# AN EXACT CONSTANT-FIELD SOLUTION FOR A SIMPLE MEMBRANE

RICHARD A. ARNDT, JAMES D. BOND, *and* L. DAVID ROPER

*From the Department of Physics, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

ABSTRACT We show that the exact steady-state solution to the electrodiffusion equations for a simple membrane is the constant electric field solution when the ion environment is electroneutral on both sides of the membrane and the total numbers of ions of the same valence on both sides are equal.

## INTRODUCTION

The electrodiffusion equations for ion transport across a membrane are nonlinear. In the process of attempting to solve these nonlinear equations on a computer, we have discovered some interesting aspects of the equations. (The bulk of this work will be published in later papers.) We consider here only a simple membrane, i.e., a homogeneous membrane with no intrinsic charge structure. One interesting result is that, given special conditions, the exact solution is the constant electric field solution (Goldman, 1943).

We shall show herein that there is a special situation for which the exact solution is the constant electric field solution; viz., the situation in which the ion environment is electroneutral on both sides of the membrane and the total numbers of ions of the same valence on both sides are equal.

## THEORY

The steady-state electrodiffusion equations are the Nernst-Planck and Poisson equations.

### *The Nernst-Planck Equation (Goldman, 1943)*

$$\frac{dn_k}{dx} - z_k \beta n_k E = -\frac{j_k}{z_k u_k RT}, \tag{1}$$

where $n_k(x)$ is the concentration in moles per volume of ion type $k$, $z_k$ is the valence, $u_k$ is the mobility per unit valence (which we consider as constant across the membrane), $j_k$ is the ion current density in the outward direction, $E$ is the total electric field in the outward direction ($E = -V/w$ for constant electric field, in terms of the potential $V$ across the membrane and the membrane width $w$), and $\beta = F/RT$.

*The Poisson Equation* (*Jackson, 1962*)

$$\frac{dE}{dx} = \frac{F}{\epsilon} \sum_k z_k n_k \equiv \rho, \tag{2}$$

where $\epsilon$ is the permittivity (assumed constant across the membrane).

We shall consider the constant-field solution to Equation 1 and show that under special conditions it is also a solution of Equation 2. The general constant-field solution to Equation 1 is (Goldman, 1943):

$$n_k(x) = n_k^{(i)} + (n_k^{(o)} - n_k^{(i)}) \frac{e^{\beta z_k E x} - 1}{e^{\beta z_k E w} - 1}, \tag{3}$$

where $n_k^{(i)}$ is the ion concentration at the inside membrane boundary ($x = 0$) and $n_k^{(o)}$ is the ion concentration at the outside boundary ($x = w$).

We assume that we have the following special conditions.

($a$) The positive ions all have the same valence, $z_+$, and the negative ions all have the same valence, $z_-$.

($b$) The ion environment is electroneutral on both sides of the membrane:

$$\text{inside: } z_+ \sum_+ n_k^{(i)} = |z_-| \sum_- n_k^{(i)}; \text{ outside: } z_+ \sum_+ n_k^{(o)} = |z_-| \sum_- n_k^{(o)}.$$

($c$) The numbers of positive ions on both sides of the membrane are equal and, therefore by conditions $a$ and $b$, the numbers of negative ions on both sides of the membrane are equal:

$$\sum_+ n_k^{(i)} = \sum_+ n_k^{(o)} \text{ and } \sum_- n_k^{(i)} = \sum_- n_k^{(o)}.$$

Now we want to use these special conditions to show that Equation 3 is, also, the solution to Equation 2. For constant electric field, Equation 2 is

$$0 = \frac{F}{\epsilon} \sum z_k n_k.$$

Therefore, we must show that $\sum z_k n_k = 0$ for $n_k$ given by Equation 3 and under the three special conditions. We have

$$\sum z_k n_k = \sum z_k n_k^{(i)} + \sum z_k (n_k^{(o)} - n_k^{(i)}) \frac{e^{\beta z_k E x} - 1}{e^{\beta z_k E w} - 1}.$$

Application of conditions *a* and *b* yields:

$$\Sigma z_k n_k = z_+ \frac{e^{\beta z_+ Ex} - 1}{e^{\beta z_+ Ew} - 1} \underset{+}{\Sigma}(n_k^{(o)} - n_k^{(i)}) + z_- \frac{e^{\beta z_- Ex} - 1}{e^{\beta z_- Ew} - 1} \underset{-}{\Sigma}(n_k^{(o)} - n_k^{(i)}),$$

which is zero by condition *c*. This is what we set out to prove.

The result can be expanded to include ions of the same charge sign but different valences (removing condition *a* and replacing condition *c*).

With electroneutrality at the boundaries

$$\Sigma z_k n_k = \Sigma z_k (n_k^{(o)} - n_k^{(i)}) \frac{e^{\beta z_k Ex} - 1}{e^{\beta z_k Ew} - 1},$$

$$= \underset{k}{\Sigma} z_k \frac{e^{\beta z_k Ex} - 1}{e^{\beta z_k Ew} - 1} \underset{l}{\Sigma}(n_l^{(o)} - n_l^{(i)}),$$

where $\underset{l}{\Sigma}$ indicates a sum over all ion types with valence $z_k$ and $\underset{k}{\Sigma}$ indicates a sum over all different valences. This expression must be zero. We can make it so by requiring that $\underset{l}{\Sigma}\, n_l^{(o)} = \underset{l}{\Sigma}\, n_l^{(i)}$; i.e., that the total numbers of ions of valence $z_k$ is the same outside as inside.

## CONCLUSION

The constant-field Goldman equation (1943) for the current density,

$$j_k = -\frac{z_k^2 F u_k V}{w} \frac{n_k^{(i)} - n_k^{(o)} e^{\beta z_k V}}{1 - e^{\beta z_k V}},$$

is an exact solution of the electrodiffusion equations for the experimental conditions set forth in this paper. Since some natural and artificial membranes show rectification properties characteristic of a simple membrane (no negative resistance regions), it would be desirable to measure current density vs. clamping potential for such a membrane with the experimental conditions given here to see if the results can be fitted by the Goldman equation.

For a single uniunivalent solute (say NaCl) on both sides of the membrane, our experimental conditions are

$$n_k^{(i)} = n_k^{(o)} \equiv n_k \equiv n,$$

and

$$j_k = -\frac{F u_k n_k V}{w},$$

and

$$J(V) = -(u_+n_+ + u_-n_-)\frac{FV}{w} = -n(u_+ + u_-)\frac{FV}{w},$$

a straight line. This straight line behavior is a simple test whether a membrane is simple or not. If one of the ions (say the anion) is certain to have a very small mobility, the slope of the straight line gives a direct measure of the other ion's mobility.

For two uniunivalent solutes with identical anions (say NaCl and KCl) on both sides of the membrane, our experimental conditions are

$$n_-^{(i)} = n_-^{(o)} \equiv n_- \quad \text{and} \quad n_{1+}^{(i)} + n_{2+}^{(i)} = n_{1+}^{(o)} + n_{2+}^{(o)} = n_-.$$

The anion current density vs. potential is a straight line, but the two cation current densities are not. Thus, the total current density shows rectification:

$$J(V) = -\frac{FV}{w}\left[u_-n_- + \frac{u_{1+}n_{1+}^{(i)} + u_{2+}n_{2+}^{(i)} - (u_{1+}n_{1+}^{(o)} + u_{2+}n_{2+}^{(o)})e^{\beta V}}{1 - e^{\beta V}}\right],$$

$$= -\frac{FV}{w}\left[u_-n_- + u_{1+}n_{1+}^{(o)} + u_{2+}n_{2+}^{(o)} + \frac{(u_{1+} - u_{2+})\Delta n_+}{1 - e^{\beta V}}\right],$$

where $\Delta n_+ \equiv n_{2+}^{(o)} - n_{2+}^{(i)} = -(n_{1+}^{(o)} - n_{1+}^{(i)})$. The deviation from a straight line for $J(V)$ is a measure of the difference between the mobilities for the two cations.

For a single diunivalent solute (say $CaCl_2$) on both sides of the membrane, our experimental conditions are

$$n_+^{(i)} = n_+^{(o)} \equiv n_+ \quad \text{and} \quad n_-^{(i)} = n_-^{(o)} \equiv n_- = 2n_+.$$

Then

$$j_+ = \frac{4Fu_+n_+V}{w}, j_- = \frac{Fu_-nV}{w},$$

and

$$J(V) = -(4u_+n_+ + u_-n_-)\frac{FV}{w} = -2n_+(2u_+ + u_-)\frac{FV}{w},$$

a straight line.

For two uniunivalent solutes and one diunivalent solute with identical anions (say NaCl, KCl, and $CaCl_2$) on both sides of the membrane, our experimental conditions are

$$n_-^{(i)} = n_-^{(o)} \equiv n_-, \quad n_{Ca}^{(i)} = n_{Ca}^{(o)} \equiv n_{Ca}, \quad \text{and}$$
$$n_{Na}^{(i)} + n_K^{(i)} = n_{Na}^{(o)} + n_K^{(o)} = n_- - n_{Ca}.$$

The anion and Ca current densities are straight lines, but the univalent cation current densities are not.

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## REFERENCES

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