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Investigation of ion concentration and electric potential distributions in charged membrane/electrolyte systems

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ABSTRACT

The ion concentration, electrical potential and current distributions of a membrane/electrolyte system under equilibrium conditions are investigated numerically. The membrane is modeled as an array of finite-length charged pores with uniform distributed surface charge density and in contact with single- or multi-component electrolytes in both sides of the membrane. The numerical model is verified using the theoretical results from Donnan, Nernst and the surface potentials.

For cases involving equal electrolyte bulk concentrations in both sides of the membrane, it is found that the dimensionless Debye length and surface charge density characterize the ion concentration and potential distributions in the system. The electrical potential difference between the membrane and external bulk electrolyte depends on the degree of increase in counter-ion concentration inside the pore relative to the bulk electrolyte. Higher potential difference can be resulted as the dimensionless Debye length decreases or the surface charge density increases. In a membrane/multi-component system, the resulting potential difference between the membrane and external bulk electrolyte is smaller as compared with the membrane/single-component electrolyte system due to the increase in dimensionless Debye length.

For systems with unequal electrolyte bulk concentrations in contact with the membrane, current flow appears in the system due to the establishment of concentration and potential gradients in the system. The current flow increases with the increase in the bulk electrolyte concentration difference. The current flow in the multi-component electrolyte system is found to be smaller than that for the single-component system due to the increase in dimensionless Debye length.

1. Introduction

Charged porous membranes can be found in various processes such as water treatment filtration [1,2], electrokinetic energy conversion [3,4], fuel cell proton exchange [5,6] and ion transport through biological tissues [7–9]. When the membrane is in equilibrium with an electrolyte solution, electrical potential difference is generally established between the membrane and the solution. The establishment of this potential difference is due to the electrical charge distributed inside the membrane.

Because of the importance in practical applications, the potential difference between membrane and solution in equilibrium condition has been extensively studied [10,11]. There are two approaches used to formulate this potential difference based on these studies. One approach is to consider the potential difference to be the Donnan equilibrium potential. In this approach the charge is considered to be uniformly distributed inside the membrane with a certain density. The potential difference between the membrane and solution can be obtained by satisfying the electro-neutrality condition. This is known as Donnan equilibrium formalism [12]. The other approach involves the surface potential, in which it is assumed that all charges are located on the membrane surface with a certain density. The resulting surface potential is described using the Grahame relation [12,13]. In both approaches, ions are assumed to have Boltzmann distributions inside the membrane and the solutions are obtained based on the requirement of electro-neutrality. The spatial ion concentration and electrical potential distributions cannot be predicted from these two approaches.

Because of the structural characteristics, the charged membrane can be considered as composed of an array of identical parallel charged capillary pores. The charge inside the membrane can be considered uniformly distributed on the capillary walls with a certain charge density and the ions in the electrolyte are allowed to penetrate through the pore. This is referred to as the charged capillary model. Considerable effort has been devoted to the charged capillary model which has demonstrated that it is able to describe the coupling between the ion concentration and electrical fluxes through the charged membranes in many experi-

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mental situations [14–16]. However, these studies assumed that the membrane thickness is infinitely large and ignores any axial variations in ion concentration and electric potential. Such assumptions allow the use of a stationary radial ion concentration distribution in the pore, which is obtained from solving the one-dimensional Poisson–Boltzmann equation. The obvious limitation of such an approach is the inability to predict the axial ion concentration and potential variations, which could vary significantly across the pore thickness, especially at the membrane/electrolyte interface.

Recently, a numerical model using the Nernst–Planck equation coupled with the Poisson equation has been developed and used to study ion transport in the micro/nano scale channels [17–19]. In this model, the computational domain includes the inlet and outlet reservoirs connecting with the channel. The radial and axial variations in ion concentration are solved directly from the Nernst–Planck equation without the Boltzmann distribution assumption. According to the results predicted using this model, substantial axial ion concentration variation was found across the channel length.

In this study we explore greater understanding of the various phenomena in the equilibrium membrane/solution system. These phenomena include the ion concentration and electrical potential distributions, the developments of Donnan and Nernst potentials, the surface potential and current flow. Because most of the previous studies concerning these phenomena considered a single salt electrolyte, the multi-component electrolyte effect, which is often encountered practically, will also be addressed [20–22]. The charged capillary model will be adopted and the fundamental equations governing the multi-ion transport and electrical potential distribution are to be solved simultaneously for finite-thickness membrane without the Boltzmann distribution assumption for the ions.

2. Physical model

The charged capillary membrane model used in this study is schematically shown in Fig. 1. The membrane is modeled as consisting of an array of cylindrical pores having the radius $\alpha = 5$ nm and length $L = 50$ nm, respectively. The pore size is chosen based on the study of Liu et al. [23] in which the translocation of charged particle through a nanopore with radius of 5 nm was investigated. Because of the advance in nanofabrication techniques [24,25], the membrane in this study may be thought as the fabricated synthetic nanopores in mimicking the biological membranes [26,27]. The wall of the capillary tube is considered to have a surface charge density of σ. To focus on the effects of surface charge density and types of electrolyte on the ion concentration and potential distributions, the detail of surface charged mechanism, membrane material and structure are not considered in this study [13,28,29]. The membrane is in contact with electrolytes on the right- and left-hand sides of the membrane. In general, the electrolytes on both sides of the membrane may have different bulk concentrations and contain different components. As indicated in Fig. 1, c_{i0R} and c_{i0L} are used to designate the bulk molar concentration of the ith ion in a multi-component electrolyte on the right- and left-hand sides of the pore, respectively.

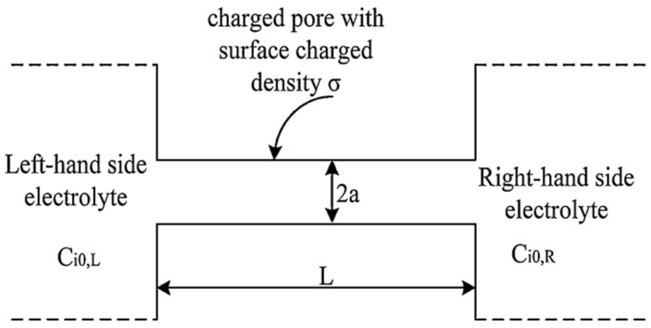

Fig. 1. Physical model of the charged membrane in contact with electrolyte.

Because of the existence of a surface charge at the wall and no other external forcing source, such as electrical voltage or pressure difference involved in the system, the ions inside the capillary would redistribute due to the surface charge and finally reach an equilibrium state. The ion distribution is due purely to the ion diffusion and electro-migration. In dealing with this kind of problem, the Debye length is usually employed as a length scale to characterize the ion and potential distributions. In this study, we use c_{i0L} as the reference bulk concentration and the Debye length is given as,

$$\kappa^{-1} = \left(\frac{\varepsilon_0 \varepsilon RT}{\sum_{i=1}^{N} z_i^2 F^2 c_{i0L}} \right)^{1/2} \tag{1}$$

where z_i is the valence of the ith ion, ε is the dielectric permittivity, ε_0 is the permittivity of vacuum, F is the Faraday constant, R is the universal gas constant, T is the temperature of the electrolyte and N is the number of ions present in the electrolyte. Physically, the Debye length is a length scale that indicates the distance from the charged wall where the electrical energy and thermal energy are balanced [30]. Using the capillary radius as the characteristic length of the system, the dimensionless Debye length is κa.

3. Theoretical solutions

Because the system is under equilibrium the ion concentration and potential distributions must satisfy electro-neutrality and constant electrochemical potential conditions throughout the system. Based on these requirements, the potential difference between the membrane and external electrolyte and surface potential at the charged capillary wall can be described theoretically. In the following, brief derivations of these theoretical models are given under the conditions of $c_{i0R} = c_{i0L} = c_{i0}$.

3.1. Donnan potential

In the literature, there are two approaches to describe the potential difference between the membrane and the contacted electrolyte. One of these approaches is based on the Donnan equilibrium formalism in which all ions are assumed to freely penetrate the membrane. Because of the membrane charge, a potential difference relative to the external bulk electrolyte, known as the Donnan potential, must be established in order to satisfy the electro-neutrality condition. According to Boltzmann distribution, the ion concentration distribution can be expressed as [10],

$$c_i = c_{i0} \exp\left(-\frac{z_i F \psi_D}{RT} \right) \tag{2}$$

where ψ_D is the Donnan potential. The charge neutrality equation becomes,

$$z_f c_f + \sum_{i=1}^{N} z_i c_{i0} \exp\left(-\frac{z_i F \psi_D}{RT} \right) = 0 \tag{3}$$

where z_f and c_f are the valence and molar concentration of the charges on the pore wall, respectively. c_f can be converted from the surface charge density using the relation,

$$c_f = \frac{2\sigma}{aF} \tag{4}$$