ON THE CONVECTIVE DIFFUSION UNDER PARTIAL SLIP AT WALL

Ondřej WEIN and Petr KUČERA*

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Received June 6, 1988
Accepted September 7, 1988

Extended Leveque problem is studied for linear velocity profiles, $v_x(z) = u + qz$. The existing analytic solution is reconsidered and shown to be inapplicable for the accurate calculation of mean mass-transfer coefficients. A numerical solution is reported and its accuracy is checked in detail. Simple but fairly accurate empirical formulas are suggested for the calculating of local and mean mass-transfer coefficients.

Both the thermoanemometrical and electrodiffusion flow measurements are based on the phenomenon of convective diffusion. There are, however, substantial differences in their relationship to the corresponding mathematical theory. The calibration measurements for a given liquid under given temperature are unavoidable in the thermoanemometry due to both geometrical imperfections of the sensing elements and rather complex nature of their thermal interactions with the body of probe[1]. On the contrary, the electrodiffusion measurements under the actual condition of limiting diffusion current[2] allow to perform various absolute measurements – the determination of the concentration c_0 or diffusivity D of certain depolarizers as well as the measuring of the wall shear rate q under given flow conditions – as the electrodiffusion sensors can be manufactured with the necessary geometrical perfection of the surface[3]. The absolute nature of carefully performed electrodiffusion measurements allowed to discover the anomalous flow behaviour of suspensions and polymer solutions in an extremally thin "slip" layer close to a solid surface[4,5]. In this sense, the laboratory practice of electrodiffusion measurements is encouraging also the development of the corresponding transport theories.

In the hydrodynamics of Newtonian liquids, the assumptions are commonly taken of no slip at solid surfaces, homogeneity and isotropy of liquid even in an intimate neighbourhood of the wall. Under these conditions, the velocity profile, at least within the diffusion layer, is given by the relation $v_x(z) = qz$. Then, also the integral effect of convection is represented by a single kinematic parameter, the wall shear

* Present adress: State Research Institute for Construction of Machines, 250 97 Prague 9-Běchovice.

rate q. The corresponding formulas for calculating q from electrodiffusion data

$$q = DL(\tfrac{2}{3}/\beta_0\delta)^3 = D^{-2}L(\tfrac{2}{3}I/\beta_0 nFc_0\Omega)^3 , \quad (1)$$

$$\beta_0^{-1} = \int_0^\infty \exp(-s^3/9)\,ds = \Gamma(\tfrac{1}{3})/3^{1/3} , \quad (2)$$

represent the well-known result[3] which has been first given by Leveque.

In an analogous analytic way it is possible to solve slightly more general problem of steady convective diffusion for the power-law velocity profile inside a diffusion layer,

$$v_x(z) = az^p , \quad (3)$$

with the explicite result for the mean current density[6]:

$$\frac{I}{nFc_0\Omega} = D/\delta = \frac{2+p}{1+p}\frac{(2+p)^{p/(2+p)}}{\Gamma(1/(2+p))} D\left(\frac{a}{LD}\right)^{1/(2+p)} . \quad (4)$$

Unfortunately, this result cannot form a sufficiently general basis for the electrodiffusion investigation of velocity profiles at wall because the kinematical assumption (3) is unreal at the solid surface and outside of the slip layer as well. Both the experimental[4] and theoretical[7] evidences have shown that the velocity profile outside of a narrow slip region under condition of constant shear stress can be represented by the linear relation

$$v_x(z) = u + qz . \quad (5)$$

Here, the apparent slip velocity u represents the anomalous wall effects taking place within the slip region which is assumed to be thin enough as compared with the diffusion thickness. The shear rate q represents the regular flow patterns outside of the slip region under conditions of constant shear stress in the bulk of a homogeneous liquid which can exhibit non-Newtonian flow behaviour.

The corresponding problem of convective diffusion has been treated by using standard analytic methods[8] and, at least in the chemical engineering literature[7], it is considered to be succesfully solved. It is the purpose of the present paper to develop working formulas analogous to Eqs (1), (4), for this problem. First, the analytic solution[8] is reconsidered and shown to be of a little interest for treating experimental data on mass-transfer coefficient. Further, the numerical solution is presented with a high accuracy guaranteed. As a result, the simple working formulas, Eqs (41) to (44), are given.

THEORETICAL

Problem Statement, Analytic Solution

Starting formulation comprises the equation of steady convective diffusion for the concentration field $c = c(z, x)$ of a depolarizer,

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

the condition of a limiting diffusion current, i.e. of the total depletion of the depolarizer at the electrode surface,

$$c = 0\,; \quad \text{for} \quad z = 0\,, \tag{7}$$

and the condition of the fresh solution in the bulk of liquid, i.e. outside of the diffusion layer,

$$c \rightarrow c_0\,; \quad \text{for} \quad z \rightarrow \infty\,. \tag{8}$$

By introducing the normalized variables, as defined in the List of symbols, the following boundary-value parabolic two-dimensional problem is obtained:

$$\begin{aligned} &\partial^2_{ZZ}C^* - (1 + Z)\,\partial_X C^* = 0\,,\\ &C^* = 0\,; \quad \text{for} \quad Z = 0\,,\\ &C^* \rightarrow 1\,; \quad \text{for} \quad X \rightarrow 0, Z > 0\,,\\ &C^* \rightarrow 1\,; \quad \text{for} \quad Z \rightarrow \infty\,. \end{aligned} \tag{9}$$

The most important part of the solution is represented by the local and mean mass-transfer coefficients or the corresponding diffusion thicknesses. In the dimensionless form, they are given through the normalized concentration field:

$$\begin{aligned} &K(X) = \partial_Z C^*|_{Z=0}\,, \quad \bar{K}(H) = H^{-1}\textstyle\int_0^H K(X)\,\mathrm{d}X\,,\\ &B(X) = 1/K(X)\,, \qquad B(H) = 1/\bar{K}(H)\,. \end{aligned} \tag{10}$$

The problem so stated has been treated in the work[8] by using the Laplace transform, expanding the image of $K(X)$ into series and inverting them term-by-term. Unfortunately, after giving rather general framework, the authors[8] presented only the first two terms in the resulting expansions for local mass-transfer coefficients. Their approach has been completely realized in an unpublished research report[9], with the following results.

The low-X series expansion ($X \to 0$) can be written in the form of partial sums,

$$K(X) \approx K_{LN}(X) \equiv \sum_{i=0}^{N} a_i X^{(i-1)/2} / \Gamma\left(\frac{i+1}{2}\right), \qquad (11)$$

where

$$a_0 = 1\,, \qquad a_i = r_i - \sum_{j=1}^{i} s_j a_{i-j}\,,$$
$$r_0 = 1\,, \quad r_j/r_{j-1} = -(6j+1)(6j-7)/48j\,, \qquad (12)$$
$$s_0 = 1\,, \quad s_j/s_{j-1} = -(6j-1)(6j-5)/48j\,.$$

In particular, for $X \to 0$:

$$K_L(X) \approx \alpha_0 X^{-1/2} + \alpha_1 + \alpha_2 X^{1/2} + \alpha_3 X + \ldots\,, \qquad (13)$$

with

$$\alpha_0 = \pi^{-1/2}\,, \quad \alpha_1 = \tfrac{1}{4}\,, \quad \alpha_2 = -\tfrac{5}{16}\alpha_0\,, \quad \alpha_3 = \tfrac{15}{64}\,,$$

and, in general, $\alpha_i = a_i/\Gamma(i + 1/2)$.

The high-X series expansion can be expressed by using an analogous sequential algorithm:

$$K(X) \approx K_{HN}(X) \equiv \sum_{i=0}^{N} b_i X^{-(i+1)/3} / \Gamma\left(\frac{2-i}{3}\right), \qquad (14)$$

where

$$\sigma = 3^{1/3}\Gamma(\tfrac{2}{3})/\Gamma(\tfrac{1}{3})\,,$$
$$b_0 = \sigma\,, \quad b_i = r_i - \sum_{j=1}^{i} s_j b_{i-j}\,,$$
$$r_0 = \sigma\,, \quad r_1 = 0\,, \quad r_2 = -\frac{1}{2\sigma}\,, \quad r_j/r_{j-3} = \frac{1}{j(j-2)}\,, \qquad (15)$$
$$s_0 = 1\,, \quad s_1 = -\sigma\,, \quad s_2 = 0\,, \quad s_j/s_{j-3} = \frac{1}{j(j-1)}\,.$$

In particular, for $X \to \infty$:

$$K_H(X) \approx \beta_0 X^{-1/3} + \beta_1 X^{-2/3} + \beta_3 X^{-4/3} + \beta_4 X^{-5/3} + \ldots \qquad (16)$$

with

$$\beta_0 = 3^{1/3}/\Gamma(\tfrac{1}{3}) \doteq 0.538366\,,$$
$$\beta_1 = \sigma^2/\Gamma(\tfrac{1}{3}) \doteq 0.198383\,,$$

$$\beta_3 = (-\tfrac{1}{3}\sigma^3 + \tfrac{1}{9})\,\beta_0 \doteq -0.009709\,,$$
$$\beta_4 = (-\tfrac{2}{3}\sigma^3 + \tfrac{5}{18})\,\beta_1 \doteq 0.003866\,,$$

and, in general, $\beta_i = b_i/\Gamma((2-i)/3)$.

By applying the formal term-by-term integration of the series (*14*), in accordance with the definition (*10*), the following expressions can be obtained for the mean mass-transfer coefficients:

$$\bar{K}(H) \approx \bar{K}_{LN}(H) \equiv \sum_{i=0}^{N} a_i H^{(i-1)/2} / \Gamma\left(\frac{i+3}{2}\right); \qquad (17)$$

for $X \to 0$, and

$$\bar{K}(H) \approx \bar{K}_{HN}(H) = \sum_{i=0}^{N} b_i H^{-(i+1)/3} / \Gamma\left(\frac{5-i}{3}\right); \qquad (18)$$

for $X \to \infty$. It should be noticed that only the first two terms can be correctly applied in the series (*18*),

$$\bar{K}_H(H) = \tfrac{3}{2}\beta_0 H^{-1/3} + 3\beta_1 H^{-2/3}\,, \qquad (19)$$

as the formal integration of a power-function, $f(X) = X^p$, with the lower limit $X = 0$ is obviously incorrect for $p \leqq -1$.

The first 500 coefficients α_i, β_i have been computed and the following result was found in an empirical way:

$$\lim_{i\to\infty} |\alpha_i / i\alpha_{i-2}| = \infty\,, \quad \lim_{i\to\infty} |\beta_i / i\beta_{i-3}| = \infty\,. \qquad (20)$$

This indicates the asymptotic nature of all the series (*11*), (*14*), (*17*), (*18*) which therefore must necessarily be divergent for any finite value of the argument X. For a practical calculation of mass-transfer coefficients it means that only certain estimates can be made by using these expansions.

A few sample-calculations are given in Fig. 1 which show the divergency of the partial sums for mass-transfer coefficients. The way of optimizing of the upper and lower estimates is also shown there. The resulting optimized estimates of K and $\bar{K}$ are plotted in the Figs 2 and 3. For a better distinguishing over rather broad region of X and H, the estimates of mass-transfer coefficients are normalized there by using the first terms of the corresponding low-X expansions,

$$K_{LO}(X) = (\pi X)^{-1/2}\,, \quad \bar{K}_{LO}(H) = 2(\pi H)^{-1/2}\,. \qquad (21)$$

The uncertainty of these estimates is about 2% for local and more than 5% for mean mass-transfer coefficients. The corresponding quantitative information must therefore be found in another way, e.g. by applying finite-difference methods.

Numerical Solution

An acceptable accuracy can be guaranteed at solving a boundary-value problem by finite-difference methods only if the actual formulation to the problem includes no singularity. The extended Leveque problem exhibits a weak singularity in the corner

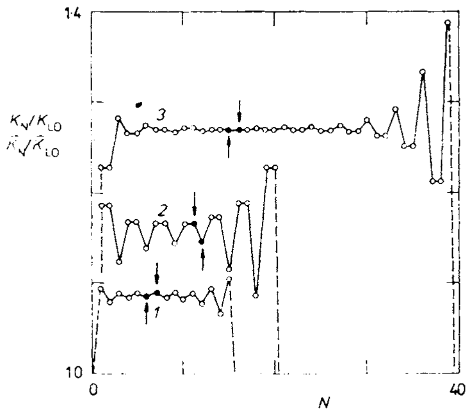

FIG. 1

Divergency of partial sums representing local and mean mass-transfer coefficients; *1* $H = 0{\cdot}2$, mean, low-H asymptote, Eq. (*17*); *2* $X = 0{\cdot}2$, local, high-X asymptote, Eq. (*14*); *3* $H = 0{\cdot}2$, mean, high-H asymptote, Eq. (*18*); the arrows show the optimized lower and upper estimates

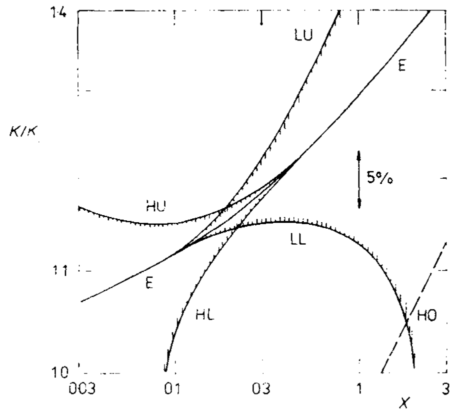

FIG. 2

Local mass-transfer coefficients; E exact numerical solution; HO Leveque solution, i.e. the single term in high-X expansion; HU, HL upper and lower estimates by high-X expansion; HU, HL upper and lower estimates by high-X expansion; LU, LL upper and lower estimates by low-X expansion

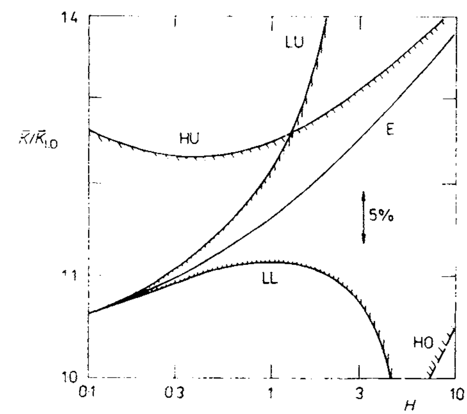

FIG. 3

Mean mass-transfer coefficients. The meaning of symbols is same as in Fig. 3. The estimate HL is identical with the single-term asymptote HO

$(Z, X) = (0, 0)$. This can be removed by using any "similarity" transformation of the type

$$C(w, b) = C^*(Z, X), \quad w = Z/b, \quad b = b(X), \tag{22}$$

where $b(X) \sim X^{1/2}$ for $X \to 0$.

A special choice has been made of the normalizing function $b(X)$ by defining it implicitly, as the positive root of the cubic equation

$$(\alpha_0 b)^2 + (\beta_0 b)^3 = X. \tag{23}$$

By applying this similarity transformation, the starting problem is modified into the following form:

$$C'' + A(1 + bw) wC' = A(1 + bw) b\partial_b C, \tag{24}$$

$$C(0, b) = 0, \tag{25}$$

$$C(w^\infty, b) = 1, \tag{26}$$

$$A \equiv b \,.\, \mathrm{d}b/\mathrm{d}X = 1/(2\alpha_0^2 + 3\beta_0^3 b). \tag{27}$$

It can be easily seen that this formulation allows two asymptotic similarity solutions:

$$C \approx \begin{cases} \int_0^w \exp(-s^2/4\alpha_0^2)\, \mathrm{d}s\,; & \text{for} \quad b \to 0, \\ \int_0^w \exp(-s^3/9\beta_0^3)\, \mathrm{d}s\,; & \text{for} \quad b \to \infty. \end{cases} \tag{28}$$

It can be expected that the dependence of the exact solution, $C = C(w, b)$, on the longitudinal coordinate b is rather weak even over the transient region of medium values of b, i.e. that the field $C(w, b)$ exhibits the similarity structure in an acceptable approximation. This assumption has been implied tacitly, by using the symbol $'$ for the partial derivatives with respect to w, $C' = \partial_w C$, etc.

In principle it should be set $w^\infty = \infty$. However, it can be shown that the sufficient accuracy of six valid digits for $C'(0, b)$ is reached by choosing the value $w^\infty \geqq 4$. The choice $w^\infty = 4{\cdot}2$ was made in the present numerical analysis.

The normalized local diffusion thickness B and the corresponding mass-transfer coefficient K can be now expressed in the following way,

$$B(X) = 1/K(X) = b(X)/G(X), \tag{29}$$

where $G = G(X)$ stands for the wall gradient of the similarity concentration profile:

$$G(X) = C'(0, b(X)). \tag{30}$$

It follows from Eq. (*28*) that $G(X) \approx 1$ holds for the both asymptotes. This suggests that the same equality could hold, within some approximation, over the whole domain of X. Slight deviations of the difference G-1 from zero hence present the main object for the following numerical study.

The Crank–Nicholson method[10] of integrating parabolic differential equations allows to compute the next concentration profile (at $b^j = b + \Delta b$) if a previous one (at $b^{j-1} = b$) is given. This method can be used with no modification in the considered case as the initial conditions are given by the asymptotical concentration profile (*28*) for $X \to 0$. By introducing the discrete representation of the concentration field on rectangular two-dimensional mesh with given m, Δb:

$$C_i^j = C(w_i, b^j)\,, \quad w_i = i\,.\,\Delta w\,, \quad b^j = j\,.\,\Delta b\,, \qquad (31)$$
$$\Delta w = w^\infty/m\,, \quad i = 0, \ldots, m\,, \quad j = 0, 1, \ldots\,,$$

the following linear system of equations is obtained for C_i^j, $i = 1, \ldots, m - 1$:

$$C_i^j = [Q_i + C_{i+1}^j + C_{i-1}^j + S_i^j(C_{i+1}^j - C_{i-1}^j)]/(2 + R_i) \qquad (32)$$

with

$$\begin{aligned} Q_i &= C_{i+1}^{j-1} + C_{i-1}^{j-1} + S_i^{j-1}(C_{i+1}^{j-1} - C_{i-1}^{j-1}) - (2 - R_i)\,.\,C_i^{j-1}\,, \\ R_i &= ((\Delta w)^2/\Delta b)\,(b^{j-1}T_i^{j-1} + b^j T_i^j)\,, \\ S_i^j &= \tfrac{1}{2}(\Delta w)^2\, i T_i^j\,, \\ T_i^j &= (1 + b^j w_i)\, A(b^j)\,. \end{aligned} \qquad (33)$$

The system of $m - 1$ linear equations is closed by the pair of boundary conditions at $w_0 = 0$ and $w_m = w^\infty$:

$$C_0^j = 0\,, \quad C_m^j = 1\,. \qquad (34)$$

The wall gradient G was calculated in several ways. First, the common method has been used of truncated Taylor series,

$$G_M = G_M(X(b^j)) = \sum_{i=0}^{M} d_i^M C_i^j\,, \qquad (35)$$

for $M = 1, 2, 3, 4$, with the coefficients d_i^M given e.g. in the reference book[10]. Further, the formula

$$C'(0, b) = bA(b) \int_0^\infty \{(1 + \tfrac{1}{2}bw)\,(1 - C) - (1 + bw)\,\partial_b C\}\,\mathrm{d}w \qquad (36)$$

can be derived by integrating the original differential equation (*24*). By using the Simpson rule for quadratures and the first difference for the derivative $\partial_b C$ at $b = b^j$

$\Delta b/2$, the formula (*36*) results in another estimate of $G = G(X)$ which will be marked by the symbol G_S in the subsequent discussion.

Discussion of Accuracy

There are the three adjustable parameters, w^{∞}, m, Δb, which can effect the accuracy of the numerical solution. It has been found in numerical experiments that the accuracy does not depend on further increasing w^{∞} above $w^{\infty} = 4{\cdot}2$ or on further diminishing Δb below $\Delta b = 0{\cdot}02$. These values have therefore been used in all the numerical calculations referred to in the following text.

The choice of an appropriate number of mesh points, m, has shown to be a delicate problem. The values about $m = 40$ represent a minimum necessary to reaching a meaningful result. On the other hand, the number of mesh points above $m = 500$ resulted in unacceptably long computational times. The dependency of the resulting estimates of G on the number of mesh points is shown in Table I.

Some conclusions can be drawn from these results. First, G_4 is rather independent of thinning of the mesh and therefore it can be taken as the best of the estimates at hand. Second, the difference $(G_4 - G_S)$ seems to be the most sensitive criterion of the accuracy reached. Third, the differences between the G_4 estimates for $m = 200$ and $m = 400$ are negligible as compared to the desired accuracy of 5 to 6 valid digits. In result, the G_4 estimate of G in the region $X < 50$ is believen to be an appropriate representation of exact solution with the said accuracy. Nevertheless, the accuracy of the G_4 estimates at higher values of X remains uncertain as the difference $(G_4 - G_S)$ is still remarkable there.

Fortunately, there is another way of checking the accuracy because the analytic asymptotes to the exact solution are known. The normalized concentration gradient G can be expressed from the definition (*29*) as the product

$$G(X) = K(X)\, b(X) \tag{37}$$

of the two functions which both have the known asymptotic representations. In particular, $b(X)$ can be expressed from its definition by Eq. (*23*):

$$b \approx \begin{cases} (X^{1/2}/\alpha_0)\,\{1 - \frac{1}{2}(\beta_0/\alpha_0)^3\, X^{1/2} + \frac{5}{8}(\beta_0/\alpha_0)^6\, X + \ldots\} \\ (X^{1/2}/\beta_0)\,\{1 - \frac{1}{3}(\alpha_0/\beta_0)^2\, X^{-1/3} + \frac{1}{9}(\alpha_0/\beta_0)^4\, X^{-2/3} + \ldots\}\,, \end{cases} \tag{38}$$

and the asymptotic expansions for $K(X)$ are given in Eqs (*13*), (*16*). By substituting these expressions into Eq. (*37*), the following final asymptotic representations are obtained for $X \to 0$:

$$G_L \approx 1 + f_1 X^{1/2} + f_2 X + \ldots\,, \tag{39a}$$

and for $X \to \infty$:

$$G_H \approx 1 + g_1 X^{-1/3} + g_2 X^{-2/3} + \dots, \qquad (39b)$$

with

$$f_1 = \alpha_1/\alpha_0 - \tfrac{1}{2}(\beta_0/\alpha_0)^3 \doteq 0.008676,$$
$$f_2 = \alpha_2/\alpha_0 - \tfrac{1}{2}(\alpha_1/\alpha_0)(\beta_0/\alpha_0)^3 + \tfrac{5}{8}(\beta_0/\alpha_0)^6 \doteq -0.033164,$$
$$g_1 = \beta_1/\beta_0 - \tfrac{1}{3}(\alpha_0/\beta_0)^2 \doteq 0.002410,$$
$$g_2 = 0 - \tfrac{1}{3}(\beta_1/\beta_0)(\alpha_0/\beta_0)^2 + \tfrac{1}{9}(\alpha_0/\beta_0)^4 \doteq -0.000883.$$

The final comparison of the various estimates of G is shown in Fig. 4. The numerical data $G_4 = G_4(X)$ for $m = 400$ merge into the both analytic asymptotes (*39a, b*) with an accuracy of 5 to 6 valid digits. An empiric formula has been found for representing

TABLE I

Effect of mesh dividing on the accuracy of results. $e_a = (G_a - 1)^* 100\%$, for $a = 1, 2, 3, 4, S$

m	b	X	e_1	e_2	e_3	e_4	e_S
50	0·1	0·003	−0·14	0·38	0·04	0·03	−0·25
	0·2	0·014	−0·10	0·38	0·06	0·05	−0·24
	0·5	0·099	−0·05	0·37	0·08	0·08	−0·24
	1·4	1·052	−0·01	0·29	0·05	0·07	−0·31
	3·5	10·59	−0·03	0·17	−0·02	0·02	−0·42
100	0·1	0·003	−0·01	0·13	0·04	0·04	−0·03
	0·2	0·014	0·02	0·15	0·07	0·07	0·01
	0·5	0·099	0·07	0·18	0·10	0·10	0·02
	1·4	1·052	0·09	0·16	0·11	0·11	0·02
	3·5	10·59	0·06	0·10	0·06	0·07	−0·04
200	0·1	0·003	0·03	0·06	0·04	0·04	0·03
	0·2	0·014	0·06	0·09	0·07	0·07	0·05
	0·5	0·099	0·10	0·13	0·11	0·11	0·10
	1·4	1·052	0·11	0·13	0·12	0·12	0·10
	3·5	10·59	0·08	0·09	0·08	0·08	0·05
	7·2	74·74	0·05	0·05	0·05	0·05	0·02
400	0·1	0·003	0·04	0·05	0·04	0·04	0·04
	0·2	0·014	0·07	0·08	0·07	0·07	0·07
	0·5	0·099	0·11	0·11	0·11	0·11	0·11
	1·4	1·052	0·12	0·12	0·12	0·12	0·12
	3·5	10·59	0·08	0·09	0·08	0·08	0·08
	7·2	74·74	0·05	0·05	0·05	0·05	0·04
	10·0	187·9	0·04	0·04	0·04	0·04	0·03

these numerical data,

$$G_E = 1 + f_1 X^{1/2}/[1 + (f_1/g_1)^{3/2} X^{1/2}]^{5/3}, \tag{40}$$

which contains only the parameters f_1, g_1 taken from the analytic solution to the problem. This formula merges in the both asymptotes exactly and represents a sound extrapolation of the numerical data for $m \to \infty$ as well. There are reasons to believe that the formula (*40*) guarantees the accuracy better than 0·01% in calculating $G(X) = C'(0, X)$.

Mean Diffusion Thickness

It should be noticed that the deviation of G-1 from zero does not exceed 0·001 and therefore it can be neglected in experimental data treating. The assumptions $G = 1$ and $B = b$ are equivalent each to other, see Eqs (*23*), (*29*). They result in the implicite formula for calculating the local mass-transfer coefficients $K = K(X)$ or the local diffusion thicknesses $B = B(X)$,

$$(\alpha_0 B)^2 + (\beta_0 B)^3 = X. \tag{41}$$

By integrating this equation in accordance with the definitions (*10*), the simple working formula is obtained for mean diffusion thicknesses in the parametric form,

$$\bar{B}(H)/B_H = [1 + (\beta_0^3/\alpha_0^2) B_H]/[2 + \tfrac{3}{2}(\beta_0^3/\alpha_0^2) B_H], \tag{42a}$$

where $B_H = B(H)$ is the root of a cubic equation,

$$(\alpha_0 B_H)^2 + (\beta_0 B_H)^3 = H. \tag{42b}$$

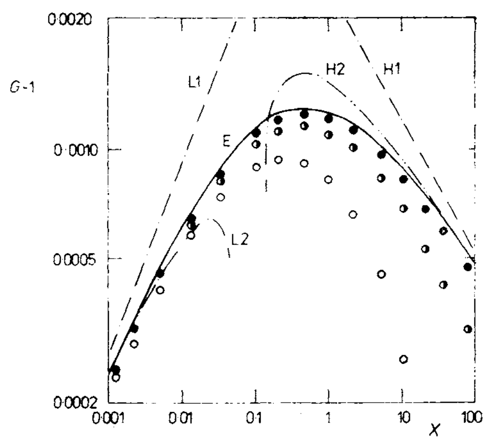

FIG. 4

Accuracy check on numerical solution; L1 low-X asymptote, $N = 1$; L2 low-X asymptote, $N = 2$; H1 high-X asymptote, $N = 1$; H2 high-X asymptote, $N = 2$; ○ mesh $\Delta b = 0{\cdot}02$, $m = 50$; ◑ mesh $\Delta b = 0{\cdot}02$, $m = 100$; ● mesh $\Delta b = 0{\cdot}02$, $m = 200$ and $m = 400$

An additional simplifying empiricism consists in approximate representation of the function $\bar{B} = \bar{B}(H)$ in a form analogous to Eq. (*42b*):

$$(2\alpha_0\bar{B})^2 + (\tfrac{3}{2}\beta_0\bar{B})^3 = H\,, \qquad (43)$$

which provides the values of $\bar{B}$ within an accuracy of 1%. This equation can be re-written into the following dimensional form

$$DL/\bar{\delta}^2 = u(2\alpha_0)^2 + q(\tfrac{3}{2}\beta_0)^3\,\bar{\delta}\,. \qquad (44)$$

With a known value of D, the pair of kinematic parameters u, q can be determined by treating the data on mean diffusion thickness, $\bar{\delta}$, for a serie of geometrically similar electrodes of different sizes L, under identical flow conditions, i.e. under the constant shear stress at wall.

CONCLUSION

Instead of the existing analytic solution[8] which does not provide the desired quantitative information, the numerical solution to the problem has been constructed, and the resulting concentration gradient at wall is represented by the simple but accurate empirical formula (*40*). The final result, as represented by Eq. (*44*), can be straightforwardly used for treating electrodiffusion data by common statistical methods. This equation contains two numerical coefficients which have been given for the case of rectangular (band) electrodes in the present paper.

For the more common, circular, shape of working electrodes, the corresponding formula has the same general structure as Eq. (*44*), with the electrode radius R instead of the length L and with different values of the numerical coefficients. This can be derived by using the approach given in the recent work[11]. Within an acceptable accuracy, the Eq. (*44*) can be used with no change if the effective length $L = 1{\cdot}64R$ is introduced[11].

This work has been done during the stay of one of the authors (O. W.) at the University Dortmund, F.R.G. The kind interest of Prof. U. Onken as well as the help of the staff of his department in using the department computers are gratefully acknowledged.

LIST OF SYMBOLS

a_i coefficients in asymptotic expansions for $X \to 0$
$A = b\,\mathrm{d}b/\mathrm{d}X$
b auxiliar longitudinal coordinate, Eqs (*22*), (*23*)
Δb mesh step in the longitudinal direction
$B = \delta q/u$, normalized local diffusion thickness
$\bar{B} = \bar{\delta}q/u$, normalized mean diffusion thickness
b_i coefficients in asymptotic expansions for $X \to \infty$

c_0 depolarizer concentration in the bulk of solution
$c(z, x)$ concentration field of a depolarizer
$C^*(Z, X) = c(z, x)/c_0$, normalized concentration field
$C(w, b) = C^*(Z, X)$, similarity concentration profiles with the axial coordinate b as a parameter
C' gradient of the similarity concentration profile
C_i^j value of C in the mesh point (w_i, b^j)
D diffusivity of depolarizer
nF the charge transferred on working electrode by the reaction of 1 mole of a depolarizer
$G(X) = C'(0, b(X))$, similarity concentration gradient at wall
G_M estimate of G based on Taylor series and using M inner mesh points, $i = 1, \ldots, M$
G_S estimate of G based on the macroscopical balance (*36*)
G_L, G_H asymptotic estimates of G for $X \to 0$ and $X \to \infty$, resp.
G_E empiric representation of exact G, Eq. (*40*)
f_i, g_i coefficients in asymptotic representations of G
$H = LDq^2/u^3$, dimensionless electrode length
I limiting diffusion current
i, j non-negative indexes (0, 1, 2, ...)
$k = D\partial_z c|_{z=0}/c_0$, local mass-transfer coefficient
$\bar{k} = L^{-1} \int_0^L k \, dx$, mean mass-transfer coefficient
$K = ku/qD$
$\bar{K} = \bar{k}u/qD$
K_L, K_H asymptotic representations of K for $X \to 0$, $X \to \infty$, resp.
$\bar{K}_L, \bar{K}_H$ asymptotic representations of $\bar{K}$ for $X \to 0$, $X \to \infty$, resp.
$K_{LN}, K_{HN}, \bar{K}_{LN}, \bar{K}_{HN}$ — partial sums truncated after N^{th} term
$K_{LO} = (\pi X)^{-1/2}$
$\bar{K}_{LO} = 2(\pi H)^{-1/2}$
L length of a band working electrode
L length of a band working electrode in the direction of flow
m number of mesh points on the w — coordinate
N number of terms in truncated series, see Eqs (*11*), (*14*), (*17*), (*18*)
q shear rate at wall, see also Eq. (*5*)
R radius of a circular working electrode
u slip velocity, see also Eq. (*5*)
$v_x(z)$ profile of longitudinal velocities
$w = Z/b(X)$, similarity argument
Δw mesh step in the similarity argument
w^∞ actual infinity in the numerical solution
x longitudinal coordinate, distance from the forward edge of the working electrode
$X = xDq^2/u^3$
z perpendicular coordinate, distance from the surface of the working electrode
$Z = zq/u$
α_i, β_i coefficients in the resulting asymptotic representations of mass transfer coefficients, Eqs (*13*), (*16*)
Γ Euler's gamma function
$\delta = D/k$, local diffusion thickness
$\bar{\delta} = D/\bar{k} = nFDc_0/I$, mean diffusion thickness
Ω area of working electrode

REFERENCES

1. Boerner Th., Leutheuser H. J.: DISA Info. *29*, 10 (January 1984).
2. Selman J. R., Tobias Ch. W.: Adv. Chem. Eng. *10*, 211 (1978).
3. Hanratty T. J., Campbell J. in: *Fluid Mechanics Measurements* (R. J. Goldstein, Ed.). Hemisphere Publishing Company, Washington 1983.
4. Tovchigrechko V. V., Kovalevskaya N. D., Pokryvaylo N. A., Wein O.: *Paper presented on 8th International Congress CHISA,* Prague 1984.
5. Wein O., Mistchka P., Tovchigrechko V. V., Kovalevskaya N. D., Yushkina T. V. ,Pokryvaylo N. A.: Chem. Eng. Commun. *32*, 153 1985.
6. Astarita G.: Ind. Eng. Chem. Fund. *5*, 14 (1966).
7. Mashelkar R. A., Dutta A.: Chem. Eng. Sci. *37*, 969 (1982).
8. Beek W. J., Bakker C. A. P.: Appl. Sci. Res. A *10*, 241 (1961).
9. Wein O., Kučera P.: Res. Rep. No. 62., Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 1986.
10. Kubíček M.: *Numerical Algorithms of Solving the Chemical Engineering Problems.* SNTL/ALFA, Prague 1983 (in Czech).
11. Wein O., Kovalevskaya N. D.: Collect. Czech. Chem. Commun. *49*, 1297 (1984).

Translated by the autor (O.W.)