Several ways to simulate time dependent liquid junction potentials by finite differences

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ABSTRACT

Several ways of simulating time-dependent migration effects at an electrolytic liquid junction are explored, for a simple uni-univalent electrolyte, both with the full Nernst-Planck-Poisson (NPP) equation set and the reduced set from the electroneutrality condition (ENC) assumption. Using the NPP approach, the system can be simulated using all three variables (method **AB ψ**), the two concentrations and the potential, or the two concentrations and the potential field (method **ABE**), or in principle by substituting for the potential field, thereby reducing to the two concentration variables (method **AB**). The two first methods are about equally efficient, whereas the latter method is seen to be quite inaccurate. Results at long times compare very well with the Henderson equation. Using the full NPP set, junction potentials are time-dependent but not when applying the ENC, where the potential rises to the Henderson value immediately. Results for KCl and HCl are presented, with left/right concentration ratios equal to 0.1 in both cases.

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1. Introduction

Liquid junctions between electrolytes of different composition or ionic strength have attracted attention since the time of Nernst [1,2], Planck [3] and Henderson [4]. These authors derived equations of the junction potential, assuming the electroneutrality condition (see below), presumably because it made analytical solution possible. More recent analytical works include those of Schlögl [5], MacGillivray [6] (justifying electroneutrality), Hickman [7] (using electroneutrality) and Jackson [8] (avoiding it), Aguilera et al [9] (also using it), to mention a few. These were long-time solutions, time dependent solutions (still) not being amenable. For these, simulation techniques must be resorted to. In electrochemistry, apart from the interest in potentials across the tips of salt bridges, where two different electrolytes meet, or if an electrolyte in which electrolysis is carried out does not contain rather strong supporting electrolyte, migrational effects appear, which must be included in theoretical treatments of the behaviour of such cells.

There is a set of classical works cited in almost every paper on the simulation of migration. Probably the earliest simulation paper is that of Helfferich [10] simulating migration in an ion exchange

bead, whereas Cohen and Cooley [11] are usually cited as a very early effort, using an explicit method [12,13]. Scharfetter and Gummel [14] simulated *n* and *p* drift-diffusion in a semiconductor, which obeys the same mathematics as ion electro-diffusion [15] in solution, and this paper is interesting for several reasons, to be gone into later. Buck [16] wrote a review of ionic transport, describing the shortcomings but also the wide applicability of the Nernst-Planck equation. Many others have written about this subject and some will appear in what follows, in various contexts.

The system to be simulated is as follows, see Fig. 1. There are two chambers stretching along distance variable *x*, $-l \leq x \leq l$ containing the salt AB, cation A⁺ and anion B[−]. In the left half AB is at concentration *c_L* and in the right half at *c_R* uniformly initially, with a sharp boundary at *x*=0, where we set it at (*c_L* + *c_R*)/2 initially. The length *l* is chosen so that the cell is essentially semi-infinite in both directions away from the center. Therefore, the simulated system is a *free-diffusion junction* [17] with a boundary without a separating membrane, initially at *x*=0.

This system depicted in Fig. 1 describes the case for a length where concentrations are held constant at each end. It could be a membrane between two well stirred solutions. Experimentally, the situation of a watery boundary can also be realised in microchannels, involving dual-stream laminar flow of two aqueous solutions along each other carrying different electrolyte salts at various concentrations [18–22] forming a *flowing junction* [17]. Good agreement between the calculated values of the diffusion

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Fig. 1. Liquid junction of length $2L$. At the dashed line, the two different concentrations meet at $T=0$.

potential using the Henderson equation [20] and numerical solutions of the Nernst-Planck equation [21,22] and the measured open-circuit potentials has been found.

In the following, the abbreviation NPP refers to the full Nernst-Planck-Poisson equation set, whereas NP refers to the Nernst-Planck equations without the Poisson equation.

2. Local electroneutrality or Poisson equation?

There is continuing discussion in the literature on the applicability (or otherwise) of the local electroneutrality condition (ENC). The Poisson equation relates the charge distribution to the electrical potential. For electrolyte solutions the Poisson equation is

$$\phi_{xx} = -\frac{\mathcal{F}}{\epsilon_r \epsilon_0} \sum_{i=1}^s z_i c_i \quad (1)$$

where ϕ_{xx} is the second derivative of the potential with respect to the space variable x , $\mathcal{F}$ the Faraday constant, ϵ_r the relative permittivity of the medium (e.g. for water, $\epsilon_r = 80$), ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.854188 \times 10^{-12} \text{ F/m}$), z_i and c_i are the charge and concentration, respectively of ion i of a total of s species present in solution.

It is known that local charge separation is extremely small in magnitude [23,24]; if it were not, huge potential gradients would appear. Therefore, the Poisson equation is often replaced by

$$\sum_i z_i c_i = 0, \quad (2)$$

the electroneutrality assumption (see also later).

We cite only a few representative works here. Classically, Nernst [1,2], Planck [3] and Henderson [4] applied this condition in order to obtain their equilibrium solutions for liquid junction potentials. Strong support for ENC is given by Newman [17]; Oldham and Bond argue [25] for it, coining the term “electrodisparity” for its opposite; Myland and Oldham [26] call it “a requirement”, and Smyrl and Newman [27] used it to compute a large number of liquid junction potentials, a useful standard of comparison.

On the other hand, many have pointed out that at short times or short distances (e.g. thin membranes, of the order of only a few Debye lengths) the Poisson equation is required. Mafé et al [23] write that digital simulations do not become easier using the ENC; Jackson, who obtained an analytical solution rejected it [8] writing that “The charge density does indeed go to zero as t^{-1} ” but needs of the order of 10^{-9} seconds to do so. Smith and White [28] mention that ENC cannot be used for simulation of very small spheres. Instead of the ENC, Goldman [29] introduced the constant field assumption ($E = \text{constant}$), which becomes consistent with the Poisson equation if the Debye length and the diffusion length are of the same size [24].

Some review articles have been written, in an attempt to dispel the apparent contradiction between the ENC assumption and the fact that potentials do emerge from theory making that assumption [30,31], to name just two.

3. Theory

For the partial derivatives, we use the notation, for example, A_t as the first time derivative, A_x as the first spatial derivative and A_{xx} as the second spatial derivative.

The governing Nernst-Planck (NP) and Poisson equations, as normally expressed, are for the system as specified above

$$\begin{aligned} a_t &= D_A(a_{xx} + a_x \phi_x + a \phi_{xx}) \\ b_t &= D_B(b_{xx} - b_x \phi_x - b \phi_{xx}) \\ 0 &= \frac{\mathcal{F}}{\epsilon_r \epsilon_0} (a - b) + \phi_{xx} \end{aligned} \quad (3)$$

where ϕ is the potential, t the time, D_A and D_B the diffusion coefficients of A^+ and B^- , respectively, $\mathcal{F}$ the Faraday constant, ϵ_r the relative permittivity of the medium, and ϵ_0 the permittivity of free space (values provided above). The last equation is the Poisson equation for the present uni-univalent electrolyte. It has been pointed out by Buck [16] that the NP equations have several failings, that apply at very short times ($< 10^{-12}$ s) and distances smaller than the Debye length, as well as at higher concentrations, where cross terms apply, that is, ions act to limit the transport of each other. Mafé et al [23] also refer to “the approximate” nature of the NPP equations. These problems do not concern us here, as we are outside the regimes where they are of concern.

There are various possibilities for normalising the variables; concentrations could be normalised by the higher one, e.g. c_R on the right, or the expected final concentration at equilibrium; let whatever we choose be c^* , for example c_R as is often chosen.

Distance can be normalised by the Debye length as used by Hickman [7] and later by Dickinson et al [32] and defined by Mafé et al [23,24],

$$L_D = \sqrt{\frac{\epsilon_r \epsilon_0 RT}{\mathcal{F}^2 c^*}}. \quad (4)$$

Diffusion coefficients D_A and D_B are normalised by some chosen reference value D^* , for example $\sqrt{D_A D_B}$ or (as is often done) by D_B (chosen here). The dimensionless variables are then

$$\begin{aligned} A &= a/c^* \\ B &= b/c^* \\ C_L &= c_L/c^* \\ C_R &= c_R/c^* \\ \psi &= \frac{\mathcal{F}}{RT} \phi \\ X &= x/L_D \\ L &= l/L_D \\ \tau &= D^* t / L_D^2 \\ d_A &= D_A/D^* \\ d_B &= D_B/D^* \end{aligned} \quad (5)$$

In the following, several methods are described. There are other possibilities. The Poisson equation, perhaps reduced to the electroneutrality condition by elimination of ψ , can always be used to reduce one of the unknowns to one fewer. This is done, as will be seen, in methods AB and ENC.

3.1. Using A , B and ψ

The three $pdes$ are then

$$\begin{aligned} A_\tau &= d_A(A_{XX} + A_X \psi_X + A \psi_{XX}) \\ B_\tau &= d_B(B_{XX} - B_X \psi_X - B \psi_{XX}) \\ 0 &= A - B + \psi_{XX} \end{aligned} \quad (6)$$

Boundary conditions are

$$\begin{aligned} \tau = 0, \quad -L \leq X < 0: \quad A &= B = C_L \\ \tau = 0, \quad 0 < X \leq L: \quad A &= B = C_R \\ \tau = 0, \quad X = 0: \quad A &= B = (C_L + C_R)/2 \\ \tau = 0, \quad -L \leq X \leq L: \quad \psi &= 0 \\ \tau > 0, \quad X = -L: \quad A &= B = C_L; \quad \psi = 0 \\ \tau > 0, \quad X = +L: \quad A &= B = C_R; \quad \psi_X = 0 \end{aligned} \quad (7)$$

The potential ψ , is floating, and is set arbitrarily to zero somewhere, for example at $X = -L$, so that the total potential drop is the value at $X = +L$. The potential field E , defined in (8), was computed from the potential profile sequence at any point X_i by numerical differentiation using a central five-point window and a subroutine based on Fornberg [33], except at the ends where one-sided approximations were applied. The very end points are of course set to zero.

The above will be named **AB ψ** , that is, it uses the three variables A , B and ψ .

3.2. Using A , B and E

It is seen that in the above equations, ψ only appears as its first or second spatial derivatives. The potential field E , given by

$$E = -\frac{d\psi}{dX}, \quad (8)$$

can also be used, so that the equations become

$$\begin{aligned} A_\tau &= d_A(A_{XX} - A_X E - A E_X) \\ B_\tau &= d_B(B_{XX} + B_X E + B E_X) \\ 0 &= A - B - E_X \end{aligned} \quad (9)$$

Boundary conditions are slightly simpler (and slightly simpler to implement in a computer program),

$$\begin{aligned} \tau = 0, \quad -L \leq X < 0: \quad A &= B = C_L \\ \tau = 0, \quad 0 < X \leq L: \quad A &= B = C_R \\ \tau = 0, \quad X = 0: \quad A &= B = (C_L + C_R)/2 \\ \tau = 0, \quad -L \leq X \leq L: \quad E &= 0 \\ \tau > 0, \quad X = -L: \quad A &= B = C_L; \quad E = 0 \\ \tau > 0, \quad X = +L: \quad A &= B = C_R; \quad E = 0 \end{aligned} \quad (10)$$

The condition that E is zero at both ends arises from the fact that, as mentioned, L is chosen sufficiently large. For this method, the potentials were computed by numerical integration of E , using a Simpson-like routine adapted for unequal intervals.

This approach will be named **ABE**.

3.3. Using A and B only

A third possibility is to eliminate the potential from the equations. Given the third equation of the $pdes$, (6), we can substitute for ψ in the first two, replacing ψ_{XX} by $B - A$, and ψ_X by the integral of $B - A$ from $-L \dots X$. This does involve an integration step every time

we need a potential field value, but it reduces the system to two $pdes$ and thus the Jacobian matrix to 2/3 the size for the same grid dimensions, which might speed up the computation. The equations are then

$$\begin{aligned} A_\tau &= d_A(A_{XX} + A_X I(X) + A(B - A)) \\ B_\tau &= d_B(B_{XX} - B_X I(X) - B(B - A)) \end{aligned} \quad (11)$$

where we define

$$I(X) = \int_{u=-L}^X (B(u) - A(u)) du \quad (12)$$

Boundary conditions are

$$\begin{aligned} \tau = 0, \quad -L \leq X < 0: \quad A &= B = C_L \\ \tau = 0, \quad 0 < X \leq L: \quad A &= B = C_R \\ \tau = 0, \quad X = 0: \quad A &= B = (C_L + C_R)/2 \end{aligned} \quad (13)$$

The potential field was computed by integrating $B - A$, and the potential itself by integrating the resulting E .

This method will be called **AB**.

3.4. Eliminating one concentration

This is possible in principle, using the Poisson equation in (6) to substitute for B by setting $B = A - E_X$. However, one then obtains terms in E_{XT} and the third spatial derivative E_{XXX} and this was deemed not worth the effort. However, as will be seen, with the ENC, where there is no potential (field) in what remains of the Poisson equation, it is indeed worth while and was done.

3.5. Assuming local electroneutrality

One way to apply the ENC is to replace the Poisson equation in (6) simply by

$$0 = A - B \quad (14)$$

and simulate the resulting three equations. This in fact works. However, given the assumed equality of A and B everywhere, it is even better to make use of that and reduce the set of equations to two:

$$\begin{aligned} A_\tau &= d_A(A_{XX} + A_X \psi_X + A \psi_{XX}) \\ A_\tau &= d_B(A_{XX} - A_X \psi_X - A \psi_{XX}) \end{aligned} \quad (15)$$

This is more efficient and also works (although, as will be seen, not very well). The method will be called **ENC**.

4. Discretisation, simulation methods

Here the procedure for method **AB ψ** will be described, and that for the others will then follow in an obvious manner.

The cell length L is divided into M intervals, producing $N = 2M + 1$ points from left to right indexed as number 1 at the left-hand end and N at the right-hand end. There are three variable vectors **A**, **B**, and **ψ** , each of length N and they are arranged in a single long vector $\mathbf{U} \equiv [A_1, B_1, \psi_1, A_2, B_2, \psi_2, \dots, A_N, B_N, \psi_N]^T$. Vector **U** is of length $N_U = 3N$ for the computation. For most programs, the three-point backward differentiation formula (BDF) [34,35] was used, started with a single backwards implicit (BI) step (Laasonen [36]); this preserves the $O(\delta T^2)$ of the BDF [37]. For these programs, equal steps in time were taken. In the case of expanding time intervals (see later), this was not convenient, as unequal time intervals reduce the order of three-point BDF to $O(\delta T)$, so four-point BDF would be needed to achieve the same order [38]. It was more convenient in this case to use backward implicit with extrapolation [39–42], which is also $O(\delta T^2)$ (for the simple second-order extrapolation method). The

method requires three operations per time step rather than one, but as comparatively very few time steps were needed if they were expanding with time, computation was extremely fast, as will be seen.

Discretisation in time for a given concentration variable Y was then, for BI,

$$Y_T \approx \frac{Y' - Y}{\delta T} \quad (16)$$

and for BDF

$$Y_T \approx \frac{Y' - 4Y + 3Y'}{2\delta T} \quad (17)$$

where Y' is the previous value, Y the present one and Y' the next, unknown one, to be computed.

The points along the spatial coordinate were arranged in a sigmoidally exponentially expanding sequence (see Appendix A) in both directions away from the centre of the diffusion space at $X=0$. In this way very small intervals in X near the centre were obtained (typically 0.0001), expanding outwards but with the expansion limited near the ends, so as not to overdo the interval sizes there, since for ψ , derivative boundary conditions hold at the ends and this was desired to be discretised with good accuracy. Typically, M was chosen at about 400, which resulted in an expansion factor γ_1 of no more than about 1.1. It has been established [43] that a value no more than 1.2 is optimal.

There is therefore a sequence of N points along X at positions $X_1, X_2, \dots, X_N$ and at any point indexed i along this sequence we have a first derivative approximation in the bulk (away from edges)

$$Y_X(i) \approx \beta_1 Y_{i-1} + \beta_2 Y_i + \beta_3 Y_{i+1} \quad (18)$$

In what follows, we denote this as δY_i for brevity.

There is also in some cases a need for first derivative approximations at the right-hand end point (boundary condition for ψ) and here we use the one-sided formula

$$Y_X(N) \approx \beta_1 Y_{N-2} + \beta_2 Y_{N-1} + \beta_3 Y_N \quad (19)$$

We also need second spatial derivatives, expressed as

$$Y_{XX} \approx \alpha_1 Y_{i-1} + \alpha_2 Y_i + \alpha_3 Y_{i+1} \quad (20)$$

These will be denoted by $\delta^2 Y_i$. The β and α coefficients were computed for each i in advance using the algorithm of Fornberg [33].

We are now ready to express the discrete forms of the *pdes* in (6). It is convenient to lump the constants d_A and d_B with the time interval δT into the new constants $f_A = d_A \delta T$ and $f_B = d_B \delta T$. For index $i = 1$ we have the three equations

$$\begin{aligned} A_1 &= C_L \\ B_1 &= C_L \\ \psi_1 &= 0 \end{aligned} \quad (21)$$

(ψ_1 is arbitrarily set to zero at the left-hand end). In the bulk, for the BI step we have at any index i ,

$$\begin{aligned} \frac{A'_i - A_i}{f_A} &= \delta^2 A'_i + \delta A'_i \delta \psi_i + A'_i \delta^2 \psi \\ \frac{B'_i - B_i}{f_B} &= \delta^2 B'_i - \delta B'_i \delta \psi_i - B'_i \delta^2 \psi \\ 0 &= A'_i - B'_i + \delta^2 \psi_i \end{aligned} \quad (22)$$

which equations are rearranged suitably such that the unknowns are on the left-hand side and the knowns on the right.

At the end point index N we have

$$\begin{aligned} A_1 &= C_R \\ B_1 &= C_R \\ 0 &= \beta_1 \psi_{N-2} + \beta_2 \psi_{N-1} + \beta_3 \psi_N \end{aligned} \quad (23)$$

(although the β coefficients depend on the index i and here refer to the point $i=N$, we do not include it, so as not to clutter the notation needlessly).

The above holds for the (first) BI step. Taking a single example, in the bulk, for species A, the subsequent BDF steps lead to

$$\frac{A'_i - 4A_i + 3A'_i}{2f_A} = \delta^2 A'_i + \delta A'_i \delta \psi_i + A'_i \delta^2 \psi \quad (24)$$

which again is reorganised as above. These discrete approximations now form the equation system in $\mathbf{U}$

$$\mathbf{MU}' = \mathbf{R} \quad (25)$$

where $\mathbf{M}$ is the coefficient matrix and $\mathbf{R}$ the knowns vector. This is clearly a coupled nonlinear system and requires an iterative process to solve it, and the Newton-Raphson method [44] was used. Generation of the Jacobian from $\mathbf{M}$ is straight-forward, and in most cases, just 1–3 iterations (often 1–2) were sufficient to reduce the (Euclidian) norm of the correction vector $\delta \mathbf{U}$ to the tolerance limit, here set to 10^{-5} (this is much larger than the value used by Bieniasz [45], but he used the norm maximum, that is, the maximum absolute value of the correction vector, as criterion). Solution was at first by plain lower-upper decomposition (LUD [44]), not taking into account the sparse nature of $\mathbf{M}$, in which each row has entries only along a stretch of 9 consecutive points. It was recognised that the matrix can also be represented as a block-matrix with 3×3 blocks and total dimension $N \times N$ for method **AB ψ** and only 2×2 for methods **AB** and **ENC**. Vector $\mathbf{U}$ is now of length N and each element is itself a vector of length 3; similarly for the vector $\mathbf{R}$. To make this clearer, the above system, expressed in this way, produces a Jacobian block-matrix of the form

$$\mathbf{J} = \begin{bmatrix} I & & & & & \\ L_2 & C_2 & R_2 & & & \\ & \ddots & & \ddots & & \\ & & L_i & C_i & R_i & \\ & & & \ddots & & \ddots \\ & & & & L_{N-1} & C_{N-1} & R_{N-1} \\ & & & & & L_N & C_N & R_N \end{bmatrix} \quad (26)$$

with I being the 3×3 unit matrix and for $1 < i < N$,

$$\begin{aligned} L_i &= \begin{bmatrix} \alpha_{i1} + \beta_{i1} \delta \psi_i & 0 & \beta_{i1} \delta A_i + \alpha_{i1} A_i \\ 0 & \alpha_{i1} - \beta_{i1} \delta \psi_i & -\beta_{i1} \delta B_i - \alpha_{i1} B_i \\ 0 & 0 & \alpha_{i1} \end{bmatrix} \\ C_i &= \begin{bmatrix} \alpha_{i2} - 1/f_A + \beta_{i2} \delta \psi_i + \delta^2 \psi_i & 0 & \beta_{i2} \delta A_i + \alpha_{i2} A_i \\ 0 & \alpha_{i2} - 1/f_B - \beta_{i2} \delta \psi_i - \delta^2 \psi_i & -\beta_{i2} \delta B_i - \alpha_{i2} B_i \\ 1 & -1 & \alpha_{i2} \end{bmatrix} \\ R_i &= \begin{bmatrix} \alpha_{i3} + \beta_{i3} \delta \psi_i & 0 & \beta_{i3} \delta A_i + \alpha_{i3} A_i \\ 0 & \alpha_{i3} - \beta_{i3} \delta \psi_i & -\beta_{i3} \delta B_i - \alpha_{i3} B_i \\ 0 & 0 & \alpha_{i3} \end{bmatrix} \end{aligned} \quad (27)$$

and at the end point, $i = N$,

$$L_N = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \beta_{N1} \end{bmatrix}; \quad C_N = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \beta_{N2} \end{bmatrix};$$

$$R_N = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \beta_{N3} \end{bmatrix}. \quad (28)$$

The tridiagonal block system can now be solved by the block-Thomas algorithm as described in Appendix B. Block solutions have been used by Scharfetter and Gummel [14], Newman [17] and Aguilera et al [46]; Isaacson and Keller [47] and Golub [48] describe block-LUD solution.

In the case of method **AB** we have a small problem. The two equations eliminate the potential field E and its first derivative in (11) by substituting $B - A$ for E_X and the integral of $B - A$ for E itself, equation (12). The integral $I(X)$ is computed, in effect, as a weighted sum of all $B_i - A_i$, and therefore this should result in a whole N -length row entry in the Jacobian since, in principle, the integral should be updated at every Newton-Raphson step. However, using a constant integral was found to converge but upon more iterations.

Lastly, the aim of the computations was to obtain profiles for the concentrations, potentials and potential fields across the cell length for a given set of T values for two chosen example substances. This was done using, initially, rather small equal time intervals (typically, δT was set at 0.01). Since we were not interested in other than the given set of T values, it was decided to use sigmoidally exponentially expanding time intervals (see Appendix A for such a sequence). This always resulted in a time sequence not including the wanted T values and the problem was solved by setting those nearest to them equal to them. This procedure reduced the number of steps in time greatly and thus computing time also, as will be seen below.

5. Computational details

Programs were run (i) under Windows 7 (64 bits) on a PC equipped with an AMD Athlon® II X4 processor, using the gfortran 95/2003 compiler V.4.6 and (ii) under Linux running on an Amitech Blueline PC and Intel Fortran 90/95 V.11.3. All computations were run using IEEE 754 Standard double precision, giving approximately 16-decimal precision.

5.1. A note on COMSOL

Parallel to the Fortran code the NP equation together with the Poisson equation or the ENC were solved with the commercial finite element software COMSOL Multiphysics® (version 3.5a). The main purpose of this was to have an independent numerical approach to check the results from our Fortran code. For the NPP simulation, the Nernst-Planck equation without electroneutrality (a part of the Chemical Engineering module) was solved together with the Poisson equation from the PDE mode. For the NP-ENC system, the Nernst-Planck with electroneutrality application mode of the Chemical Engineering module was used. The coefficients for the pdes were chosen according to the dimensionless form, Eqs. (6) and (14), rendering the COMSOL Multiphysics® simulations dimensionless, so that direct comparison with the Fortran results was possible. The (one dimensional) domain was meshed by line elements with a maximal size of 10^{-5} around $X=0$ and an expansion factor of 1.05. Convergence tests showed that these parameters deliver reliable results.

Fig. 2. Spatial profiles of (A) concentrations, (B) Potentials and (C) potential fields, for KCl, initially $C_L = 0.1$, $C_R = 1$, at times $T = 0.1, 1, 10, 100$, as marked in the plots. Solid lines: results from method **AB**; circles: COMSOL Multiphysics® simulations.

6. Results

Method **AB** was found quite inaccurate, although the Newton-Raphson process did converge, usually after 3–4 iterations, slightly more than for the other methods, where usually 1–2 iterations were sufficient. The potential values went through a (false) maximum in time before converging on the Henderson value. Presumably this is due to the problem of the integral $I(X)$ mentioned above. The method will therefore be left out of consideration now, interesting though the idea of it was.

We present profiles of concentration, potential and the potential field for some T values for the two electrolytes KCl and HCl. In both cases the values $C_L = 0.1$ and $C_R = 1.0$ were set. The dimensionless diffusion coefficients were calculated from the ionic mobilities tabulated in Bard and Faulkner [49, p.68] and they were, for K^+ , 0.9630 and for H^+ , 4.582, respectively, d_B being unity in both cases. The number of points (expanding as described above) M was set at 400 and for the expanding time intervals, δT_0 was set at 0.0001, expanding to a maximum of about 0.6 with a starting expansion γ_1 (computed as) 1.037. Initially, before implementing variable time intervals, these were a constant 0.01. This number of points is unusually large for expanding intervals, where typically a few tens of points are sufficient for good accuracy [13]. We find that for fewer points, the calculated cell potential remains the same at large times but the potential profile becomes inaccurate, especially at the left-hand end. Also, the sigmoidal exponentially expanding point sequence, used here for this reason, evidently requires more points than the traditional undamped exponentially expanding sequence.

Fig. 2 shows the profiles for some T values, applying the full NPP set. Note the time dependence of the potential profiles, which even

Fig. 3. Similar to Fig. 2 but using electroneutrality.

at $T=100$ have not quite reached the Henderson value (normalised) 0.0432. On the other hand, Fig. 3 shows the same KCl system but using the ENC, and the potentials rise to the Henderson value without time delay. This follows from the concept of the ENC which does not allow the resolution of the potential build-up process. Fig. 4 is a plot of cell potential at a larger range of times, showing approach to the Henderson value with increasing T . 95% of the Henderson value 0.0432 is reached at about $T=5$, and 99% at $T=15$.

Fig. 5 shows the results for HCl, again with the full NPP set and with COMSOL values superimposed. Note here the (small) difference between the profiles for A and B. These curves deviate noticeably in the potential field peaks from those presented by Dickinson et al [32]. Since we ran two independent computations

Fig. 4. Cell potential for the KCl system in Figure 2 as function of T . The potential according to the Henderson equation is presented by the dashed line.

Fig. 5. Similar to Fig. 2 but for HCl, for $T=0.1, 1, 10, 100$ as marked. Empty circles are for ion H^+ while filled circles are for Cl^- . Note the slight separation of the ions' concentrations at $T < 1$ seen in (A), better resolved in A1, where the X scale has been expanded 10 times.

and checked with COMSOL Multiphysics®, which agreed closely with our Fortran results (although there are slight differences seen for HCl), we are confident that our results are correct. We have not been able to find publications of such profiles other than those of Dickinson et al. We did find plots of the total cell potential developing with time [50] albeit for a different electrolyte. There are tabulated total cell potentials in the literature, such as [51,52], to name just two, for KCl and HCl.

Table 1 compares computation times for the various approaches. Methods AB ψ and AB were for equal time intervals and solving

Table 1

Cpu times for the four algorithms, going to $T=100$

Algorithm	CPU (m:s)
AB ψ	17:51
ABE	19:00
ENC	19:37
block AB ψ	00:11
block ABE	00:10
block ENC	00:07
var. T block AB ψ	00:01.2

with LUD of the full Jacobian matrix; the algorithms labeled “block-” use the Jacobian’s block structure, and finally, the last entry uses both block structure and 100 variable time steps. Clearly, using the block-tridiagonal structure reduces cpu time greatly and, not surprisingly, fewer expanding time intervals reduce it drastically more still. The cpu time ratios for methods **ABE** and **ENC** are about 0.7, see Table 1. This ratio remains the same for coarser grids. The number of arithmetic operations for one Newton iteration, using the tridiagonal block solution, is proportional to M , so this is not surprising; the ratio simply reflects the amount of calculation required for the operations on the block matrices. There is some uncertainty in the cpu times, however, arising from the number of Newton iterations needed at each step; this varies from unity to about 8 in some cases, seemingly randomly. The effect of this is that the cpu time needed plotted against M fluctuates around linearity especially for high $M > 400$ and differently for the two methods, so that the ratio also fluctuates somewhat.

7. Conclusions

The NPP set of equations presents a non-linear system of *pdes* describing ionic fluxes under the influence of concentration gradients and an electric field or potential. The systems of equations were solved numerically using finite differences in one space dimension and in the time domain. Three different approaches were applied to include the electric field. As an simulation example, the liquid junction potentials for KCl and HCl were presented, with left/right concentration ratios equal to 0.1 in both cases. The three approaches were tested for efficiency and the results compared well with finite element simulations using COMSOL Multiphysics®, ensuring confidence into the accuracy of the computed profiles of concentration, potential and electric field over a range of times.

Methods **AB ψ** and **ABE** were found about equally efficient, whereas method **AB** was found, not unexpectedly, to be quite inaccurate (but faster, as also expected). Results at long times compared very well with the Henderson equation. Using the full NPP set, the development of the electric potential (or field) was simulated, approaching 95% of the Henderson value at dimensionless times $T \approx 8$ and 99% of the value at $T \approx 15$. As expected, when applying the ENC, the potential rises to the Henderson value immediately.

All the methods described can be used for the simulation of any problem involving migrational effects but clearly, we prefer **AB ψ** and **ABE**.

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Appendix A. Sigmoidally exponentially expanding sequence

There are situations where it is better not to have too large intervals at an outer boundary when using exponentially expanding intervals. One way to achieve this is to apply a damping function to the expansion factor γ , so that we have the sequence of points X_i , $i = 0 \dots N$, defined by the cumulative sum of the intervals H

$$H_i = \gamma_i H_{i-1}, \quad i = 2, \dots, N, \quad (29)$$

with $X_0 = 0$ and H_1 being set at a suitable value (see later), where

$$\gamma_i = \gamma_1 + (\gamma_1 - 1) \exp(-6X_i). \quad (30)$$

Here γ_1 is the base factor, and the constant 6 has been found a practically useful value. We set H_1 and find that value of γ_1 , using

Fig. 6. Sigmoid exponentially expanding grid (sig-exp) compared with plain exponentially expanding (exp-exp) grid as function of the running index i . Parameters were $\delta X_0 = 10^{-5}$ and $N = 400$. Only every 10th point was plotted. (A) X itself and (B) δX .

a binary search, which results in $X_N = \sum_{i=1}^N X_i = L$. Fig. 6 compares such a sequence of points with the plain exponentially expanding sequence.

In practice, this needs to be run only for a single L (e.g. $L = 1$), and for other values of L we can simply scale H_1 accordingly. If this is used for a sequence of time values and we wish to have output at definite time values, the ones closest to these in the computed sequence are set equal to them.

Appendix B. Block-tridiagonal solution

We choose as the example system (26) to be solved, using **AB ψ** . We start at the top, where we know $\delta U_1 = -F_1$ and we set, for convenience,

$$\delta U_1 = v_1 \delta U_2 + w_1 \quad (31)$$

where clearly v_1 is the zero matrix and $w_1 = -F_1$. Row 2 expands to

$$L_2 \delta U_1 + C_2 \delta U_2 + R_2 \delta U_3 = -F_2 \quad (32)$$

and substituting for δU_1 ,

$$(L_2 v_1 + C_2) \delta U_2 + R_2 \delta U_3 = -(L_2 w_1 + F_2) \quad (33)$$

from which we get

$$\delta U_2 = v_2 \delta U_3 + w_2 \quad (34)$$

where

$$v_2 = -(L_2 v_1 + C_2)^{-1} R_2 \quad (35)$$

$$w_2 = -(L_2 v_1 + C_2)^{-1} (L_2 w_1 + F_2).$$

We go on doing this and in general at index i ,

$$\delta U_i = v_i \delta U_{i+1} + w_i \quad (36)$$

where

$$v_i = -(L_i v_{i-1} + C_i)^{-1} R_i \quad (37)$$

$$w_i = -(L_i v_{i-1} + C_i)^{-1} (L_i w_{i-1} + F_i) \quad .$$

All v_i and w_i must be kept. This process stops at $i = N - 1$, where

$$\delta U_{N-1} = v_{N-1} \delta U_N + w_{N-1} \quad (38)$$

with the last row as defined in (28). We already have substitutions for δU_{N-2} and δU_{N-1} so the expanded N th line,

$$L_N \delta U_{N-2} + C_N \delta U_{N-1} + R_N \delta U_N = -F_N \quad (39)$$

becomes, upon substitution,

$$\begin{aligned} L_N(v_{N-2} \delta U_{N-1} + w_{N-2}) + C_N(v_{N-1} \delta U_N + w_{N-1}) + R_N \delta U_N &= -F_N \\ L_N(v_{N-2}(v_{N-1} \delta U_N + w_{N-1}) + w_{N-2}) + C_N(v_{N-1} \delta U_N + w_{N-1}) + R_N \delta U_N &= -F_N \\ (L_N v_{N-2} v_{N-1} + C_N v_{N-1} + R_N) \delta U_N &= -(L_N(v_{N-2} w_{N-1} + w_{N-2}) + C_N w_{N-1} + F_N) \end{aligned} \quad (40)$$

which we solve for δU_N , and then zip back to get all the others. Note that although we formally included F_N in these equations, it is in fact zero at all times.

For the ABE the last trio is not needed, as we have fixed values for A_N , B_N and E_N , and can immediately go into the backwards substitution loop.

This is similar to the mechanism described in [13, p.140–].

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