

THE EFFECT OF MIGRATION IN LAMINAR DIFFUSION LAYERS

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Newman's similarity model of convective diffusion of ions through multi-ionic concentration boundary layer in the presence of electric field is generalized for non-linear velocity profiles in the diffusion layer, and put into a form that can be integrated by the Runge-Kutta method. The results of a numerical solution are compared with voltammetric data from the literature.

Quantitative treatment of electrochemical data obtained in electrodiffusion diagnostics of convection processes¹ and in electroanalytical chemistry² is based on phenomenological models of transport processes in electrolytic cells³. Usually, it is necessary to model phenomena in three subregions arranged in series: at the surface of the working electrode, in a thin adjacent diffusion layer, and in the bulk of the solution^{3,4}. The dynamics of the electrode process is represented by the dependence of the current density on the composition of the solution at the electrode surface and on the surface overpotential. In the bulk of the liquid, the problem of current conduction at constant composition and conductivity must be solved. The solution of the convective diffusion problem in a thin diffusion layer for arbitrary surface concentrations gives the difference between the concentration and potential at the electrode surface and at the outer boundary of the diffusion layer as functions of the current density J . This information permits to join the description of the electrode reaction kinetics with that of the transport in the diffusion layer to give complex boundary conditions for the solution of the problem about potential and current density distributions in the bulk of the liquid⁵.

The mathematical description of the transport phenomena in solutions containing more than two ionic components is much complicated by taking the migration into account³⁻⁶ even in the limiting current regime, where the depolarizer concentration at the surface of the working electrode is negligible against that in the bulk. Whereas without migration the transport equations for the particular species are linear and mutually interrelated only by the stoichiometry of the electrode reaction, in the presence of the migration transport a system of simultaneous differential equations bound through migration terms with the unknown potential gradient must be considered. For multi-ionic systems, only particular numerical solutions are known, published for several systems with 3-5 components³⁻⁶ using tabulated values of the diffusion coefficients⁷. Such results are only of limited significance for quantitative treatment of the measured limiting current densities to obtain the real diffusivities, since the diffusion coefficients of the ionic species are strongly dependent on the ionic strength even in very dilute solutions⁸.

The contemporary state of the computer technique and its extent of exploitation caused a principal change in the views about working with complicated mathematical models. Tabulated data from isolated numerical solutions are no more in the focus of interest, but either correlations based on extensive data calculated for wide regions of input parameters, or the relevant application programs suitable for users who are not specialists in the theory or in numerical mathematics are desired.

The present work is a continuation of that of Newman^{4,5}, who showed that for a concentration boundary layer in a laminar flow regime, the electric potential field can be expressed by using the same similarity transformation as for the concentration field. The sort of problems considered by Newman^{4,5} is here, at the same similarity structure of the resulting boundary value problem, generalized for cases with non-zero depolarizer concentration at the electrode surface and for non-linear velocity profiles in the diffusion layer, which is important when non-Newtonian liquids are considered.

The results of the classical theory of the concentration boundary layer³, in which the migration effects are neglected, are considered as a special case of the general theory, for which the results, especially the current density distribution at the electrode surface, $J_{\text{dif}} = J_{\text{dif}}(x, t)$, are known. The influence of migration on the measured currents in a real electrochemical experiment is then expressed as $E = J/J_{\text{dif}}$, where $J = J(x, t)$ is the local current density at a given composition of the bulk solution.

For the numerical solution of the resulting system of simultaneous non-linear equations, a new and highly effective algorithm is proposed. Its structure is described to a limited extent, which is indispensable for working with the application program MIGR-1.

THEORETICAL

Starting Transport Equations in the Diffusion Layer Approximation

Phenomenological description of isothermal transport of ionic species in not too concentrated strong electrolyte solutions in the presence of a not too strong electric field is based on the following four equations:

$$\sum z_i c_i = 0, \quad (1)$$

$$\mathbf{N}_i = c_i \mathbf{v} - D_i c_i \nabla \tilde{\mu}_i / RT, \quad (2)$$

$$\partial_t c_i + \nabla \cdot \mathbf{N}_i = 0, \quad (3)$$

$$\mathbf{J} = F \sum z_i \mathbf{N}_i. \quad (4)$$

The dependences of the activity coefficients and diffusion coefficients on the composition of the solution can be expressed as functions of a single independent parameter, namely ionic strength of the solution, defined as

$$\Gamma \equiv \frac{1}{2} \sum z_i^2 c_i. \quad (5)$$

The assumptions $D_i = \text{const.}$ and

$$c_i \nabla \tilde{\mu}_i / RT = \nabla c_i + z_i c_i \nabla P \quad (6)$$

are therefore plausible not only for infinitely dilute solutions ($\Gamma \rightarrow 0$), but also for such cases where it can approximately be assumed that $\Gamma = \text{const}$.

Substitution of the thermodynamic constitutive equation (6) into the transport constitutive equation (2) leads to the usual expression for the fluxes

$$\mathbf{N}_i = -D_i(\nabla c_i + z_i c_i \nabla P) + c_i \mathbf{v}, \quad (7)$$

which is compatible with the Nernst–Einstein relation between diffusivities and mobilities of ions. The basic transport equation in molar concentrations follows by substituting Eq. (7) into (3) and observing the condition of incompressibility $\nabla \cdot \mathbf{v} = 0$:

$$\partial_t c_i + \mathbf{v} \cdot \nabla c_i = D_i \nabla \cdot (\nabla c_i + z_i c_i \nabla P). \quad (8)$$

In typical electrodiffusion experiments^{1,2}, the concentration changes due to a heterogeneous reaction at the working electrode are only significant in a thin solution layer adjacent to the electrode surface. The notion of the diffusion layer⁴ based on this fact permits to simplify both the transport equations (8) and the boundary conditions, which can now be situated at the boundaries of the diffusion layer.

At a given velocity field close to the working electrode, it is possible to choose orthogonal curvilinear coordinates (z, x, y) so that z is the distance from the electrode surface and x is the distance between a point on the electrode surface and the leading edge of the electrode along the streamline. Assuming that the thickness of the diffusion layer is much smaller than the dimensions of the electrode, we may neglect both the macroscopic curvature of its surface and the longitudinal component of the concentration gradient. If the electric field in the diffusion layer is only due to electrode processes at the working electrode and the corresponding transport of ions, the longitudinal component of the intensity of the electric field can be neglected as well. The resulting transport equations in the diffusion layer approximation can be written as follows:

$$\begin{aligned} (\mathbf{N}_i)_x &= c_i v_x, \quad (\mathbf{N}_i)_y = 0, \\ (\mathbf{N}_i)_z &= c_i v_z - D_i(\partial_z c_i + z_i c_i \partial_z P) \end{aligned} \quad (9)$$

$$\dot{c}_i = \partial_t c_i + v_x \partial_x c_i + v_z \partial_z c_i = \partial_z D_i(\partial_z c_i + z_i c_i \partial_z P). \quad (10)$$

Summation of the transport equations (10) multiplied by z_i , observing the electro-neutrality condition (1) and integrating gives the basic result of the theory of multi-ionic diffusion layer, viz., that the current density at a given point is independent of the z coordinate, $\partial_z J_z = 0$,

$$J_z = -F(\sum z_i D_i \partial_z c_i + \partial_z P \sum z_i^2 D_i c_i) \quad (11)$$

and equal to the current density at the electrode surface, J :

$$J_z = J(x, t). \quad (12)$$

The electrode process can be formulated by the stoichiometric relation



For the species consumed in the reaction (further: working depolarizers), we have $s_i > 0$, while for those produced (further: auxiliary depolarizers) $s_i < 0$, and for other (indifferent) species $s_i = 0$. The stoichiometry of the reaction leads to the balance of the charge transferred

$$n^* = -\sum z_i s_i \quad (14)$$

and to the balances of the fluxes at the electrode surface, $z = 0$

$$N_i = D_i(\partial_z c_i + z_i c_i \partial_z P) = s_i J / n^* F, \quad (15)$$

representing the boundary conditions for our problem at the inner boundary of the diffusion layer. Its outer boundary can, with regard to the transport inside the diffusion layer, be situated at an "infinite" distance from the electrode surface, $z \gg \delta_0(x)$, i.e. in the bulk of known composition, c_{Bi} :

$$c_i|_{z \rightarrow \infty} = c_{Bi}. \quad (16)$$

When the existence and uniqueness of the solution for the transport model of the diffusion layer is considered, it should be kept in mind that this model forms only a part of a broader description of processes in an electrolytic cell, which, in general, must take into account the ohmic voltage drop in the bulk of the liquid and the kinetics of the electrode reaction as function of the overpotential between the working and auxiliary electrodes. Nevertheless, isolated study of transport processes in the diffusion layer can be based on the circumstance that the system of transport equations (10) with boundary conditions (15) and (16) supplemented by the local electroneutrality condition (1) and eventual initial equilibrium conditions for $t = 0$

$$c_i|_{t \rightarrow 0} = c_{Bi} \quad (17)$$

has a single remaining degree of freedom. This can be fixed, e.g., by assuming that the current density is given as $J = J(x, t)$. However, not every such a priori given function is compatible with the condition that $c_i \geq 0$ for all concentration distribu-

tions in the diffusion layer. As a special case, when the current density is gradually increased to reach its limiting value, $J \rightarrow J_{\text{lim}}$, the surface concentration of one of the working depolarizers approaches zero, $c_{wi} \rightarrow 0$. This species is the "clue" depolarizer limiting the intensity of the electrode process at a given bulk composition, c_{Bi} , and a given stoichiometry of the electrode process, s_i . In the text below, the distribution of the current densities over the electrode surface, $J = J(x, t)$, as function of the assumed distribution of the surface concentration of the clue depolarizer will be considered as the solution of the problem. The clue depolarizer is denoted by the subscript $i = 1$, its stoichiometric number $s_1 = 1$, and its surface concentration is given as

$$w = c_{w1}/c_{B1} . \quad (18)$$

It should be noted that the calculations of migration currents published hitherto were done for the limiting conditions, i.e.

$$w = 0 . \quad (19)$$

The problem about the influence of the concentration parameter w on the transport in the diffusion layer was solved recently⁹ on the basis of the Nernst stagnant layer approximation.

Similarity Formulation

The system of partial differential equations (10) lacks the initial conditions such as definitions of starting concentration profiles $c_i(z)$ for $x = 0$. This circumstance is not accidental but is related with the local character of the transport model in the boundary layer approximation. To calculate the local current density at a given $w = w(x, t)$ and a given velocity field v_x, v_z , it is sufficient to know these parameters in a relatively small region around the point considered on the electrode surface. The existence of so-called similarity solutions is a formal reflexion of the local character of the transport equations for the diffusion layer.

The similarity solutions are formulated on the assumption that the concentration and potential fields can be expressed by functions of a single similarity argument, Z , as

$$c_i(x, z, t) = c_{B1} C_i(Z) , \quad (20)$$

$$P(x, z, t) = P(Z) , \quad (21)$$

$$Z = z/\delta_o , \quad (22)$$

$$\delta_o = \sigma(x, t) D_1^{1/(2+p)} . \quad (23)$$

In this formulation, the concentration fields are normalized by the concentration of the clue depolarizer in the bulk, c_{B1} . The parameter δ_0 represents an estimate of the local diffusion thicknesses, the function $\sigma(x, t)$ and the constant p depend on the transport regime only, i.e. on the velocity field and on the function $w(x, t)$.

Substitution of the equations (20)–(22) into the transport equation (10) for the stationary state and the assumption $C_i = C_i(Z)$ lead to the differential equation

$$b_i H'(Z) C_i'(Z) + (C_i' + z_i C_i P')' = 0, \quad (24)$$

where

$$b_i = D_1 / D_i. \quad (25)$$

The following equation is important for the similarity transformation:

$$H'(Z) = \frac{z}{D_1} \left(v_x \frac{d\delta_0}{dx} - v_z \frac{\delta_0}{z} \right). \quad (26)$$

This expresses not only the definition of the function $H'(Z)$, but also the assumption that $\delta_0(x)$ can be found such that the expression on the right-hand side be function of $Z = z/\delta_0(x)$, i.e. of a single argument, in the considered range of the variables x and z .

A sufficient condition for the existence of such a transformation in the local sense is the existence of a representation of the longitudinal velocity field in the product form

$$v_x = \beta(x) \frac{d^2 h(z)}{dz^2}, \quad (27)$$

where the function $h(z)$ is further expressed as

$$h(z) \sim z^{p+2}. \quad (28)$$

The equation of continuity written for the boundary layer in curvilinear x, z coordinates

$$\partial_x(rv_x) + \partial_z(rv_z) = 0 \quad (29)$$

gives the following expression for the normal velocity component in the central region of the diffusion layer

$$v_z = - \frac{dh}{dz} \beta(x) \frac{d \ln r \beta}{dx}. \quad (30)$$

Substitution of the velocity fields according to equations (27)–(30) into the condition (26) leads to an expression for the function $H'(Z)$ in the form of Eq. (28)

$$H(Z) = Z^{p+2} \quad (31)$$

and to the following differential equation for the effective thickness of the diffusion layer

$$\frac{\delta_0^{p+2}}{D_1} \frac{\beta(x)}{x} \left[(p+1) \frac{d \ln \delta_0}{d \ln x} + \frac{d \ln r}{d \ln x} \right] = 1 \quad (32)$$

with a known solution $\delta_0 = D_1^q \sigma(x)$, where

$$q = 1/(p+2), \quad (33)$$

$$\sigma(x) = (r\beta)^{-(p+1)} \left[(p+2)^2 \int_0^x (\beta r^{p+2})^{1/(p+1)} dx \right]^{1/(p+2)}. \quad (34)$$

For linear velocity profiles, $p = 1$, this procedure is known as the Lighthill–Acrivos transformation⁴; for other p values an analogous transformation is considered in refs^{10,11}.

It is not necessary to assume that the function $H(Z)$ can be expressed in a power form. For example, for streaming in the forward critical region, where the normal velocity profile is independent of the longitudinal coordinate, $v_z = h'(z)$, the function $H(Z)$ can be introduced implicitly by the following definition involving an arbitrary constant parameter δ_0 :

$$H(z/\delta_0) = \int_0^z v_z dz. \quad (35)$$

The form parameter p is then defined as

$$p+1 = \left. \frac{d \ln v_z}{d \ln z} \right|_{z=\delta/2}, \quad (36)$$

where δ is the true diffusion thickness and the quantity σ depends somewhat on the diffusion coefficient.

The similarity system of differential equations (24) is also obtained in some problems concerning transient transport phenomena after stepwise change of conditions on the electrode surface. This is especially the case of Cottrellian diffusion (penetration of the diffusion layer into motionless liquid^{4,12} under potentiostatic conditions) and of the transient process on a dropping electrode growing at a constant volume

rate^{4,13}. In these cases, Eqs (10) must be solved with the initial condition

$$c_{w1} = \begin{cases} c_{B1} & (t < 0) \\ wc_{B1} & (t > 0) \end{cases} \quad (37)$$

and the similarity transformations are given by Eqs (20)–(23), where

$$p = 0, \quad \sigma = K \sqrt{t}. \quad (38)$$

The dimensionless constant K ensuring the normalized form $H'(Z) = 2Z$ depends on the type of the process considered. For Cottrellian diffusion^{4,12} we have $K = 2$, for a growing Hg drop $K = \sqrt{(12/7)}$. The similarity equations (24) have the same form as in steady-state convective transport involving perfect sliding of the liquid over the electrode surface¹⁴.

In addition to the Cottrellian diffusion model, also the Nernst model of the stagnant layer^{4,15} can be included in the class of problems considered. In this case we have $p \rightarrow \infty$; obviously

$$\lim_{p \rightarrow \infty} H'(Z) = \begin{cases} 0 & \text{for } Z < 1 \\ \infty & \text{for } Z > 1 \end{cases} \quad (39)$$

and $\delta = \delta_0$ is an arbitrary constant.

Substitution of the transformation equations (20)–(23) into Eq. (11) for the current density leads to the equation

$$-J^* = \sum b_i^{-1} z_i C_i + (\sum b_i^{-1} z_i^2 C_i) P' = \text{const.}, \quad (40)$$

where

$$J^* \equiv J\sigma(x, t)/(FD_1^{1-a} c_{B1}) \quad (41)$$

is the "eigenvalue" of the boundary value problem considered, for which the calculation of the constant parameter J^* represents the main goal.

The similarity formulation of boundary conditions and local electroneutrality conditions is obviously

$$C_i|_{Z \rightarrow \infty} = C_{Bi} = c_{Bi}/c_{B1}, \quad (42)$$

$$(C'_i + z_i C_i P')|_{Z=0} = C'_{wi} + z_i C_{wi} P'_w = s_i b_i J^*/n^*, \quad (43)$$

$$C_1|_{Z=0} = w, \quad (44)$$

$$\sum z_i C_i(Z) = 0; \quad Z \in (0; \infty). \quad (45)$$

For discussion of the analytical properties of the solution it is convenient to introduce some "concentration invariants" following from Eqs (24) and (43) with regard to the condition of electroneutrality. A typical example of a concentration invariant is Eq. (40), which follows by summation of Eqs (24) multiplied by z_i/b_i , integrating the result and determining the integration constant from the conditions (43). By substituting the intensity P' ,

$$P' = \frac{J^* + \sum b_i^{-1} z_i C_i'}{\sum b_i^{-1} z_i^2 C_i}, \quad (46)$$

and the divergence P'' expressed analogously,

$$P'' = - \frac{\sum z_i (b_i H' + z_i P') C_i'}{\sum z_i^2 C_i}, \quad (47)$$

into the transport equations (24) and conditions (43), the potential can be eliminated from the formulation of the problem.

The expression for the surface intensity

$$P'_w = P'(Z)|_{Z=0} \quad (48)$$

in terms of the concentration fields is important. In addition to the general representation (46) used for $Z = 0$, i.e. $C_i' = C'_{wi}$, $C_i = C_{wi}$, independent expression for P'_w can be found by summation of the boundary conditions (43) multiplied by z_i :

$$G_w P'_w = -S^* J^* / n^*. \quad (49)$$

Here we have introduced

$$-S^* = \sum s_i b_i z_i \quad (50)$$

and $G_w = G(Z)$ for $Z = 0$, where generally

$$G = \sum z_i^2 C_i. \quad (51)$$

By combining Eqs (46) and (49), P'_w can be expressed independent of the current density as

$$P'_w = \frac{\sum b_i^{-1} z_i C'_{wi}}{\sum (-b_i^{-1} + n^*/S^*) z_i^2 C_{wi}}. \quad (52)$$

In addition to the normalized current density J^* and normalized surface concentrations C_{wi} , the normalized surface intensity of the electric field is another important parameter whose calculation is aimed at.

ANALYTICAL SOLUTIONS AND APPROXIMATIONS

Analytical solutions of the problem represented by Eqs (24) with the conditions (42)–(45) are known for three simple cases which will be briefly discussed below by using the new notation.

Diffusion Asymptote

This asymptote is introduced ad hoc⁴ by ignoring all migration terms, i.e. $P' = 0$. In this case, the simultaneous non-linear system (24) for the ionic species $i = 1, \dots, N$ splits into differential equations $H'b_i C'_i + C''_i = 0$ with the obvious analytical solution

$$C_i = C_{wi} + C'_{wi} \int_0^Z \exp(-b_i H) dZ, \quad (53)$$

where

$$C'_{wi} \equiv C'_i(Z=0) = \frac{C_{Bi} - C_{wi}}{\int_0^\infty \exp(-b_i H) dZ}. \quad (54)$$

As a special case, for the usual power form of the function $H(Z)$,

$$C'_{wi} = (C_{Bi} - C_{wi}) b_i^q / \Gamma(q+1), \quad (55)$$

where Γ is the Euler gamma function and $q = 1/(p+2)$. The corresponding value of the diffusion current density follows from Eq. (43) for the clue depolarizer in the form

$$\frac{J_{dif}^*}{n^*} C'_{w1} = \frac{1-w}{\Gamma(q+1)}. \quad (56)$$

For other depolarizers, $s_j \neq 0$, the surface concentration gradients are also given by the conditions (43), whence it follows

$$C'_{wj} = s_j b_j \frac{1-w}{\Gamma(q+1)}. \quad (57)$$

The concentrations of indifferent species are constant for the diffusion asymptote,

$$C'_{wk} = 0, \quad C_k = C_{Bk}. \quad (58)$$

This solution does not satisfy the condition of local electroneutrality, hence the concentration invariants (46), (49), and (52) give profoundly different estimates of the

surface electric intensity:

$$P'_W = 0, \quad (59a)$$

$$P'_W = \frac{(1-w)S^*}{\Gamma(1+q)} \left/ \left[G_B - (1-w) \sum z_i^2 b_i^{1-q} s_i \right] \right., \quad (59b)$$

and

$$P'_W = \frac{(1-w)S^*}{\Gamma(1+q)} \left/ \left[\sum \left(\frac{S^*}{n^*} - b_i \right) z_i^2 (b_i^{-1} C_{Bi} - (1-w) b_i^{-q} s_i) \right] \right.. \quad (59c)$$

Somewhat more realistic estimates of P'_W , J^* , and C_{wi} can be obtained on the assumption that the terms $C_i P''$ in Eqs (24) are negligible against $C'_i P'$. The equations can then be integrated and the result for $P \approx P'_W Z$, $P'_W \rightarrow 0$ is the following:

$$\frac{C_{Bi} - C_{wi}}{C'_{wi}} = \int_0^\infty \exp(-b_i H - z_i P) dZ \approx \frac{\Gamma(1+q)}{b_i^q} \left(1 - \frac{z_i P'_W}{b_i^q} \frac{\Gamma(2q+1)}{2\Gamma(q+1)} \right). \quad (60)$$

By introducing this into the boundary conditions (43) and the concentration invariants (46), (49), and (52) we obtain a self-consistent estimate of P'_W :

$$P'_W = \frac{1-w}{\Gamma(1+q)} X + O(X^2), \quad (61)$$

$$\frac{J^*}{n^*} = \frac{1-w}{\Gamma(1+q)} \left[1 + \left(w + (1-w) \frac{\Gamma(2q+1)}{2\Gamma^2(q+1)} \right) z_i X \right] + O(X^2), \quad (62)$$

where, in accord with Eq. (59b),

$$X \equiv S^*/G_B. \quad (63)$$

Binary Electrolyte Solution

This case can be solved exactly⁴ by elementary methods, since the condition of electroneutrality, $z_1 C_1 + z_3 C_3 = 0$, permits to simplify the system considerably. The potential can be eliminated by adding Eqs (24) for both components. The intermediate result $H'(b_1 C'_1 + b_3 C'_3) + (C'_1 + C'_3)' = 0$ can be rearranged by using the relation $C'_3 = -(z_1/z_3) C'_1$ to the considered form $b_s H' C'_1 + C''_1 = 0$, where

$$b_s \equiv D_1/D_s = (z_1 b_1 - z_3 b_3)/(z_1 - z_3). \quad (64)$$

The concentration field problem has hence a solution analogous to (46), whence

$$C'_{w1} = \frac{(1-w)b_s^q}{\Gamma(1+q)}, \quad C'_{w3} = -(z_1/z_3) C'_{w1}, \quad C_{w3} = -(z_1/z_3) w. \quad (65)$$

By adding the boundary conditions (43) for both components, the potential is eliminated and we arrive at the following expression for the current density:

$$\frac{J^*}{n^*} = \frac{C'_{w1} + C'_{w3}}{1 + s_3 b_3} = \frac{(1-w) b_3^q (1 - z_1/z_3)}{(1 + s_3 b_3) \Gamma(1+q)}. \quad (66)$$

Physically, only a single ionic species can be discharged, $s_3 = 0$.

The ratio of D_1/D_s is usually expressed by means of the transference number, t_1 , i.e. in our case

$$\frac{D_1}{D_s} = b_s = \frac{1}{(1-t_1)(1-z_1/z_3)}. \quad (67)$$

From this we arrive at the result in the usual form⁴

$$\frac{J^*}{n^*} = \frac{1-w}{\Gamma(1+q)} \frac{(1-z_1/z_3)^{1-q}}{(1-t_1)^q}. \quad (68)$$

The influence of migration on the current density is apparent by comparing Eq. (68) with Eq. (56), which does not involve migration.

Improved Nernst's model

With neglect of the convective and accumulation terms, $H'(Z) = 0$, the transport equations (24) can be integrated to obtain the form corresponding to the so-called Nernst model

$$C'_i + z_i C_i P' = s_i b_i J^* / n^*. \quad (69)$$

The influence of the convection and accumulation processes is represented here by the diffusion thickness for the clue depolarizer

$$\delta_1 \equiv D_1 (c_{B1} - c_{w1}) n^* F / J_{\text{dif}}, \quad (70)$$

which is considered as known from the solution of the corresponding equations of convective diffusion or some transport correlations. An inadequacy of this model, which has often been criticized, is that it ignores the dependence of the mass-transfer coefficients of individual species on their diffusivity. In addition, it also ignores the effect of convective diffusion of the indifferent species of different diffusivities on the electric potential profile. Both these inadequacies can be widely suppressed by an empirical modification of Eqs (69) to the form

$$C'_i + \zeta_i C_i P' = s_i b_i^{1-q} J^* / n^*. \quad (71)$$

Here, the right-hand side involves a correction for the true diffusion thicknesses of the depolarizers in accord with the familiar relation $\delta_i \sim D_i^{\frac{1}{2}}$. The coefficients ζ_i can be empirically adjusted, e.g. so that the final solution gives the known exact values of limiting current densities in the laminar diffusion layer for binary electrolyte solutions.

Already Eucken¹⁵, integrating Eqs (69), used substitution of the potential for an independent variable. By summation of Eqs (71) multiplied by z_i we obtain the concentration invariant

$$P' = \frac{\sum s_i b_i^{1-q} z_i J^*}{\sum z_i \zeta_i C_i n^*} \quad (72)$$

and another form of Eqs (71)

$$\frac{dC_m}{dP} + \zeta_m C_m = \frac{s_m b_m^{1-q}}{\sum s_i b_i^{1-q} z_i} \sum z_i \zeta_i C_i. \quad (73)$$

For indifferent species, $s_k = 0$, the solution is obviously

$$C_k = C_{Bk} \exp [\zeta_k (P_B - P)]. \quad (74)$$

It remains to solve the subsystem of Eqs (73) for ionic depolarizers. Although systems with more than two ionic depolarizers have been considered in the literature¹⁶, it is practically sufficient to consider only those with at most two ionic depolarizers, $j = 1, 2$. In such a case, the solution can be expressed in a relatively simple form⁹

$$C_1 = C_{B1} E_\lambda + \sum_k \frac{(\lambda - \zeta_1)(\zeta_2 - \zeta_k) z_k C_{Bk}}{(\zeta_2 - \zeta_1)(\lambda - \zeta_k) z_1} (E_\lambda - E_k), \quad (75)$$

$$C_2 = C_{B2} E_\lambda + \sum_k \frac{(\lambda - \zeta_2)(\zeta_1 - \zeta_k) z_k C_{Bk}}{(\zeta_1 - \zeta_2)(\lambda - \zeta_k) z_2} (E_\lambda - E_k).$$

Here, summation is carried out over all indifferent ionic species. The functions E_λ and E_k are defined as

$$E_\lambda \equiv \exp [\lambda (P_B - P)], \quad E_k = \exp [\zeta_k (P_B - P)], \quad (76)$$

$$\lambda = \zeta_1 \zeta_2 \frac{(z_1/\zeta_1) s_1 b_1^{1-q} + (z_2/\zeta_2) s_2 b_2^{1-q}}{z_1 s_1 b_1^{1-q} + z_2 s_2 b_2^{1-q}}. \quad (77)$$

The integration constant P_B is the root of the equation

$$w = \exp (\lambda P_B) + \sum \frac{(\lambda - \zeta_1)(\zeta_2 - \zeta_k) z_k C_{Bk}}{(\zeta_2 - \zeta_1)(\lambda - \zeta_k) z_1} [\exp (\lambda P_B) - \exp (\zeta_k P_B)]. \quad (78)$$

To determine the current density, the method according to Eucken¹⁵ is the most straightforward. Integration of the starting transport equation (71) for the clue depolarizer over the thickness of the diffusion layer leads to the equation

$$\frac{J^*}{n^*} = 1 - w + \zeta_1 \int_0^{P_B} C_1 dP, \quad (79)$$

where $C_1 = C_1(P)$ is a known function of the potential P . The migration coefficient introduced by Newman is hence given by

$$E = \frac{J^*}{J_{\text{dif}}^*} = 1 + \frac{\zeta_1}{1 - w} \int_0^{P_B} C_1 dP. \quad (80)$$

The parameters ζ_i in the starting equations are still undetermined. They must satisfy the following requirements:

(1) The values of ζ_i should depend on the bulk composition and on the diffusion coefficients of the present species only.

(2) For stagnant diffusion layers, $q = 0$, it should hold good that $\zeta_i = z_i$.

(3) At equal diffusivities of all species it should hold good that $\zeta_i = z_i$.

(4) The choice of ζ_i must not influence the diffusion asymptote of the solution for $S^*/G_B \rightarrow 0$.

(5) The choice of ζ_i should ensure the exact value of J^*/J_{dif}^* for binary electrolyte solutions.

From Eqs (56) and (68) we obtain the following expression for the ratio of J^*/J_{dif}^* for laminar diffusion layers in binary electrolytes:

$$\frac{J^*}{J_{\text{dif}}^*} = \frac{(1 - z_1/z_3)^{1-q}}{(1 - t_1)^q} = \left(\frac{b_3^{-1} - z_1/z_3}{1 - z_1/z_3} \right)^q (1 - z_1/z_3). \quad (81)$$

The solution for the Nernst model, Eqs (71) for $i = 1, 3$ and $s_3 = 0$, gives the simple result

$$J^*/J_{\text{dif}}^* = 1 - \zeta_1/\zeta_3. \quad (82)$$

The coefficients ζ_i can be adjusted in accord with the requirements (1)–(5) in several ways, one of which will be used here. For the species participating in the electrode reaction we set

$$\zeta_j = z_j, \quad (83a)$$

and for indifferent ionic species

$$\zeta_k = z_k \frac{1 - \varepsilon_k}{(D_e/D_k)^q - \varepsilon_k}, \quad (83b)$$

where $\varepsilon_m = z_m^2 C_m / \sum z_i^2 C_i$, $D_e = \sum \varepsilon_i D_i$. Hence, for the binary electrolyte solution $\zeta_1 = z_1$ and

$$\zeta_3 = z_3 \frac{1 - z_3/(z_3 - z_1)}{(1 - D_1 z_1 / D_3 z_3)^q - z_3/(z_3 - z_1)}, \quad (84)$$

whence it follows easily that

$$1 - \zeta_1/\zeta_3 = (D_3/D_1 - z_1/z_3)^q (1 - z_1/z_3)^{1-q}. \quad (85)$$

For the opposite situation, i.e. excess of indifferent ions, $S^*/G_B \rightarrow 0$, the potential difference P_B is so small that the exponential functions in Eqs (78) and (79) can be expanded in series according to the Taylor theorem. This leads to the asymptotic result

$$\frac{1 - w}{P_B} = \frac{\sum z_i \zeta_i C_{Bi}}{\sum z_i s_i b_i^{1-q}} - z_1, \quad (86)$$

$$\frac{J^*}{J_{dif}^*} = 1 + \frac{1 + w}{2} \frac{z_1 P_B}{1 - w}. \quad (87)$$

User Program MIGR-1

The analytical solutions described above are useful mainly for understanding the nature of the migration effects in multiionic systems and for qualitative considerations. For quantitative treatment of data, e.g. in determining the true diffusion coefficients by electrodiffusion methods, it is desirable to know the migration coefficients $E = J/J_{dif} = J^*/J_{dif}^*$ with an accuracy of 0.1 per cent. To this end, it is necessary to know the exact solution which can only be obtained by numerical integration of the transport equations with the boundary conditions.

In the Runge-Kutta integration method, the integrated differential equations (24) must be rearranged to the form giving the derivatives of the highest order as functions of the other local quantities,

$$-C_1'' = b_1(p + 2) Z^{p+1} + z_1 P' C_1' + z_1 P'' C_1. \quad (88)$$

The gradient P' and the divergence P'' of the electric potential are expressed as functions of concentrations and their gradients by Eqs (46) and (47). The boundary

conditions give the solution composition in the bulk, $C_i(\infty) = C_{Bi}$, and the surface concentration of the clue depolarizer, $C_1(0) = w$. Other parameters must be determined during solving the problem.

In the Runge-Kutta method, the solution procedure consists in integrating the equations (88) with the initial conditions

$$P'_w = -S^*J^*/n^*G_w, \quad (89)$$

$$C'_{wi} = s_i b_i J^*/n^* - z_i C_{wi} P'_w = (J^*/n^*) (s_i b_i + z_i C_{wi} S^*/G_w), \quad (90)$$

$$J^*/n^* = C'_{wi}/(1 + z_i w S^*/G_w), \quad (91)$$

where $G_w = \sum z_i^2 C_{wi}$. To specify the initial conditions fully, it is thus sufficient to know all surface concentrations and the surface concentration gradient of the clue depolarizer.

The task of numerical solution is thus reduced to seeking a suitable iteration strategy for finding the unknown parameters in the initial conditions. The following strategy proved well (and suitable for automatic calculations of large ensembles of problems) even at very low concentrations of the indifferent electrolyte under limiting conditions:

(1) The results for a purely diffusion asymptote, Eqs (55) to (58), are used as starting estimates.

(2) Integration is carried out on an interval $Z \in (0, Z_\infty)$ sufficiently long to attain the conditions $\text{Max } |C'_i| > \varepsilon_D (= 10^{-7})$. This leads to certain estimates of the concentrations in the bulk, C_{Qi} .

(3) New estimates of the initial conditions are made on the assumption of linearity and independency of the solutions for the particular species

$$C_{wi} = C_{wi} + C_{Bi} - C_{Qi}$$

$$C'_{wi} = C'_{wi}(1 - w)/(C_{Qi} - w)$$

(4) Iterations are repeated until the values of C_{Qi} attain the preset values of C_{Bi} with an accuracy of ε_Q , i.e. $\text{Max } |C_{Qi} - C_{Bi}| < \varepsilon_Q (= 10^{-5})$.

In common cases, i.e. with solutions containing indifferent electrolytes in usual concentrations, or for other than limiting regimes, $w \neq 0$, ten to fifteen iterations are needed to attain a relative accuracy of 10^{-7} . More iterations are only necessary in calculating the limiting currents in almost binary electrolytes. The integration is carried out by the Runge-Kutta-Merson method with automatic increase of the step length. At an initial step $\Delta Z = 0.001$, the upper estimate of the inaccuracy in C_{Qi} is about 10^{-5} . The mean time required for the calculation of one variant on

A Commodore PC 10 computer is 30 s, so the greater problem is the repeated keying-in of input data about transport regimes and electrochemical systems. For the purpose of automation, the user program MIGR-1 was equipped with auxiliary subroutines to organize the keying-in of data with the use of a mini-data bank containing the necessary physico-chemical constants (diffusivities, charge numbers, and stoichiometric coefficients) for common electrochemical systems. A diskette with the program and auxiliary modules is available by the author.

RESULTS AND DISCUSSION

A typical output from the computer is reproduced in Table I.* We consider a three-ion system, H^+ , K^+ , and Cl^- with charge numbers $z_i \equiv z[i]$, diffusivity ratios $b_i^{-1} \equiv d[i]$, and stoichiometric coefficients $s_i \equiv s[i]$. The second part of the table contains parameters indicating that the calculations were performed for the Light-hill-Acrivos transport regime, $p \equiv \text{preg} = 1$, under limiting conditions $C_{w1} \equiv$

TABLE I

An example of computer output

```

MIGR1                                     5.3.1987  11:59:0

elchem. system considered:                file " hypocl "
i      component      cb[i]  z[i]  d[i]  s[i]
1  hydroxonium      1.0000  1  1.00000  1
2   potassium      1.0000  1  0.21016  0
3   chloride      2.0000 -1  0.21821  0

preg :    1.0000          cdf :  -1.1198          h : 0.0001
cw[1] :  0.0000          eps :  4.0E-005

          variation of bulk conc. ratio

   rat  cb[2]  cw[2]  cw[1]  dcw[1]  cur/cdf  potm  S/gb
0.9000  9.0000  9.4798  0.0000  1.2144  1.0845  -0.1469  -0.0500
0.8000  4.0000  4.4629  0.0000  1.3115  1.1711  -0.2401  -0.1000
0.6667  2.0000  2.4372  0.0000  1.4482  1.2932  -0.3099  -0.1667
0.5000  1.0000  1.3979  0.0000  1.6402  1.4647  -0.3322  -0.2500
0.3333  0.5000  0.8458  0.0000  1.8752  1.6745  -0.2827  -0.3333
0.2000  0.2500  0.5361  0.0000  2.1255  1.8980  -0.1570  -0.4000
0.1000  0.1111  0.3278  0.0000  2.3979  2.1413  0.0736  -0.4500
0.0400  0.0417  0.1873  0.0000  2.6606  2.3758  0.4421  -0.4800
0.0100  0.0101  0.0864  0.0000  2.9031  2.5924  1.0774  -0.4950

MIGR1                                     5.3.1987  12:21:8

```

* The sign of identity is used in the text below to denote equivalence between mathematical symbols (on the left-hand side) and the symbols used in the program and printed output.

$\equiv cw[1] = 0$. Then follows the datum about the limiting diffusion current, $J^* \equiv \equiv cdf = n^*/\Gamma(4/3) = -1.1198$. The parameters h and ϵ give the initial integration step and the required accuracy of the calculation of C_{Q_i} .

The third part of Table I contains the numerical results. In the given case, the concentration ratio

$$r = - \frac{z_{N-1} C_{B,N-1}}{z_N C_{BN}} \equiv \text{rat} \quad (92)$$

is changed automatically. The parameters necessary for specifying the initial conditions, $C_{w_i} = cw[i]$, $C'_{w_i} = dcw[i]$, the migration coefficient $E \equiv cur/cdf$, and the parameter of the potential profile

$$P_M = \lim_{Z \rightarrow \infty} [P(Z) - ZP'(Z)] \equiv \text{potm}$$

are indicated. The last parameter, $S^*/G_B \equiv S/gb$, serves for correlation of the data.

The calculation exemplified in Table I corresponds to the conditions considered by Newman (Table II in ref.⁵) for the "drop" regime. For $r > 1/3$ the results agree very well, larger deviations are apparent at low concentrations of the indifferent

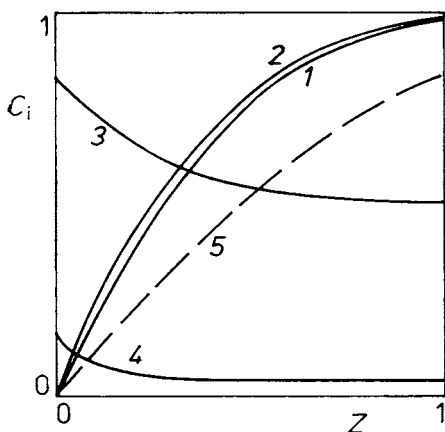


FIG. 1

Concentration profiles for the depolarizer, H^+ , and indifferent electrolyte ion, K^+ , in polarography with a dropping electrode ($p = 0$) in HCl-KCl system. 1, 2 Depolarizer; 3, 4 K^+ ions; 1, 3 $r = [K^+]/[Cl^-] = 0.5$; 2, 4 $r = 0.04$; 5 concentration profile of H^+ ions at a great excess of K^+

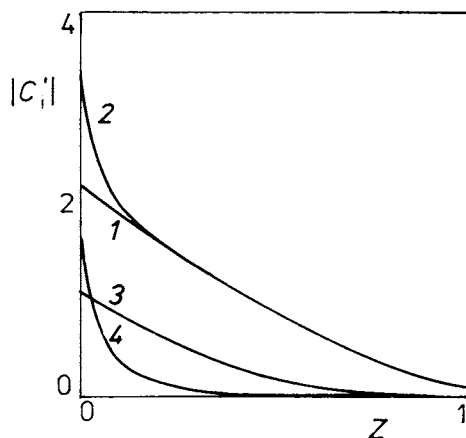


FIG. 2

Profiles of concentration gradients in HCl-KCl system. The symbols have the same meaning as in Fig. 1

electrolyte. They are probably caused by the relatively large integration step, $\Delta Z = 0.01$, used by Newman⁵ in the finite difference method. It is apparent from Figs 1 and 2 that for $r < 1/3$ both the concentration of the indifferent electrolyte and its gradient near the surface change too rapidly for the system of equations to be integrated accurately enough by using steps $\Delta Z = 0.01$.

Exact values of the migration coefficients E for the system $H^+ - K^+ - Cl^-$ for $w = 0$, $p = 1$ are shown graphically in Fig. 3 in comparison with some approximations. It can be seen that none of the considered approximations can be used for quantitative evaluation of E . It is surprising that the oldest and simplest empirical formula

$$E = 1/(1 - t_1) \quad (93)$$

proposed by Heyrovský¹³ gives for $r > 0.1$ still the best estimate. Failure of the asymptotic expansion (62), curve 6, suggests that the terms $P''C_i$ cannot be neglected against $P'C_i$ even for $G_B \rightarrow \infty$.

In Fig. 4 the dependences of E on the transport index p are shown at limiting conditions, $w = 0$, for the system $Cu^{2+} - H^+ - SO_4^{2-}$. It can be seen that this depen-

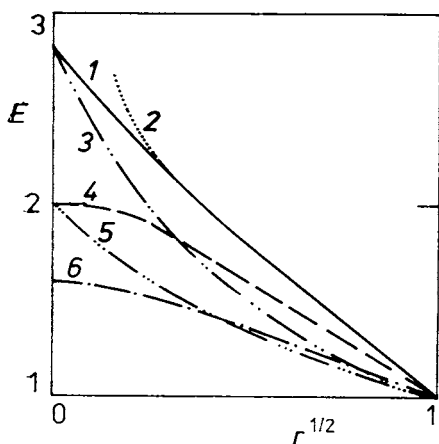


FIG. 3

Migration coefficient $E = J/J_{dif}$ in polarography of a solution of HCl and KCl with a dropping electrode. 1 Exact numerical solution; 2 Newman's numerical solution, 3 improved Nernst's model, Eq. (8); 4 Heyrovský's approximate formula $E = 1/(1 - t_1)$; 5 Nernst's model, Eqs (56) and (68); 6 diffusion asymptote, Eq. (62)

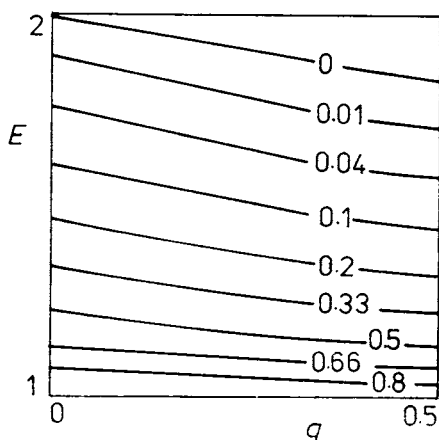


FIG. 4

Dependence of migration coefficient in a solution of $CuSO_4$ and H_2SO_4 on transport conditions, characterized by the exponent $q = 1/(2 + p)$. The numbers refer to the values of $r = [H^+]/2[SO_4^{2-}]$

dence is very weak; to estimate it, it is sufficient to know E for three values of $q = 1/(p + 2)$, corresponding to the Nernst stagnant layer ($q = 0$), laminar concentration layer ($q = 1/3$), and potentiostatic transition ($q = 1/2$). For a binary solution ($r = 0$), Eq. (68) gives the following simple result

$$E = (1 - b_3 z_1/z_3)^q (1 - z_1/z_3)^{1-q}. \quad (94)$$

For redox electrode reactions with ionic products, e.g. for the systems hexacyanoferrate(III) and (IV), iodide-triiodide, etc., the estimates come much closer to the exact values⁹.

To calculate the migration coefficient under limiting conditions, it is sufficient to know the concentrations of the species in the bulk, their diffusivities, and the type of the transport regime. Thus, it is possible to calculate the correct values of $E = J/J_{\text{diff}}$ corresponding to the primary literature data. The new treatment of the data about migration effects is illustrated in Figs 5–9 for two types of transition potentiodynamic experiments^{17,18}. All these experiments, in which the thickness of the diffusion layer is proportional to the square root of the time, belong to a single class of transport situations, $p = 0$. In all cases considered, the solutions contain

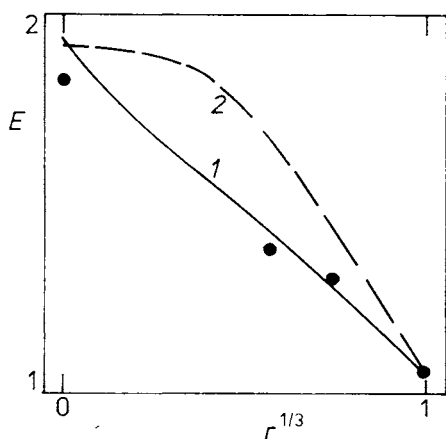


FIG. 5

Migration coefficients in chronopotentiometry of solutions of Tl_2SO_4 and K_2SO_4 . 1 Exact numerical solution; 2 approximate formula according to Heyrovský; experimental data were published by Morris and Lingane¹⁷ in numerical form; diffusivities are from standard tables⁷

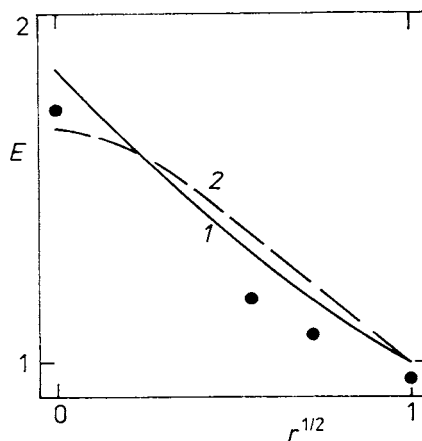


FIG. 6

Migration coefficient in chronopotentiometry of solutions of CuSO_4 and K_2SO_4 . 1 Exact numerical solution; 2 approximate formula according to Heyrovský; experimental data were published by Morris and Lingane¹⁷ in numerical form; diffusivities are from standard tables⁷

three ionic species, $N = 3$, one of which is the depolarizer. The relative composition of such solutions can be characterized⁵ by a single parameter, r , according to Eq. (92). The classical theory for a stagnant Nernst layer^{3,15} implies that the data can suitably be presented by using the argument

$$r^{z_2/(z_1 - z_3)},$$

since the dependence of E on it is roughly linear.

FIG. 7

Migration coefficient in voltammetry of $TlNO_3$ - KNO_3 solutions. 1 Exact numerical solution; 2 Heyrovský's approximate formula; experimental data were published in graphical form¹⁸, diffusivities are from the same source¹⁸

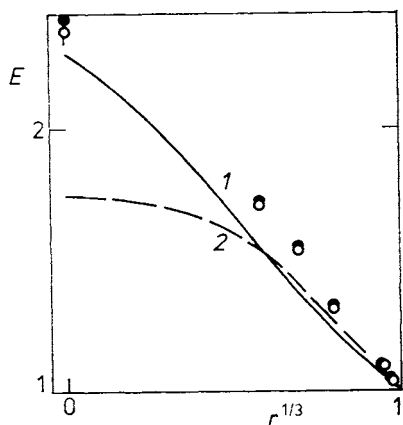
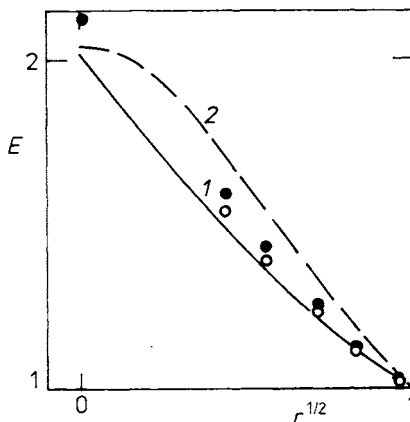


FIG. 8

Migration coefficient in voltammetry of $Cd(NO_3)_2$ - KNO_3 solutions. For explanation see Fig. 7

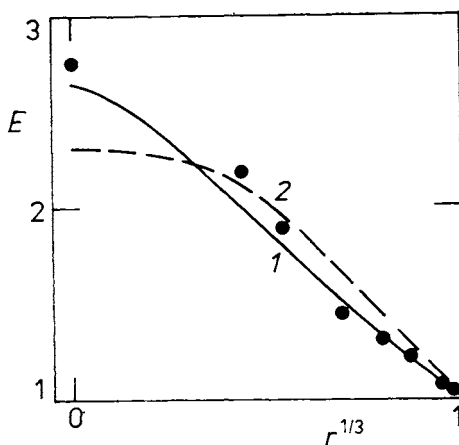


FIG. 9

Migration coefficient in voltammetry of Cu acetate-Li acetate solutions. For explanation see Fig. 7

A very good agreement between theory and experiments is observed for solutions of Tl^+ ions, Figs 5 and 7, and for acetate solutions. In other cases, the agreement lies within the errors of 10%, which are common in electrodiffusion experiments owing to lack of informations about the concentration dependences of diffusion coefficients. For comparison, approximate values of E calculated from Eq. (93) according to Heyrovský are included in the figures.

CONCLUSIONS

1) The transport model of the laminar diffusion layer is adequate for description of transport processes in most regimes encountered in electrodiffusion experiments. It is therefore suitable for quantitative description of electrodiffusion data. Its further refinement is possible by including the dependence of diffusivities and activities of the particular species on the solution composition, which will form the subject of a further communication.

2) The underlying phenomenological description of the laminar diffusion layer according to Newman was generalized for non-linear velocity profiles at the electrode surface and non-zero surface concentrations of the working depolarizer.

3) The new formulation of Newman's model, mainly the explicit formulae for the gradient and divergence of the potential in terms of concentration gradients, permits the use of standard numerical techniques. A user program MIGR-1 was written in PASCAL for the purpose of laboratory calculations.

4) The influence of migration observed in voltammetric and chronopotentiometric transients was for the first time compared with theoretical calculations. The agreement is surprisingly good; the deviations may be due to inaccurate diffusivity data or non-fulfilment of the condition $\delta \sim \sqrt{t}$ in the experiments.

5) Since the corrections for migration can be calculated exactly without difficulties, quantitative electrodiffusion measurements can be carried out without using a large excess of indifferent electrolyte, wherever it may be convenient from the experimental point of view.

The author is grateful to the Alexander von Humboldt Foundation, Bonn, F.R.G., for the liberal donation of the Commodore PC 10 computer.

LIST OF SYMBOLS

$b_i = D_1/D_i$	diffusivity ratio
c_i	concentration of species i
c_{B1}, c_{wi}	values of c_i in the bulk and at the electrode surface
$C_i(Z) = c_i/c_{B1}$	normalized concentration profile
$C_i'(Z)$	normalized concentration gradient
D_i	diffusivity, defined by Eq. (2)

D_s	diffusivity of binary salt solution, Eq. (64)
$D_c = \sum \varepsilon_i D_i$	
$E = J/J_{dif}$	migration coefficient
F	Faraday's constant
$G = z_i^2 C_i$	normalized ionic strength
$H'(Z)$	normalized streaming velocity
J	current density in the bulk
J	current density on the electrode surface
J_{dif}	current density calculated without regard to migration
$J^* = J\delta_o / Fc_{B1}D$	normalized current density
$M_i^{z_i}$	ionic species i with charge number z_i
N	number of ionic species in solution
N_i	flux intensity of species i
$n^* = -\sum s_i z_i$	stoichiometric coefficient of electrode reaction
P	normalized electrostatic potential
p	exponent characterizing transport in the diffusion layer
$q = 1/(p + 2)$	parameter
r	metric coefficient of the boundary layer coordinates; concentration ratio of in-different electrolyte
R	gas constant
$S^* = -\sum s_i z_i b_i$	transport-stoichiometric coefficient of electrode reaction
T	absolute temperature
t	time
t_i	transference number
\mathbf{v}	velocity vector
$w = c_{W1}/c_{B1}$	parameter
x, y, z	boundary layer coordinates
$Z = z/\delta_o$	normalized coordinate in the diffusion layer
z_j	charge number
$\beta(x)$	longitudinal velocity profile
ζ_i	modified parameter of the Nernst model
$\Gamma = \frac{1}{2} \sum z_i^2 c_i$	ionic strength
$\Gamma(x)$	gamma function
$\delta_j = F(c_{Bj} - c_{Wj}) D_j n^* / s_j J_{dif}$	Nernst thickness
δ_o	effective diffusion thickness
$\varepsilon_m = z_m^2 c_m / \sum z_i^2 c_i$	parameter
λ	parameter of the solution for Nernst's model
$\tilde{\mu}_i$	electrochemical potential
σ	convective parameter of the similarity transformation

Subscripts

B refers to the bulk of the solution, i to species i in solution, j to a depolarizer ($j = 1$ refers to the clue depolarizer), k to an indifferent species, m to species m in solution, Q to value obtained by integration from $Z = 0$ to $Z = \infty$, and W refers to the electrode surface.

The first and second derivatives with respect to the similarity variable are denoted by primes (' and "). The sign of summation, \sum , with subscript i, j or k refers, respectively, to all species, to depolarizers, and to indifferent ions.

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