Introduction

To gain analytical insight into the transport of ions across charged or uncharged media, simplifying must be made. One of the most important and commonly used assumptions is that of electroneutrality which states that due to the strong electrical forces between charged species in solution and their high mobilities, "significant separation of charge does not occur" [1]. Specifically in the transport of charged ions through a membrane, another important assumption is that of a Gibbs-Donnan equilibrium at the membrane surface. In 1968, A. D. MacGillivray demonstrates how these assumptions may be derived for the transport of ions across a charged membrane that obeys the Nernst-Planck and Poisson equations [2].

Up to 1968 electroneutrality had been observed as a very reasonable assumption but lacked an analytical basis as well as grounds for when this assumption is valid. For example, if one assumes electroneutrality while solving Poisson's equation in one dimension they find the solution of the potential to be a straight line. This result is physically impossible because the solution for potential found by solving the Nernst-Planck transport equation under the same assumptions is non-linear. Before 1968, the justification made in literature was that "if this nonlinear potential is substituted into Poisson's equation, the charge distribution, although not zero, is small" [2, 3, 4].

The purpose of this paper is to demonstrate how the electroneutrality equation may be derived from Poisson's equation and under what grounds it is valid by following MacGillivray's technique, as well as to show how the Nernst-Planck equation in conjunction with Poisson's equation implies the existence of a Gibbs-Donnan equilibrium at the membrane surface [2].

Methods

The problem we are considering is the transport of ions through a charged membrane. The governing equations for this type of problem are the Nernst-Planck equation and Poisson's equation. The Nernst-Planck equation describes the total flux (N_i) of species i in terms of its concentration (C_i) and the potential distribution (ϕ):

$$N_i = C_i v - D_i\left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla\phi\right) \tag{1}$$

In in this equation v represents the bulk velocity, D_i and z_i are the diffusion coefficient and charge of species i respectively, F is Faraday's constant, R is the gas constant, and T is the temperature. Poisson's equation relates the Laplacian of the potential to the charge density and is given by the equation:

$$\nabla^2\phi = -\frac{\rho_e}{\xi} \tag{2}$$

where ξ is the constant dielectric permittivity and ρ_e is the volumetric charge density given by:

$$\rho_e = F\sum_i z_i C_i \tag{3}$$

To solve these equations, like all other transport problems, some sort of boundary condition is necessary. One such assumption is the existence of a Gibbs-Donnan equilibrium with the surface of the membrane. Gibbs-Donnan equilibrium occurs when a semipermeable membrane allows for the transport of smaller ions across its surface but not larger ones, thus resulting in varying equilibrium concentrations on each side of the membrane [5]. A Gibbs-Donnan equilibrium is characterized by the equation:

$$\left(\frac{A}{\tilde{\tilde{C}}_A}\right)^{z_A} = \left(\frac{B}{\tilde{\tilde{C}}_B}\right)^{z_B} = e^{-D} \tag{4}$$

where A and B are the dimensionless concentrations of species A and B inside the membrane that are "close" to the wall but not at the wall, $\widetilde{C_A}$ and $\widetilde{C_B}$ are their dimensionless concentrations outside of the membrane, and D is some constant.

To solve this problem, we will need to use a singular perturbation scheme. Singular perturbation is very similar to regular perturbation but is used in the case that the small dimensionless parameter ϵ that is otherwise small, becomes large in certain limits of the system (for example close to the walls as in our problem). A singular perturbation problem may be identified from a regular perturbation problem when ϵ approaching zero reduces the order of the differential equation, thus losing important information about the problem. Singular perturbation solves this problem by splitting the problem into two: 1) using perturbation to solve for the solution in the bulk (known commonly as the outer solution), and 2) using a change of variables followed by perturbation to solve for the solution close to the wall (known as the inner solution). The two solutions may then be woven together via asymptotic matching. For further discussion on singular perturbation beyond the example discussed in this paper please refer to Deen [6].

To derive the electroneutrality equation from Poisson's equation and prove the existence of a Gibbs-Donnan equilibrium at the membrane surface, we will consider the one-dimensional transport of charged species 1 and 2 through a charged membrane of length L. We will begin with the following assumptions: Let species 1 have a $+1$ charge and species 2 have a -1 charge and that both are able to cross the membrane wall, let species 3 have a $+1$ charge and be fixed within the membrane at a constant concentration of C_n, assume no convection and that the Nernst-Einstein relationship is true. We will provide the boundary conditions as:

$$C_1(0) = C_0 \qquad C_1(L) = C_0 + \Delta C \tag{5}$$

$$C_2(0) = C_0 \qquad C_2(L) = C_0 + \Delta C \tag{6}$$

$$\phi(0) = 0 \qquad \phi(L) = \Delta\phi \tag{7}$$

We first begin by non-dimensionalizing our balance equations. From an order-of-magnitude analysis we find that $x \sim L$, $C_1 {\sim} C_2 {\sim} C_n {\sim} \Delta C$, and $\Delta\phi {\sim} \frac{RT}{F}$. This suggests the following dimensionless variables:

$$\tilde{x} = x/L \tag{8}$$

$$\tilde{C}_1 = C_1/\Delta C \tag{9}$$

$$\tilde{C}_2 = C_2/\Delta C \tag{10}$$

$$\tilde{C}_n = C_n/\Delta C \tag{11}$$

$$\tilde{\phi} = \phi F/RT \tag{12}$$

Plugging these into equations (1) and (2) results in the following:

$$\widetilde{N}_1 = -\tilde{C}_1 \frac{d\tilde{\phi}}{d\tilde{x}} - \frac{d\tilde{C}_1}{d\tilde{x}} \tag{13}$$

$$\widetilde{N}_2 = \tilde{C}_2 \frac{d\tilde{\phi}}{d\tilde{x}} - \frac{d\tilde{C}_2}{d\tilde{x}} \tag{14}$$

$$\left(\frac{RT\xi}{F^2L^2\Delta C}\right)\frac{d^2\tilde{\phi}}{d\tilde{x}} = -\left[\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n\right] \tag{15}$$

Furthermore, if we let $\epsilon^2 = \frac{RT\xi}{F^2L^2\Delta C}$ Equation (15) reduces to:

$$\epsilon^2 \frac{d^2\tilde{\phi}}{d\tilde{x}} = -\left[\tilde{C}_1 - \tilde{C}_2 + \tilde{C}_n\right] \tag{16}$$

If ϵ is small (which is often the case), this would suggest a perturbation scheme. ϵ becomes small either when L is large compared to the Debye length (analogous to the thickness of the boundary layer for ϕ), or when ΔC is small compared to C_0 (which would result in $\tilde{C}_1$, $\tilde{C}_2$, and $\tilde{C}_n$ being large).

We can readily prove from Equation (16) that the electroneutrality equation can be derived from Poisson's equation. Taking the limit of Equation (16) ϵ goes to zero and rearranging we have the following:

$$0 = C_1 - C_2 + C_3 = \sum_i z_i C_i \quad (17)$$

which is the definition of electroneutrality.

We begin to solve these equations using singular perturbation by letting:

$$\tilde{C}_1 = \tilde{C}_1^{(0)} + \epsilon \tilde{C}_1^{(1)} + O(\epsilon^2) \quad (18)$$

$$\tilde{C}_2 = \tilde{C}_2^{(0)} + \epsilon \tilde{C}_2^{(1)} + O(\epsilon^2) \quad (19)$$

$$\tilde{\phi} = \tilde{\phi}^{(0)} + \epsilon \tilde{\phi}^{(1)} + O(\epsilon^2) \quad (20)$$

$$\widetilde{N}_1 = \widetilde{N}_1^{(0)} + \epsilon \widetilde{N}_1^{(1)} + O(\epsilon^2) \quad (21)$$

$$\widetilde{N}_2 = \widetilde{N}_2^{(0)} + \epsilon \widetilde{N}_2^{(1)} + O(\epsilon^2) \quad (22)$$

Plugging these expressions into equations (13), (14), and (16) and rearranging we get the following for zeroth order in ϵ:

$$\widetilde{N}_1^{(0)} + \widetilde{N}_2^{(0)} = \tilde{C}_n \frac{d\tilde{\phi}^{(0)}}{d\tilde{x}} - \frac{d}{d\tilde{x}}\left[\tilde{C}_1^{(0)} + \tilde{C}_2^{(0)}\right] \quad (23)$$

$$\widetilde{N}_1^{(0)} - \widetilde{N}_2^{(0)} = -\left[\tilde{C}_1^{(0)} + \tilde{C}_2^{(0)}\right] \frac{d\tilde{\phi}^{(0)}}{d\tilde{x}} \quad (24)$$

$$0 = -\left[\tilde{C}_1^{(0)} - \tilde{C}_2^{(0)} + \tilde{C}_n\right] \quad (25)$$

These equations represent the outer solution, which could then be solved to give us the concentration and potential profiles in the bulk. To prove the existence of a Gibbs-Donnan equilibrium we don't actually have to solve these, so we won't. It will be sufficient to assume that a solution exists and that the limits of that solution are as follows:

$$\lim_{\tilde{x}\to 0} \tilde{C}_1^{(0)}(\tilde{x}) = A \quad (26)$$

$$\lim_{\tilde{x}\to 0} \tilde{C}_2^{(0)}(\tilde{x}) = B \quad (27)$$

$$\lim_{\tilde{x}\to 0} \widetilde{\Phi}(\tilde{x}) = D \quad (28)$$

We then solve for the inner solution using a change of variables. Noticing that as $\tilde{x}$ approaches zero, the second derivative of potential becomes large enough that the entire left-hand side of Equation (16) must be on the order of one to become significant, we suggest a change of variable:

$$x_\eta = \frac{\tilde{x}}{\epsilon} \quad (29)$$

such that on substitution into Equation (16) the left-hand side becomes zeroth order in ϵ. Substituting this change of variable into equations (13), (14), and (16) along with the expansions in equations (18-22) we get the following for zeroth order in ϵ:

$$0 = -\hat{C}_1^{(0)} \frac{d\widehat{\Phi}^{(0)}}{x_\eta} - \frac{d\hat{C}_1^{(0)}}{x_\eta} \quad (30)$$

$$0 = \hat{C}_2^{(0)} \frac{d\hat{\phi}^{(0)}}{x_\eta} - \frac{d\hat{C}_2^{(0)}}{x_\eta} \quad (31)$$

$$\frac{d^2\hat{\phi}^{(0)}}{dx_\eta^2} = -\left[\hat{C}_1^{(0)} - \hat{C}_2^{(0)} + \tilde{C}_n\right] \quad (32)$$

Note the change in notation from $\tilde{C}_1^{(0)}$, $\tilde{C}_2^{(0)}$, and $\tilde{\phi}^{(0)}$ to $\hat{C}_1^{(0)}$, $\hat{C}_2^{(0)}$, and $\hat{\phi}^{(0)}$ to represent the inner solution. Using integrating factors and applying boundary conditions we get the following solution for the concentration profiles near the wall of the membrane:

$$\hat{C}_1^{(0)}(x_\eta) = \tilde{C}_0 e^{-\hat{\Phi}^{(0)}(x_\eta)} \tag{33}$$

$$\hat{C}_2^{(0)}(x_\eta) = \tilde{C}_0 e^{\hat{\phi}^{(0)}(x_\eta)} \tag{34}$$

where $\tilde{C}_0 = C_0/\Delta C$.

To connect the inner and outer solutions we use asymptotic matching, where the limit of the outer solution as $\tilde{x}$ approaches zero must equal the limit of the inner solution as x_η approaches infinity. Matching equations (33) and (34) with equations (26), (27), and (28) under these limits results in:

$$A = \tilde{C}_0 e^{-\hat{\phi}^{(0)}(\infty)} \tag{35}$$

$$B = \tilde{C}_0 e^{\hat{\phi}^{(0)}(\infty)} \tag{36}$$

$$\hat{\Phi}^{(0)}(\infty) = D \tag{37}$$

Which satisfy Equation (4).

Results and Discussion

Using MacGillivray's technique of applying perturbation to Poisson's equation we were able to derive the electroneutrality equation. As shown in Equation (17), we found that in the limit as ϵ approaches zero Poisson's equation becomes the electroneutrality equation. From this derivation we gain insight into what conditions validate the assumption of electroneutrality. We have shown that electroneutrality is valid when the length scale of the system is large compared to the Debye length of the charged particles in question or when the change in concentration across the system is small compared to the overall bulk concentration.

Using singular perturbation MacGillivray proved that a system obeying the Nernst-Planck and Poisson equations results in Gibbs-Donnan equilibrium boundary conditions at the walls. Figure 1 shows an example system illustrating both electroneutrality and Gibbs-Donnan Equilibrium. In this system the orange ions cannot pass the membrane and thus create a concentration gradient across the membrane surface which affects the concentrations of both blue and green ions at equilibrium. Regardless of the concentrations of individual ions, the net charge on either side of the membrane is kept at zero, thus maintaining electroneutrality.

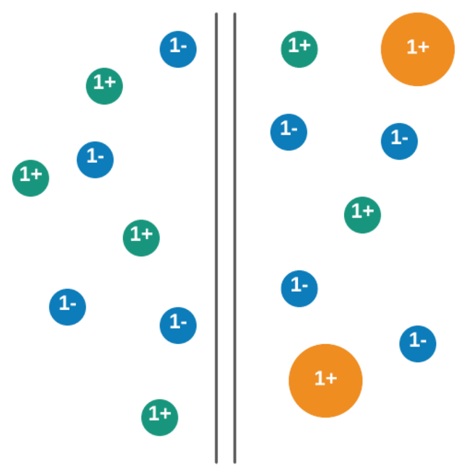

Figure 1: Example of a system obeying both electroneutrality and Gibbs-Donnan Equilibrium

Conclusion

MacGillivray's 1968 publication on the electroneutrality and Gibbs-Donnan equilibrium assumptions provides a sound analytical argument for how these assumptions work together with the Nernst-Planck and Poisson equations as well as give grounds for their validity other than solely experimental observation. While these equations were derived specifically in the case of ions moving across a charged membrane, they may be applied on a much larger scale. Electroneutrality is almost always a valid assumption in the bulk solution due to the strong attraction of electrical forces and the high mobility of small ions in solution. Gibbs-Donnan equilibrium refers to specifically the equilibrium across a membrane, but same principles may be applied to any phase boundary in an electrochemical system. In modern electrochemistry calculations the assumption of electroneutrality is nearly always assumed. Knowing the limits of this assumption is important in case they are ever approached in a future situation.

In doing this report I learned several knew things that I think are valuable to my understanding of graduate-level transport phenomena. In order to solve this problem, I had to learn about singular perturbation, both how to solve problems using it and how to identify when it is needed. While reading MacGillivray's paper and attempting to solve the problem I gained a greater understanding of what an order-of-magnitude analysis and why it is useful for defining dimensionless variable, something that I did not fully grasp the first time we covered it. To better understand the problem, I was solving I read both our textbook and sources online to learn about the governing equations for electrochemical transport. That has really helped me make the connection between what we have learned in our transport class to the field of research that I am studying.

References

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