Biophysical Journal Volume 74 June 1998 2903–2905

Derivation of Unstirred-Layer Transport Number Equations from the Nernst-Planck Flux Equations

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ABSTRACT Since the late 1960s it has been known that the passage of current across a membrane can give rise to local changes in salt concentration in unstirred layers or regions adjacent to that membrane, which in turn give rise to the development of slow transient diffusion potentials and osmotic flows across those membranes. These effects have been successfully explained in terms of transport number discontinuities at the membrane-solution interface, the transport number of an ion reflecting the proportion of current carried by that ion. Using the standard definitions for transport numbers and the regular diffusion equations, these polarization or transport number effects have been analyzed and modeled in a number of papers. Recently, the validity of these equations has been questioned. This paper has demonstrated that, by going back to the Nernst-Planck flux equations, exactly the same resultant equations can be derived and therefore that the equations derived directly from the transport number definitions and standard diffusion equations are indeed valid.

INTRODUCTION

In the late 1960s it was clearly demonstrated that the passage of current across a planar membrane could give rise to local changes in salt concentration close to the membranes that resulted in both the development of slow changes in the diffusion potentials and local osmotic flows across those membranes (Barry and Hope, 1969b). A companion paper (Barry and Hope, 1969a) demonstrated that these effects, sometimes also referred to as polarization effects, could be explained in terms of transport number differences across the membrane-solution interfaces and resulting local concentration changes in the unstirred layers (USLs) adjacent to those membranes together with standard diffusion equations. The transport number (transference number), representing the fraction of current carried by an ion in a particular phase, generally differs between membrane and solution. A number of papers followed this work and showed that a number of transient potential responses and current-induced volume flows across cell membranes could be explained in terms of these transport number effects (e.g., Wedner and Diamond, 1969; Barry and Adrian, 1973; MacDonald, 1976; Barry 1977, 1981, 1984; Barry and Dulhunty, 1984; Barry and Diamond, 1984). The equations used to derive the theoretical analytical treatments made use of the simple definition of transport numbers along with normal diffusion equations.

A question, raised over recent years as to whether the original transport number equations were valid and were consistent with a derivation from first principles from the Nernst-Planck flux equations, was brought to my attention at the recent 1997 International Union of Physiological Sciences (IUPS) Congress (Dr. Robert Nielsen, personal communication).

The aim of this short paper is to show that the unstirred-layer transport number equations used in the literature (e.g., as cited above) and defined in this paper as transport number equations are consistent with those derived directly from the Nernst-Planck flux equations and result from the fundamental definitions of the transport numbers together with the standard solute diffusion equations. To achieve this aim, the paper will demonstrate the identity of the two approaches for the same physical situation under the final steady-state conditions.

It should also be noted that there had been an earlier analysis by Segal (1967) of a transport number contribution to low-frequency capacitance with infinite USLs. He had derived his response by starting with the Nernst-Planck equations and ended up with more standard electrolyte diffusion equations.

DESCRIPTION OF UNSTIRRED-LAYER SITUATION AND ASSUMPTIONS

The situation to be considered will be that of a current crossing a planar membrane adjacent to an USL (see Fig. 1). The solution will be considered to be a simple uni-univalent electrolyte and the membrane will be considered to be potentially permeable to both ions.

1) It will be assumed that within the USL there is no stirring and that beyond it stirring is perfect, a situation reasonably well approximated in many situations (see Barry and Diamond, 1984; Pedley, 1983). 2) It will also be assumed that, before the current starts, everything is at equilibrium with no solute flux across the membrane.

3) Any second-order effects, such as those of convective flow due to local osmotic water flows or the presence of any solute back fluxes down local concentration gradients, will be neglected.

Received for publication 23 December 1997 and in final form 5 March 1998.

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0006-3495/98/06/2903/03 $2.00

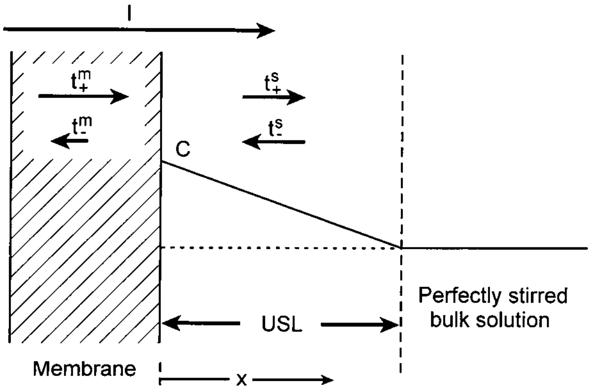

FIGURE 1 The steady-state concentration profile during the passage of current *I* across a membrane and adjacent unstirred-layer (USL). This is the situation considered for the derivation, from first principles, of transport number equations from the Nernst-Planck flux equations. The transport numbers t_+ and t_- represent the fractions of current (strictly the nondiffusive fractions) carried by the cations and anions, respectively, the superscripts m and s refer to the membrane and solution phases and the sizes of the arrows reflect the arbitrary magnitudes of the transport numbers (with typically $t_+^m > t_+^s$). *C* refers to the concentration profile of the uni-univalent electrolyte, and it is assumed that there is no stirring within the USL and perfect stirring beyond it.

4) It will be assumed that there will be no concentration changes within the membrane and that the transport numbers within the membrane will not change during the passage of current.

5) In the treatments using both approaches, ionic activities will be considered to be well approximated by concentrations.

THE STEADY-STATE TRANSPORT NUMBER EQUATIONS FOR A PLANAR MEMBRANE AND AN ADJACENT USL

The transport number of an ion represents the fraction of current *I* carried by that ion. More strictly, it actually represents the nondiffusive fraction of current carried by the ion (see Eq. 3 below and discussion following). A transport number difference between a membrane and the adjacent solution ($t_+^m - t_+^s$) will result in salt being generated (if $t_+^m > t_+^s$) or lost (if $t_+^m < t_+^s$) in the USL at the interface between the USL and the membrane whenever a current is passed across the membrane. In the steady state, this generation of salt is simply balanced by the diffusion of the salt away from the membrane and across the USL (Fig. 1). The transport number definitions automatically conserve electroneutrality.

This rate of salt generation, Φ, is given by

$$\Phi = (t_+^m - t_+^s)I/F, \tag{1}$$

where *F* is the Faraday. The transport number *t* for each ion (e.g., for cations) is, in turn, given by

$$t_+ = u_+C_+/(u_+C_+ + u_-C_-) = u_+/(u_+ + u_-) \tag{2}$$

where *u* is ion mobility and C its concentration. The final transport number equation at $x = 0$ thus simply becomes

$$-D(dC/dx)_{x=0} = (t_+^m - t_+^s)I/F, \tag{3}$$

with t_+^m and t_+^s representing the transport numbers in membrane and solution, respectively, with the solution value being given by Eq. 2, *D* being the diffusion coefficient for the electrolyte, and in this steady state-situation dC/dx being constant throughout the USL. Equation 3 shows clearly that the difference between the cation component of current in the membrane ($t_+^m I$) and the transport number component ($t_+^s I$) in the solution represents a diffusive component, $-D(dC/dx)F$. In the case of anions, there is a diffusive component of equal magnitude but opposite sign for the equivalent difference in their transport number components ($t_-^m - t_-^s)I$. It should be noted that the sum of both cation and anion transport number components equals the total current, as the two diffusive components cancel out.

THE NERNST-PLANCK DERIVATION OF TRANSPORT NUMBER EFFECTS

From the definition of chemical potential for ions in a solution, the Nernst-Planck equation for a flux J can be readily shown to be given by

$$J = -uRT(dC/dx) - uCzF(d\varepsilon/dx) \tag{4}$$

(e.g., Schwartz, 1971), where ε is electrical potential, *z* is ionic valency, *R* is the gas constant and *T* the temperature in °*K*. For a cation and anion, the flux equations in the solution respectively become

$$J_+^s = -u_+RT(dC_+/dx) - u_+C_+F(d\varepsilon/dx) \tag{5}$$

$$J_-^s = -u_-RT(dC_-/dx) + u_-C_-F(d\varepsilon/dx) \tag{6}$$

From the Poisson equation:

$$d\varepsilon/dx = \rho/(\epsilon\epsilon_o) = F(C_+ - C_-)/(\epsilon\epsilon_o) \tag{7}$$

where ρ is charge density, ϵ is dielectric constant and ϵ_o is the permittivity of free space. However, given reasonably long (more than a micron) USL widths, to a reasonable approximation, it can be assumed that $C_+ \approx C_- \approx C$, and hence it should not be necessary to have to use the Poisson equation.

In the steady state, $dC/dt = 0$ everywhere. This means that, in this situation, the cation flux leaving the membrane will now equal the cation flux flowing through the solution. Thus, at $x = 0$, we have from Eq. 5 that

$$J_+^m = J_+^s = -u_+RT(dC/dx) - u_+CF(d\varepsilon/dx) \tag{8}$$

As the cation flux in the membrane, J_+^m, is related to the cation current component in the membrane by $J_+^m = I_+^m/zF$ (where $z = +1$), by substituting into Eq. 8 and multiplying by $+F$, we obtain

$$I_+^m = t_+^m I = -u_+RTF(dC/dx) - u_+CF^2(d\varepsilon/dx) \tag{9}$$

Using the same approach for the anion flux and anion current component, we similarly obtain

$$I_-^{\mathrm{m}} = (1 - t_+^{\mathrm{m}})I = +u_-RTF(dC_-/dx) - u_-CF^2(d\varepsilon/dx) \tag{10}$$

Hence, from Eq. 10:

$$-u_-CF^2(d\varepsilon/dx) = I_-^{\mathrm{m}} - u_-RTF(dC/dx) \tag{11}$$

Hence, substituting from Eq. 11 into Eq. 9, we have

$$I_+^{\mathrm{m}}/u_+ = -2RTF(dC/dx) + I_-^{\mathrm{m}}/u_-, \tag{12}$$

so that

$$(I_+^{\mathrm{m}}/u_+) - (I_-^{\mathrm{m}}/u_-) = -2RTF(dC/dx) \tag{13}$$

Now multiplying both sides of the equation by $u_+u_-/(u_+ + u_-)$, we obtain

$$\begin{aligned}(I_+^{\mathrm{m}}u_- - I_-^{\mathrm{m}}u_+)/(u_+ + u_-)&\\ = -[2u_+u_-/(u_+ + u_-)]RTF(dC/dx)&\end{aligned} \tag{14}$$

However, for a uni-univalent electrolyte, the salt diffusion coefficient D can readily be shown from the Nernst-Planck flux equations (see Appendix) to be given by

$$D \equiv [2u_+u_-/(u_+ + u_-)]RT \tag{15}$$

Hence,

$$[(I_+^{\mathrm{m}}u_- - I_-^{\mathrm{m}}u_+)/(u_+ + u_-)]/F = -D(dC/dx) \tag{16}$$

On substituting for the membrane components in terms of membrane transport numbers, we can see that

$$\begin{aligned}(I_+^{\mathrm{m}}u_- - I_-^{\mathrm{m}}u_+)/(u_+ + u_-) &= I(t_+^{\mathrm{m}}u_- - (1 - t_+^{\mathrm{m}})u_+)/\\ (u_+ + u_-) &= I(t_+^{\mathrm{m}}u_- - u_+ + t_+^{\mathrm{m}}u_+)/(u_+ + u_-)\\ &= I[t_+^{\mathrm{m}}(u_+ + u_-) - u_+]/(u_+ + u_-)\\ &= I[t_+^{\mathrm{m}} - u_+/(u_+ + u_-)] = (t_+^{\mathrm{m}} - t_+^{\mathrm{s}})I\end{aligned}$$

Hence, Eq. 16 becomes equal to

$$-D(dC/dx) = (t_+^{\mathrm{m}} - t_+^{\mathrm{s}})I/F, \tag{17}$$

which is identical to the original transport number equation given in Eq. 3.

CONCLUSION

By considering the steady-state situation for local concentration changes in an USL adjacent to a planar membrane, this paper has demonstrated that the transport number equations used in the literature can also be derived from first principles from the Nernst-Planck flux equations.

APPENDIX

From Eqs. 5 and 6, the ionic fluxes, J_+ and J_-, are given by:

$$J_+ = -u_+RT(dC_+/dx) - u_+C_+F(d\varepsilon/dx) \tag{A1}$$

$$J_- = -u_-RT(dC_-/dx) + u_-C_-F(d\varepsilon/dx) \tag{A2}$$

For fluxes down a concentration gradient in the absence of any current $J_+ = J_- = J$. Therefore, adding Eqs. A1 and A2 after dividing by u_+ and u_-, respectively, and as $C_+ = C_- = C$, we obtain

$$J[(1/u_+) + (1/u_-)] = -2RT(dC/dx) \tag{A3}$$

Hence,

$$J = -2[(u_+u_-)/(u_+ + u_-)]RT(dC/dx) \tag{A4}$$

And by analogy with the normal diffusion equation ($J = -D(dC/dx)$):

$$D \equiv [2u_+u_-/(u_+ + u_-)]RT \tag{A5}$$

I acknowledge both the initial challenge from Dr. Robert Nielsen, of the August Krogh Institute at the University of Copenhagen, to validate the transport number equations and to silence their critics, together with his helpful and critical reading of the manuscript. The constructive critical comments on the manuscript by Dr. David Levitt were also very much appreciated.

This work was supported by the Australian Research Council and the National Health and Medical Research Council of Australia.

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