



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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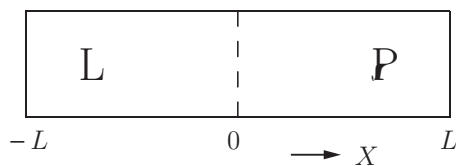


Fig. 1. Liquid junction of length $2L$. At the dashed line, the two different concentrations meet at $T=0$.

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 ($\epsilon_0 = 8.854188 \times 10^{-12}$ 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.

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