Pergamon

0013–4686(94)–00359–9

DIFFUSION–MIGRATION TRANSPORT IN A SYSTEM WITH BUTLER–VOLMER KINETICS, AN EXACT SOLUTION

Artjom V. Sokirko* and Fritz H. Bark

Department of Mechanics, Royal Institute of Technology, Stockholm, Sweden

Abstract — Steady one-dimensional electrolysis of a metal salt in a system with a supporting electrolyte is considered. The electrolyte in the system investigated is made up of three ionic species, one of which takes part in the electrode reactions. Attention is restricted to the quite common cases where the transfer coefficient in the Butler–Volmer law for the electrode kinetics is $\frac{1}{2}$. For reasons of algebriac simplicity, the main part of the paper deals with the special case with two species of cations of charge numbers 2 and 1, respectively, and one species of anions of charge number 1. However, all results are easily generalized to any set of charge numbers. In the special case of a binary electrotype, an exact explicit simple expression is computed for the polarizarion curve. Also the drops in ohmic potential, concentration overpotential in the electrolyte and the surface overpotentials. are computed as functions of the electric current density. In the general case with three ionic species, an exact expression for the polarization curve is given in implicit form. In the limiting case of the polarization curve and the aforementioned parts of the difference in potential between the electrodes. For the diffusion layer configuration, and explicit expression for the polarization curve is computed for a system with arbitrary charge numbers and a more general form of the Butler–Volmer law.

Key words: Butler–Volmer law, diffusion metal salt, migration.

NOMENCLATURE

C	nondimensional constant of integration
$C_i, i = 1, 2, 3$	dimensional concentrations of species *1, 2,* 3 mol m^{-3}
$C_i^0, i = 1, 2, 3$	dimensional initial concentrations of species *1,2* and 3 mol m^{-3}
$c_i, i = 1, 2, 3$	dimensionless concentrations of species *1,* 2, 3
D_1	diffusivity for species *1*
e^-	unit electron charge
$E_{1/2}$	dimensionless half-wave potential
$f(c_1)$	dimensionless function entering Butler–Volmer law
f_0	$f(c_1(0))$
f_1	$f(c_1(1))$
F	Faraday's constant C mol^{-1}
$g(c_1)$	dimensionless function entering Butler–Volmer law
g_0	$g(c_1(0))$
g_1	$g(c_1(1))$
i	dimensional electric current density Am^{-2}
i_0	dimensional exchange current density Am^{-2}
j	dimensionless electric current density
j_0	dimensionless exchange current density
j_*	dimensionless limiting current density
$\mathscr{J}(\mathscr{V})$	dimensionless polarization curve
k	dimensionless initial concentration of species 1
L	dimensional distance between electrodes m
M	notation of species 1
M^{z_1+}	notation of species 1 as cation
$\mathscr{M}(y)$	auxiliary function
$\mathscr{N}(y)$	auxiliary function
x	dimensional spatial coordinate m
R	gas constant JK^{-1} mol^{-1}
T	absolute temperature K
V	dimensional difference in electric potential between electrodes V
$\mathscr{V}$	dimensionless difference in electric potential between electrodes
y	auxiliary variable
y_*	upper bound for the auxilliary variable y
$z_i, i = 1, 2, 3$	absolute value of charge number of species i
$Z_i, i = 1, 2$	normalized absolute values of charge numbers of species *1* and *2*
α	symmetry coefficient, dimensionless
$\Delta\phi$	dimensionless drop in electric potential in electrolyte
$\Delta\phi_{ohmic}$	dimensionless ohmic potential drop in electrolyte

* Present address: Department of Chemistry, Trent University, Peterborough, Ont. Canada.
† Author to whom correspondence should be addressed.

$\Delta\phi_{conc}$	dimensionless drop in concentration overpotential in electrolyte
κ	dimensionless initial concentration of species 1 from formula 52
ξ	dimensionless spatial coordinate
ϕ	dimensionless electric potential in electrolyte
ϕ_0	auxiliary dimensionless variable
Φ	dimensional electric potential in electrolyte V

INTRODUCTION

In the literature, there is a large documented body of empirical and theoretical knowledge, often made use of in technical applications, of transport in electrochemical systems with a supporting electrolyte and operating in the regime of nonlinear reaction kinetics. The theoretical studies of ionic transport in electrochemical systems can be said to have started with the classical work on binary electrolytes by Nernst[1], who constructed a simplified but still physically realistic model by neglecting migration and assuming that the variation of the concentration near an electrode is linear. Outside the so called diffusion layer near an electrode, Nernst assumed that the concentration is constant. This model can, among other things, be used to explain, in a qualitative sense, the limiting current phenomenon. In all its simplicity, the diffusion layer, which in the literature is frequently labelled the Nernst layer, is a good model for *eg* the rotating disc electrode.

Numerous studies have supplemented and improved upon the Nernst model[1]. Brunner[2, 3] accounted for migration and was able to compute an expression for the limiting current density for a nonsymmetric binary electrolyte with charge numbers $z_1 \neq z_2 = 1$. The results by Brunner were extended to a general binary electrolyte by Baars[4]. The modifications of the Nernst model to account for a supporting electrolyte were given by Eucken[5]. As an example of later generalizations of Eucken's work, one may mention the study by Hsieh and Newman[6], in which a system with three ions of arbitrary charge numbers were considered. In none of these studies was reaction kinetics accounted for.

A large number of papers in the literature deal with the role of reaction kinetics on transport in electrochemical systems. Therefore, only a few of the most pertinent contributions are mentioned here. Two-dimensional transport due to migration was considered by Wagner[7], who derived analytic solutions for the quite common cases in which the Butler–Volmer law for the reaction kinetics can be locally linearized. In the work by Heyrovsky and Ilkovic[8], diffusion transport and nonlinear reaction kinetics was investigated and an approximate model of semiempirical nature was proposed. In that work, the useful concept of the half-wave potential was introduced. This matter was further elaborated upon by Brdicka[9] in a study of reversible and irreversible electrochemical systems. Reaction kinetics was also approximately accounted for in the work by Vorotyntsev[10], where the general solution of the one-dimensional version of the Planck–Nernst equations was derived.

In textbooks, see *eg* Vetter[11], Levich[12], Bard and Faulkner[13] and Newman[14], and, to the knowledge of the authors of the present paper, in the scientific literature on basic electrochemistry, some of which have been briefly reviewed above, the analytic mathematical treatment of potentiostatic electrolysis of systems operating under conditions of nonlinear reaction kinetics is, with one exception to be discussed below, incomplete in the sense that some kind of approximation procedure has always been resorted to. From a mathematical point of view, the most common type of approximation is linearization, which is valid at low current densities or for modest variations of the electric current. There are two other limiting cases that are frequently considered in the literature. In the first of these, which is sometimes labelled reaction controlled, it is assumed that effects of transport of reagents in the electrolyte can be neglected. Almost all of the potential drop between the electrodes is assumed to be made up by the overpotentials at the surfaces of the electrodes. For the mathematical modeling of such systems, one may often use a simple Tafel law or some modification thereof to correct for effects of transport, see *eg* [8]. For the second limiting case, the transport of reagents is crucial and the concentration of carriers of charge is usually taken to be small near one of the electrodes. In other words, one is then restricting the analysis to current densities that are close to the limiting current density.

As far as approximations made in the derivation of formulae for polarization curves, an exceptional study by Pritzker[15] has recently appeared in the literature. In this work, no approximation are used for the solution of the governing equations. However, when constants of integration are determined from prescribed boundary conditions, a system of four nonlinear algebraic equations has to be solved by numerical methods. In addition to numerical results, Pritzker[15] gives some interesting explicit solutions for the cases of small current densities and for current densities that are close to the limiting current density. Pritzker restricts attention to a system of the diffusion layer variety. In the present work, emphasis is put on the somewhat more complicated case with two electrodes. The diffusion layer is briefly discussed in A p p e n d Ax

Other analytic simplification procedures for diffusion–migration problems, which in the end rely on simple numerical computations, have been recently developed by Baker *et* al.[16], Oldham[17], Baker[18] and Myland and Oldam[19]. An interesting approximate analytic solution for the growth of spherical clusters has been obtained by Milchev[20]. The computation of polarization curves may, of course, also be carried out by using numerical methods from the outset. In the literature, there is a large number of papers in which such methods are used, see *eg* Gu *et* al.[21] and Mao *et* al.[22] and the references therein.

Although results from different approximation procedures have, in a large number of cases, formed the basis for indeed very successful experimental procedures for *eg* determination of kinetic parameters for performance of certain electrical systems, the lack of exact solutions of realistic basic model equations

has had some undesirable consequences. Firstly, the accuracy of measured kinetic parameters such as the exchange current density is sometimes not satisfactory. For several systems, only one digit has been determined. This may at least partly be due to the fact that, as was clearly pointed out by Pritzker[15], the approximate analytical formulae, to which experimental data are to be fitted by adjusting kinetic parameters in the mathematical model, have a limited range of validity. Thus, only limited ranges of experimental data can be used. Secondly, from a fundamental point of view, it is a bit unsatisfactory to compute the limiting current density at that value at which the concentration(s) of the species that transport charge is (are zero. Although the procedure is formally correct, the result does not tell how the limiting current density is approached as the primary control variable of the system, the difference in voltage between the electrodes, becomes large.

In the present paper, an exact solution, the implicit form, is given for the polarization curve for a system of quite general nature. A one-dimensional system, in which transport takes place due to diffusion and migration, is considered. Thus, advective transport is left out which means that the validity of the results are formally restricted either to systems with a solid electrolyte or, in case of a liquid electrolyte, to systems having horizontal electrodes being arranged so that the electrolyte is always stably stratified. The system considered is made up of three ionic species, which is often the situation at hand for an aqueous solution of a metallic salt with a supporting electrolyte. A standard form of the Butler–Volmer law with the value $\frac{1}{2}$ of the transfer coefficient is chosen as model for the reaction kinetics.

As only exact solutions or accurate approximations thereof are considered in this paper, use will only be made for the physical concepts electric current, overpotential and electric potential. There is thus no need to subdivide, as is sometimes done in the literature, the electric current into primary, secondary and tertiary current. When appropriate, however, the contributions to the total potential drop from the ohmic, concentration and surface potential drops are commented upon.

The organization of the present paper is as follows. In Section 2, the mathematical formulation of the problem is given. The solution of the problem is derived in Section 3. Although the mathematics used in this derivation is elementary, the manipulations are a bit lengthy* and of unusual nature. Among other things, the calculus involves extensive algebra with unknown boundary values of the dependent variables. The main obstacle in the derivation is thus algebraic organization rather than mathematical analysis. Therefore, those readers, who may not be particularly interested in formal details, may well proceed directly to Section 4, which gives a summary of the formulae derived and a discussion of some general properties of the solution. In Section 5, some interesting limiting cases are discussed and some simple approximate explicit solutions are

given. Section 6 contains a discussion of some typical polarization curves. The essentials of the paper are summarized in Section 7. In Appendix A, results are given for the diffusion layer configuration. Results for a more general Butler-Volmer law than the one used in the main body of the paper but still restricted to the value $\frac{1}{2}$ of the transfer coefficient are given in Appendix B.

2. PROBLEM FORMULATION

Consider the steady, one-dimensional potentiostatic electrolysis of a dilute electrolyte that, in addition to the solvent, consists of three ionic species. Attention is restricted to cases such that species 1 and 2 are cations and species 3 is an anion. Furthermore, it is assumed that only species 1 participates in the reactions at the electrodes, which is typical for a metallic salt. In other words, if species 1 is labelled M, the electrode reaction at the anode is given by the simple formula

$$M \rightarrow M^{z_1+} + z_1 e^-.$$
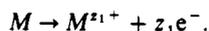
At the cathode, the same reaction is assumed to proceed in the opposite direction. None of the assumptions made so far are really important for the development in this paper and can be dispensed with at the cost of some algebraic complications. The transport mechanisms to be accounted for are diffusion and migration but not advection, ie the electrolyte is assumed to be motionless. Thus, the system considered can either be thought of as one in which there is a separator of low permeability between the electrodes or a system with a liquid electrolyte that is contained between two horizontal electrodes under conditions such that no free convection occurs. The case with a vigorously stirred electrolyte, for which the diffusion layer model is applicable, is dealt with in Appendix A.

The position between the electrodes is denoted by the coordinate x. The cathode is at $x = 0$ and the anode at $x = L$. It turns out to be convenient to choose the reference level of the electric potential such that the potential of the cathode is zero. The electric potential of the anode is taken as V. In the electrolyte, the electric potential Φ under conditions of current flow is defined relative to the equilibrium potential distribution in the cell. It is assumed that there is no potential redistribution in diffuse double layers during current flow. As will be apparent below, the definition leads to an algebraically simple form of the Butler–Volmer law.

In the case of a dilute electrolyte, the Nernst-Einstein relation for the mobility is valid and the following equations are to be solved for the concentration fields $C_i(x)$, i = 1, 2, 3, and the electric potential $\Phi(x)$:

$$D_1 \frac{dC_1}{dx} + \frac{z_1 F D_1}{RT} C_1 \frac{d\Phi}{dx} = -\frac{i}{Fz_1}, \quad (1)$$

$$\frac{dC_2}{dx} + \frac{z_2 F}{RT} C_2 \frac{s\Phi}{dx} = 0, \quad (2)$$

$$\frac{dC_3}{dx} - \frac{z_3 F}{RT} C_3 \frac{d\Phi}{dx} = 0, \quad (3)$$

---

* Most of the algebra carried out in Section 3 has been checked by using automatic symbolic manipulation.

$$z_1 C_1 + z_, C_, = z_3 C_3. \tag{4}$$

The constants that appear in these equations are D_1, the diffusion coefficient of species 1, z_i, $i = 1, 2, 3$, which are here taken as the absolute values of the charge numbers for the three species, Faraday's constant F, the gas constant R, the absolute temperature T and the constant, but so far unknown, electric current density i that flows across the system. Equation (1), which is Faraday's law combined with the Planck–Nernst law for the mass flux of species 1, states that the electric current is carried by species 1 only whereas equations (2) and (3) imply that there is no flux of species 2 and 3. The condition of local electroneutrality is stated by equation (4).

At the electrodes, the electric current density i is specified in terms of the surface overpotentials at cathode and anode, which are $\Phi(0)$ and $V - \Phi(L)$, respectively, by the following Butler–Volmer law:

$$i = i_0\left\{e^{-\alpha z_1 F/RT\,\Phi(0)} - \frac{C_1(0)}{C_1^0}e^{(1-\alpha)z_1 F/RT\,\Phi(0)}\right\}$$
$$\text{cathode} \quad (5)$$

$$i = i_0\left\{\frac{C_1(L)}{C_1^0}e^{(1-\alpha)z_1 F/RT\,[\Phi(L)-V]} - e^{\alpha z_1 F/RT\,[V-\Phi(L)]}\right\}$$
$$\text{anode.} \quad (6)$$

Here i_0 is the exchange current density at a reference concentration C_1^0 of species 1 that will be specified in a moment. a is the transfer coefficient. The factors $C_1(0)/C_1^0$ and $C_1(L)/C_1^0$ in these formulas account for the concentration dependence of the anodic relation at the cathode and the cathodic reaction at the anode. A more general form of the Butler–Volmer law is considered in Appendices A and B.

Because the reactions at anode and cathode, by assumption, proceed at the same rate, one has to specify conservation conditions for the three species, ie how much of each species that is present per unit length and width of the cell. Thus, the following conditions are prescribed:

$$\int_0^L C_i\,dx = C_i^0 L, \; i = 1, 2, 3, \tag{7}$$

where C_i^0 are initial concentrations that, due to the condition of electroneutrality, see equation (4), cannot be specified independently, cf. formula (9) below.

In order to proceed without excessive algebra, a special case will be considered in the remaining part of this section. Attention will be restricted to cases where the transfer coefficient a is equal to $\frac{1}{2}$. This restriction is crucial for the mathematical solution procedure made use of in this work. Also, the values $z_1 = 2$, $z_2 = z_3 = 1$ are chosen. The case dealt with may thus be exemplified by eg an aqueous solution of $CuSO_4$ with H_2SO_4 as a supporting electrolyte. At reasonably low concentrations, H_2SO_4 dissociates mainly into H^+ and HSO; . If the concentration of copper sulphate is less than half of that of the sulphuric acid, species 1, 2 and 3 can be taken as Cu^{2+}, H^+ and HSO_4^-. Electrolytes with arbitrary change numbers are considered in Appendices A and B.

The formulation of the mathematical problem is now complete. The problem addressed is to compute C_i, 4 and the unknown current density i in terms of V for given values of the physical constants of the system. Before the derivation of the solution is given, the mathematical problem will be formulated in dimensionless form.

It turns out to be expedient to use the reference concentration C_3^0 as the concentration scale. Dimensionless concentrations c, are thus defined as

$$c_i = \frac{C_i}{C_3^0}. \tag{8}$$

Instead of defining dimensionless reference concentration in the same way, it is, according to the remark following formula (7) above, more appropriate to introduce a quantity k, which relates C_i^0, $i = 1, 2$ and C_3^0 as follows:

$$\frac{C_1^0}{C_3^0} = k, \quad \frac{C_2^0}{C_3^0} = 1 - 2k. \tag{9}$$

The quantity k is thus restricted by the inequality $0 < k \leqslant \frac{1}{2}$. Dimensionless length coordinate ξ, electric potential ϕ and current density j are defined by the formulae

$$\xi = \frac{x}{L}, \quad \phi = \frac{F\Phi}{RT}, \quad j = -\frac{Li}{FD_1 C_3^0}. \tag{10}$$

It should be noted that the dimensional current density i in the present problem is negative, which means that the dimensionless current density j, as defined above, is positive. Also, the following dimensionless parameters will appear:

$$\mathscr{V} = \frac{FV}{RT}, \quad j_0 = \frac{Li_0}{FD_1 C_3^0} \tag{11}$$

The parameter j_0 is thus the ratio between the exchange current density and the absolute value of the limiting diffusion current density. The values of j_0 that appear in applications can be either very large, of order unity or very small. As is well known, this offers possibilities for approximations, ie the Nernst approximation for $j_0 \gg 1$ and the Tafel approximation for $j_0 \ll 1$. However, this aspect of the problem to be dealt with will not be considered here. j_0 is thus assumed to be a fixed quantity.

In terms of the dimensionless quantities defined above, one finds the following dimensionless equations to be solved:

$$\frac{dc_1}{d\xi} + 2c_1\frac{d\phi}{d\xi} = \frac{j}{2}, \tag{12}$$

$$\frac{dc_2}{d\xi} + c_2\frac{d\phi}{d\xi} = 0, \tag{13}$$

$$\frac{dc_3}{d\xi} - c_3\frac{d\phi}{d\xi} = 0, \tag{14}$$

$$2c_1 + c_2 = c_3. \tag{15}$$

The dimensionless versions of the boundary condi-

tions (5) and (6) are

$$j = j_0 \left[\frac{c_1(0)}{k} e^{\phi(0)} - e^{-\phi(0)} \right], \quad \text{cathode,} \quad (16)$$

$$j = j_0 \left[e^{\mathscr{V} - \phi(1)} - \frac{c_1(1)}{k} e^{\phi(1) - \mathscr{V}} \right], \quad \text{anode.} \quad (17)$$

The dimensionless form of the conservation conditions (7) is

$$\int_0^1 (c_1, c_2, c_3) \, d\xi = (k, 1 - 2k, 1). \quad (18)$$

The potential drop in the electrolyte, which will be discussed in some detail later, can, according to equation (12), be written in the following form

$$\phi(1) - \phi(0) = \frac{j}{4} \int_0^1 \frac{d\xi}{c_1(\xi)} + \frac{1}{2} \ln \frac{c_1(0)}{c_1(1)}. \quad (19)$$

In this expression, the first term is the ohmic potential drop and the second the concentration overpotential drop. These quantities are henceforth labelled $\Delta\phi_{ohmic}$ and $\Delta\phi_{conc}$, respectively.

3. SOLUTION FOR A BINARY ELECTROLYTE

In this section, an expression for the polarization curve in the simplest case, ie that for a binary electrolyte, will be computed. For $k = \frac{1}{2}$ and $c_2 = 0$, one obtains in terms of the concentration variable $c = 2c_1 = c_3$ the following reduced version of the problem that was formulated in the last part of the previous section:

$$\frac{dc}{d\xi} + 2c \frac{d\phi}{d\xi} = j, \quad (20)$$

$$\frac{dc}{d\xi} - c \frac{d\phi}{d\xi} = 0. \quad (21)$$

The solution of these equations has to fulfil the boundary conditions

$$j = j_0 [c(0)e^{\phi(0)} - e^{-\phi(0)}], \quad \text{cathode,} \quad (22)$$

$$j = j_0 [e^{\mathscr{V} - \phi(1)} - c(1)e^{\phi(1) - \mathscr{V}}], \quad \text{anode,} \quad (23)$$

and the constraint

$$\int_0^1 c(\xi) \, d\xi = 1. \quad (24)$$

Elimination of ϕ between equations (20) and (21) leads to a simple ordinary differential equation for c, whose solution is

$$c = \frac{1}{3}(j\xi + C), \quad (25)$$

where C is a constant of integration that is determined by the constraint (24). A minor computation gives that

$$c = \frac{1}{3}\left(j\xi - \frac{j}{2} + 3\right). \quad (26)$$

In the present non-dimensionalization, the value of the limiting current j, is thus

$$j_* = 6, \quad (27)$$

a result first obtained by Baars[4]. The ohmic potential drop and the concentration overpotential drop can now be computed from formula (19), whereby one finds that

$$\Delta\phi_{ohmic} = \frac{3}{2} \ln \frac{6 + j}{6 - j} \quad (28)$$

and

$$\Delta\phi_{conc} = -\frac{1}{2} \ln \frac{6 + j}{6 - j}. \quad (29)$$

The formula for the $\Delta\phi_{conc}$ is of the expected form whereas that for $\Delta\phi_{ohmic}$ is perhaps a little surprising. One would tend to believe that $\Delta\phi_{ohmic}$ would be proportional to the electric current density j but this is so only for small values of j. The singular behaviour of $\Delta\phi_{ohmic}$ as j approaches j, is due to the fact that the resistivity, which is $\sim c$, then approaches zero locally at a cathode.

It remains to compute the surface overpotentials at the anode and cathode, respectively, ie $\phi(0)$ and $\mathscr{V} - \phi(1)$. Equations (22) and (23) are second order algebraic equations for $e^{\phi(0)}$ and $e^{\mathscr{V} - \phi(1)}$. Solution of these equations and substitution of expression (26) in the results given the following formulae

$$\phi(0) = \ln\left[\frac{3\sqrt{j^2 + 4j_0^2(1 - j/6)} + j}{j_0(1 - j/6)} \right], \quad (30)$$

$$\mathscr{V} - \phi(1) = \ln\left[\frac{\sqrt{j^2 + 4j_0^2(1 + j/6)} + j}{j_0} \right]. \quad (31)$$

The first of these formulae shows clearly the well known singular behaviour of the surface overpotential at the cathode as the limiting current is approached. This singularity is a consequence of the fact that the rate of the cathodic reaction at the cathode, which dominates over the anodic reaction except for very small current densities, is proportional to the concentration, see formula (22). As the concentration at the cathode approaches zero, an infinite surface overpotential is needed to sustain a finite electric current.

Collecting the results given above leads to the following expression for the polarization curve for a binary electrolyte

$$\mathscr{V} = 2 \ln \frac{6 + j}{6 - j} + \ln\left[\frac{\sqrt{j^2 + 4j_0^2(1 - j/6)} + j}{\sqrt{j^2 + 4j_0^2(1 + j/6)} - j} \right]. \quad (32)$$

4. SOLUTION FOR THE CASE WITH A SUPPORTING ELECTROLYTE

For the case to be dealt with in this section, it turns out to be expedient to use a solution procedure that is a little different from that used for the binary electrolyte. The solutions of equations (13) and (14) in Section 2 can be written as

$$c_2 = c_2(0)e^{-[\phi(\xi) - \phi(0)]} \quad (33)$$

$$c_3 = \mathcal{N} c_2(0) e^{[\phi(\xi) - \phi(0)]}, \qquad (34)$$

where $c_2(0)$ and $\mathcal{N}$ are two constants of integration to be determined. The first step of the solution procedure that is given in this section is to derive a relation of the form $\mathcal{N} = \mathcal{F}(\Delta\phi)$ between $A\# = \phi(1) - \phi(0)$, which is the so far unknown difference in electric potential in the electrolyte at the anode and cathode, respectively, and $\mathcal{N}$, which is also unknown a *priori.* Thereafter, the current density **j** and the difference in electric potential between the electrodes $\mathcal{V}$ will be computed in terms of $\mathcal{N}$ and $\Delta\phi$, which gives an implicit form of the sought relation $\mathbf{j} = \mathcal{J}(\mathcal{V})$. Somewhat unfortunate, as the quantities $\mathcal{N}$ and **A 4** are parts of the solution itself, the parameterization chosen does not directly involve quantities that are closely related to the enternally controllable parameters **k** and $\mathcal{V}$ of the system. However, this is a price that has to be paid for reasonable algebraic convenience. As was pointed out in the introduction, the solution procedure is a little technical. Therefore, the reader, who is mainly interested in the results, may well go directly from here to the next section where results are summarized.

Combination of equations **(12)**–**(15)** gives the useful relation

$$\frac{d\xi}{d\phi} = \frac{1}{j}(3c_3 - c_2). \qquad (35)$$

The third of conservation conditions **(18)** can be written

$$\int_0^1 c_3 \, d\xi = \int_{\phi(0)}^{\phi(1)} c_3 \frac{d\xi}{d\phi} \, d\phi = 1. \qquad (36)$$

Substitution of expressions **(34)** for c_3 and **(35)** for $d\xi/d\phi$ then gives, after a little computation, that

$$\frac{\mathcal{N} c_2(0)^2}{2j} [3\mathcal{N}(y - 1) - \ln y] = 1, \qquad (37)$$

where the quantity y, which will henceforth be used frequently, is defined as

$$y = e^{2\Delta\phi}. \qquad (38)$$

Using the second of conservation conditions **(18)** one finds, in an analogous way, that

$$\frac{c_2(0)^2}{2j} [3\mathcal{N} \ln y + y^{-1} - 1] = 1 - 2k. \qquad (39)$$

By dividing equation **(37)** by equation **(39)**, one finds a second order algebraic equation for $\mathcal{N}$ in terms of y, whose solutions are

$$\mathcal{N} = [(2 - k) \ln y$$
$$\frac{\pm \sqrt{(2 - k)^2 \ln^2 y + 3(y - 1)(y^{-1} - 1)(1 - 2k)]}}{[3(y - 1)(1 - 2k)]}. \qquad (40)$$

It can be shown that only the solution with the **+** sign preceding the square root leads to physically realistic results. (The details of the proof are a bit

tedious and are therefore not given here.) As pointed out in the beginning of the section, the relation **(40)** between $\mathcal{N}$ and $\Delta\phi$ forms the basis of the parametric representation of the solution.

The next step is to compute the current density **j** as function of $\mathcal{N}$ and **A4**. Equations **(37)** and **(39)** are insufficient for this purpose and an additional relation between $c_2(0)$, **j**, $\mathcal{N}$ and **y** is needed. The relation needed is obtained by using equation **(35)** and the identity

$$\int_{\phi(0)}^{\phi(1)} \frac{d\xi}{d\phi} \, d\phi = 1, \qquad (41)$$

which, after using equations **(33)** and **(34)** and some algebra, gives that

$$\frac{c_2(0)}{j} [3\mathcal{N}(y^{1/2} - 1) + y^{-1/2} - 1] = 1. \qquad (42)$$

From equation **(37)** and **(42)** one then finds the following expression for $c_2(0)$ in terms of y and $\mathcal{N}$

$$c_2(0) = \frac{2(3\mathcal{N} - y^{-1/2})(y^{1/2} - 1)}{\mathcal{N}[3\mathcal{N}(y - 1) - \ln y]}, \qquad (43)$$

which will be used in a moment, and that

$$j = \frac{2[3\mathcal{N}(y^{1/2} - 1) + y^{-1/2} - 1]^2}{\mathcal{N}[3\mathcal{N}(y - 1) - \ln y]}. \qquad (44)$$

So far use has not been made of the Butler–Volmer law, eg formulae **(16)** and **(17)**, which are the relations needed to compute **Y** in terms of $\mathcal{N}$ and $\Delta\phi$. However, in order to make use of these formulae, expressions of $c_1(0)$ and $c_1(1)$ are needed. These expressions are obtained from the condition of electroneutrality, *ie* equation **(15)**, and expressions **(33)** and **(34)** for c_2 and $c_{,,}$ respectively. One finds that

$$c_1(0) = \tfrac{1}{2}(\mathcal{N} - 1)c_2(0) \qquad (45)$$

and

$$c_1(1) = \tfrac{1}{2}(\mathcal{N} y^{1/2} - y^{-1/2})c_2(0), \qquad (46)$$

where $c_2(0)$ is given by formula **(43)**. Formula **(16)** can now **be** solved as a second order algebraic equation for $e^{\phi(0)}$ in terms quantities that are known functions of y and $\mathcal{N}(y)$. One finds that the physically realistic solution of that equation gives that

$$\phi(0) = \ln\left[\frac{\sqrt{(kj)^2 + 4kj_0^2 c_1(0)} + kj}{2j_0 c_1(0)}\right] \qquad (47)$$

A similar expression can be derived for $\mathcal{V} - \phi(1)$ from equation **(17)**. Using the definition **(38)** one has the following identity

$$\phi(1) = \phi(0) + \tfrac{1}{2} \ln y, \qquad (48)$$

which, when combined with the aforementioned expressions for $\phi(0)$ and $\mathcal{V} - \phi(1)$ gives that

$$\mathcal{V} = \ln\left[\frac{\sqrt{y} c_1(1)}{c_1(0)} \frac{\{\sqrt{j^2 + 4j_0^2 c_1(0)/k} + j\}}{\{\sqrt{j^2 + 4j_0^2 c_1(1)/k} - j\}}\right]. \qquad (49)$$

5. SUMMARY OF FORMULAE

In the previous section, the following formulae for $\mathcal{N}(y)$ and $j(y, \mathcal{N})$ were derived

$$\mathcal{N}[(y) = (2 - k) \ln y$$
$$+ \frac{\sqrt{(2 - k)^2 \ln^2 y + 3(y - 1)(y^{-1} - 1)(1 - 2k)]}}{[3(y - 1)(1 - 2k)]}, \tag{50}$$

$$j = \frac{2[3\mathcal{N}(y^{1/2} - 1) + y^{-1/2} - 1]^2}{\mathcal{N}[3\mathcal{N}(y - 1) - \ln y]}. \tag{51}$$

Formula **(49)** can, by using expressions **(43–46)** and **(51)**, be written in the following form

$$\mathcal{V} = \ln \left| \frac{(\mathcal{N} y - 1)}{(\mathcal{N} - 1)} \times \right.$$

$$\left. \times \frac{\sqrt{1 + \frac{\mathcal{N}(\mathcal{N} - 1)[3\mathcal{N}(y - 1) - \ln y] j_0^2}{k[3\mathcal{N}(y^{1/2} - 1) + y^{-1/2} - 1]^3} + 1}}{\sqrt{1 + \frac{\mathcal{N}(\mathcal{N} y - 1)[3\mathcal{N}(y - 1) - \ln y] j_0^2}{ky^{1/2}[3\mathcal{N}(y^{1/2} - 1) + y^{-1/2} - 1]^3} - 1}} \right|. \tag{52}$$

These three formulae constitute, in implicit form, the exact solution of the problem stated. In general, one cannot eliminate $\mathcal{N}$ and y from the solution to obtain the function $j = \mathcal{J}(Y)$ in implicit form but one has to use some simple numerical evaluations of elementary functions. The solution procedure is to compute, for a given value of k, $\mathcal{N}$ as function of y from equation **(50)**. The quantity y varies monotonically between 1 and a number $y, > 1$ that will be specified in a moment. One then obtains j and Y as functions of y (and, of course, the parameters j_0 and k), between which y can be eliminated leading to the function $j = \mathcal{J}(\mathcal{V})$. Some comments on the general character of the solution are in order.

At low current densities j, the potential drop A\$ in

the electrolyte is small, which means that, see definition **(38)**, y is slightly larger than **1**. Series expansion of formula **(50)** then gives that

$$\mathcal{N} = \frac{1}{1 - 2k} \left[\frac{3}{2} - y + 0\{(y - 1)'\}\right]. \tag{53}$$

The singular behaviour of $\mathcal{N}$ as $k \to \frac{1}{2} - 0$ is just of formal nature and comes from the parameterization chosen. For k being close to $\frac{1}{2}$, the electrolyte is almost binary, see conservation conditions **(18)**. The concentration c_2 is then small, which means that $\mathcal{N}$, according to its definition **(34)**, has to be large for $c_3(0)$ to be finite. An approximate expression for $j = \mathcal{J}(\mathcal{V})$ for small current densities is given in the next section.

At the limiting current density, where $c_1(0) = 0$ and $c_2(0) = c_3(0)$, one finds that $\mathcal{N} = 1$. The corresponding value of y, which is henceforth labelled $y,,$ is to **be** computed from the equation

$$k = \frac{1}{2} \left[1 - \frac{3 \ln y_* + y_*^{-1} - 1}{3(y_* - 1) - \ln y_*} \right], \tag{54}$$

which is readily derived from formula **(50)**. According to equation **(54)**, $k -, \frac{1}{2} - 0$ implies that $y_* \to \infty$. This quantifies the well known fact that as $Y \to \infty$, the potential drop $\Delta \phi$ in the electrolyte between anode and cathode approaches ∞ if the electrolyte is binary but stays finite for a finite concentration of supporting electrolyte. Roughly speaking, the reason for this behaviour is that, for a binary electrolyte, the conductivity is locally zero at the cathode, but is finite if a supporting electrolyte is present.

Figures **1** and **2** show the auxiliary functions $\mathcal{N}(y)$ and $y_*(k)$, which are defined by formulae **(50)** and **(54)**. These functions do not have a clear physical interpretation but are shown to provide the reader with some feeding for the nature of the solution that is given by formulae **(50, 51)** and **(52)**. The concentration profiles in a typical case are shown in Fig. **3**.

The results for the case of a binary electrolyte, which were derived in Section **3**, are recovered from formulae **(50-52)**, the limit $k \to \frac{1}{2} - 0$.
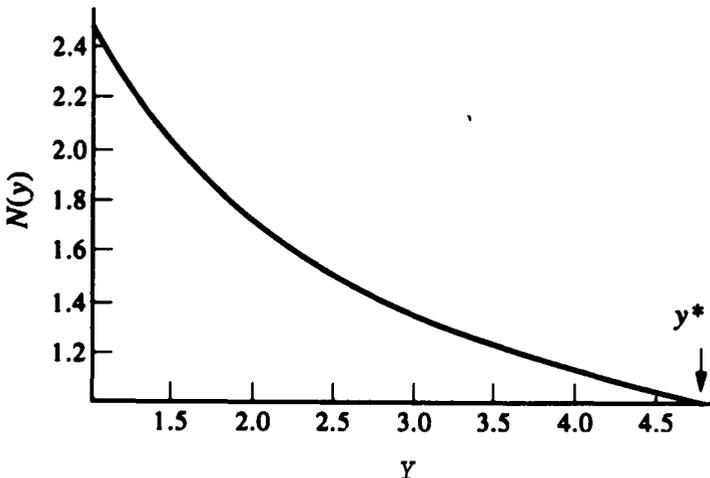

Fig. 1. The auxiliary function $\mathcal{N}(y)$ for k = 0.3 and j_0 = 1. In this case y_* = 4.76552.
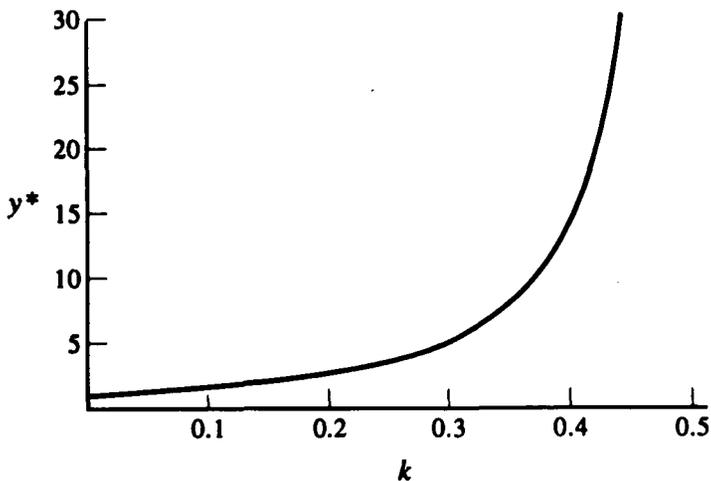
Fig. 2. Magnitude of the potential drop $\Delta\phi$ in the electrolyte, here measured as $y_*(k) = e^{2\Delta\phi}$, as function of k at the limiting current density. Note that $y_*(0) = 1$.
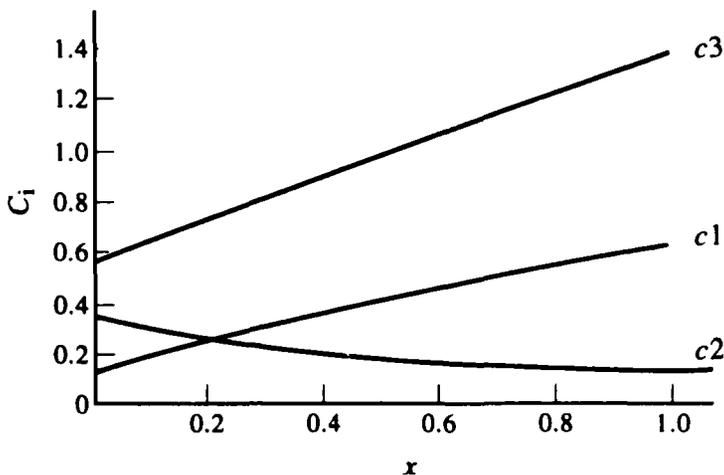

Fig. 3. Concentration profiles in a case with a supporting electrolyte. $k = 0.425, j = 2.4, j_* = 3.43$.

6. SOME LIMITING CASES

In this section, some physically interesting and algebraically transparent limiting cases of the implicit solution that is defined by formulae (50–52) are given. Some of these formulae are well known in the literature whereas others are not.

A particularly simple case is the limit of *small current density*, for which the potential drop in the electrolyte, measured in terms of y, is close to 1. After some algebra, one obtains the well known result that

$$\mathscr{V} \approx \left(\frac{1}{j_0} + \frac{1}{4k}\right)j. \qquad (55)$$

In the right hand side of this equation, the first term represents the reaction resistance and the second term the ohmic resistance, sometimes called the diffusion resistance. The corresponding formula for a diffusion layer was given by Pritzker[15].

The opposite limit, *ie* when the current density **j** *approaches the limiting current density* j_*, say, the

corresponding expression is more complicated. One finds the following formula

$$j \approx \left\{1 + \frac{2k\sqrt{y_*}}{j_0} \mathscr{A}e^{-\mathscr{V}}\right\}j_*, \qquad (56)$$

where the constant $\mathscr{A}$ is given by the following limit

$$\mathscr{A} = \lim_{y \to y_*} \left[\frac{c_1(1) \dfrac{dj}{dy}}{c_2(0)\left\{\sqrt{\left(\dfrac{kj}{2j_0}\right)^2 + k^2 c_1(0)} - \dfrac{kj}{2j_0}\right\} \dfrac{d\mathscr{N}}{dy}} \right].$$

The expression for $\mathscr{A}$ in terms of k, y_* and j_0 is complicated and is therefore not given here. Formula (56) is a mathematical demonstration of the empirically well known fact that the current density approaches the limit current density exponentially as the voltage $\mathscr{V}$ between the electrodes increases. A similar formula for the diffusion layer configuration was given by Pritzker[15].

Another limit of significant interest is that of *a large excess of supporting electrolyte*. Because, in the

scaling chosen, the concentration of the charge carrying species, will then be small, $ie \sim k,$ and so will the variation of the potential in the electrolyte. The approximate solution, with an error ■ k^3, of equation (54) for y_* at the limiting current density is

$$y_* = 1 + 4k\left(1 + \frac{7k}{3}\right) + \cdots. \qquad (57)$$

A suitable parameterization of the variation of y is thus

$$y = 1 + 4\beta k\left(1 + \frac{7k}{3}\right) + \cdots, \quad 0 \leqslant \beta \leqslant 1. \quad (58)$$

One finds, after some algebra, from formula (50) that

$$\mathcal{N} = 1 + 2(1 - \beta)k\left[1 + \frac{2k(7\beta - 6)}{3}\right] + \cdots \quad (59)$$

In this particular case, formula (52) turns out to be a bit inconvenient from an algebraic point of view. Some algebra can be dispensed with by using formula (49) directly and use the formulae (58) and (59) in formulae (43)–(46) to compute $\mathbf{j}, c_1(0)$ and $c_1(1)$ to second order in k. The results are

$$j = 4k\beta\left[1 - \frac{2k(3\beta - 5)}{3}\right] + \cdots, \qquad (60)$$

$$c_1(0) = k(1 - \beta)\left[1 - \frac{4\beta k}{3}\right] + \cdots \qquad (61)$$

and

$$c_1(1) = k\left[1 + \beta - \frac{4\beta k(2\beta - 1)}{3}\right] + \cdots \qquad (62)$$

In the present notation, the limiting current is thus given by the expression

$$j_* = 4k + \frac{16k^2}{3} + \cdots, \qquad (63)$$

the lowest order of which is frequently given in the literature but whose origin appears to be unclear. Using the aforementioned expressions for $\mathbf{j}$ and j* one can express β approximately in terms of j/j_* with the following result

$$\beta = \frac{j}{j_*}\left[1 - 2k\left(1 - \frac{j}{j_*}\right)\right] + \cdots \qquad (64)$$

Combination of formulae (64), (60)–(62) and (49) then gives, with an error $\sim k^2$ for all values of $\mathbf{j}$, the following relation between $\mathcal{V}$ and $\mathbf{j}$

$$\mathcal{V} = \ln\left[\frac{j_* + j}{j_* - j}\right]$$

$$+ \ln\left[\frac{\sqrt{j^2 + 4kj_0^2(1 - j/j_*)(1 + 2kj/3j_*)} + j}{\sqrt{j^2 + 4kj_0^2(1 + j/j_*)(1 - 2kj/3j_*)} - j}\right] + \frac{j}{6} + \cdots$$

$$(65)$$

As expected, this formula shows that $\mathcal{V}$ becomes infinite as k approaches zero. The nature of this singularity will be elucidated in a moment.

In the same way as was done for the binary electrolyte, one can compute the separate contributions to the difference in voltage $\mathcal{V}$ between the electrodes. The computations are simple but a little tedious. Therefore, for brevity's sake, the results are stated directly without deviation. One finds that

$$\Delta\phi = \frac{2kj}{j_*} + \cdots \qquad (66)$$

$$\Delta\phi_{\text{ohmic}} = \frac{1}{2}\ln\left[\frac{j_* + j}{j_* - j}\right] + \frac{4kj}{3j_*} + \cdots \qquad (67)$$

$$\Delta\phi_{\text{conc}} = -\frac{1}{2}\ln\left[\frac{j_* + j}{j_* - j}\right] + \frac{2kj}{3j_*} + \cdots \qquad (68)$$

$$\phi(0) = \ln\left[\frac{\sqrt{j^2 + 4j_0^2(1 - j/j_*)(1 + 2kj/3j_*)} + j}{2kj_0(1 - j/j_*)(1 + 2kj/3j_*)}\right] + \cdots$$

$$(69)$$

$$\mathcal{V} - \phi(1)$$

$$= \ln\left[\frac{\sqrt{j^2 + 4j_0^2(1 + j/j_*)(1 - 2kj/3j_*)} + j}{2j_0}\right] + \cdots$$

$$(70)$$

Formulae (67) and (68), which to these authors knowledge have not been given in the literature before, show that the differences in both ohmic potential and concentration overpotential across the electrolyte are singular as the limiting current is approached. However, the singular parts of these two contributions cancel when adding up to the (well known) small value of $\Delta\phi$ that is given by formula (66). As was found to be the case for a binary electrolyte, $\Delta\phi_{\text{ohmic}}$ is proportional to $\mathbf{j}$ only for small values of this quantity. The singular behaviour of the surface overpotential $\phi(0)$ at the cathode as the limiting current is approached is of the same nature as for the binary electrolyte, cf formula (30). For the very same physical reason, the cathodic surface overpotential is singular in the limit k approaching zero.

Other interesting cases, which are possible to examine in a rigorous way, are higher order corrections of known lowest order results in the limits $j_0 \rightarrow 0+$ and $j_0 \rightarrow \infty$ for a fixed value of k. One may also, by taking further terms in the approximate expressions used, compute explicit corrections to formulae (65) and (32). In the former case, the corrections would account for higher order effects of a small but finite concentration of species 1. The corrections to formula (32) would quantify modifications on a system with a binary electrolyte due to a small but finite concentration of a supporting electrolyte. However, these matters will not be pursued in this work but will be reported on elsewhere.

7. EXAMPLES OF POLARIZATION CURVES

Figure 4 shows some polarization curves for different values of k for a fixed value of j_0. The general behaviour of the curves are as expected. The decreasing magnitude of the limiting current density is simply a consequence of the normalization used. For
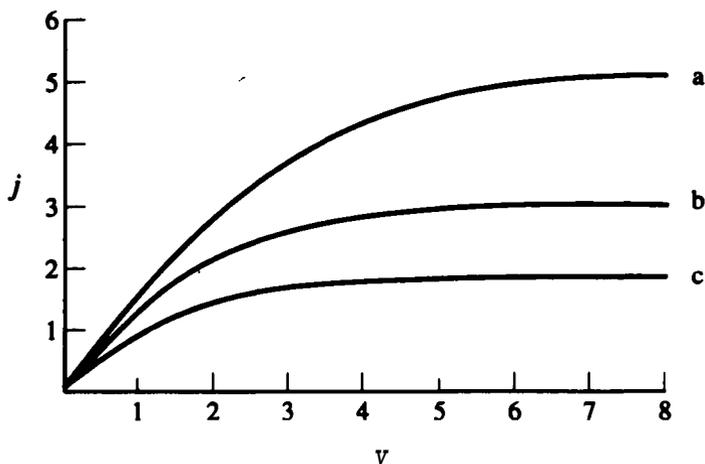
Fig. 4. Some polarization curves for $j_0 = 1$ and different values of k. (a) k = **0.49** (b) k = **0.4** (c) k = **0.30**.

smaller values of k, there are less carriers of charge available. An interesting property of the curves in Fig. 4 is that the limiting current density is approached slower at large values of $\mathscr{V}$ as k is increased. This reflects the fact, which is perhaps not altogether unexpected, that depletion of species 1 near the cathode takes place for smaller values of $\mathscr{V}$ for smaller concentrations, ie smaller values of k.

The magnitude of the limiting current density, normalized with the dimensionless concentration 2k of species 1, as function of k is shown in Fig. 5. This graph shows the square root behaviour of j_* near $k = \frac{1}{2}$ that was first demonstrated by Eucken[5].

The change of character of the polarization curve as the exchange current increases for given value of k is illustrated in Fig. 6. As j_0 is increased above a certain value, an inflection point appears in the polarization curve. As is well known from experiments and semi-empirical theories, there are two possible shapes of the polarization curve. The character of the polarization curve is frequently used to classify the reaction kinetics as either "facile' or

"sluggish", see eg Bard and Faulkner[13]. The possible values of j_0 for which an inflection point appears for a given value of k can be inferred from Fig. 7, which shows the magnitude of the half-wave potential $E_{1/2}$ where it exists. For traditional reasons, the lg-function has here been used instead of the ln-function for the abscissa.

In Fig. 8, an exact polarization curve is compared with the approximate formula (55) for small current densities, formula (56) for large values of $\mathscr{V}$ and the classical Tafel law. This graph shows that the ranges of accuracy for formulae (55) and (56) are quite limited whereas that of the Tafel approximation is quite large.

8. CONCLUSIONS

An exact solution in implicit form has been computed for the polarization curve for a system with symmetric reactions but arbitrary charge numbers and an arbitrary Butler–Volmer law. The special case
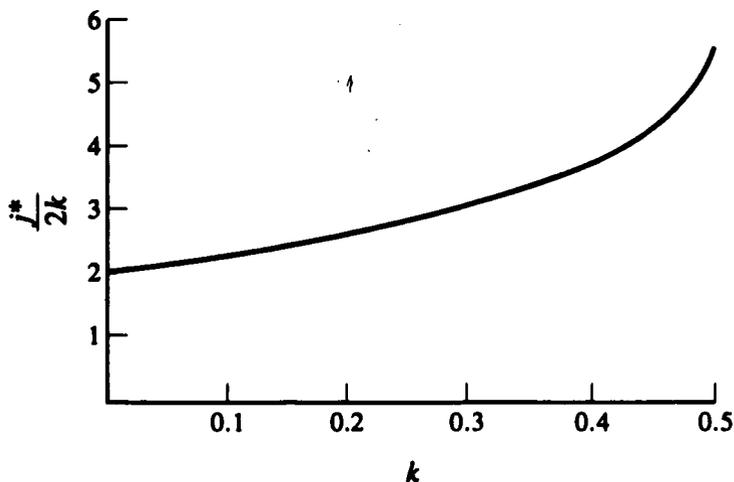

Fig. 5. Magnitude of the limiting current density j_* normalized by twice the concentration of species 1, *ie* 2k, as function of **k**.
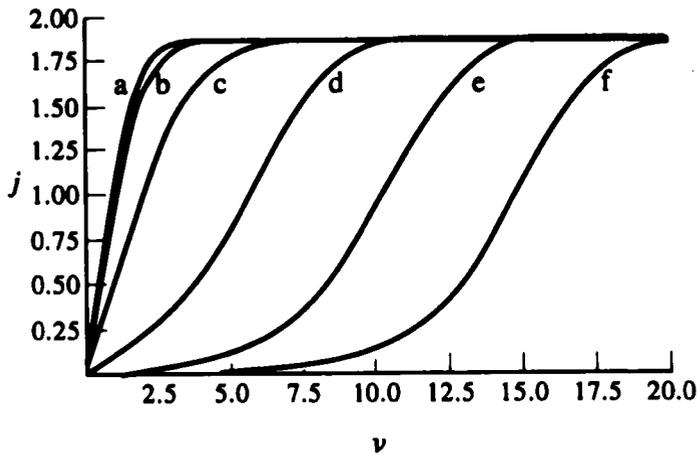
Fig. 6. Polarization curves for $k = 0.3$ and different values of j_0. (a) $j_0 = \infty$, (b) $j_0 = 10$, (c) $j_0 = 1$, (d) $j_0 = 10^{-1}$, (e) $j_0 = 10^{-2}$, (f) $j_0 = 10^{-3}$.
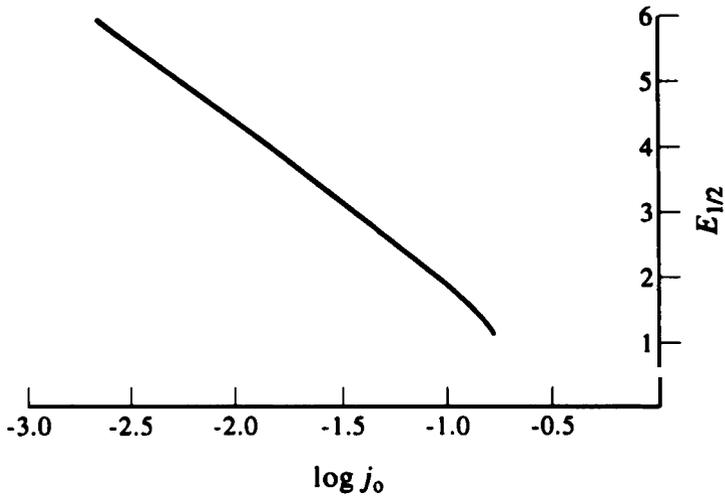

Fig. 7. Magnitude of the half-wave potential and the range where it exists as function of j_0 for $k = 0.3$. There is no half-wave potential for $\lg j_0 > -0.738$.
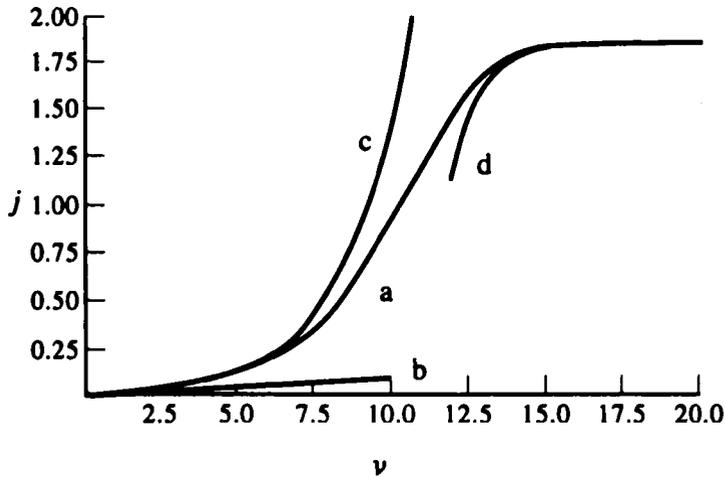

Fig. 8. A comparison between an exact polarization curve and different common approximations for $k = 0.3$ and $j_0 = 10^{-2}$. (a) exact, (b) small current density approximation, (c) Tafel approximation, (d) large approximation.

with an anion of charge number 1 and two cations of charge numbers 1 and 2, respectively, and a simple but commonly used form of the Butler–Volmer law was treated in some detail. An exact explicit formula for the polarization curve for a binary electrolyte was given. An approximate formula was given for a system with a large surplus of supporting electrolyte. In contrast to previously given approximate formulae, the present results are valid for any magnitude of the exchange density. It is believed that some of the results in this paper will be of value for experimental determination of kinetic parameters. For instance, as was pointed out by Pritzker[15], an incorrect Tafel slope may be inferred from experimental data if effects of transport are not properly accounted for. The results given may also serve as tests for numerical methods.

REFERENCES

1. W. Nernst, *Z.phys. chem.* 47, 52 (1904).
2. E. Brunner, *Z.phys. chem.* 47, 56 (1904).
3. E. Brunner, *Z.phys. chem.* 58, 1(1907).
4. E. Baars, *Handbuch der Physik* 13, 558(1928).
5. A. Eucken, *Z.phys. chem.* 59, 72 (1907).
6. L. Hsieh, and J. Newman, *Ind. Eng. chem. Fund.* 10(4), 615 (1971).
7. C. Wagner, *J. electrochem. Soc.* 98(3), 116 (1951).
8. J. Heyrovsky and D. Ilkovic, *Coll. Czech. chem. Commun.* 7, 198 (1935).
9. R. Brdicka, *Coll. Czech. chern. Commun.* 19, 41 (1954).
10. M. A. Vorotyntsev, In *Advances in Science and Technology, Electrochemistry,* Vol. 14, pp. 57. VINITI, Moscow (1979).
11. K. Vetter, *Elecrrochemische Kinetik.* Springer, Berlin (1961).
12. V. G. Levich, *Physicochemical Hydrodynamics.* Prentice-Hall, Englewood Cliffs, NS (1962).
13. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications.* Wiley, New York (1980).
14. J. S. Newman, *Electrochemical Systems,* 2nd edn. Prentice-Hall, Englewood Cliffs, NS (1991).
15. M. D. Pritzker, *J. electroanal. Chem.* 296, 1 (1990).
16. D. R. Baker, M. W. Verbrugge and J. Newman, *J. electroanal. Chem.* 314, 23 (1991).
17. K. B. Oldham, *J. electroanal. Chem.* 337, 91 (1992).
18. D. R. Baker, SIAM *J. appl. Math* 53, 419 (1993).
19. J. C. Mykand and K. B. Oldham, *J. electroanal. Chem.* 347, 49 (1993).
20. A. Milchev, *Electrochim. Acta* 37, 2229, (1992).
21. H. Gu, T. V. Nguyen and R. E. White, *J. electrochem. Soc.* 134, 2953 (1987).
22. Z. Mai, R. E. White and B. Jay, *J. electrochem. Soc.* 138, 1615 (1991).

APPENDIX A

The diffusion layer for a system with arbitrary charge numbers and a general Butler–Volmer law with transfer coeflcient ½

The diffusion layer version for the problem dealt with in the main part of this paper offers some significant algebraic simplifications. Therefore, a considerably more general electrochemical system can be dealt with without much additional effort. Firstly, the charge numbers of the three ions are in this appendix kept arbitrary. Secondly, a very general form of the Butler–Volmer law can be considered. However, it turns out that, in order to obtain a reasonably simple solution, one is still forced to restrict the development to reactions whose transfer coefficient is ½. Attention is also restricted to cases such that only one species, here labelled species 1, carries charge. In Appendix 2, results for the more general system but in the configuration discussed in Sections 2–7 are given.

As is customary in the electrochemical literature, the thickness L of the diffusion layer is assumed to be known. The initial concentration c_3^0 for species 3 is taken as concentration scale also in the present diffusion layer problem. The dimensionless quantities ξ, j and j_0 are defined as before, *ie* according to formulae (10) and (11), respectively. However, the dimensionless electric potential ϕ and dimensionless difference in electric potential between the electrode and the edge of the diffusion layer, *ie* $\mathscr{V}$, are in this appendix defined by the formulae

$$(\phi, \mathscr{V}) = \frac{z_3 F}{R T} (\Phi, V).$$

As the charge numbers z_i, $i = 1, 2, 3$, are now arbitrary, the quantity k that appears in formulae (9) cannot be used as defined. In view of the general form of the condition for local electroneutrality, it turns out to be convenient to introduce another quantity κ that relates the initial concentrations for species 1 and 2 to that of species 3 by the following relations:

$$\frac{z_1 C_1^0}{z_3 C_3^0} = \kappa, \quad \frac{z_2 C_2^0}{z_3 C_3^0} = 1 - \kappa, \qquad (A1)$$

where, as before, $C_{1,2}^0$ are the initial concentrations for species 1 and 2, respectively. Furthermore, it turns out to be expedient to define normalized charge numbers according to the following formulae:

$$Z_1 = \frac{z_1}{z_3}, \quad Z_2 = \frac{z_2}{z_3}.$$

These normalized charge numbers may, of course, be fractional and there is *a priori* no restriction on whether Z_2 is positive or negative.

In terms of the dimensionless quantities that were defined above, the generalized versions of equations (12)–(15) are found to be

$$\frac{dc_1}{d\xi} + Z_1 c_1 \frac{d\phi}{d\xi} = \frac{j}{Z_1}, \qquad (A2)$$

$$\frac{dc_2}{d\xi} + Z_2 c_2 \frac{d\phi}{d\xi} = 0, \qquad (A3)$$

$$\frac{dc_3}{d\xi} - c_3 \frac{d\phi}{d\xi} = 0, \tag{A4}$$

$$Z_1 c_1 + Z_2 c_2 = c_3. \tag{A5}$$

At the edge of the diffusion layer, ie at $\xi = 1$, the following boundary conditions are prescribed:

$$c_1(1) = \kappa, \quad c_2(1) = 1 - \kappa, \quad c_3(1) = 1, \quad \phi(1) = 0. \tag{A6}$$

The first three of these boundary conditions simply state that the electrolyte outside the diffusion layer is unaffected by the transport inside the layer, which is not an unreasonable model for eg a rotating disc electrode. The fourth boundary condition states that the electric potential at the edge of the diffusion layer is equal to a constant. This value can, without loss of generality, be set equal to zero. This is an often idealization, which may perhaps be a little hard to realize in an experiment, but is here chosen for its simplicity. Results for such an idealized case are still believed to be of significant didactic value.

At the electrode, ie at $\xi = 0$, the following Butler-Volmer law is prescribed:

$$j = j_0 \{ f(c_1(0)) e^{z_1[\mathscr{V} - \phi(0)]/2} - g(c_1(0)) e^{z_1[\phi(0) - \mathscr{V}]/2} \}, \tag{A7}$$

where $f(c_1)$ and $g(c_1)$ are any given functions of c_1.

Taking $\phi_0 = \phi(0)$ instead of y as the parameter in the implicit form of the solution and using the methodology outlined in Section 3, it is not hard to derive the following counterparts of equations (43), (45) and (51)

$$c_2(0) = \frac{(1 - \kappa)}{Z_2} e^{-Z_2 \phi_0}, \tag{A8}$$

$$c_1(0) = \frac{1}{Z_1} [e^{\phi_0} - Z_2 c_2(0)], \tag{A9}$$

$$j = (1 + Z_1)(1 - e^{\phi_0}) + (1 - \kappa)(Z_1 - Z_2)(1 - e^{\phi_0}). \tag{A10}$$

Using the notation

$$f_0 = f(c_1(0)), \quad g_0 = g(c_1(0)), \tag{A11}$$

For any given functions f and g that depend on the concentration fields $c_{1,2}$, formulae (80-82), with expressions (A8)-(A9) substituted into f and g, define the polarization curve $j = \mathscr{J}(\mathscr{V})$ in implicit form. The general properties of the solution is very much like that given in Section 4.

APPENDIX B

Extension of the results given in Section 4 to a more general system

In this appendix, the same kind of electrochemical system as the one considered in Sections 2–7 is considered but for the more general electrolyte and reaction kinetics that was dealt with in Appendix A. This means that the system of equations to be solved are equations (A2)–(AS). The boundary condition at the cathode, ie equation (A7), will remain the same whereas that at the edge of the diffusion layer has to be replaced by

$$j = j_0 \{ g_1 e^{z_1[\mathscr{V} - \phi(1)]/2} - f_1 e^{z_1[\phi(1) - \mathscr{V}]/2} \}, \quad \text{anode} \tag{B1}$$

where, in analogy with equation (A11), the following notation has been used

$$f_1 = f(c_1(1)), \quad g_1 = g(c_1(1)). \tag{B2}$$

The solution of equations (A2)–(AS) subject to the boundary conditions (A7) and (B1) and the conservation conditions (A1) proceeds essentially along the same lines as in Section 3. However, the algebra involved is a little more complicated. Therefore, only the results are given here. The detailed manipulations are available on request from the authors.

It turns out to be algebraically convenient to make a minor adjustment in the definition of the quantity y, which was used in Section 3 as the parameter in the implicit representation of the solution, see definition (38). In this appendix, y is defined as follows

$$y = e^{[\phi(1) - \phi(0)]/2}.$$

For the more general system considered here, one has to introduce two auxiliary functions, $\mathscr{N}(y)$ and $\mathscr{M}(y)$. These functions are defined by the following formulae:

$$\mathscr{N}(y) = \frac{Z_2^{1/2}}{(1 - Z_2)^{1/2}(1 + Z_1)(y^2 - y^{-2})} \left\{ \left(Z_1 - Z_2 + \frac{1 + Z_1}{1 - \kappa} \right)(y^{1 - Z_2} - y^{Z_2 - 1}) \right.$$

$$\left. + \left[\left\{ \left(Z_1 - Z_2 + \frac{1 + Z_1}{1 - \kappa} \right)(y^{1 - Z_2} - y^{Z_2 - 1}) \right\}^2 + \frac{(1 + Z_1)(1 - Z_2)(Z_1 - Z_2)(y^2 - y^{-2})(y^{-2Z_2} - y^{2Z_2})}{(1 - \kappa)} \right]^{1/2} \right\}, \tag{B3}$$

$$\mathscr{M}(y) = \frac{2(1 - Z_2)[\mathscr{N}(y)(1 + Z_1)(y - y^{-1}) + (Z_1 - Z_2)(y^{-2Z_2} - y^{2Z_2})]}{\mathscr{N}(y)(1 - Z_1)(1 - Z_2)(y^2 - y^{-2}) - 2Z_2(Z_1 - Z_2)(y^{1 - Z_2} - y^{Z_2 - 1})} \tag{B4}$$

one can then, by using equations (80) and (77) compute the following expression

$$\mathscr{V} = \frac{2}{z_1} \left\{ \phi_0 - \ln \left[\frac{\sqrt{j^2 + 4j_0^2 f_0 g_0} - j}{2g_0 j_0} \right] \right\}. \tag{A12}$$

In terms of these functions and the variable y itself, one can express the electric current density j implicitly in terms of the difference in voltage $\mathscr{V}$ between the electrodes with the concentration variable κ and the dimensionless exchange current density j_0

appears as parameters. The results are as follows:

$$j = \mathcal{M}(y)\Bigg[(1 + Z_1)(y - y^{-1})$$

$$+ \frac{1}{\mathcal{N}(y)}(Z_1 - Z_2)(y^{-z_2} - y^{z_2})\Bigg], \quad \text{(B5)}$$

$$\mathcal{V} = 2 \ln y + \frac{2}{Z_1} \ln \frac{g_1}{g_0} \Bigg[\frac{\sqrt{j^2 + 4j_0^2 f_0 g_0} + j}{\sqrt{j^2 + 4j_0^2 f_1 g_1} - j}\Bigg]. \quad \text{(B6)}$$

In these expressions, one has to insert the expression for the concentration c_1 at $x = 0, 1$ into the functions f and g, respectively, see the definitions (B2)

and (A11). The expressions required are

$$c_1(0) = \frac{\mathcal{M}(y)}{Z_1}\left(\frac{1}{y} - \frac{Z_2}{\mathcal{N}(y)} y^{z_2}\right),$$

$$c_1(1) = \frac{\mathcal{M}(y)}{Z_1}\left(y - \frac{Z_2}{\mathcal{N}(y)} y^{-z_2}\right), \quad \text{(B7)}$$

$$c_2(0) = \frac{\mathcal{M}(y)}{\mathcal{N}(y)} y^{z_2}, \quad c_2(1) = \frac{\mathcal{M}(y)}{\mathcal{N}(y)} y^{-z_2}. \quad \text{(B8)}$$

If so desired, approximate formula for limiting cases such as a binary electrolyte or a system with an excess of supporting electrolyte can be derived in the same manner as was done in Section 5. However, these formulae will not be given here.