TRANSIENT CONVECTIVE DIFFUSION FOR THE HYDRODYNAMIC REAR STAGNANT REGION, WITH AN APPLICATION IN ELECTROCHEMISTRY

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Time dependence of mean current densities after the step change in concentration of depolarizer on the surface of convective electrode under conditions of limiting diffusion currents for the axially symmetrical configuration of the rear critical region is approximately determined by a new type of the similarity integral method.

Studies of the transient electrochemical process under potentiostatic conditions and in the regime of limiting diffusion currents in the region of operating electrode open some interesting possibilities in hydrodynamic and convective mass transfer studies in electrolytic systems. By this experimental technique, at the known longitudinal dependence of velocity gradient at the wall of the convective electrode, it is possible to determine diffusivity of the depolarizer simultaneously at two considerably different transport regimes. The penetration regime for $t \rightarrow 0$ differs from the steady regime for $t \rightarrow \infty$ by current densities higher by orders of magnitude and by independence of local current densities both on flow kinematics and position (so-called conditions of uniform accessibility of the electrode surface). At the known velocity gradient on the wall of the electrode it is possible, by the analysis of the transient current characteristics, to determine simultaneously the velocity gradients and diffusivity of the depolarizer. This last possibility is significant *e.g.* in electrochemical studies of flow of polymer solutions as the polymer content affects both diffusivities and viscoelastic flow properties.

In this study the approximative theory of potentiostatic transient process is constructed in the rear critical flow region. The considered axially symmetric configuration is demonstrated in Fig. 1. Among the realisation of this kinematics belongs *e.g.* the Bödewadts flow (liquid rotation above the stationary wall)[1,2] and the rear region of bodies in the creeping flow[3]. A similar flow character can be met also in creeping rotation of the spindles in viscoelastic liquids as elastic normal stresses cause strong centripetal flow[4,5]. In studies[1-3] is solved the problem of steady mass transfer in the rear critical region. The corresponding transient problem has not yet been solved.

THEORETICAL

Formulation of the Problem

Mathematical model of the process is considered in the usual approximation of the transport boundary layer, *i.e.* with neglection of the streamwise diffusion, for which there holds

$$0 = D\,\partial^2_{zz}c - v_z\,\partial_z c - v_r\,\partial_r c - \partial_t c\,, \tag{1}$$

and with the linear description of the velocity profile $v_r(z)$ at the wall of the electrode in the form

$$v_r = -Azr\,,\quad v_z = Az^2\,. \tag{2a, b}$$

Under limiting current conditions the transient potentiostatic experiment is characterised by concentration boundary conditions of the first kind

$$c \to c_0 \quad \text{for} \quad t \to 0 \quad \text{or} \quad r \to R \quad \text{or} \quad z \to \infty \tag{3a, b, c}$$

$$c = 0 \quad \text{for} \quad t > 0 \quad \text{and} \quad r < R \quad \text{and} \quad z = 0\,. \tag{4}$$

As the solution of the problem is considered the time dependence of local and current densities, for which there holds

$$I(r, t) = F_v D(-\partial_z C|_{z=0})\,, \tag{5}$$

$$\bar{I}(t) = (\pi R^2)^{-1} \int_0^R I(r, t)\, 2\pi r\, dr\,. \tag{6}$$

In the normalised variables the problem has the form

$$0 = \mathscr{R}[C] \equiv \partial^2_{ZZ}C - Z(Z\,\partial_Z C + X\,\partial_X C) - \partial_T C \tag{7}$$

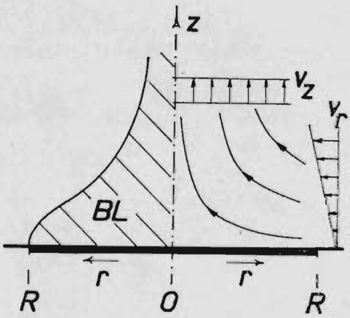

FIG. 1

Concentration boundary layer in the rear critical region; v_z, v_r axial and radial velocity component, BL region of boundary layer, $\eta \leqq 1$

$$C \to 0 \quad \text{for} \quad T \to 0 \quad \text{or} \quad X \to 1 \quad \text{or} \quad Z \to \infty \tag{8}$$

$$C = 1 \quad \text{or} \quad T > 0 \quad \text{and} \quad X > 1 \quad \text{and} \quad Z = 0 \tag{9}$$

with the two familiar asymptotic solutions for $T \to 0$ and $T \to \infty$, as follows.

Penetration asymptote for $T \to 0$ corresponds to the planary propagation of the concentration impulse at preserved condition of uniform accessibility of the electrode surface, $\partial_X C = 0$, for which can be written

$$C = C_P(\zeta) = g(\zeta)/g(0)\,, \quad \zeta = ZT^{-1/2} \tag{10}$$

$$g(\zeta) = \int_{\zeta^2/4}^{\infty} \exp(-s)\, s^{-1/2}\, ds\,. \tag{11}$$

The local mean current densities according to the penetration asymptote are, with regard to the condition of uniform accesibility, equal *i.e.*

$$\bar{I}_P(r, t) = \bar{I}_P(t) = F_v c_0 D^{1/2} (\pi t)^{-1/2}\,. \tag{12}$$

Steady asymptote for $T \to \infty$ when $\partial_T C = 0$, has been obtained by use of the Lighthill's transformation constructed by Newman[2] in the form

$$C = C_S(\eta) = f(\eta)/f(0)\,, \quad \eta = Z(X^3 - 1)^{-1/3} \tag{13}$$

$$f(\eta) = 3^{-2/3} \int_{\eta^3/3}^{\infty} \exp(-s)\, s^{-2/3}\, ds\,. \tag{14}$$

The corresponding current densities are given by relations

$$\bar{I}_S = F_v c_0 D^{2/3} A^{1/3} / f(0) \tag{15}$$

$$I_S(r) = \bar{I}_S (X^3 - 1)^{-1/3}\,. \tag{16}$$

In analogous transient problems for kinematics of the front critical region[6,7], kinematics of the shear flow[8,9] or kinematics of the hydrodynamic boundary layer[10] it is possible to find similarity transformations which decrease the number of independent variables to two. In the given case such transformation has not been found. Thus here we will content with the approximative solution of the given three-dimensional problem by the typical technique of the boundary layer theory.

Similarity Approximation

The usual integral methods in the theory of unsteady concentration boundary layer[11,12] operate with polynomial concentration profiles and with the macroscopic balance of the transported component. Resulting approximative estimates of transient characteristics $\bar{I}(t)$ differ from the familiar exact solutions[6-10] by up to 10%. In the following part of this study is given the modification of the integral similarity approximation analogous to that which has been constructed by Ruckenstein[13] in solution of unsteady absorption problems. Two degrees of freedom, which are manifested by possibility to select the similarity concentration profile and weighted integral residuum, are optimised so that asymptotes of transient characteristics $I(r, t)$ according to the approximative solution are identical with the exact asymptotes according to Eqs (*12*) and (*16*).

The concentration field is superimposed in the form

$$C(Z, X, T) \approx C_S(\xi)\,, \quad \xi = Za(X, T) \tag{17}$$

where $a(X, T)$ is the normalised reciprocal value of the momentous local thickness of the concentration boundary layer. For $T \to 0$ or $X \to 1$ the local current densities become infinite. It is thus required, that

$$a(X, T) \to \infty \quad \text{for} \quad T \to 0 \quad \text{or} \quad X \to 1\,. \tag{18}$$

The complete dependence of $a(X, T)$ is determined by the method of the weighted integral residua so that it is requested that

$$0 = \int_0^\infty \mathscr{R}\,[\mathrm{C}]\;\Phi(Z, X, T)\,\mathrm{d}Z\,, \tag{19}$$

where the local residua $\mathscr{R}[\mathrm{C}]$ defined by Eq. (7) are identically equal to zero on the whole region (Z, X, T) only for exact solution C. When into Eq. (*19*) the approximation of the field C is substituted according to Eq. (*17*) and for the not yet defined weight function Φ is assumed that there holds $\Phi = \Phi(\xi)$, the nonlinear partial differential first order equation for the field $a(X, T)$ is obtained

$$0 = a^4 + a + X\,\partial_X a + 2ba\,\partial_T a\,. \tag{20}$$

On the choice of the weight function depends only the value of coefficient b. In the case $\Phi = \Phi(\xi)$ b is a constant, so that there holds

$$b = \int_0^\infty \xi f'(\xi)\,\Phi(\xi)\,\mathrm{d}\xi \Big/ \int_0^\infty 2\xi^2 f'(\xi)\,\Phi(\xi)\,\mathrm{d}\xi\,. \tag{21}$$

At a fixed choice of b the field $a(X, T)$ is fully determined by the boundary problem according to Eqs (*18*) and (*20*).

It is possible to see that Eq. (*20*) has two particulate solutions each of which depends only one of the variables X and T.

The time independent solution which can be written

$$a_\infty(X) = (X^3 - 1)^{-1/3} \tag{22}$$

leads to the exact steady asymptote according to Eqs (*13*)–(*16*), independent of the coefficient b.

The coefficient b only corrects the scale of the newly normalised time variable for which it is suitable to introduce an independent symbol

$$\Theta = T/b\,. \tag{23}$$

The second, on axial geometric coordinate X independent particular solution, limited according to Eqs (*20*) and (*23*) by the differential equation $a^4 + a + 2a\,\partial_\Theta a = 0$ with the condition $a \to \infty$ for $\Theta \to 0$, can be expressed implicitely in the form

$$\Theta = \Theta(a_0) = 2\int_{a_0}^{\infty}(1 + s^3)^{-1}\,\mathrm{d}s\,, \tag{24}$$

or by the corresponding series on the definition region $\Theta(0;\,\Theta_0)$ for which there holds

$$a_0(\Theta) = \begin{cases}\Theta^{-1/2} - \frac{1}{5}\Theta - \frac{3}{200}\Theta^{5/2}\,; & \Theta \to 0\,,\\ \frac{1}{2}(\Theta - \Theta_0) + \frac{1}{64}(\Theta - \Theta_0)^4 + \frac{1}{3584}(\Theta - \Theta_0)^7\,; & \Theta \to \Theta_0\,,\end{cases} \tag{25a, b}$$

where

$$\Theta_0 = 2\int_0^{\infty}(1 + s^3)^{-1}\,\mathrm{d}s = 4\,3^{-3/2}\,\pi\,. \tag{26}$$

At the choice

$$b = b_0 = [f(0)/g(0)]^2 \tag{27}$$

the particular solution $a_0(\Theta)$ for $T \to 0$ or $\Theta \to 0$ leads to expression of the momentous current densities which are identical with the exact asymptote according to Eq. (*12*).

On basis of the given particular solutions a_0, a_∞ it is possible to construct completely continuous, piecewise smooth solution of the boundary problem according to

Eqs (*18*) and (*20*)

$$a(X, T) = \begin{cases} a_0(\Theta) & \text{for} \quad X \geqq X_c(\Theta) \\ a_\infty(X) & \text{for} \quad 1 < X \leqq X_c(\Theta) \end{cases} \tag{28}$$

The critical front $X_c = X_c(\Theta)$ of the transition of the unsteady particular solution a_0 into the steady one a_∞, is defined by requirement of the continuity of the field $a(X, T)$

$$a_\infty(X_c) = a_0(\Theta) = a_c\,. \tag{29}$$

Analytical description of the function $X_c(\Theta)$ then results from Eqs (*22*), (*24*) and (*28*) in the form

$$\Theta = 2 \int_{(X_c^3 - 1)^{-1/3}}^{\infty} (1 + s^3)^{-1}\, ds\,. \tag{30}$$

This function is plotted in Fig. 2.

So constructed solution obviously corresponds to the coexistence of both asymptotic regimes below the surface of the electrode. At the periphery of the electrode a steady regime is reached immediately after the step change in the surface concentration which spreads toward the centre of the electrode. In the internal region an unsteady regime exists in which are – similarly as in the case of the rotating disc electrode[6,7] – preserved the conditions of uniform accessibility of the electrode beyond the region of validity of the own penetration asymptote. The time for reaching the steady regime on the whole electrode is finite and according to Eqs (*25*) to (*27*) is given by the value

$$t_S = b_0 \Theta_0 D^{-1/3} A^{-2/3} = 1{\cdot}277 D^{-1/3} A^{-2/3}\,. \tag{31}$$

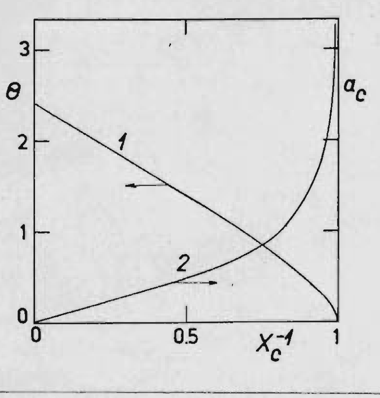

FIG. 2

Characteristics of the critical front. *1* Motion of critical front, $(r/R)\,\text{crit} = X_c^{-1}$; *2* growth of critical thickness of the boundary layer, $\delta_{\text{crit}} = (A/D)^{1/3}\, a_c^{-1}$

Transient Characteristics

The final looked for result is the transient characteristics of the electrode under the given convective conditions, *i.e.* the time dependence of mean current densities. From the corresponding definition relations results

$$\bar{N} = \bar{I}(t)/\bar{I}(\infty) = 2\int_0^\infty a(X, T)\, X^{-3}\, \mathrm{d}X\,. \tag{32}$$

The piecewise smooth solution according to Eq. (*28*) leads to the following representation of the normalised transient characteristics

$$\bar{N}(\Theta) = \int_1^{X_c} a_\infty(X)\, 2X^{-3}\, \mathrm{d}X + \int_{X_c}^\infty a_0\, 2X^{-3}\, \mathrm{d}X =$$

$$= (1 - X_c^{-3})^{2/3} + a_0 X_c^{-2} = (1 + a_0^3)^{1/3}\,, \tag{33}$$

where a_0 and X_c are known functions of time which are according to Eqs (*24*) and (*30*) related by the relation

$$a_0 = (X_c^3 - 1)^{-1/3}\,. \tag{34}$$

After elementary arrangements of Eqs (*25a, b*) it is possible to obtain the next representation

$$\bar{N}(\Theta) = \begin{cases} \Theta^{-1/2}(1 + \frac{2}{15}\,\Theta^{3/2} + \frac{13}{1800}\Theta^3)\,, & \text{for} \quad \Theta \leqq 1{\cdot}2 \\ 1 + \frac{1}{24}(\Theta_0 - \Theta)^3 + \frac{5}{2304}(\Theta_0 - \Theta)^6\,, & \text{for} \quad \Theta \in (1{\cdot}2;\, \Theta_0) \\ 1\,, & \text{for} \quad \Theta \geqq \Theta_0 \end{cases} \tag{35}$$

The polynomials given in Eq. (*35*) guarantee the accuracy of the expression $\bar{N}(\Theta)$ better than 0·2% as compared with the primary parametric representation according to Eqs (*24*) and (*30*).

DISCUSSION AND CONCLUSIONS

As the demonstrated technique of approximate solution of unsteady problems of the theory of concentration boundary layer is applicable in any type of steady flow around the convective electrode, the problem of applicability of the final relation for $\bar{I}(t)$ at description of the real potentiostatic experiment is considered here more thoroughly.

It is suitable to divide the theoretical prediction of $\bar{I}(t)$ into two parts. The first one concerns the *shape* of the transient characteristics, expressed by the normalised function $\bar{N}(\Theta)$. The second one concerns the *values* of normalisation parameters $\bar{I}_\infty$ and t_0 in definition relations

$$\bar{N} = \bar{I}(t)/\bar{I}_\infty\,, \quad \Theta = t/t_0\,. \tag{36}$$

The best theoretical estimate $\bar{I}_\infty = \bar{I}(\infty)$ results from the solution of the corresponding steady electrochemical problem. $\bar{I}_S$ is its approximation according to the theory of concentration boundary layer. The value t_0 results from the corresponding initial penetration asymptote, being de facto defined as the time coordinate of the intercept of the penetration and steady asymptote

$$\bar{I}_\infty t_0^{1/2} = \lim_{t\to 0} \bar{I}(t)\, t^{1/2} = F_v c_0 (D/\pi)^{1/2}\,. \tag{37}$$

The parameter t_R is then the approximation t_0 according to the theory of concentration boundary layer, *i.e.* for $\bar{I}_\infty = \bar{I}_S$.

The extent of deviations of the theoretical prediction of transient characteristics according to Eqs (*24*) and (*30*) or (*35*) and its measured dependence at an actual transient electrochemical experiment depends on the following groups of circumstances: *a*) accuracy of solution of equations of the concentration boundary layer, *b*) adequate simplifying assumptions of the theory of concentration boundary layer[1,2] (neglected axial diffusion, linearisation of velocity profiles), *c*) side effects of convective diffusion[17,18] (free convection, geometric nonideality of walls in the region of convective electrode, concentration dependence of diffusivity), *d*) electrochemical side effects[14,16] (kinetics of the electrode process, quality of the electrode surface, capacity of the double layer, migration of ions, transient impedance of the auxiliary electrode) *e*) quality of control and record of the process (stability of the potentiostate, distortion of the signal during recording, accuracy of adjustment and stability of hydrodynamic conditions, temperature *etc.*).

Accuracy of the approximate solution can be judged only when there is simultaneously at the disposal accurate solution of the transient problem. For the kinematics of the front critical region the approximately determined[12,19] $\bar{N}(\Theta)$ differs from the accurate solution of equations of the concentration boundary layer[6,7] by less than 1·5% in the values $\bar{N}$. For the kinematics of shear flow when there exist two equivalent exact solutions[8,9,20] is the approximately determined $\bar{N}(\Theta)$ identical with one of exact solutions and from the second one it differs by less than 0·5%. For the kinematics of the rear critical region the exact solution in the frame of the theory of concentration boundary layer is not known. The character of flow in the decisive front region as well as the dependence of $\bar{N}(\Theta)$ according to Eq. (*35*) is for this case very close to the situation for kinematics of shear flow (Fig. 3). It is thus possible to expect that the approximate solution according to Eq. (*35*) is affected by an error smaller than 1%.

Within the theory of complete convective diffusion there seems probable that the main source of inaccuracies are simplification of the theory of boundary layer according to *b*) and the convective side-effects according to *c*). As these effects are the more expressive the greater is the Nernst's thickness of the concentration boundary layer their effect will be most profound in the steady regime while the start of the transition can be satisfactorily described by the penetration asymptote.

The magnitude of interfering effects of the electrochemical nature according to *d*) and of the apparature according to *e*) can be quite different in individual cases which could differ in values of transient half-life periode t_0 even by several orders of magnitude. In general it is possible to say that in the case of the resulting steady limiting diffusion currents these interfering effects are concentrated in the initial transient phase of the experiment.

At the data processing it is possible to avoid the distortion of final results in the following way: *1*) to eliminate the initial data with too high current densities which, at the corresponding steady state (*e.g.* at higher values of kinematic parameter A), are situated beyond the region of limiting diffusion currents, *2*) to eliminate the effect of additional transient impedances and retardation in the records by introduction of an additional empirical parameter – time lag t_E in the definition of the normalised time variable, given by

$$\Theta = (t - t_E)/t_0 \qquad (38)$$

3) to include the effect of convective side effects into the theory of steady process, *i.e.* into the theoretical expression of the value I_∞.

In the case when, according to assumptions of the concentration boundary layer theory for the regime of limiting diffusion currents, there hold $\bar{I}_\infty = \bar{I}_S$, $t_0 = t_R$ it is possible, without regard to the resulting values t_E, to transfer the results of regression

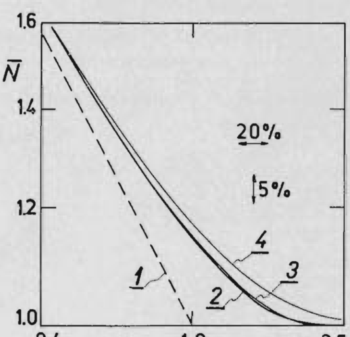

FIG. 3

Transient characteristics. *1* Penetration asymptote, *2* dependence for the rear critical region, Eq. (*36*), *3* exact dependence for the shear flow[20], $\bar{N} = \Theta^{-1/2} + (4/27)\,\Theta$, *4* exact dependence for the front critical region[6,7] data evaluation to data on kinematic parameter A and diffusivity of the depolarizer D, according to relations

$$A = 0{\cdot}216 F_v c_0 t_0^{-2} \bar{I}_\infty^{-1} \quad (39)$$

and

$$D = 3{\cdot}14 \bar{I}_\infty^2 t_0 / (F_v c_0)^2 \,. \quad (40)$$

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LIST OF SYMBOLS

a reciprocal normalised thickness of the concentration boundary layer
a_0, a_∞ particular solutions of Eq. (*20*)
A kinematic parameter according to Eqs (*2a,b*)
b, b_0 adjustable parameter of integral balance (*21*), its optimised value according to Eq. (*27*)
c concentration of depolarizer
c_0 initial concentration
$C = (c_0 - c)/c_0$
C_P, C_S asymptotic concentration field for $t \to 0$, and $t \to \infty$
D diffusivity of depolarizer
F_v charge exchanged by 1 kmol of depolarizer
$f(\eta), g(\zeta)$ asymptotic solution of transient problem
$f(0) = 1{\cdot}28790$
$g(0) = 1{\cdot}77245$
$I(r, t)$ local momentous current densities
$\bar{I}(t)$ momentous mean current densities
$\bar{I}_\infty, \bar{I}_S$ steady mean current density and its value according to the boundary layer theory, Eq. (*15*)
$N = I(r, t)/I(r, \infty)$
$\bar{N} = \bar{I}(t)/\bar{I}_\infty$
r radial coordinate
R radius of disc electrode
$\mathscr{R}[C]$ momentous local residuum according to Eq. (*7*)
t_0 half-life period of transient process according to Eq. (*37*)
t_S finite time of steadying
$t_R = 0{\cdot}528 D^{-1/3} A^{-2/3}$ half-life period of transient process according to Eqs (*15*) and (*37*)
t time
$T = D^{1/3} A^{2/3} t$
$X = R/r$
z axial coordinate
$Z = A^{1/3} S^{-1/3} z$
$\zeta = Z T^{-1/2}$
$\xi = aZ$
$\eta = Z X^{-1/3}$
$\Theta = T/b_0$
$\Theta_0 = 2{\cdot}4148$

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