CrossMark

Theoretical study of electrolyte transport in nanofiltration membranes with constant surface potential/charge density

Ilya I. Ryzhkov [a,b,*], Andrey V. Minakov [a,b]

[a] Institute of Computational Modelling SB RAS, Akademgorodok, 660036 Krasnoyarsk, Russia
[b] Siberian Federal University, Svobodny 79, 660041 Krasnoyarsk, Russia

A B S T R A C T

The pressure–driven electrolyte transport through nanofiltration membrane pores with constant surface potential or charge density is investigated theoretically. Two approaches are employed in the study. The first one is based on one–dimensional Nernst–Planck equation coupled with electroneutrality, zero current, and Donnan equilibrium conditions. This model is extended to account for interfacial effects by using a smooth approximation of step function for the volume charge density. The second approach is based on two–dimensional Nernst–Planck, Poisson, and Navier–Stokes equations, which are solved in a high aspect ratio nanopore connecting two reservoirs with much larger diameter. The modification of equations on the basis of Slotboom transformation is employed to speed up the convergence rate. The distributions of potential, pressure, ion concentrations and fluxes due to convection, diffusion, and migration in the nanopore and reservoirs are discussed and analyzed. It is found that for constant surface charge density, the convective flux of counter–ions in the nanopore is almost completely balanced by the opposite migration flux, while for constant surface potential, the convective flux is balanced by the opposite diffusion and migration fluxes. The co–ions in the nanopore are mainly transported by diffusion. A particular attention is focused on describing the interfacial effects at the nanopore entrance/exit. Detailed comparison between one– and two–dimensional models is performed in terms of rejection, pressure drop, and membrane potential dependence on the surface potential/charge density, volume flux, ion concentration, and pore radius. A good agreement between these models is found when the Debye length is smaller than the pore radius and the surface potential or charge density are sufficiently low.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nanofiltration (NF) is a pressure–driven membrane process, which is used to remove ionic species and organic solutes from aqueous solutions [1]. Nanofiltration membranes are characterized by effective pore diameter ranging from one to a few nanometers, and the molecular weight cut–off between a few hundred to a few thousand Dalton. The range of operating pressure starts from a few bars up to 10–20 bars. These characteristics lie between those of reverse osmosis (RO) and ultrafiltration (UF) membranes [2]. NF membranes combine the advantages of a high water flux at relatively low operating pressure and high salt and organic matter rejection rate [3]. Nanofiltration has received much attention in the last decades due to its applications in textile, paper, and food industries including water desalination [1–4].

The separation mechanisms of NF membranes include not only steric, but also electric effects. Most of such membranes acquire an electric charge when brought in contact with a polar medium due to dissociation of functional groups or adsorption of charged species from the solution onto the pore walls. In nanometer–sized pores, the electric double layers from the opposite walls overlap, which leads to the favored transport of counter–ions and exclusion of co–ions. If the pore walls are made of conductive material, the wall charge can be altered by applying a prescribed potential to the membrane. In this way, the membrane selectivity characteristics can be externally varied and controlled [5,6]. A comprehensive review of charged membranes applications can be found in [7].

The development of adequate mathematical models for nanofiltration is extremely important for better understanding of complex transport mechanisms and prediction of separation characteristics [8]. A charged membrane is usually modeled as an array of identical parallel charged pores. It is now well established that the pressure–driven transport of ions in charged membrane pores can be described by the system of Nernst–Planck, Poisson,

* Corresponding author at: Institute of Computational Modelling SB RAS, Akademgorodok, 660036 Krasnoyarsk, Russia.
   E-mail addresses: rii@icm.krasn.ru (I.I. Ryzhkov),
tov-andrey@yandex.ru (A.V. Minakov).

and Navier–Stokes equations [9]. However, the direct application of this model requires much computational resources even in two–dimensional statement. Due to that, a number of simplified approaches have been developed. In the homogeneous approximation [10], the uniform distribution of fixed charged in membrane pores is assumed, and the radial variation of electric potential and ion concentrations in the pores is neglected. It is a valid assumption when the Debye screening length is much larger than the pore radius, and the fixed charge density is sufficiently low. In this case, the model reduces to one–dimensional Nernst–Planck equation extended by convective transport term, the electroneutrality and zero current conditions, and Donnan equilibrium at the pore entrance and exit. This is known as Uniform potential (UP) model, and also as Teorell–Meyer–Sievers (TMS) model, although the original TMS theory [11] does not include the fluid flow. The UP model was successfully applied for interpreting the experimental data on reverse osmosis in charged membranes in [12]. The Donnan–steric partitioning pore model (DSPM) [13] takes into account the finite ion size by introducing diffusive and convective hindrance factors. The fitting of experimental rejection data to this model allowed obtaining such membrane parameters as pore radius, volume charge density, and effective membrane thickness [14–16]. The influence of dielectric effects on ion rejection in nanofiltration membranes was actively investigated in recent decades. These effects are related to the interaction of ions with polarized interface between membrane and solution due to the difference in their dielectric constants [17,18] and lowering of solution dielectric constant inside nanopores [19]. It was found that dielectric effects are especially relevant in determining the rejection of divalent counter–ions. Critical assessment of nanofiltration models was performed in [20] showing that the rejection does not explicitly depend on membrane thickness.

The effect of concentration polarization on salt rejection was investigated in [21] by coupling the DSPM model with convection–diffusion equations in the boundary layer adjacent to the membrane. The contribution of convection, diffusion, and migration to electrolyte transport through nanofiltration membranes was studied in [22]. It was found that convection is dominant at low membrane charge density and/or high permeate volume flux, while the transport is mainly governed by diffusion when the membrane is strongly charged. Migration becomes dominant when the co–ion diffusion coefficient exceeds that of counter–ion. The effect of inhomogeneous charge distribution on the pressure–driven ionic transport was considered in [23,24]. It was suggested that the rejection capability of nanopores can be optimized by the appropriate fixed charge distribution. The osmotic flow across an ion–exchange membrane was studied in [25] with the help of mathematical framework based on the two–fluid model.

The radial variation of potential and ion concentrations in the pore as well as the impact of electroosmotic flow on ion transfer are taken into account in the space–charge (SC) model, which was originally developed in [26]. The electrolyte osmosis through charged membrane pores was investigated theoretically on the basis of SC model in [27]. Experimental verification of this model was performed by comparing the theoretical predictions for streaming potential, pore conductivity, and diffusion potential with the measured data [28]. A good agreement for monovalent ions was found. Detailed comparison between results obtained from SC and TMS models [29] showed a good agreement for pores with small radius (less than 2 nm) and low surface charge density. Otherwise, a strong overestimation of rejection by the TMS model in comparison with the SC model was found. Similar conclusion was made with respect to membrane potentials of monovalent and multivalent electrolytes calculated from the above two models in [30]. The SC model was revisited in [31] by using the flux–force formalism with Onsager symmetry properties, which allowed a

significant simplification of working formulas. A simplification of SC model, which assumes a parabolic velocity profile (Poiseuille flow) in the pore, was suggested in [32].

The effect of membrane/solution interface on the distribution of potential and ion concentrations in the absence of pressure–driven flow was investigated in [33] by solving two–dimensional Nernst–Planck and Poisson equations in two reservoirs connected by a charged nanopore. The cases of equal and unequal electrolyte concentrations in the reservoirs were considered. In the latter case, it was found that unequal migration and diffusion currents resulted in non–zero total current flow in the system. A simplified analytical approach to describing potential distribution in the interfacial region was suggested in [34]. It was concluded that Donnan equilibrium conditions with discontinuous potential and ion concentrations at the interface are valid only if the membrane thickness is much greater than the Debye length. The impact of pressure–driven flow on the ion transfer in the nanopore connecting two reservoirs with equal electrolyte concentrations was investigated numerically in [35]. In addition to counter–ion enrichment and co–ion depletion in the nanopore, the increase/decrease of electrolyte concentration near the pore entrance/exit was found. The latter effect became stronger with increasing the applied pressure drop. The impact of electric force on pressure–driven flow (the electroviscous effect) in reservoir–connected flat and circular nanochannels was studied numerically in [36,37]. A simple analytical model was suggested for prediction of the pressure drop and correlated with the numerical results. It should be noted that in the above–mentioned works, the nanopore diameter was of order 10–100 nm, while the length to the diameter ratio was of order 10. The considered electrolyte concentrations were 1 mol/m^3 and lower except the work [33] (the pressure–driven flow was not considered there). However, typical nanofiltration membranes have the pore diameter of a few nanometers and the aspect ratio of order 100–1000, while the considered electrolyte concentration can be as high as 1000 mol/m^3 [1–5].

The main aim of this work is to investigate theoretically the pressure–driven electrolyte transport through nanofiltration membrane pores of realistic geometry in a wide range of ion concentrations. The cases of constant surface charge density and constant surface potential are considered. Note that the former case has not been studied in much detail in the literature. Two approaches are employed in the study. The first one is based on one–dimensional Nernst–Planck equation coupled with electroneutrality, zero current, and Donnan equilibrium conditions. This model is extended to account for interfacial effects by using a smooth approximation of step function for the volume charge density. The second approach is based on two–dimensional Nernst–Planck, Poisson, and Navier–Stokes equations, which are solved in a high aspect ratio nanopore, which connects two reservoirs with much larger diameter. The modification of equations on the basis of Slotboom transformation is employed to speed up the convergence rate. Detailed comparison between the two approaches is performed in terms of rejection, pressure drop, and membrane potential dependence on the applied potential/charge density, volume flux, ion concentration, and pore radius. A particular attention is focused on describing the interfacial effects at the nanopore entrance/exit.

The paper is organized as follows. The mathematical models and their numerical implementation are presented in Section 2, while the obtained results are analyzed and discussed in Section 3. The main findings are summarized in conclusion.