ON THE TRANSIENT LEVEQUE'S PROBLEM WITH AN APPLICATION IN ELECTROCHEMISTRY

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The electrochemically induced unsteady mass transfer to a uniform shear flow from a local wall electrode subjected to a step change in electrochemical potential is studied. Due to neglecting the streamwise diffusion, the problem has two solutions which however differ only insignificantly. The resulting transient characteristics of current densities have a simple analytical form suitable for an efficient data treatment.

Electrochemical measurement of mass transfer rates by the limiting-current technique offers number of possibilities for experimental studies on convective diffusion[1] and flow kinematics[2] in vicinity of a polarized electrode. Under the supposed regime of limiting diffusion currents the mathematical description of transport processes is reduced to the familiar model of convective diffusion with the fixed concentrations on boundaries of the system[3]. Numerous steady and transient problems of this type have been solved in relation to the convective heat transfer.

Majority of these studies is related to the approximative theory of transport boundary layer *i.e.* to the asymptotics $Pe \to \infty$ when the effect of streamwise diffusion can be neglected. It is well known that the boundary layer approximation only exceptionally describes adequately the heat transfer process. In addition to a strong thermal dependence of transport properties and relatively low Peclet and Prandtl numbers, at comparison of theoretical and experimental results, there appears the disturbing effect of heat conduction through the walls and-with unsteady processes-thermal capacity of walls. Perhaps this was the reason why accuracy of approximations of some theoretical studies[4] is only about 10%, while in others[5,6] the results are obtained in the form which prevents direct comparison with the experimental data.

Considerably favourable is the situation as concerns the relation of the linear theory of transport boundary layer to electrochemical experiments performed in the regime of limiting diffusion currents. With regard to very low diffusivity in liquids the Prandtl and Peclet numbers are sufficiently high so that the effect of axial diffusion is negligible. Negligibility of the other electrochemical side effects (migration of ions of the depolarizer, finite rate of electrode reaction. resistances in the external electrical circuit) is just typical of the regime of limiting diffusion currents. If we take into account that the high, better than 1%, accuracy of the electrochemical measurement of the instantaneous mass transfer rates, the present interest in accurate solutions of linear problems of the transport boundary layer becomes understandable.

THEORETICAL

Accurate solution of the transient Leveque's problem is considered especially determination of time dependence of the mean current density on the electrode after a step change of concentration of the depolarizer on its surface. Configuration of the process is demonstrated in Fig. 1, whose normalised mathematical model in the boundary-layer approximation is given by the following boundary problem for $C(Z, X, T)$

$$\partial^2_{ZZ}C - Z\,\partial_X C - \partial_T C = 0 \quad (1)$$

$$C \to 0 \quad \text{for} \quad T \to 0, X > 0, \ Z > 0 \quad (2a)$$

$$C \to 0 \quad \text{for} \quad T > 0, \ X \to 0, Z > 0 \quad (2b)$$

$$C \to 0 \quad \text{for} \quad T > 0, \ X > 0, Z \to \infty \quad (2c)$$

$$C = 1 \quad \text{for} \quad T > 0. \ X > 0, Z = 0 \,. \quad (3)$$

In equations (*2a*, *b*, *c*) it is necessary to understand the relations $T > 0$, $X > 0$, $Z > 0$ so that is is possible to choose at the mentioned limiting process for T, X, Z an arbitrary, but fixed positive value.

By introduction of the similarity variables η, τ it is possible to formulate the problem alternatively with two independent variables

$$\partial^2_{\eta\eta}C + \tfrac{1}{3}\eta^2\,\partial_\eta C - (1 - \tfrac{2}{3}\eta\tau)\,\partial_\tau C = 0 \quad (4)$$

$$C \to 0 \quad \text{for} \quad \tau \to 0, \ \eta > 0 \quad (5a)$$

$$C \to 0 \quad \text{for} \quad \tau \to \infty, \ \eta\tau^{-1/2} > 0 \quad (5b)$$

$$C \to 0 \quad \text{for} \quad \tau > 0, \ \eta \to \infty \quad (5c)$$

$$C = 1 \quad \text{for} \quad \tau > 0, \ \eta = 0 \,. \quad (6)$$

To the limiting formulation (*5a*, *b*, *c*) there hold the same remarks as at formulations (*2a*, *b*, *c*).

The problem given by Eqs (*1*), (*2a*, *b*, *c*), (*3*) has been in principle already solved analytically[5,6]. Two aspects, which deserve the attention are considered here: *1*) in analytical studies[5,6] the transient characteristics for the total fluxes are not given, although these are only interesting from the experimental point of view, *2*) the boundary value problem according to (*1*), (*2a*, *b*, *c*), (*3*) does not have a single one but at least two different solutions.

Duplicity of solution is worth notice with regard to the fact that the automodel boundary problems of analogous type[4,7] were until now considered as corectly formulated with a single solution. From the practical point of view it is significant to decide which of both solutions has the assumed physical significance and to bring the formal solution into the form of a simply generable regression function expressing the time dependence of mean current densities.

Singular Solution

The boundary problems (*1*)–(*3*) have two asymptotic solutions. The first one for which identically $\partial_X C = 0$ represents the familiar penetration asymptote according to Higbie, for $T \rightarrow 0$. The second one for which identically $\partial_T C = 0$ represents the familiar steady asymptote according to Leveque, for $T \rightarrow \infty$. Both these asymptotes have a simple analytical solution expressed in the automodel variables η, τ.

The penetration asymptote is the solution of the automodel problem (*4*)–(*6*) for $\tau \rightarrow 0$, where Eq. (*4*) is reduced to the form $\partial^2_{\eta\eta} C - \partial_\tau C = 0$, with the familiar results

$$C = C_P(\eta, \tau) = g(\eta\tau^{-1/2})/g_0 , \tag{7}$$

where

$$g(\zeta) = \int_{\zeta^2/4}^{\infty} \exp(-s)\, s^{-1/2}\, ds . \tag{8}$$

The steady asymptote is the solution of the problem (*4*)–(*6*) for $\tau \rightarrow \infty$, $\partial_\tau C = 0$, $\partial^2_{\eta\eta} C + \frac{1}{3}\eta^2\, \partial_\eta C = 0$, with the familiar result

$$C = C_S(\eta, \tau) = f(\eta)/f_0 \tag{9}$$

where

$$f(\eta) = 3^{-1/3} \int_{\eta^3/9}^{\infty} \exp(-s)\, s^{-2/3}\, ds . \tag{10}$$

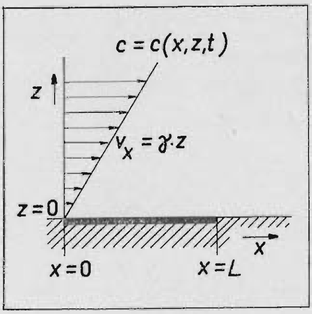

FIG. 1
Configuration of the Leveque's problem

These two simple automodel expressions represent the asymptotic solutions of all linear transient problems of the transport boundary layer theory. The speciality of the transient Leveque's problem is, in the literature so far unsubstantiated fact, that these asymptotic solutions exactly satisfy the complete differential equation (*1*) of this problem. As these two asymptotic solutions also fit all the boundary conditions (*2a, b, c*), (*3*) in the required sense, it is possible to formulate on their basis the following singular solution of the given problem

$$C = C_{PS}(\eta, \tau) = \begin{cases} C_P(\eta, \tau)\,; & \tau < \tau_c(\eta) \\ C_S(\eta, \tau)\,; & \tau > \tau_c(\eta)\,. \end{cases} \qquad (11a, b)$$

The critical area of contact of both regions $\tau = \tau_c(\eta)$ is given by the condition of continuity of solutions $C_{PS}(\tau, \eta)$ for $\eta \in (0; \infty)$:

$$C_P(\eta, \tau_c(\eta)) = C_S(\eta, \tau_c(\eta))\,; \qquad (12a)$$

i.e.

$$\tau_c^{1/2} g(\eta \tau_c^{-1/2}(\eta)) = f(\eta)\,. \qquad (12b)$$

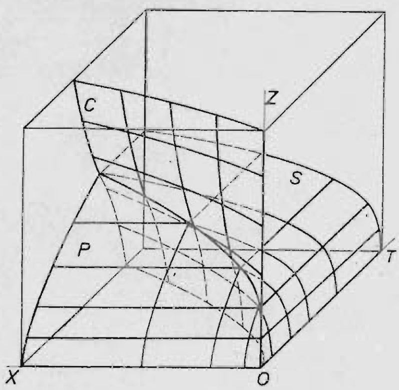

FIG. 2

Structure of singular solution in the space Z, X, T. O Origin, P, S surfaces of constant concentration for penetration and steady asymptote, C singular front separating the whole phase space (Z, X, T) to the region of validity of penetration or steady asymptote

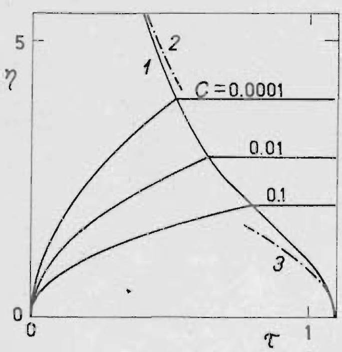

FIG. 3

Singular front in the space η, τ. *1* Singular front $\tau = \tau_c(\eta)$, *2*, *3* asymptotic representations of function $\tau_c(\eta)$ according to (*13a,b*). Plotted are also lines of constant concentration for $C = 0{\cdot}0001$, $0{\cdot}01$ and $0{\cdot}1$

Physically it is possible to consider the critical area $\tau = \tau_c(\eta)$ as the singular front moving along the axis X by a finite velocity. The structure of singular solution in the three-dimensional phase space $Z = 0$, $X = 0$, $T = 0$ is demonstrated in Fig. 2 with the emphasis to the character of areas $C = \text{const.}$ In Fig. 3 is plotted in coordinates η, τ the function $\tau_c(\eta)$ defined by Eq. (*12*) their asymptote inclusive, which is

$$\tau_c(\eta) \approx \begin{cases} \tau_0/(1 + \eta^2/(12\tau_0))^2 \, ; & \eta \to 0 \\ 9/(4\eta) \, ; & \eta \to \infty \, . \end{cases} \qquad (13a, b)$$

The profiles of the moving singular front and the corresponding level of constant concentration $C = 0{\cdot}1$ are demonstrated in Fig. 4.

It is worth noting that the velocity of the singular front at the surface of the electrode $(\partial X/\partial T)_{\text{front},z=0}$, is given by the relation $\frac{2}{3}\tau_0 X^{-1/3}$, which corresponds to the local convective liquid velocity at the boundary of the steady concentration boundary layer.

Analytical Solution

Concentration field according to the analytical solution[5] constructed by the technique of the double Laplace transformation can be expressed by the functional series

$$C = C_a(\eta, \tau) = C_S(\eta, \tau) + \sum \frac{3}{a_n Ai'(-a_n)} F_n(\eta, \tau) \qquad (14)$$

$$F_n(\eta, \tau) = \text{Im} \int_0^\infty \exp\left(-s^3 + a_n \varkappa^2 s^2 \tau\right) Ai(-a_n + \varkappa s \eta) \, \text{d} \ln s \, , \qquad (15)$$

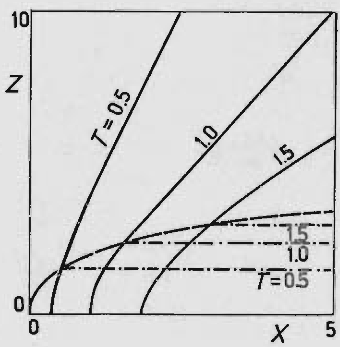

FIG. 4

Movement of singular front in the plane Z, X. Solid lines are representing momentous profiles of the singular front for $T = 0{\cdot}5$, $1{\cdot}0$, $1{\cdot}5$. Dash and dotted lines represent the corresponding development of concentration profiles in the penetration region on the level $C = 0{\cdot}1$. Dashed line corresponds to the surface $C = 0{\cdot}1$ in the steady region where $Ai(z)$ is the Airy's function of first kind, $(-a_n)$ are their zeros on the negative axis, $\varkappa = (1 + i\sqrt{3})/2$, $i = \sqrt{-1}$.

The normalised concentration gradient at the wall

$$J^*(\tau) = X^{1/3}\,\partial_Z C\big|_{Z=0} = \partial_\eta C\big|_{\eta=0} \tag{16}$$

can be expressed according to Eqs (*14*) and (*15*) by the series

$$J^*_a(\tau) = f_0^{-1}\left(1 + \frac{6^{1/6}}{\Gamma(2/3)}\sum a_n^{-1} G(2^{1/3}a_n\tau)\right), \tag{17}$$

where $G(u)$ given according to the Eq. (*15*) by the Lebesque's integral[5]

$$G(u) = \mathrm{Re}\int_0^\infty \exp\left[-(1 + i)\,s^{3/2} + i\pi/4 + i\,su\right] s^{-1/2}\,ds \tag{18a}$$

can be expressed by use of the Airy's function[6]

$$G(u) = 2^{5/6}\,3^{-1/3}\pi\,\exp\left(-u^3/27\right) Ai(18^{-2/3}u)\,. \tag{18b}$$

The equivalence of relations (*18a*) and (*18b*) can be seen by the elementary procedure: By introduction of the new integration variable $w = s^{3/2}$, three-fold derivation of the right side of Eq. (*18a*) according to the parameter u and elimination of all integral expressions the differential equation can be obtained with the real argument u, whose integral with initial conditions resulting from (*18a*) for $u \to 0$ is given by relation (*18b*). The asymptotic representations $G(u)$ are given by relations

$$G(u) \approx \begin{cases} 1{\cdot}377940 - 0{\cdot}146257u^2 + 0(u^3)\,; & u \to 0 \\ (\pi/4)^{1/2}\exp\left(-\frac{2}{27}u^3\right)(1 + 0(u^{-3}))\,; & u \to \infty\,. \end{cases} \tag{19a, b}$$

The shape of function $G(u)$ and the boundaries of applicability of asymptotic relations (*19a, b*) are obvious from Fig. 5.

Local and Mean Current Densities

According to Eq. (*16*) it is possible to express the local current densities by equation

$$I(x, t) = F_v D(-\partial_z c)\big|_{z=0} = F_v c_0 D^{2/3}\gamma^{1/3}\,J^*(\tau)\,x^{-1/3}\,. \tag{20}$$

As the steady asymptotic value $J^*(\infty)$ is known, it seems suitable to introduce the normalised instantaneous local stream densities $N = N(\tau) = J^*(\tau)/J^*(\infty)$.

It is easy to see that the singular solution according to (*11a, b*) leads to the following representation of $N(\tau)$

$$N_{PS}(\tau) = \begin{cases} (\tau/\tau_0)^{-1/2} ; & \tau < \tau_0 \\ 1 ; & \tau > \tau_0 . \end{cases} \qquad (21a, b)$$

The nontrivial problem of numerical realisation of the function $N_a(\tau) = f_0 \,.\, J_a^*(\tau)$ according to the formal prescriptions (*17*) and (*18b*) is in detail discussed in the study[6], where the tabulated numerical values are also given to sufficient extent. Both alternative shapes of functions $N(\tau)$ according to the analytical and singular solution are plotted in Fig. 6. It is obvious that the difference between the both versions is small and is concentrated to a small region in vicinity of $\tau = \tau_0$.

From the experimental point of view there appear to be more interesting the data on mean current densities averaged over the surface of the electrode

$$\bar{I}(t) = L^{-1} \int_0^L I(x, t)\, \mathrm{d}x \,. \qquad (22)$$

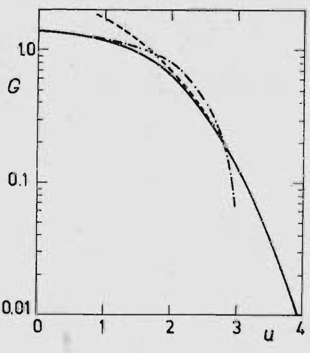

FIG. 5

Kernel function of analytical solution, $G(u)$. Solid line represents the exact form of Eq. (*18b*), dash and dotted is the asymptote (*19a*) for $u \to 0$, dashed the asymptote (*19b*) for $u \to \infty$

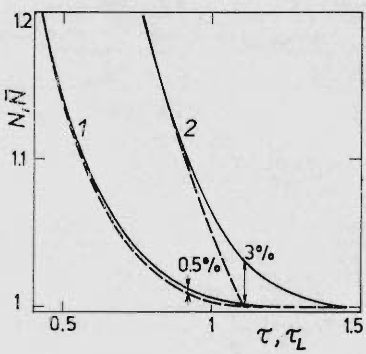

FIG. 6

Time dependence of normalised current densities. *1* Local current densities N, *2* current density $\bar{N}$, averaged over the surface of the electrode. Solid lines represent dependences of $N_a(\tau)$, $\bar{N}_a(\tau_L)$ according to the analytical solution and $N_{PS}(\tau)$, $\bar{N}_{PS}(\tau_L)$ according to the singular solution

The time dependence of normalised mean current densities $\bar{N} = \bar{N}(\tau_L)$ can be, according to definitions summarised in the List of symbols, expressed on basis of the familiar time dependence of local current densities

$$\bar{N}(\tau_L) = \tau_L \int_{\tau_L}^{\infty} N(\tau)\, \tau^{-2}\, d\tau\,. \qquad (23)$$

To the singular solution according to (*21a, b*) thus corresponds the transient characteristics

$$\bar{N}_{PS}(\tau_L) = \begin{cases} \frac{2}{3}(\tau_L/\tau_0)^{-1/2} + \frac{1}{3}(\tau_L/\tau_0)\,; & \tau_L < \tau_0 \\ 1\,; & \tau_L > \tau_0\,. \end{cases} \qquad (24a, b)$$

The shape of transient characteristics on basis of the analytical solution (*17*) has been constructed by a numerical integration according to relations

$$\bar{N}_a(\tau_L) = \bar{N}_{PS}(\tau_L) + \Delta\bar{N}(\tau_L) \qquad (25)$$

$$\Delta\bar{N}(\tau_L) = \tau_L \int_{\tau_L}^{\infty} (N_a(\tau) - N_{PS}(\tau))\, \tau^{-2}\, d\tau\,. \qquad (26)$$

TABLE I

Analytical solution of the transient Leveque's problem

τ, τ_L	$N_a(\tau)$	$\Delta\bar{N}(\tau_L)$	$\bar{N}_a(\tau_L)$
0·1	3·3135	0·0006	2·2402
0·2	2·3428	0·0012	1·6241
0·3	1·9136	0·0018	1·3684
0·4	1·6569	0·0024	1·2285
0·5	1·4820	0·0030	1·1428
0·6	1·3529	0·0036	1·0877
0·7	1·2525	0·0042	1·0517
0·8	1·1724	0·0048	1·0287
0·9	1·1092	0·0051	1·0147
1·0	1·0628	0·0047	1·0069
1·1	1·0323	0·0029	1·0029
1·2	1·0147	0·0011	1·0011
1·3	1·0058	0·0004	1·0004
1·4	1·0020	0·0001	1·0001
1·5	1·0006	0·0000	1·0000

The results of numerical integration, supported by data in Table I can be represented with the accuracy of $\pm 0{\cdot}00005$ by semiempirical relations

$$\Delta \bar{N}(\tau_L) = \begin{cases} 0{\cdot}0060\tau_L - 0{\cdot}0013(\tau_L)^{11{\cdot}0}\,; & \tau_L < \tau_0 \\ 0{\cdot}077\tau_L^{-3{\cdot}5} \exp\left(-1{\cdot}89\tau_L^3\right)\left(1 - 0{\cdot}42\tau_L^{-2}\right); & \tau_L > \tau_0\,. \end{cases} \qquad (27a, b)$$

The resulting dependences of functions $\bar{N}_{PS}(\tau_L)$, $\bar{N}_a(\tau_L)$ are plotted in Fig. 6. The differences do not exceed $\pm 0{\cdot}5\%$ and are concentrated in close vicinity of the point $\tau_L = 0{\cdot}9\tau_0$.

Approximative Similarity Solution

The usual methods of approximative solution of transient problems of the theory of transport boundary layer[4,7] can be easily modified so that the final approximation of the transient characteristics of current densities would have for $t \to 0$, $t \to \infty$ asymptotes identical with the exact solution. It is generally sufficient in the automodel problems with two independent variables η, τ to suppose the concentration field in the approximative similarity form

$$C(\eta, \tau) = f_0^{-1} f(\xi)\,, \quad \xi = \eta / A(\tau) \qquad (28)$$

and instead of the usual integral balance (for which is $\Phi = 1$) to require for $A(\tau)$ that the more general integral condition is satisfied, *i.e.*

$$\int_0^\infty \left[\partial^2_{\eta\eta} C + \tfrac{1}{3}\eta^2\, \partial_\eta C - \left(1 - \tfrac{2}{3}\eta\tau\right) \partial_\tau C\right] \Phi(\eta, \tau)\, d\eta = 0\,, \qquad (29)$$

where $\Phi(\eta, \tau)$ is the in advance not determined function.

Substitution of Eq. (*28*) into (*29*) leads to a differential equation for $A(\tau)$

$$A^2 - A^{-1} + 2(b - \tau A)\frac{dA}{d\tau} = 0\,, \qquad (30)$$

where the numerical coefficient b depends only on the selection of the weight function $\Phi(\eta, \tau)$. Especially, for $\Phi = \Phi(\xi)$ there holds

$$b = \frac{3}{2}\int_0^\infty \Phi(\xi)\, \xi\, f'(\xi)\, d\xi \Big/ \int_0^\infty \Phi(\xi)\, \xi^2 f'(\xi)\, d\xi\,. \qquad (31)$$

It is possible to find out that for the steady asymptote $dA/d\tau = 0$ there results from Eq. (*30*) independently of selection of b the result $A(\tau) = 1$, $C(\eta, \tau) = C_S(\eta, \tau)$, identical with the exact solution. The coefficient b can be thus chosen so that for $\tau \rightarrow 0$ would be, in agreement with the exact penetration asymptote, satisfied the relation

$$\partial_\eta C|_{\eta=0} = (A(\tau) f_0)^{-1} = g_0^{-1} \tau^{-1/2} . \tag{32}$$

This requirement is satisfied by the selection $b = \tau_0$. It is possible to demonstrate that the corresponding $\Phi(\xi)$ can be selected by infinite number of ways. One of the possibilities is very close to the function $\Phi(\xi) = (f'(\xi))^{1/2}$.

For so selected b the differential equation (*30*) with the initial condition $A(0) = 0$ has only a single one piecewise smooth solution

$$A(\tau) = \begin{cases} (\tau/\tau_0)^{-1/2} ; & \tau < \tau_0 \\ 1 ; & \tau > \tau_0 . \end{cases} \tag{33}$$

The corresponding approximative expression of transient characteristics $\mathrm{N}(\tau)$, $\bar{N}(\tau_L)$ is obviously identical with the result of the exact singular solution according to Eqs (*21a*, *b*), (*24a*, *b*).

DISCUSSION

The fact that the transient Leveque's problem, which has been considered until now as the "well posed", has at least two equivalent solutions is obviously related to the neglection of the axial diffusion. Which of the two solutions is the "legitimate" asymptote of the complete problem (with the inclusion of axial diffusion) for $Pe \rightarrow \infty$ is the question which should be answered by a profesional mathematician. The present state of theory, when the effect of axial diffusion is considered on basis of the perturbation around the known asymptotes for $Pe \rightarrow \infty$ hints that a considerably complicated problem is considered which is not solvable by the present techniques.

In the transient Leveque's problem appears worth noting the fact that the automodel formulation (*4*) is not simplifying the mathematical solution. On the contrary, new problems are encountered with the adequate formulation of boundary conditions In study[5] the problem is defined only by three conditions which are here given as Eqs (*5a*), (*5c*) and (*6*). But without condition (*5b*) the problem has another parasite solution on the whole region (η, τ) in the form $C(\eta, \tau) = C_P(\eta, \tau)$. Already from this fact is obvious that the numerical solution of problems of this type by the mesh method must fail. Besides, with the transient Leveque's problem do fail even the most usual analytical methods. The Laplace transformation fails, as Eq. (*4*) is not a differential equation with constant, *i.e.* on τ independent coefficients. The Fourier's method[8,9] and the method of singular perturbations fail totally because the asymptotes C_P and C_S, around which are constructed the corresponding functional series, satisfy the differential Eq. (*4*) identically. To the analytical solution leads only the considerably refined technique of two-fold Laplace transformation[5,6]. On the other hand it is possible "to guess" the equivalent singular solution of the problem directly form the automodel formulation which is written alternately in variables (η, τ) or (ζ, τ).

Nevertheless, from the practical point of view both exact solutions seem to be well applicable. The local inaccuracy of theoretical mean expressions for current densities does not exceed 0·5% and will be always smaller in comparison with the inaccuracy of data on geometry of electrodes, flow velocity, concentration of depolarizer *etc.*, let alone the electrochemical effects which have been mentioned in the introduction. It seems that in these connections the problem of the effect of axial diffusion becomes of secondary significance. For purposes of quantitative evaluation of experimental data is obviously more advantageous to use the simpler of the exact theories according to Eq. (*24a, b*). By introduction of a pair of normalisation parameters $\bar{I}(\infty)$, t_0 and the corresponding normalised variables, Eq. (*24a, b*) can be written in the form

$$\bar{N}(\tau_L) = \begin{cases} \Theta^{-1/2} + \frac{4}{27}\,\Theta\,; & \Theta < 9/4 \\ 1\,; & \Theta > 9/4\,. \end{cases} \qquad (34)$$

Here, the relaxation time of the experiment t_0 has the geometric significance of the time coordinate of intersection of the power asymptotes $\bar{I} \sim t^{-1/2}$ and $\bar{I} = \text{const.}$ which in the coordinates $\log \bar{I} - \log t$ appear as straight lines.

LIST OF SYMBOLS

A normalised thickness of the concentration boundary layer, Eq. (*28*)
c concentration of depolarizer
c_0 initial concentration
c_w concentration on polarized electrode
$C = (c_0 - c)/(c_0 - c_w)$
D diffusivity of depolarizer
F_v charge transferred by one mole of depolarizer
$f(\eta)$ defined by Eq. (*10*)
$f_0 = f(0) = 3^{-1/3}\Gamma(1/3) = 1{\cdot}8574723$
$g(\zeta)$ defined by Eq. (*8*)
$g_0 = g(0) = \Gamma(1/2) = 1{\cdot}7724538$
$G(u)$ Kernel function of analytical solution, Eq. (*18a,b*)
$I(x, t) = F_v\, J(x, t)$ momentous local current density on electrode
$I(\infty) = 0{\cdot}80755 F_v c_0 D^{2/3} \gamma^{1/3} L^{-1/3}$ mean steady current density, according to Eq. (*22*)
$J(x, t) = D\, \partial_z c|_{z=0}$ diffusion flux of depolarizer toward the surface of electrode
$J^*(\tau)$ normalized momentous fluxes at the wall, Eq. (*16*)
$J^*(\infty) = f_0^{-1}$
L length of electrode in the flow direction
$N = I(x, t)/I(x, \infty)$
$\bar{N} = \bar{I}(t)/\bar{I}(\infty)$
ΔN defined by Eq. (*26*)

$Pe = \gamma L^2/D$ Péclet number of the Leveque's problem
t time measured from the moment of the step change of the electrode potential
$t_0 = 0{\cdot}48810 D^{-1/3} \gamma^{-2/3} L^{2/3}$ relaxation time of the transition process
$T = \gamma t$
x, z longitudinal and normal coordinates, Fig. 1
$X = (\gamma/D)^{1/2} x$
$Z = (\gamma/D)^{1/2} z$
γ constant shear rate, Fig. 1
$\xi = Z/A(\tau)$
$\zeta = \eta\tau^{-1/2} = ZT^{-1/2}$
$\eta = ZX^{-1/3}$
$\Theta = t/t_0 = (9/4)(\tau_L/\tau_0)$
$\tau = TX^{-2/3}$ time variable of local description
$\tau_c(\eta)$ function describing the advance of the singular front, Eq. (*12a,b*)
$\tau_L = D^{1/3}\gamma^{2/3}L^{-2/3}t$ time variable of global description
$\tau_0 = (f_0/g_0)^2$

Superscripts

— mean value over surface of electrode

Subscripts

a analytical solution
P penetration asymptote
S steady asymptote
PS singular solution
C singular front

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