(2+p)(2w)^{1+p}\,(wF_{n-1} - F_{n-1}') \qquad (19)$$

with the boundary conditions

$$F(0) = F(\infty) = 0\,, \qquad (20a,b)$$

and the generator $wF_0 - F_0' = \exp(-\frac{1}{2}w^2)$.
This system was solved numerically on a PC computer, by using the Runge–Kutta method. The unknown initial conditions $F_n'(0)$ were determined manually, by the trial and error searching in a dialogue regime.

Orthogonal Series for Finite Times

The formal series (*17*) with the zero radius of convergence are the asymptotic expansions only, which do not provide a complete solution to the problem. For larger times, $\Theta > 1$, it is necessary to introduce another representation of the field $C(Z, T)$. To this aim, Newman[11] suggested to find the solutions as a perturbation to the known steady solution $C_s(Z)$:

$$C_s(Z) = \int_Z^\infty \exp(-s^{2+p})\, ds \Big/ \Gamma\left[\frac{3+p}{2+p}\right]. \qquad (21)$$

We modify the original Newman's approach slightly, by introducing an exponential weighting function into the exponential series representation:

$$C(Z, T) = C_s(Z) + \exp(-\tfrac{1}{2}Z^{2+p}) \sum_{n=1}^{\infty} b_n G_n(Z) \exp(-k_n T) . \quad (22)$$

The corresponding representation of the normalized fluxes is

$$N(\Theta) = 1 + \sum_{n=1}^{\infty} \beta_n \exp(-\varkappa_n \Theta) , \quad (23)$$

where

$$\beta_n = b_n \Gamma\left[\frac{3+p}{2+p}\right], \quad \varkappa_n = k_n/B . \quad (24a,b)$$

The sets k_n, b_n can be determined by solving the corresponding eigenvalue problem for $n = 1, 2, \ldots$. In the first stage, the boundary-value problem

$$G_n'' - \left(1 + \frac{p}{2}\right) Z^p \left(1 + p + \left(1 + \frac{p}{2}\right) Z^{2+p}\right) G_n = -k_n G_n \quad (25)$$

with the extended boundary-value conditions,

$$G(0) = G(\infty) = 0 , \quad G'(0) = 1 \quad (26a,b,c)$$

is solved by adjusting iteratively the eigenvalues $0 < k_1 < k_2 < \ldots$. In the second stage, the orthogonality of the set of the eigenfunctions G_n, $\int_0^\infty G_m(Z) G_n(Z) \, dz = 0$, $m < n$, is used to determing the Fourier coefficients b_k:

$$b_k = - \int_0^\infty \exp(\tfrac{1}{2}Z^{2+p}) C_s(Z) G_n(Z) \, dZ / \int_0^\infty G_n^2(Z) \, dZ . \quad (27)$$

It should be noticed that this last equation follows from the initial condition (*8a*), written now in the form

$$0 = C_s(Z) + \exp(-\tfrac{1}{2}Z^{2+p}) \sum_{n=1}^{\infty} b_n G_n(Z) , \quad (28)$$

for the series representation of $C(Z, 0)$, see Eq. (*22*).

The technique of the numerical solving the problem for a few first eigenfunctions was the same as for the short-time expansion, referred to in the preceding paragraph. The quadratures in Eq. (*27*) was evaluated by integrating the corresponding first-order differential equations simultaneously with integrating the differential equations which define the functions C_s and G_n.

RESULTS

The course of diffusion fluxes is represented in the normalized form $N(\Theta) = j(t)/j(\infty)$, $\Theta = t/t_0$, see Eqs (*11, 13*). This solution to the transient problem under consideration is represented here by the power-law series for the short-times,

$$N(\Theta) = \Theta^{-1/2}\left(1 + \sum_{n=1}^{4} \alpha_n \Theta^{(1+p/2)n}\right), \quad \Theta > \Theta_c, \tag{29a}$$

and by the exponential series for the long times:

$$N(\Theta) = 1 + \sum_{n=1}^{3} \beta_n \exp\left(-\varkappa_n \Theta\right), \quad \Theta > \Theta_c. \tag{29b}$$

The constants α_n for $n = 1 \div 4$, and $(\beta_n, \varkappa_n)$ for $n = 1 \div 3$ are given in Tables I and II for several values of the parameter p which represents a power-law non-linearity of the velocity profiles under apparent-slip conditions, see Eqs (*3, 4*). The optimum bounds Θ_c, giving the regions where the alternative representations (*29a,b*) should be used, were found for different p by a numerical experiment and are included in Table I.

It has been found during these calculations that the four terms in the short-time expansion (*29a*), and the three terms in the exponential series (*29b*) provide the resulting $N(\Theta)$ with the accuracy $\pm 0{\cdot}1\%$. The check procedure consisted in *a*) calculating 10 terms in the both series for all the values of p under consideration, *b*) in comparing the new data on $N(\Theta)$ for $p = 1$ with the older ones[10,11] and *c*) in comparing the new data on $N(\Theta)$ for $p = 0$ with the exact analytical result.

$$N(\Theta) = \left[1 - \exp\left(-\Theta\right)\right]^{1/2}. \tag{30}$$

A family of the normalized transient curves $N = N(\Theta; p)$ for $0 \leqq p \leqq 1$ is shown in Fig. 1.

DISCUSSION

The data treating can be based on the following three-parametric form of the theoretical prediction[3,6]:

$$j(t) = j(\infty)\, N(t/t_0; p). \tag{31}$$

In the log (j) vs log (t) graph, the variation of $j(\infty)$ or t_0 corresponds to horizontal or vertical shifts, respectively, while p acts as a form parameter. The family of $N = N(\Theta; p)$ curves in log–log coordinates is shown in Fig. 1. Taking into consideration our previous experience[4–6,12] in treating the transient data for "difficult" liquids, we believe that the difference $\Delta p = 1/6$ will be well detectable for the 12-bit transient data provided that a harmonical background is well filtered out.

TABLE I

Coefficients in the short-time series, Eq. (*17*)

p	α_1	α_2	α_3	α_4	Θ_c
1·0000	0·169995	0·002453	−0·002932	−0·000024	0·84
0·8333	0·178826	0·003040	−0·002755	−0·000027	0·90
0·6667	0·189034	0·003804	−0·002633	−0·000034	0·98
0·5000	0·200875	0·004807	−0·002560	−0·000043	1·08
0·3333	0·214678	0·006144	−0·002533	−0·000055	1·22
0·1667	0·230868	0·007947	−0·002549	−0·000072	1·40
0·0000	0·250000	0·010417	−0·002604	−0·000098	1·64

TABLE II

Coefficients in the long-time series, Eq. (*24*)

p	$\varkappa_1$	β_1	$\varkappa_2$	βa	$\varkappa_3$	β_3
1·0000	1·8317	1·0074	4·6094	0·8082	7·9184	0·7061
0·8333	1·7187	0·9342	4·2036	0·7459	7·1050	0·6479
0·6667	1·5954	0·8560	3·7818	0·6793	6·2769	0·5864
0·5000	1·4616	0·7730	3·3461	0·6083	5·4411	0·5216
0·3333	1·3173	0·6856	2·9000	0·5333	4·6074	0·4538
0·1667	1·1630	0·5943	2·4488	0·4552	3·7883	0·3837
0·0000	1·0000	0·5000	2·0000	0·3750	3·0000	0·3125

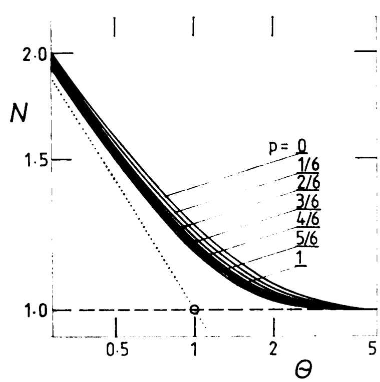

FIG. 1

Transient curves in log–log coordinates. Solid lines: exact courses with the labels giving the p-values; dashed line: steady asymptote, $N = 1$; dotted line: Cottrell asymptote, $N = \Theta^{-1/2}$

When the p-value is known, it is the good practice[6] to treat the transient data in the coordinates $jt^{1/2}$ vs $t^{1+p/2}$. The main reason for doing it is the linear course of the data in these coordinates for $\Theta \ll 1$, which makes it easy to develop an extrapolation procedure of determining the Cottrell coefficient from its definition[3]

$$c_0(D/\pi)^{1/2} = j(\infty)\, t_0^{1/2} = \lim_{t \to 0} (jt^{1/2}) \,. \tag{32}$$

Two examples of the master curves in the linearized coordinates are given in Figs 2, 3 for the cases $p = 1$ and $p = 0$, respectively. These figures demonstrate well that the transient curves for different values of p can be safely distinguished when treated properly.

CONCLUSIONS

It has been shown that certain types of convective electrodes can be uniformly accessible even when used for the microdispersion liquids which exhibit apparent slip at walls.

The theory of the transient process has been developed in which the apparent slip is represented by the power-law velocity profiles with the exponent p, different from unity. The presented final form of the theory allows ones to determine the three parameters of the process – the depolarizer diffusivity D and the parameters a, p of the normal velocity profile.

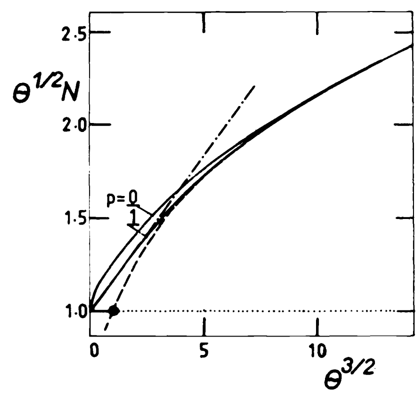

FIG. 2

Transient curves in linearizing coordinates for $p = 1$. The meaning of solid, dotted, and dashed lines is the same as in Fig. 1; dot-and--dashed line corresponds to the formula $N\Theta^{1/2} = 1 + \alpha_1 \Theta^{1+p/2}$

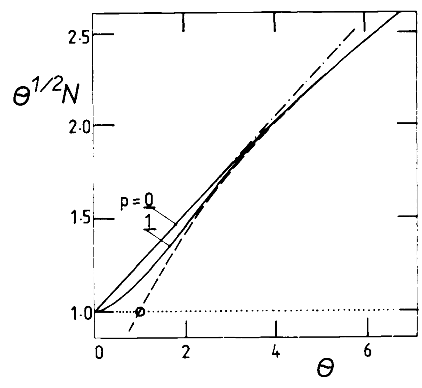

FIG. 3

Transient curves in linearizing coordinates for $p = 0$. The meaning of individual lines is the same as in Fig. 2

SYMBOLS

a, b	coefficients in the representations (*3*), (*4*) of flow field
b_n	Fourier coefficients to the problem (*7*), (*8*), see Eq. (*22*)
B	conversion factor between T and Θ, see Eq. (*14*)
c	field of depolarizer concentration
c_0	initial value of c
D	constant depolarizer diffusivity
F_n, G_n	eigenfunctions
j	density of diffusion flux
$j(\infty)$	steady value of j for $t \to \infty$, Eq. (*13b*)
k_n	eigenvalues to the problem given by Eqs (*25*), (*26*)
$M(T)$	normalized transient fluxes, Eqs (*9*), (*10*)
$N(\Theta)$	transient fluxes in practical normalization, Eqs (*12*)
p	form-factor of velocity profiles, see Eqs (*3*), (*4*)
t	time
t_0	transient half-time, Eq. (*13a*)
T	normalized time, Eq. (*6*)
v_x, v_z	longitudinal and normal velocity components
x, z, σ	geometrical coordinates
α_n, β_n, $\varkappa_n$	coefficients in resulting series (*29a,b*), see Tables I, II
Θ	normalized time, Eqs (*11b*), (*14*)
Θ_c	optimal bounds between alternative representations of $N(\Theta)$

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