



Nernst Planck approach based on non-steady state flux for transport in a Donnan dialysis process



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ABSTRACT

In the present work, Nernst Planck (NP) approach based on non-steady state flux has been explored to predict the transport kinetics in a Donnan dialysis process. The calculations have been carried out for pure and mixed bi-ionic monovalent–monovalent systems. Appropriate forms of the equations have been derived and then solved numerically by finite difference method using appropriate initial and boundary conditions. The results of the calculations have been compared with the experimental transport profiles and NP calculations based on pseudosteady state approximation. It has been found that the NP method based on non-steady state flux is capable of predicting the transport kinetics for both pure and mixed ionic systems for all salt compositions. On the other hand, NP approach based on pseudosteady state approximation works only at high salt concentrations (> 0.1 M) for pure ionic systems. Also, the approach completely fails for mixed ionic systems. The NP approach with non-steady state flux is capable of accounting the accumulation of ions in the membrane and the time lag characteristics prevalent dominantly in the initial time scales of a membrane transport process.

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1. Introduction

The permselective nature of the ion-exchange membranes, due to Donnan exclusion, is extensively exploited in Donnan dialysis (DD) process which is used for enrichment, recovery and separation of trace metal ions [1,2]. Several ecofriendly applications of DD process for the separation of metal ions and charged organic species have been reported elsewhere [3–13]. The ion-exchange membranes are also widely used in electrodialysis and in electrochemical devices such as batteries [14–16], fuel cells [17–19] etc due to their ability to regulate transport of ions. For successful use of these membranes for any application, the knowledge of basic transport phenomena of ions through these membranes is important. Transport mechanism of ions and solvent through biological membranes has also some similarity with that of ion-exchange membranes [20,21]. There has been accelerated effort to model the transport of ions through ion-exchange membranes with the rationale to simulate and optimize the performance of a given ion-exchange membrane to achieve a desired separation or electrochemical response. As for example, in a Donnan dialysis process, while the equilibrium distribution of the ions is well understood, there has been continuous effort to understand and predict the transport rate. Several mathematical models have been

developed by a number of researchers to explain the transport of ions and solvent through ion-exchange membranes keeping in view the importance of the transport properties in polymer electrolyte fuel cells [22–25]. In general, two fundamental approaches based on Nernst-Planck (NP) equation [26,27] and Maxwell Stefan equation [28] have been used to calculate the membrane diffusion controlled transport rate in ion-exchange membrane. Verbugge and Hill [27] developed a general model based on NP approach for calculation of ion and solvent transport in ion-exchange membranes, applicable with or without the flow of electric current. Similarly, Yang and Pintauro [29] proposed a multicomponent space charge model for transport through ion-exchange membranes. Both these models are rather involved. For explaining the transport rate in a Donnan dialysis process, simpler models have been used based on NP equation or mass balance approach [26,30–34]. All these models use pseudosteady state approximation in which the flux of ions across the membrane is assumed to be constant and linear integration of the flux through the membrane thickness have been carried out. These models use experimental transport parameters such as self-diffusion coefficients of the ions in the membrane (D), concentration of different components in the solution/membrane interface (selectivity coefficient) and ion-exchange capacity (Q) of the membrane as input. In our earlier work [31], the NP approach based on pseudosteady state approximation was successfully applied to predict the transport rate of monovalent–monovalent and monovalent–bivalent systems at equimolar initial feed and receiver (0.5 M and 0.1 M)

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concentrations. But this approximation is not valid, especially in the initial period of a membrane diffusion process, where for a bi-ionic system, the membrane is invaded by the counterion not present in the membrane and the flux through the membrane is not constant. Also, pseudosteady state approximation assumes an average interdiffusion coefficient across the membrane and neglects its variation along the spatial co-ordinate in the membrane. This is not true due to the dependency of the interdiffusion coefficient on the concentration of the ions in the membrane which changes across the membrane nonlinearly (especially the initial time scales). Ho et al. [35] have proposed a transport model in which the non-steady state diffusion has been accounted using an integration technique developed by Caillaud and Padmanabhan [36]. However, the approach assumes the diffusivity ratio of the two ions to be same in aqueous solution and in membrane. This assumption is not true especially for ion-exchange membranes like Nafion where the diffusivity trend in membrane of ions is not same as in aqueous solution [37]. Also, along with other experimental inputs, this approach requires determination of large number of differential quadrature coefficients, α_{ij} and β_{ij} , which makes the method cumbersome. In the present work, Nernst Planck approach based on non-steady state flux has been explored to calculate the transport profiles in a Donnan dialysis process. Appropriate forms of the equations have been derived and solved numerically by finite difference method using appropriate initial and boundary conditions. The calculations have been carried out for monovalent–monovalent pure and mixed bi-ionic systems. The results have been compared with the experimental measurements. The present method of calculations has also been compared with the calculation results on the basis of pseudosteady state approximation, given in detail in earlier publications [31–34].

2. Theoretical

Consider a two compartment system where a cation exchange membrane separates the compartments, *I* and *II*, containing the electrolyte solutions *AX* and *BY* respectively at time, $t=0$. At $t > 0$, ion-exchange process $z_B A^{z_A^+} \rightleftharpoons z_A B^{z_B^+}$ will take place due to the permselectivity of the cation exchange membrane. The co-ions are assumed to be completely excluded from the membrane. The solutions in the compartments are continuously stirred thereby ensuring membrane diffusion-controlled ion-exchange process. The transport of ions along the thickness of the membrane is assumed to occur through the continuous water channels present in the membrane. The effect of membrane structure and the specific interactions of the ions with the membrane matrix are assumed to be included in their respective self-diffusion coefficients (D_i). Using Nernst Planck equation, membrane electroneutrality and mass balance condition, flux of ion, $A^{z_A^+}$ in the membrane can be expressed as [26,38]:

$$J_A = - \frac{D_A D_B (z_A^2 \bar{C}_A + z_B^2 \bar{C}_B) d\bar{C}_A}{D_A z_A^2 \bar{C}_A + D_B z_B^2 \bar{C}_B} dx \quad (1)$$

Eq. (1) shows that the flux of a particular ion depends on its concentration gradient, membrane concentration and SDC of that particular ion as well as on the membrane concentration and SDC's of the other ions present in the solution. In situations where concentration of one ion is kept very high than the other ion, the equation can be simplified to Fick's first law and can be easily solved to calculate the flux in a Donnan dialysis process, based on pseudosteady state approximation. However, in present studies, we have not made any assumption regarding concentration of ions in the two compartments. Also, in the present calculations, unsteady nature of the flux, which is very important in initial time

scales, has been accounted for. This has been done by considering the variable nature of the flux through the membrane thickness, as given by the Fick's second law:

$$\frac{\partial \bar{C}_A}{\partial t} = - \nabla \cdot J_A \quad (2)$$

Substituting Eq. (1) in Eq. (2), the concentration of ion $A^{z_A^+}$ at any time, t and membrane thickness, x is given as:

$$\frac{\partial \bar{C}_A}{\partial t} = \frac{\partial}{\partial x} \left[D_{AB} \frac{\partial \bar{C}_A}{\partial x} \right] \quad (3)$$

This nonlinear diffusion equation describes the time and space dependence of the concentration of ion $A^{z_A^+}$, \bar{C}_A in the membrane. Here D_{AB} is the interdiffusion coefficient given by:

$$D_{AB} = \frac{D_A D_B (z_A^2 \bar{C}_A + z_B^2 \bar{C}_B)}{D_A z_A^2 \bar{C}_A + D_B z_B^2 \bar{C}_B} \quad (4)$$

As seen from the equation, interdiffusion coefficient is a function of the self diffusion coefficient of the two ions and also on the concentration of the two ions in the membrane. Since these concentrations will change with time and spatial co-ordinate, the interdiffusion coefficient will also change with time and spatial co-ordinate unlike self-diffusion coefficients. Eqs. (3) and (4) are expressed in terms of dimensionless quantities by using the following relations:

$$y_A = \frac{z_A \bar{C}_A}{Q} \quad \tau = \frac{D_A t}{L^2} \quad \varepsilon = \frac{x}{L} \quad (5a-c)$$

where L is the thickness of the membrane. Here y_A represents the dimensionless variable for concentration, \bar{C}_A and is a function of dimensionless variables for time (τ) and x -co-ordinate (ε) along the membrane thickness. In terms of y_A , τ and ε , Eq. (3) can therefore be written as:

$$\frac{\partial y_A(\varepsilon, \tau)}{\partial \tau} = \frac{\partial}{\partial \varepsilon} \left[D(y_A(\varepsilon, \tau)) \frac{\partial y_A(\varepsilon, \tau)}{\partial \varepsilon} \right] \quad (6)$$

where $D(y_A)$ is the interdiffusion coefficient (in terms of dimensionless quantities), as given by:

$$D(y_A) = \frac{1 + b y_A}{1 + a y_A} \quad (7)$$

where a and b are given by:

$$a = \frac{D_A z_A}{D_B z_B} - 1 \quad b = \frac{z_A}{z_B} - 1 \quad (8a-b)$$

As seen from Eqs. (6) and (7), the interdiffusion coefficient and hence flux is a function of not the absolute value of the charges and self-diffusion coefficients of the two ions, but depends on the ratio of the charges and self-diffusion coefficients of the two ions undergoing ion-exchange. Using finite difference method, Eq. (6) can be written as:

$$y_A(\varepsilon, \tau + \Delta\tau) = y_A(\varepsilon, \tau) + \frac{\Delta\tau}{\Delta\varepsilon^2} \left[D_+(y_A(\varepsilon + \Delta\varepsilon, \tau) - y_A(\varepsilon, \tau)) - D_-(y_A(\varepsilon, \tau) - y_A(\varepsilon - \Delta\varepsilon, \tau)) \right] \quad (9)$$

where

$$D_+ = \frac{2 + b(y_A(\varepsilon + \Delta\varepsilon, \tau) + y_A(\varepsilon, \tau))}{2 + a(y_A(\varepsilon + \Delta\varepsilon, \tau) + y_A(\varepsilon, \tau))} \quad (10)$$

and

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