



A GENERAL ANALYTIC EXPRESSION BASED ON THE LOCAL ELECTRICAL NEUTRALITY DESCRIBING ION TRANSPORT THROUGH AN ION-EXCHANGE MEMBRANE

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Abstract

The local electrical neutrality has been assumed to investigate the transverse ion transport through an ion-exchange membrane with a fixed charge density. General analytical expressions satisfying the Poisson-Nernst-Planck equations were sought to reveal ion concentration and electric potential profiles within the membrane. The Donnan equations were exploited to link the concentration in the solution and the concentration in the membrane at the interface. The osmotic pressure driven convection was also taken into account

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for full consideration, in addition to molecular diffusion and electrophoresis. The resulting set of the analytical expressions are found to agree well with the numerical results based on the full Poisson-Nernst-Planck equations without assuming the local electrical neutrality. The validation of the present analytic expressions was followed by a series of computations to investigate the characteristics of various parameters associated with the ion transport through an ion-exchange membrane with a fixed charge density.

Nomenclature

| | |
|--------------------------------|---|
| c | : concentration of ion [mol/m ³] |
| c_i | : concentration of ion in the solution bath [mol/m ³] |
| c_{mi} | : concentration of Na^+ in the membrane [mol/m ³] |
| $c_{mQ} = (c_{m1} + c_{m2})/2$ | [mol/m ³] |
| D_i | : diffusion coefficient of ion in the solution bath [m ² /s] |
| D_{mi} | : diffusion coefficient of ion in the membrane [m ² /s] |
| F | : Faraday constant [96485C/mol] |
| i | : current density [A/m ²] |
| J_i | : ion flux [mol/m ² s] |
| L_p | : permeability of the membrane [m ² s/mol] |
| l_m | : membrane thickness [m] |
| R | : gas constant [8.314 J/mol K] |
| T | : temperature [K] |
| u | : velocity component in x direction [m/s] |
| v | : velocity component in y direction [m/s] |
| p | : pressure [Pa] |
| x | : vertical coordinate [m] |
| y | : transverse coordinate [m] |
| z | : valency of an ion [-] |

Greek symbols

| | |
|---------------|---|
| δ | : concentration boundary thickness [m] |
| ρ | : density [kg/m ³] |
| ϕ | : voltage [V], $\Delta\phi = \phi(0) - \phi(l_m)$ |
| ε | : dielectric permittivity [F/m] |

Subscript

| | |
|-----|--|
| i | : 1 and 2 for cation and anion, respectively |
| m | : membrane |
| 1 | : cation |
| 2 | : anion |

Introduction

Ion transport through ion-exchange membranes is of great importance, since it controls the ionic concentrations in electrodialysis cells (e.g., [1, 2]). However, such ion transport processes are quite complicated, due to coupling among cation, anion and solvents fluxes. Usually, multiple electrodialysis cells are arranged to form an electrodialysis stack with alternating anion and cation exchange membranes, in which ion transport takes place under an applied electric potential difference. The ions pass through the membrane, travelling from the solution on one side of the membrane to the other side.

Numerical simulations of such ion transport in an electrodialysis stack are quite formidable, since the length scales associated with ion concentration fields within the cells are much larger than those in the membranes which are too thin to be resolved spatially. However, such a coupling problem resulting from the difference in length scales can be overcome by introducing an analytical model to describe the ion transport within the ion-exchange membrane with a fixed charge density. Thus, without resorting to detailed numerical calculations within the thin membranes, one can couple the ion concentration fields within the membrane with those in the adjacent electrodialysis cells in the stack.

A considerable number of attempts were made to solve the problems encountered in the ion transport across the ion-exchange membrane with a fixed charge density. The set of the principal ion transport equations involve in the Nernst-Planck equation and the Poisson equation (i.e., Maxwell's first law or Gauss's law for the electric field), which is commonly referred to as the Poisson-Nernst-Planck equations (PNP). Manzanares et al. [3] and many others (e.g., Flavell et al. [4], Jasielec et al. [5]) appealed to numerical solutions of the Poisson-Nernst-Planck equations.

Since the electroneutrality does not hold in the electrical double layer adjacent to the membrane surface, the Poisson equation should be solved together with the Nernst-Planck equation to reveal the space-charge concentrations in the electrical double layer with thickness in the range of several Debye lengths, which is even thinner than the membranes (note that the electrical double diffusion layer inside the membrane is even thinner). In view of practical applications, such computations are not desirable, because of high spatial resolutions required, which one cannot afford even with a super-computer available today. Fortunately, in the diffusion boundary layer outside the electrical double layer (i.e., several Debye lengths away from the membrane surface), the local electrical neutrality holds such that the cation and anion concentrations are locally identical.

In this study, we shall exploit the local electrical neutrality assumption to consider the transverse ion transport through an ion-exchange membrane with a fixed charge density. Analytical expressions satisfying the Nernst-Planck equations are sought to reveal ion concentration and electric potential profiles within the membrane. The Donnan equations are used to link the concentration in the solution and the concentration in the membrane at the interface [6]. The osmotic pressure driven convection is also taken into account, in addition to molecular diffusion and electrophoresis since it always takes place in an electrodialysis stack consisting of feeding and concentrating cells. The analytical expressions obtained here for coupling the ion concentration fields in the membrane with those in the adjacent electrodialysis cells can readily be implemented to conduct full scale numerical computations of ion transport in a whole system of electrodialysis

cells and electrodes. Thus, the present expressions, when combined with full numerical computations within electrodialysis cells, can save considerable CPU time.

Physical Model

The membrane system under the present study is illustrated in Figure 1 in which only several compartments in an electrodialysis system are presented. One representative cell may represent any one of cells in the electrodialysis stack, since they are repeatedly arranged. Upon analyzing convective ion transport within the unit cell, we can understand how overall stack system will perform under specified feed conditions.

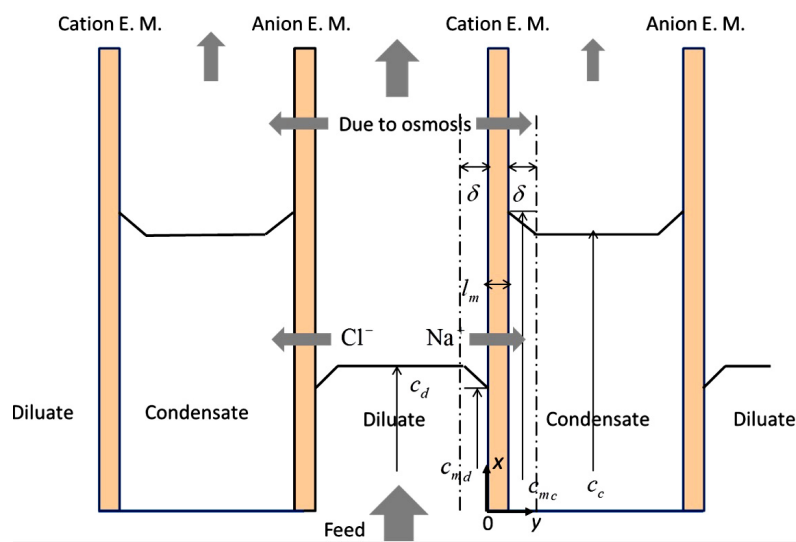


Figure 1. Physical model (electrodialysis cells).

Thus, we shall focus on the cation exchange membrane ($0 \leq y \leq l_m$) and its left hand-side (feeding side) and right hand-side diffusion boundary (concentrating side) layers, namely, those thin diffusion layers located at $-\delta \leq y \leq 0$ and $l_m \leq y \leq l_m + \delta$. The thickness of concentration boundary layer δ is very small, since a porous spacer is placed in the compartment, to enhance mechanical mixing of electrolyte solutions.

Direct current passes along the y axis in the direction perpendicular to the ion-exchange membranes. The electrolyte concentration within the solution decreases toward the interface of the left hand side of the membrane at $y = 0$. The cation exchange membrane naturally blocks the anions. Thus, the cation concentration is high within the membrane which contains fixed negatively charged groups at a uniform concentration Q , while its anion concentration is very much low, or virtually zero for the case of ideal ion-exchange membrane. Away from the right hand-side interface of the membrane at $y = l_m$, the electrolyte concentration decreases to its bulk value in the concentrating compartment which is naturally higher than the bulk concentration in the feeding compartment.

In the present analysis, we shall consider an overflow type of electrodialysis with the concentrating compartments sealed at the bottom end. In such a system, osmotic pressure driven flows across the membranes are no longer negligible. Thus, we shall also take account of the ion flux resulting from the osmotic flow in addition to diffusion and electrophoresis. Electrodialysis systems of this type have an advantage of producing high concentration concentrate and thus are commonly used in Japan.

In this paper, we shall follow Manzanares et al. [3] and many others, and consider a particular region covering an ion-exchange membrane and two adjacent diffusion layers, namely, $-\delta \leq y \leq l_m + \delta$, indicated by the two dashed lines in Figure 1. A steady state one-dimensional ion transport is considered across the membrane under the conditions of osmotic pressure driven flow with its velocity v . In an actual electrodialysis stack, an estimation of such osmotic flow velocity and bulk electrolyte concentration fields can be made by solving the set of Navier-Stokes equations and mass transfer equations in individual cells, along with the set of analytic expressions such as those derived in this paper. A coupling procedure will be presented in a separate paper in near future.

As for the present one-dimensional analysis, the Nernst-Planck equations are assumed to be valid for all three layers, namely, the membrane and two diffusion boundary layers [6, 7]. The concentrations at the membrane-

solution interfaces inside the membrane are related through the Donnan equations to the concentrations at the membrane-solution interfaces in the adjacent diffusion boundary layers. The Donnan equations are assumed to be valid even when electric current passes through the interface. The discussion on the validity of the Donnan equations may be found in [8].

Analysis in the Membrane

The sodium chloride ions are dissolved such that $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$. We shall first consider the ion transport through the membrane. The ion concentrations c_{mi} ($i = 1$ for the cations and 2 for the anions) and electric potential ϕ within the cation-exchange membrane at $0 \leq y \leq l_m$ (see Figure 1) may be investigated using the Nernst-Planck equation for the total ion flux:

$$J_i = -D_{mi} \frac{dc_{mi}}{dy} - \frac{z_i F D_{mi}}{RT} c_{mi} \frac{d\phi}{dy} + v c_{mi}, \quad (1)$$

where a locally unidirectional ion transport across the membrane is assumed. The subscript m indicates membrane, z_i is the ion valency, D_{mi} the ion diffusion coefficient in the membrane, v the osmotic pressure driven velocity, $F = 96485 [\text{C/mol}]$, $R = 8.314 [\text{J/mol K}]$ and $T [\text{K}]$ have their usual meanings, Faraday constant, ideal gas constant and absolute temperature. Writing it for individual ions:

$$J_1 = -D_{m1} \frac{dc_{m1}}{dy} - \frac{F D_{m1}}{RT} c_{m1} \frac{d\phi}{dy} + v c_{m1} : \text{Cation } \text{Na}^+, \quad (2\text{-a})$$

$$J_2 = -D_{m2} \frac{dc_{m2}}{dy} + \frac{F D_{m2}}{RT} c_{m2} \frac{d\phi}{dy} + v c_{m2} : \text{Anion } \text{Cl}^-. \quad (2\text{-b})$$

In order to determine the ion distributions c_{m1} and c_{m2} in the membrane, we may prescribe the ion fluxes J_1 and J_2 . Alternatively, we can provide the current density

$$i = F \sum_i z_i J_i = F(J_1 - J_2) \quad (3)$$

such that

$$\begin{aligned} \frac{i}{F} = J_1 - J_2 = & -D_{m1} \frac{dc_{m1}}{dy} + D_{m2} \frac{dc_{m2}}{dy} \\ & - \frac{F}{RT} (D_{m1}c_{m1} + D_{m2}c_{m2}) \frac{d\phi}{dy} + v(c_{m1} - c_{m2}) \end{aligned} \quad (4)$$

and the electroneutrality assumption:

$$c_{m1} = c_{m2} + Q \quad (5)$$

or

$$c_{m1} = c_{mQ} + \frac{Q}{2} \quad (6-a)$$

and

$$c_{m2} = c_{mQ} - \frac{Q}{2}, \quad (6-b)$$

where

$$c_{mQ} = (c_{m1} + c_{m2})/2 \quad (7)$$

Q is the negative exchange capacity of the cation exchange membrane. Following Sistat and Pourcelly [9], the foregoing equation may be re-written in terms of the new variable c_{mQ} as

$$\begin{aligned} \frac{i}{F} = & -(D_{m1} - D_{m2}) \frac{dc_{mQ}}{dy} - \frac{F}{RT} (D_{m1} + D_{m2}) \frac{d\phi}{dy} c_{mQ} \\ & - \frac{F}{RT} (D_{m1} - D_{m2}) \frac{Q}{2} \frac{d\phi}{dy} + vQ \end{aligned} \quad (8)$$

which can be transformed into:

$$\begin{aligned} & \left(\frac{i}{F} - vQ \right) \exp \left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F\phi}{RT} \right) \\ & = -(D_{m1} - D_{m2}) \frac{d}{dy} \left(\left(c_{mQ} + \frac{D_{m1} - D_{m2}}{D_{m1} + D_{m2}} \frac{Q}{2} \right) \exp \left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F\phi}{RT} \right) \right). \end{aligned}$$

Both left and right hand side terms may be integrated from 0 to y as

$$\left(\frac{i}{F} - vQ\right) = -(D_{m1} - D_{m2})$$

$$\times \left\{ \left(c_{mQ}(y) + \frac{D_{m1} - D_{m2}}{D_{m1} + D_{m2}} \frac{Q}{2} \right) \exp\left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F(\phi - \phi_0)}{RT} \right) \right. \\ \left. - \left(c_{mQ}(0) + \frac{D_{m1} - D_{m2}}{D_{m1} + D_{m2}} \frac{Q}{2} \right) \right\} \\ \frac{\int_0^y \exp\left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F(\phi - \phi_0)}{RT} \right) dy}{\int_0^y \exp\left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F(\phi - \phi_0)}{RT} \right) dy}.$$

Thus, $c_{mQ}(y)$, for given $\phi(y)$, may be evaluated from

$$c_{mQ}(y) = \frac{\left\{ c_{mQ}(0) + \frac{D_{m1} - D_{m2}}{D_{m1} + D_{m2}} \frac{Q}{2} - \frac{\frac{i}{F} - vQ}{D_{m1} - D_{m2}} \right\} \\ \times \int_0^y \exp\left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F(\phi - \phi(0))}{RT} \right) dy}{\exp\left(\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F(\phi - \phi(0))}{RT} \right)} - \frac{D_{m1} - D_{m2}}{D_{m1} + D_{m2}} \frac{Q}{2}. \quad (9)$$

This analytical expression deserves special attention in the sense that the effects of convective velocity on the ion concentration in the membrane are taken into account analytically for the first time. The cation and anion concentrations $c_{m1}(y)$ and $c_{m2}(y)$ in the membrane can be evaluated substituting equation (9) into equation (6-a) and (6-b), respectively. Furthermore, the cation and anion fluxes may be determined by the following equation obtained by integrating equation (1):

$$J_i = D_{mi} \frac{\left\{ \left(c_{mQ}(0) + z_i \frac{Q}{2} \right) \right. \\ \left. - \left(c_{mQ}(l_m) + z_i \frac{Q}{2} \right) \exp\left(z_i \frac{F(\phi(l_m) - \phi(0))}{RT} - \frac{vl_m}{D_{m1}} \right) \right\}}{\int_0^{l_m} \exp\left(z_i \frac{F(\phi(y) - \phi(0))}{RT} \right) dy}. \quad (10)$$

Hence,

$$J_1 = D_{m1} \frac{\left\{ \left(c_{mQ}(0) + \frac{Q}{2} \right) - \left(c_{mQ}(l_m) + \frac{Q}{2} \right) \exp \left(-\frac{F(\phi(0) - \phi(l_m))}{RT} - \frac{vl_m}{D_{m1}} \right) \right\}}{\int_0^{l_m} \exp \left(\frac{F(\phi - \phi(0))}{RT} - \frac{vy}{D_{m1}} \right) dy}, \quad (11-a)$$

$$J_2 = D_{m2} \frac{\left\{ \left(c_{mQ}(0) - \frac{Q}{2} \right) - \left(c_{mQ}(l_m) - \frac{Q}{2} \right) \exp \left(\frac{F(\phi(0) - \phi(l_m))}{RT} - \frac{vl_m}{D_{m2}} \right) \right\}}{\int_0^{l_m} \exp \left(-\frac{F(\phi - \phi(0))}{RT} - \frac{vy}{D_{m2}} \right) dy}. \quad (11-b)$$

Since the cation exchange membrane is homogeneous, the Poisson equation reduces to

$$\frac{d^2\phi}{dy^2} = -\frac{F(c_{m1} - (c_{m2} + Q))}{\varepsilon_m} = 0, \quad (12)$$

where ε_m is the dielectric permittivity in the membrane. Thus, across the membrane, the electric potential drops almost linearly, namely,

$$\phi - \phi(0) = -\Delta\phi \left(\frac{y}{l_m} \right), \quad (13)$$

where $\Delta\phi = \phi(0) - \phi(l_m) > 0$.

Substitution of equation (13) into (9) yields

$$c_{mQ}(y) = \frac{\left\{ c_{mQ}(0) + \frac{D_{m1} - D_{m2}}{D_{m1} + D_{m2}} \left(\frac{Q}{2} - \frac{il_m}{F} - \frac{vl_m Q}{D_{m1} - D_{m2}} \frac{RT}{F\Delta\phi} \right) \right\} \times \left(1 - \exp \left(-\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F\Delta\phi}{RT} \left(\frac{y}{l_m} \right) \right) \right)}{\exp \left(-\frac{D_{m1} + D_{m2}}{D_{m1} - D_{m2}} \frac{F\Delta\phi}{RT} \left(\frac{y}{l_m} \right) \right)} \quad (14)$$

which gives the inter-relation between the ion concentration and electric potential within the membrane. The Donnan equations should be used to match the concentrations $c_{mQ}(0)$ and $c_{mQ}(l_m)$ in the membrane with the concentrations $c(0)$ and $c(l_m)$ in the solutions as follows:

$$c_{mQ}(0) = \sqrt{(c(0))^2 + \frac{Q}{4}}, \quad (15-a)$$

$$c_{mQ}(l_m) = \sqrt{(c(l_m))^2 + \frac{Q}{4}}. \quad (15-b)$$

Note that the transverse velocity v due to the osmotic pressure is given by

$$v = L_p RT(c(l_m) - c(0)), \quad (16)$$

where L_p is the permeability of the membrane.

Thus, once the concentrations $c(0)$ and $c(l_m)$ in the solutions at the membrane interface are given, the concentration $c_{m1}(y)$ and $c_{m2}(y)$ and the electric potential difference $\Delta\phi$ within the membrane will be determined in such a way as to satisfy the Donnan equations (15-a) and (15-b).

Equations (11-a) and (11-b), for the case of linear potential distribution, reduce to

$$J_1 = \frac{D_{m1}}{l_m} \left(\frac{F\Delta\phi}{RT} + \frac{vl_m}{D_{m1}} \right) \frac{\left\{ \left(c_{mQ}(0) + \frac{Q}{2} \right) - \left(c_{mQ}(l_m) + \frac{Q}{2} \right) \exp \left(- \left(\frac{F\Delta\phi}{RT} + \frac{vl_m}{D_{m1}} \right) \right) \right\}}{1 - \exp \left(- \left(\frac{F\Delta\phi}{RT} + \frac{vl_m}{D_{m1}} \right) \right)}, \quad (17-a)$$

$$J_2 = - \frac{D_{m2}}{l_m} \left(\frac{F\Delta\phi}{RT} - \frac{vl_m}{D_{m2}} \right) \frac{\left\{ \left(c_{mQ}(0) - \frac{Q}{2} \right) - \left(c_{mQ}(l_m) - \frac{Q}{2} \right) \exp \left(\frac{F\Delta\phi}{RT} - \frac{vl_m}{D_{m2}} \right) \right\}}{1 - \exp \left(\frac{F\Delta\phi}{RT} - \frac{vl_m}{D_{m2}} \right)} \quad (17-b)$$

which, for the case of negligible osmotic water flow (i.e., $v = 0$), reduces to the Goldman-Hodgkin-Katz flux equation [10], as follows:

$$J_1 = \frac{D_{m1}}{l_m} \left(\frac{F\Delta\phi}{RT} \right) \frac{\left(c_{mQ}(0) + \frac{Q}{2} \right) - \left(c_{mQ}(l_m) + \frac{Q}{2} \right) \exp\left(-\frac{F\Delta\phi}{RT} \right)}{1 - \exp\left(-\frac{F\Delta\phi}{RT} \right)}. \quad (18)$$

Analysis in the Solutions

The boundary layer approximation may be applied to the ion transport equations in both diffusion boundary layers covering over the membrane, namely, at $-\delta \leq y \leq 0$ and $l_m \leq y \leq l_m + \delta$, respectively (see Figure 1).

$$\frac{\partial}{\partial x} u c_1 = \frac{\partial}{\partial y} \left(D_1 \frac{\partial c_1}{\partial y} + \frac{FD_1}{RT} c_1 \frac{\partial \phi}{\partial y} - v c_1 \right) = \frac{\partial}{\partial y} (-J_1), \quad (19-a)$$

$$\frac{\partial}{\partial x} u c_2 = \frac{\partial}{\partial y} \left(D_2 \frac{\partial c_2}{\partial y} - \frac{FD_2}{RT} c_2 \frac{\partial \phi}{\partial y} - v c_2 \right) = \frac{\partial}{\partial y} (-J_2). \quad (19-b)$$

Noting that the local electroneutrality holds such that $c_1 = c_2 \equiv c$ and that a near wall approximation (i.e., negligible axial convection) is valid, the foregoing equations may be combined to eliminate the potential gradient for given set of the ion fluxes, J_1 and J_2 , as

$$D_2 J_1 + D_1 J_2 = -2D_1 D_2 \frac{dc}{dy} + (D_1 + D_2) cv. \quad (20)$$

Equation (20) can easily be solved for $c(y)$ as

$$c(y) = c(-\delta) e^{\frac{D_1 + D_2}{2D_1 D_2} v(y + \delta)} + \frac{D_2 J_1 + D_1 J_2}{(D_1 + D_2) v} \left(1 - e^{\frac{D_1 + D_2}{2D_1 D_2} v(y + \delta)} \right) : -\delta \leq y \leq 0, \quad (21-a)$$

$$c(y) = c(l_m + \delta) e^{\frac{D_1 + D_2}{2D_1 D_2} v(y - l_m - \delta)}$$

$$+ \frac{D_2 J_1 + D_1 J_2}{(D_1 + D_2)v} \left(1 - e^{\frac{D_1 + D_2}{2D_1 D_2} v(y - l_m - \delta)} \right) : l_m \leq y \leq l_m + \delta. \quad (21-b)$$

For the case of negligible osmotic pressure driven flow, i.e., $v = 0$, the foregoing equations reduce to the linear concentration profiles:

$$c(y) = c(-\delta) - \frac{D_2 J_1 + D_1 J_2}{2D_1 D_2} (y + \delta) : -\delta \leq y \leq 0, \quad (22-a)$$

$$c(y) = c(l_m + \delta) - \frac{D_2 J_1 + D_1 J_2}{2D_1 D_2} (y - l_m - \delta) : l_m \leq y \leq l_m + \delta. \quad (22-b)$$

Results and Discussion

The present analytical expressions for the ion concentrations given by (14), (21-a) and (21-b) for the membrane and adjacent diffusion layers, together with auxiliary relations, (15-a), (15-b), (16), (17-a) and (17-b), may readily be used to reveal the cation and anion concentration fields in the membrane and adjacent diffusion layers. An iterative procedure must be taken to satisfy the boundary values, such that the concentrations at the boundary layer edges match with the bulk concentrations in the solutions (see Figure 1):

$$c(-\delta) = c_d \quad (23-a)$$

and

$$c(l_m + \delta) = c_c, \quad (23-b)$$

respectively. In order to accomplish this task, we shall first assume $c_{mQ}(0)$ and $\Delta\phi$ to find $c_{mQ}(l_m)$, J_1 and J_2 , using (14), (17-a) and (17-b). Then, the Donnan equations (15-a), (15-b) and (16) are used to calculate $c(0)$, $c(l_m)$ and v . These values are substituted into (21-a) and (21-b) to find the bulk concentrations in the solutions, namely, $c(-\delta)$ and $c(l_m + \delta)$. The whole process based on the Newton-Raphson method, e.g., [11] is repeated to find the correct set of $c_{mQ}(0)$ and $\Delta\phi$, which satisfies the boundary conditions in terms of the bulk concentrations, namely, equations (23-a) and (23-b).

However, in full numerical computations in electrodialysis cells in a stack, the streamwise variations of the concentrations $c(0)$ and $c(l_m)$ at the membrane interface are determined directly by solving the set of governing equations, namely, mass conservation, momentum conservation and Nernst-Planck equations (note that there is no need to assume the concentration boundary thickness δ or to estimate the bulk concentrations, $c(-\delta)$ and $c(l_m + \delta)$).

Validation of the present analysis

In order to examine the present analytical expressions based on the local electroneutrality assumption, the foregoing iterative calculations were carried out for the case of the membrane system with a cation-exchange membrane and bathing solutions under negligible osmotic pressure driven transverse flow, namely, $c(-\delta) = c(l_m + \delta) = \text{const.}$ and $v = 0$, which was treated by Manzanares et al. [3], numerically solving the Poisson-Nernst-Planck equations, without assuming the local electroneutrality. The values used for the calculations are as follows: $c(-\delta) = c(l_m + \delta) = 500 [\text{mol/m}^3]$, $i = 200 [\text{A/m}^2]$, $D_1 = 10^{-9} [\text{m}^2/\text{s}]$, $D_2 = 1.5 \times 10^{-9} [\text{m}^2/\text{s}]$, $T = 298 [\text{K}]$, $Q = 1000 [\text{mol/m}^3]$, $l_m = 1.7 \times 10^{-4} [\text{m}]$ and $\delta = 3.4 \times 10^{-4} [\text{m}]$.

The present iterative calculations converged to give $c_{mQ}(0) = 637 [\text{mol/m}^3]$, and $\Delta\phi = 4.65 \times 10^{-3} [\text{V}]$. The resulting ion concentrations are compared against the numerical results reported by Manzanares et al. [3] in Figure 2. Since the local electroneutrality prevails in the solution bath, the cation and anion concentrations are identical across the diffusion layer, namely, $c_1 = c_2 \equiv c$. In the solution bath on the feeding side (i.e., the bath on the left hand side), the ion concentration decreases towards the left hand side of the membrane interface located at $y = 0$. Then, the cation concentration jumps up to a higher level, while the anion concentration goes down to a lower level, at the membrane interface, to satisfy the Donnan equations. Both cation and anion concentrations in the membrane increase

towards the right hand side interface of the membrane. Then, the cation concentration suddenly goes down, while the anion concentration goes up, to meet each other to satisfy both Donnan equations and local electroneutrality condition at the right hand side interface. In the solution bath on the concentrating side (i.e., the bath on the right hand side), the concentration decreases to its bulk concentration.

Despite the difference in the two approaches, the present results based on the general analytical expressions are in close agreement with those obtained from full numerical calculations based on the PNP equations. This agreement substantiates the validity of the present analytical expressions to couple the concentrations in the solutions with the concentrations in the membranes.

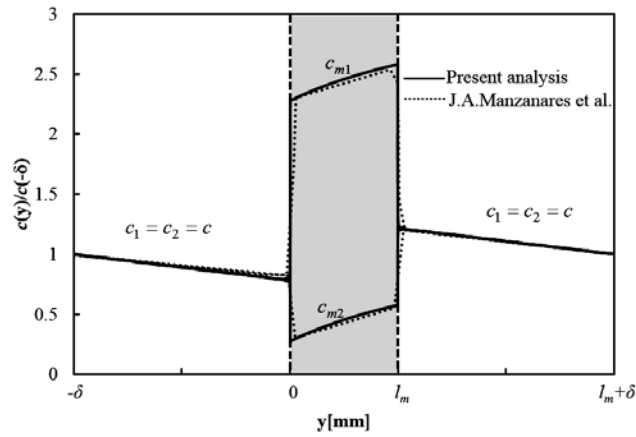


Figure 2. Comparison of the present results and the numerical results obtained by Manzanares et al.

Effects of current density on ion concentration profiles and potential drop

In order to investigate the effects of the current density i on the ion concentrations, the concentrations are plotted for the case of $c(-\delta) = c(l_m + \delta) = 591[\text{mol}/\text{m}^3]$, $D_1 = 10^{-9}[\text{m}^2/\text{s}]$, $D_2 = 1.5 \times 10^{-9}[\text{m}^2/\text{s}]$, $T = 298[\text{K}]$, $Q = 2000[\text{mol}/\text{m}^3]$, $l_m = 1.7 \times 10^{-4}[\text{m}]$, $L_p = 2.0 \times 10^{-14}[\text{m}^2\text{s}/\text{mol}]$ and $\delta = 3.4 \times 10^{-4}[\text{m}]$, with three different values of current density, namely,

$i = 100, 200$ and $400[\text{A}/\text{m}^2]$. The values of $c_{mQ}(0)$ and $\Delta\phi$ were assumed initially and updated to match the boundary conditions (22-a) and (22-b). A series of the iterative calculations were carried out and the results are plotted together in Figure 3.

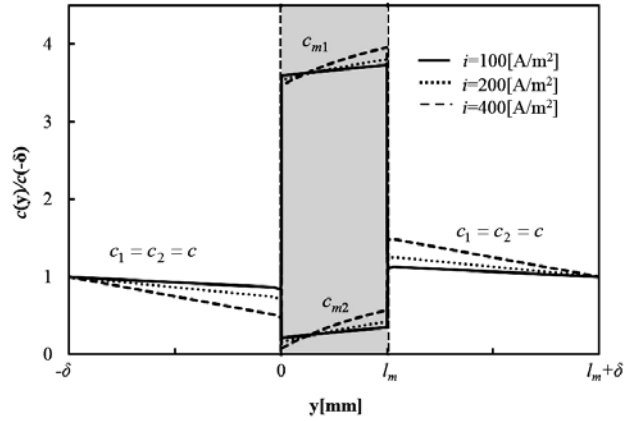


Figure 3. Effects of current density on ion concentrations.

Naturally, the net flux $(J_1 - J_2)$ increases with the current density i . Both concentration difference $(c(l_m) - c(0))$ and concentration gradient across the membrane grow with the current density i , as expected. Concentration polarization on the left hand side surface of the ion-exchange membrane proceeds further with increasing i . It would eventually yield zero concentration there, as the limit current density is attained.

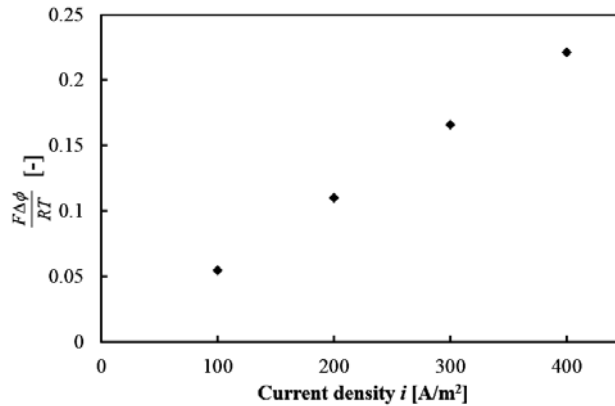


Figure 4. Potential drop across the membrane versus ion density.

The dimensionless potential drop $F\Delta\phi/RT$ for this case is plotted against the current density, in Figure 4, in which the potential drop is seen to increase almost linearly with the current density.

Effects of bulk concentration on ion concentration profiles

Calculations were conducted for various values of the bulk concentration, namely, $c(-\delta) = 591, 493$ and $380 [\text{mol/m}^3]$. The other parameters are set the same as the previous calculations. The concentration profiles within the diffusion boundary layer in the concentrating bath, shown in Figure 5, are quite insensitive to the bulk concentration $c(-\delta)$ in the feeding bath, since the net flux $(J_1 - J_2)$ is virtually controlled by the current density i , which is kept constant. However, closer observation reveals that the level of the concentration within the diffusion boundary layer in the concentrating bath is lower for the lower $c(-\delta)$, for which, the osmotic pressure driven flow is stronger so that dilution takes place within the diffusion later.

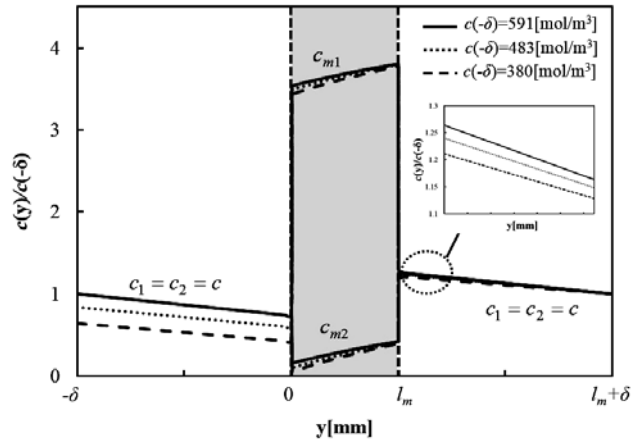


Figure 5. Effects of bulk concentration on ion concentration profiles.

Effects of negative exchange capacity on ion concentration profiles

The effects of negative exchange capacity Q on the concentration profiles are illustrated in Figure 6 for three different values, namely,

$Q = 1500, 2000$ and $2500 [\text{mol}/\text{m}^3]$. In the membrane, the cation concentration c_{m1} gets higher while the anion concentration c_{m2} gets lower, as increasing Q . Since Q is much larger than the bulk concentration on the solution, the cation concentration in the membrane on the average is roughly equal to Q . An ideal case of infinitely large Q would result in $c_{m2} = 0$ in the membrane. The figure also indicates that large Q leads to slightly high and low concentrations in the left and right hand side solution diffusion layers, respectively.

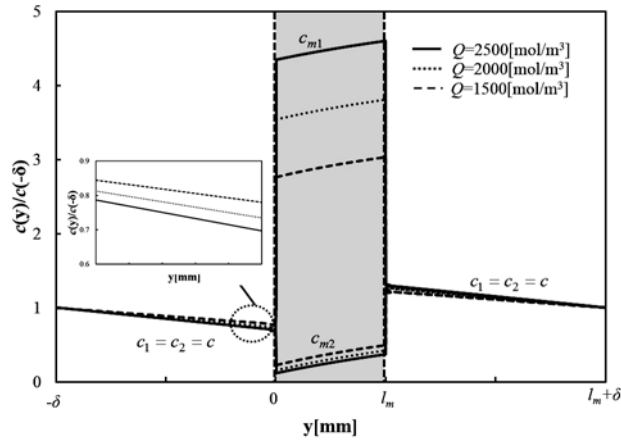


Figure 6. Effects of negative exchange capacity on ion concentration profiles.

Effects of membrane permeability on ion concentration profiles

Finally, a series of calculations were conducted for various values of the membrane permeability, namely, $L_p = 2 \times 10^{-14}$, 6×10^{-14} and $10^{-13} [\text{m}^2\text{s}/\text{mol}]$, with the potential drop across the membrane fixed at $\Delta\phi = 2.57 \times 10^{-3} [\text{V}]$. The results are plotted in Figure 7, to investigate the effects of L_p on the concentration profiles. In the overflow type of electrodialysis with the concentrating compartments sealed at the bottom end, the salt concentration in the concentrating chamber decreases due to the dilution

resulting from this osmotic pressure driven transverse flow. In actual electrodialysis desalination system, the osmotic pressure driven flow is never negligible. The osmotic flow increases with L_p , which results in dilution, lowering the concentration in the concentrating chamber. The figure clearly indicates that the osmotic pressure driven convection should be taken into full consideration.

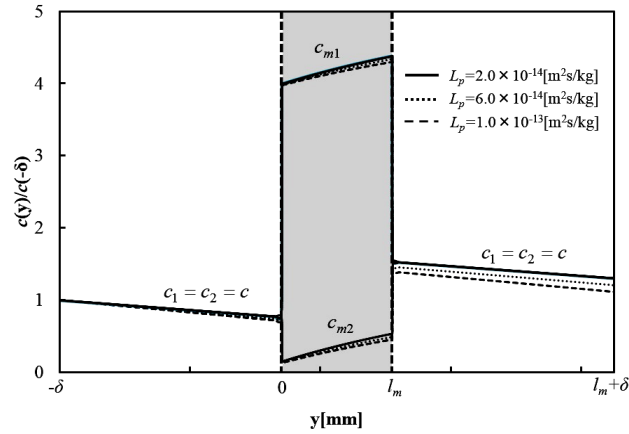


Figure 7. Effects of membrane permeability on the ion concentration profiles.

Conclusions

A general set of analytical expressions based on the local electrical neutrality are proposed, to describe the transverse ion transport with an osmotic pressure driven flow through an ion-exchange membrane with a fixed charge density. The expressions are found to agree well with the numerical results based on the full Poisson-Nernst-Planck equations without assuming local electrical neutrality. Various parameters associated with the ion-exchange membrane system, such as current density, bulk concentration in the solution, negative charge capacity and osmotic pressure driven flow are varied to investigate their effects on the ion concentrations in both solutions and membrane. The present set of analytical expressions capable of accounting for osmotic pressure driven convection can easily be coupled

with full numerical computations of ion transport within electrodialysis cells and electrode systems, using Navier-Stokes equations and mass transfer equations in individual cells.

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