

Ion Rejection Properties of Nanofiltration Membranes with Inhomogeneous Charge Distributions

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ABSTRACT

Ion rejection by nanofiltration (NF) membranes with bipolar fixed charge distributions have been investigated theoretically.

Salt flux rectification has been predicted as a result of the broken symmetry of the fixed charge distribution on the pore walls. The existence of an optimal volume flux (i.e. leading to the highest salt rejection) has been put in evidence when there is a region within the membrane pores that is more repulsive than the pore entrance with respect to a given electrolyte. For low Peclet numbers, our results show that bipolar membranes can lead to close rejections for both 2-1 and 1-2 asymmetric electrolytes. These performances result from specific properties of bipolar membranes and cannot be achieved with homogeneously charged membranes.

The present work benefits the design of nanoporous membranes with targeted distribution of ionizable surface groups for advanced separations.

Keywords: nanofiltration, charge distribution, modeling, transport, rejection

1 INTRODUCTION

Nanofiltration (NF) appears as the pressure-driven separation process with the highest expected growth in coming years. This promising technique has attracted increasing attention in the various scientific communities working at the nanometer scale and numerous works have focused on the development of models that are likely to describe the separation properties of NF membranes [1-4].

All current models used in NF are based on the assumption that ionizable surface groups that are present at the surface of most NF membranes are homogeneously distributed over the pore surface. Otherwise stated, the membrane charge density is considered to be constant over the membrane thickness.

In this work we have dropped this assumption to present a detailed theoretical account of the effects of inhomogeneous charge distributions on the salt rejection performances of nanoporous membranes. A comprehensive set of charge distributions (either unipolar or bipolar) have been considered and their influence on salt rejection has

been investigated by means of the uniform-potential approximation of the space charge model [1-4].

2 THEORY

The active layer of the membrane is described as a bundle of identical cylindrical nanopores separating the feed solution from the permeate one. The presence of the coarse-porous support layer is disregarded here since it does not affect the ion rejection properties of the membrane.

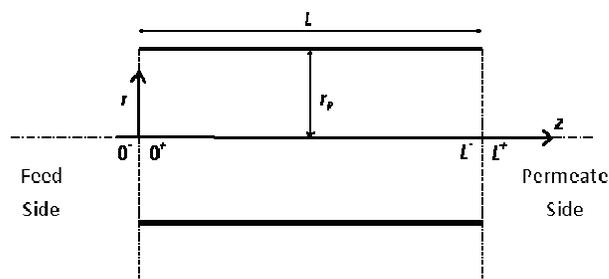


Figure 1: Schematic of the cylindrical nanopore used in the modeling; 0^- and L^+ denote the axial coordinates just outside the nanopore, 0^+ and L^- denote the axial coordinates just inside the nanopore, and r_p and L are the pore radius and the pore length, respectively.

Figure 1 shows a schematic of the system under consideration in the present work, i.e. a cylindrical nanopore of length $L = 2\mu\text{m}$ and radius $r_p = 2\text{ nm}$ (transport can then be considered as one-dimensional since $L \gg r_p$). The external solutions are assumed to be ideal and perfectly stirred (no concentration polarization). The system is considered isothermal with a temperature T of 298 K.

Within the scope of the uniform-potential approximation of the space charge model, the local ion concentrations (c_i) and electrostatic potential (ψ) inside the nanopore are defined as radially averaged quantities and the concentration gradient of an ion i inside the nanopore can be expressed this way from the extended Nernst-Planck equation [5],

$$\frac{d \langle c_i(z) \rangle}{dz} = \frac{J_V}{K_{i,d} D_i} (K_{i,c} \langle c_i(z) \rangle - C_i(L^+)) - \frac{z_i F \langle c_i(z) \rangle}{RT} \frac{d \langle \psi(z) \rangle}{dz} \quad (1)$$

where the symbol $\langle \rangle$ indicates radially averaged quantities, J_V denotes the volume flux (equivalent to the fluid velocity) induced by the pressure gradient through the nanopore, C_i is the external concentration of the ion i , z_i its charge number, D_i its bulk diffusion coefficient, F is the Faraday constant, R is the ideal gas constant, $K_{i,d}$ and $K_{i,c}$ are the hindrance factor for diffusion and convection, respectively (these hydrodynamic factors $K_{i,d}$ and $K_{i,c}$ depend on the ratio $r_{i,Stokes} / r_p$, where $r_{i,Stokes}$ denotes the Stokes radius of an ion i ; expressions for $K_{i,d}$ and $K_{i,c}$ can be found elsewhere [5]).

Eq 1 has to be coupled with an explicit expression of the local electroneutrality inside the membrane ($0^+ \leq z \leq L$),

$$\sum_i z_i c_i(z) + X(z) = 0 \quad (2)$$

where $X(z)$ denotes the local volume charge density of a membrane pore (i.e. the fixed charge concentration at a point of coordinate z within a membrane pore)

For cylindrical pores, the fixed charge concentration is related to the surface charge density (σ) by

$$X(z) = \frac{2\sigma(z)}{Fr_p} \quad (3)$$

The expression of the radially averaged electric field ($\langle E(z) \rangle$) through the membrane is derived from eqs 1 and 2,

$$\langle E(z) \rangle = -\frac{d \langle \psi(z) \rangle}{dz} = -\frac{\sum_i \frac{z_i J_V}{K_{i,d} D_i} (K_{i,c} \langle c_i(z) \rangle - C_i(L^+))}{\frac{F}{RT} \sum_i \langle c_i(z) \rangle z_i^2} - \frac{\frac{dX(z)}{dz}}{\frac{F}{RT} \sum_i \langle c_i(z) \rangle z_i^2} \quad (4)$$

The system of eqs 1 and 4 can be solved iteratively with the following boundary conditions,

$$c_i(0^+) = C_i(0^-) \phi_i \exp\left(-z_i \Delta \Psi_{D(\Delta^- | \Delta^+)}\right) \quad (5)$$

$$c_i(L^-) = C_i(L^+) \phi_i \exp\left(-z_i \Delta \Psi_{D(\Delta^- | \Delta^+)}\right) \quad (6)$$

where ϕ_i is the steric partitioning coefficient of ion i defined as the ratio between the available section (i.e. taking into account the finite size of the ion) and the pore cross section [6], and $\Delta \Psi_D$ denotes the dimensionless Donnan potential arising at each interface between the membrane and the external solution.

Eqs 5 and 6 are modified Donnan equations including steric hindrance. For the sake of simplification, the interaction between ions and polarization charges induced at the pore surface due to the dielectric discontinuity at the pore/solution interface [7] is not considered in the partitioning equations 5 and 6.

Finally, the salt intrinsic rejection rate (R_{salt}) can be computed according to its definition,

$$R_{salt} = 1 - \frac{C_i(L^+)}{C_i(0^-)} \quad (7)$$

In eq 7, subscript i can denote either the cations or the anions since, for single salt solutions, the rejection rate for ions of type i is identical to R_{salt} due to the electroneutrality condition that holds in both external bulk solutions (i.e. feed solution and permeate),

$$\sum_i z_i C_i = 0 \quad (8)$$

3 RESULTS AND DISCUSSION

Figure 2 shows three inhomogeneous fixed charge distributions that are described by the following expressions,

$$X(\bar{z}) = -30\bar{z} \quad (9)$$

$$X(\bar{z}) = 30\bar{z} - 30 \quad (10)$$

$$X(\bar{z}) = -10 \left(-1 + \frac{2}{1 + \exp(100(\bar{z} - 0.05))} \right) \quad (11)$$

where $\bar{z} = z/L$ is the dimensionless axial coordinate.

The first two distributions are unipolar (i.e. the fixed charge concentration is spatially changing but the sign of the surface charge remains the same) while the last one is a bipolar distribution (both the magnitude and the sign of the surface charge are spatially changing). Figure 3 shows the rejection rate of a uni-univalent electrolyte (with $D_+ = D_- = 10^{-9} \text{ m}^2 \text{ s}^{-1}$) as a function of the Peclet number (Pe) inside the membrane, which is defined as,

$$Pe = \frac{J_v L}{D_{salt}} \quad (12)$$

with,

$$D_{salt} = \frac{(z_+ + |z_-|)D_+ D_-}{z_+ D_+ + |z_-| D_-} \quad (13)$$

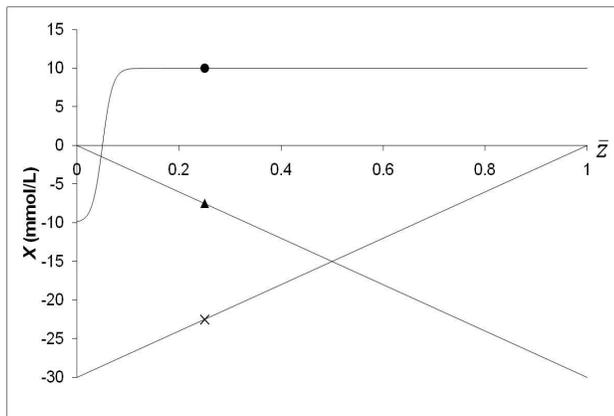


Figure 2: Inhomogeneous charge distributions inside pores; ▲: equation 9; ×: equation 10; ●: equation 11.

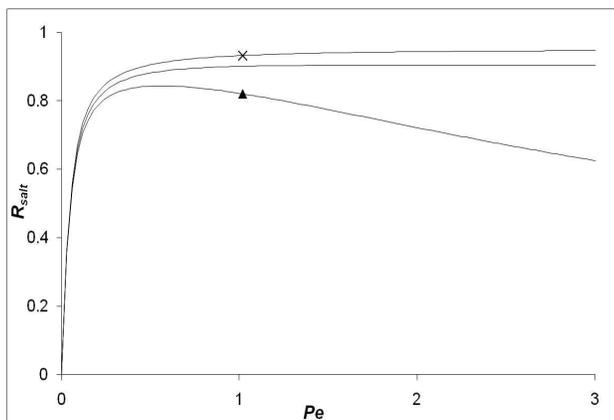


Figure 3: Rejection of a 10^{-3} mol/L solution of 1-1 electrolyte (with $D_+ = D_- = 10^{-9}$ m² s⁻¹) vs. Peclet number; ▲: inhomogeneous charge distribution given by eq 9; ×: inhomogeneous charge distribution given by eq 10; full line without symbol: homogeneous charge distributions (i.e. $X = \text{constant}$). All distributions correspond to the same average volume charge density $X_{avg} = -15$ mmol/L.

Rejection rates have been computed for the two unipolar distributions given by eqs 9 and 10 (see linear distributions shown in figure 2) and are compared with the rejection of a homogeneously charged membrane. The

average fixed charge concentration is identical for all charge distributions,

$$X_{avg} = \int_0^1 X(\bar{z}) d\bar{z} = -15 \text{ mmol/L} \quad (14)$$

The following conclusions can be drawn from results shown in figure 3.

First, it is shown that the occurrence of spatial inhomogeneities in the fixed charge concentration may lead to an enhancement of the rejection properties of membranes with respect to homogeneously charged materials. This point can be very attractive especially for desalination applications.

The comparison between the rejection rates of the two membranes characterized by the unipolar charge distributions shown in figure 2 puts in evidence a rectification phenomenon of the salt flux since results shown in Figure 3 imply that the salt rejection of a membrane with an asymmetric fixed charge distribution depends on the direction of the fluid flow. This rectification phenomenon has been also observed in recent molecular dynamics simulations performed with carbon nanotubes with artificial surface partial charge patterns [8].

Finally, figure 3 shows the presence of a maximum of the intrinsic rejection rate as function of the Peclet number (or volume flux) for the membrane which is characterized by the charge distribution given by eq 9. This is a specific behavior of membranes for which the pore entrance is not the most repulsive part of the active layer (with respect to a given electrolyte) [5, 9]. The reason is that transport in NF is controlled by different pore regions depending on the magnitude of the volume flux flowing through the membrane. For low Peclet numbers, the salt rejection is ruled by the most repulsive part of the membrane pores whereas it is controlled only by the charge density at the pore entrance for high Peclet numbers (i.e. when diffusion becomes negligible with respect to convection) [9].

Figure 4 shows the rejection rate of millimolar CaCl₂ and Na₂SO₄ solutions by membranes with different surface charge patterns. For low Pe values, figure 4 shows that both kinds of asymmetric electrolytes are rejected in a more or less similar efficiency by the membrane with the bipolar charge distribution (given by eq 11) whereas homogeneously charged membranes can reject strongly only one of these two electrolytes depending of the sign of the membrane charge (strictly speaking, this is true only if dielectric exclusion phenomena are negligible; indeed dielectric effects do not differentiate, from a qualitative point of view, between coions and counterions since they are controlled by the square of the ion charge [4, 7]).

The Peclet number is expected to be small within NF membranes because the active layers of these membranes are very thin (around 100 nm for polymer membranes) [10]. Our results therefore suggest that designing NF membranes with targeted distribution of ionizable surface sites groups

could be of great interest for industrial applications like desalination and water purification.

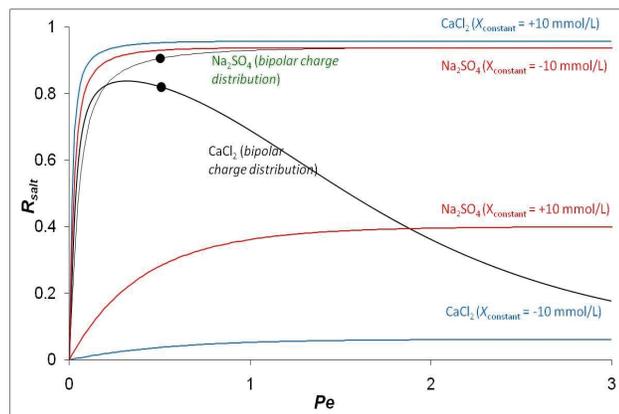


Figure 4: Rejection of 10^{-3} mol/L CaCl_2 and Na_2SO_4 solutions vs. Peclet number; ●: inhomogeneous charge distribution given by eq 11; full lines without symbols: homogeneously charged membranes with $X = \text{constant} = \pm 10$ mmol/L.

4 CONCLUSION

The effects of spatially inhomogeneous fixed charge distributions on ion transport through NF membranes have been investigated theoretically by means of a one-dimensional approximate version of the space charge model that can be used with confidence for moderately charged membranes with radius smaller than the Debye screening length of the system.

Salt rejection has been computed as a function of the Peclet number within the membrane for various fixed charge distributions and has been compared with that obtained for homogeneously charged membranes. It has been shown that the separation performances of NF membranes can be improved by an appropriate distribution of the fixed charges.

Solute transport is controlled by different pore regions depending on the magnitude of the volume flux flowing through the membrane. The existence of an optimal volume flux (i.e. leading to the highest salt rejection) has been put in evidence when a part of the nanopore is more repulsive than the pore entrance.

For the small Peclet numbers expected in NF membranes, it has been shown that membranes with bipolar fixed charge distributions may lead to similar rejections for both 2-1 and 1-2 asymmetric electrolytes. These performances cannot be achieved with homogeneously charged membranes which strongly reject electrolytes with divalent cations but are much more permeable to electrolytes with divalent counterions (in the absence of dielectric exclusion).

These findings suggest that designing advanced membranes with controlled distribution of surface groups could be beneficial for desalination purposes and water treatment.

REFERENCES

- [1] W.R. Bowen, AW Mohammad and N. Hilal, *J. Membr. Sci.* 126, 91, 1997.
- [2] J. Palmeri, P. Blanc, A. Larbot and P. David, *J. Membr. Sci.* 160, 141, 1999.
- [3] P.M. Biesheuvel and W.B.S. de Lint, *J. Colloid Interface Sci.* 241, 422, 2001.
- [4] A. Szymczyk and P. Fievet, *J. Membr. Sci.* 252, 77, 2005.
- [5] A. Szymczyk, H. Zhu and B. Balanec. *Langmuir* 26, 1214, 2010.
- [6] W.M. Deen, *AIChE J.* 33, 1409, 1987.
- [7] A.E. Yaroshchuk, *Adv. Colloid Interface Sci.*, 85, 193, 2000.
- [8] J. Goldsmith and C.C. Martens, *J. Phys. Chem. Lett.* 1, 528, 2010.
- [9] A. Szymczyk, H. Zhu and B. Balanec. *J. Phys. Chem. B.*, submitted.
- [10] S. Bason, Y. Kaufman and V. Freger, *J. Phys. Chem. B.* 114, 3510, 2010.