Ion selectivity of inhomogeneously charged NF membranes

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ABSTRACT

lon rejection properties of NF membranes having various fixed-charge distributions were investigated theoretically by considering different single-salt solutions and ternary mixtures.

It has been shown that NF membranes with bipolar charge distributions (i.e., both the sign and the concentration of the charged surface groups vary inside the membrane) exhibit specific separation properties that can be beneficial for desalination and water treatment applications.

NF experiments performed with symmetric and asymmetric electrolytes and different polymer membranes were found to support qualitatively model predictions.

1. INTRODUCTION

The last three decades, considerable effort has been invested into the development of membranes that combine the high rejection of reverse osmosis membranes with the lower pressures used in ultrafiltration (Bowen *et al.* 1997). This has resulted in the development of nanofiltration (NF) membranes. Since the first industrial applications of NF in the 80s, the market of this energy efficient and environmentally friendly process has increased dramatically and NF has found numerous applications in various industrial sectors.

Due to the increasing interest for NF, numerous works have focused on the development of models that are likely to describe the separation performances of NF membranes. Most current NF models assume implicitly that the fixed charge density is constant over the skin layer thickness (Bowen *et al.* 1997, Bowen and Mohammad 1998, Freger 2003, Lefebvre *et al.* 2004).

In this work, we have dropped this assumption in order to investigate the rejection of salts (either single-salt solutions or multi-ionic mixtures) by NF membranes whose skin layers are inhomogeneously charged. Theoretical predictions have been compared to experimental rejection rates of salts with different stoechiometries by both polyamide and polyethersulfone membranes which are membrane materials with different charge distributions.

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2. THEORY

NF membranes were described as bundles of straight cylindrical capillaries (see Fig. 1) The external solutions were assumed to be ideal and perfectly stirred so that the concentration polarization was disregarded in the present study.



Fig. 1 Schematic of a membrane pore. r_p is the pore radius, Δz is the pore length, 0⁻ and Δz^+ denote the axial coordinates just outside the pore, 0⁺ and Δz^- denote the axial coordinates just inside the pore, c_i and C_i are the concentrations inside and outside the pore, respectively.

Transport of an ion *i* (with charge z_i) through the membrane was described by means of the extended Nernst-Planck (ENP) equation, accounting for ionic diffusion under the action of the solute concentration gradient, electromigration under the action of a spontaneously arising electric field, and convection due to solvent flow in the membrane pores

$$j_{i} = -K_{i,d} D_{i,\infty} \frac{dc_{i}}{dz} - \frac{z_{i} c_{i} K_{i,d} D_{i,\infty}}{RT} F \frac{d\psi}{dz} + K_{ic} c_{i} \frac{J_{v}}{A_{k}}$$
(1)

where j_i is the molar flux of ion *i* through the pores, $D_{i,\infty}$ is its diffusion coefficient in the external solution, c_i is the local ion-concentration inside the nanopore, *z* is the axial coordinate in the flow direction, *R* is the ideal gas constant, *F* is the Faraday constant, A_k is the membrane porosity, J_v is the solution volume flux, ψ denotes the local axial electric potential inside the nanopore, $K_{i,c}$ is a drag factor accounting for the effects of the pores walls on the specie motion, and $K_{i,d}$ represents the effect of the pore to reduce the solute-solvent diffusion coefficient below its value in the free bulk solution.

The ionic molar fluxes j_i are related to solution volume flux J_v (based on the membrane area) as follows

$$j_i = \frac{J_v C_i \left(\Delta z^+\right)}{A_k} \tag{2}$$

Substitution of Eq. (2) into Eq. (1) allows the ionic concentration gradients within pores to be expressed as

$$\frac{dc_i(z)}{dz} = \frac{J_V}{K_{i,d}D_{i,\alpha}A_k} \left(K_{i,c}c_i(z) - C_i(\Delta z^+) \right) - \frac{z_iFc_i(z)}{RT}\frac{d\psi(z)}{dz}$$
(3)

Eq. (3) has to be coupled with an explicit expression of the local electroneutrality inside pores

$$\sum_{i} z_i c_i(z) + X(z) = 0 \tag{4}$$

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

Combining Eqs. (3) and (4), gives the expression of the axial electric field inside pores, E(z)

$$E(z) = -\frac{d\psi(z)}{dz} = -\frac{\sum_{i} \frac{Z_{i} J_{V}}{K_{i,d} D_{i,\infty} A_{k}} \left(K_{i,c} c_{i}(z) - C_{i}(\Delta z^{+})\right)}{\frac{F}{RT} \sum_{i} c_{i}(z) z_{i}^{2}} - \frac{\frac{dX(z)}{dz}}{\frac{F}{RT} \sum_{i} c_{i}(z) z_{i}^{2}}$$
(5)

The distribution of ions at the membrane/solution interfaces were described by the following modified Donnan equations

$$c_{i}(0^{+}) = C_{i}(0^{-})\phi_{i}\exp\left(-z_{i}\Delta\Psi_{D(0^{-}|0^{+})}\right)$$
(6)

$$c_{i} (\Delta z^{-}) = C_{i} (\Delta z^{+}) \phi_{i} \exp\left(-z_{i} \Delta \Psi_{D(\Delta z^{-} | \Delta z^{+})}\right)$$
(7)

where $0^{-} \mid 0^{+}$ and $\Delta z^{-} \mid \Delta z^{+}$ denote the membrane/solution interfaces at the feed side and the permeate side, respectively. ϕ_i is the steric partitioning coefficient of ion *i*, $\Delta \Psi_{\rm D}$ being the dimensionless Donnan potential arising at each nanopore/external solution interface.

It should be noted that dielectric effects (Yaroshchuk 2001 and Szymczyk 2005) were disregarded in the present work for the sake of clarity.

For single-salt solutions, the salt rejection rate (R_{salt}) was computed according to

$$R_{salt} = 1 - \frac{C_i \left(\Delta z^+\right)}{C_i \left(0^-\right)} \tag{8}$$

Note that the salt rejection rate can be computed as a function of the transmembrane pressure difference (ΔP) which can be derived from the average Stokes equation (Lefebvre 2004)

$$\Delta P = RT \sum_{i} \left(C_{i}(0^{-}) - c_{i}(0^{+}) \right) + \frac{8\eta \Delta z}{r_{p}^{2}} J_{V} + F \int_{z=\Delta z^{-}}^{z=0^{+}} X(z) \frac{d\psi(z)}{dz} dz + RT \sum_{i} \left(c_{i}(\Delta z^{-}) - C_{i}(\Delta z^{+}) \right)$$
(9)

For ternary mixtures the membrane selectivity, S(j/k) for an ion *j* with respect to an ion *k* (*j* and *k* having the same sign) was defined as follows

$$S(j/k) = \frac{I - R_j}{I - R_k}$$
(10)

where R_i and R_k are the individual rejection rates of ion *j* and ion *k*, respectively.

3. EXPERIMENTAL SECTION

Membranes used for this study were NF 270 (Filmtec) and NP 030 (Nadir) membranes whose skin layers are made with polyamide and polyethersulfone, respectively.

The different electrolyte solutions (NaCl, MgCl₂ and Na₂SO₄) were prepared with demineralised water. The concentration of the different solutions was 0.001 eq/L and their pH was adjusted with a decimolar HCl solution.

Filtration experiments were conducted with the Osmonics Sepa CF II cell which uses flat sheet membranes (surface area around 140cm²). A feed spacer (diameter of filaments: 0.6mm; distance between parallel filaments: 3.5mm; angle between crossing filaments: 90°) was used to limit concentration polarization.

From a 6 L feed tank, the solution was pumped into the cell where it flowed tangentially to the membrane. The transmembrane pressure difference was controlled by means of a pressure valve mounted on the retentate outlet. The feed concentration was maintained constant by recycling both the retentate and the permeate into the feed tank. Experiments were carried out at a transmembrane pressure of 10 bars. Permeate samples (30 mL) were collected in order to further determine its composition by ionic chromatography. Each permeate sample was taken after a 20 min filtration run when

constant filtration performances are reached. Experiments were performed at 20 ± 1°C.

The membrane was firstly washed by circulating demineralised water at 3 bars for 20 min three times before proceeding to a the measurement of a reference water flux up to 20 bars.

4. RESULTS AND DISCUSSION

4.1 Single-salt solutions

All calculations presented in this work were performed by setting the pore radius (r_p) and the thickness to porosity ratio ($\Delta z/A_k$) of membranes at 0.66 nm and 4.8 μ m, respectively. These values correspond to the average structural features determined by Bowen and Mohammad from twenty-nine commercial NF membranes (Bowen 1998).

Figs. 2-4 show the theoretical sequences of rejection for NaCl, MgCl₂ and Na₂SO₄ solutions (0.001 eq/L) by membranes with different fixed charge distributions.

For negatively charged membranes with either a constant charge density (Fig. 2) or a unipolar charge distribution (Fig. 3) the model predicts the rejection sequence $Na_2SO_4 > NaCl > MgCl_2$ which is easily explained by the Donnan exclusion mechanism (note that we chose arbitrarily a linear distribution of the fixed charge in Fig. 3: additional calculations performed with different unipolar distributions led to the same sequence of salt rejection).



Fig. 2 Theoretical sequence of rejection for 0.001 eq/L Na₂SO₄, NaCl and MgCl₂ solutions (at 10 bars) by a negatively charged membrane with a homogeneous charge distribution. The axial profile of the membrane charge density (*X*) is shown in the inset (the pore entrance and the pore exit correspond to $z/\Delta z = 0$ and 1, respectively).



Fig. 3 Theoretical sequence of rejection for 0.001 eq/L Na₂SO₄, NaCl and MgCl₂ solutions (at 10 bars) by a negatively charged membrane with an inhomogeneous charge distribution (unipolar distribution). The axial profile of the membrane charge density (*X*) is shown in the inset (the pore entrance and the pore exit correspond to $z/\Delta z = 0$ and 1, respectively).

On the other hand, the rejection sequence predicted for the bipolar membrane (Fig. 4) follows the order $Na_2SO_4 > MgCl_2 > NaCl_4$, i.e. both 1-2 and 2-1 asymmetric electrolytes are more efficiently rejected than the mono-monovalent electrolyte (NaCl). As shown by Zhu et al. (Zhu 2011) this rejection sequence is specific of membranes with bipolar charge distributions. Thin-film composite polyamide membranes, which are currently the main class of nanofiltration (NF) membranes for desalination and water treatment applications, are an example of membranes with bipolar charge distribution since their skin layer is most likely built of a negatively charged outer region sitting on top of an inner region possessing a positive charge density (Freger 2003). The bipolar charge distribution considered in Fig. 4 is expected to capture qualitatively the main electrostatic features of thin-film composite polyamide membranes (Freger 2003), i.e. (i) charged surface groups are distributed in a highly non uniform fashion within the skin layer, the top surface of the skin layer being negatively charged due to the presence of unreacted acid chloride groups and the inner part of the skin layer being positively charged due to the presence of unreacted amines and (ii) the charge density in the central part of the skin layer is expected to be quite low.



Fig. 4 Theoretical sequence of rejection for 0.001 eq/L Na₂SO₄, NaCl and MgCl₂ solutions (at 10 bars) by an inhomogeneously charged membrane with a bipolar charge distribution. The axial profile of the membrane charge density (*X*) is shown in the inset (the pore entrance and the pore exit correspond to $z/\Delta z = 0$ and 1, respectively).



Fig. 5 Experimental sequence of rejection at 10 bars for 0.001 eq/L Na₂SO₄, NaCl and MgCl₂ solutions at pH 4 by a polyamide NF 270 membrane



Fig. 6 Experimental sequence of rejection at 10 bars for 0.001 eq/L Na₂SO₄, NaCl and MgCl₂ solutions at pH 4 by a polyethersulfone NP 030 membrane

In order to confirm the above model predictions, we performed experimental rejection measurements with the same electrolyte solutions as in Figs. 2-4 with two types of NF membranes, namely a polyamide membrane (NF 270), as an example of membrane with bipolar charge distribution, and a polyethersulfone membrane (NP 030) which is expected to bear only negatively charged groups. Figs. 5 and 6 show the experimental sequences of rejection obtained at 10 bars for 0.001 eq/L NaCl, MgCl₂ and Na₂SO₄ solutions at pH 4 by NF 270 (polyamide) and NP 030 (polyethersulfone) membranes. Experimental results confirm our model predictions since the rejection sequence Na₂SO₄ > MgCl₂ > NaCl is obtained with the polyamide membrane (i.e. the membrane with a bipolar charge distribution) whereas the experimental sequence is Na₂SO₄ > NaCl > MgCl₂ for the NP 030 membrane which has only negatively charged groups.

4.2 Ternary mixtures

The above results showed that bipolar charge distributions could affect significantly the separation properties of NF membranes for single-salt solutions. Figs. 7 and 8 show the theoretical selectivities between monovalent and divalent ions by membranes with different charge distributions for NaCl / Na₂SO₄ and NaCl / MgCl₂ mixtures, respectively. Three different charge distributions were considered, namely homogeneous, unipolar and bipolar distributions. It is worth noting, however, that all the three distributions lead to the same average volume charge density over the membrane thickness (0.01 eq/L). As shown in the insets of Figs. 7 and 8, the bipolar distribution under consideration here has a sinusoidal shape with several positive and negative domains, and it could be viewed as a crude representation of membranes obtained by the so-called "Layer-by-Layer" technique which consists in the successive adsorption of positively and

negatively charged polyelectrolytes onto a membrane surface.



Fig. 7 Theoretical selectivity between Cl⁻ and SO₄⁻ ions as a function of the permeate volume flux by membranes with different charge distributions (shown in the inset) for a NaCl / Na₂SO₄ mixture. The mixture is characterized by [Cl⁻] = [SO₄²⁻] = 0.001 eq/L.

Fig. 7 shows that the selectivity between chloride and sulfate ions is significantly increased with the bipolar membrane with respect to both the homogeneously charged membrane and the membrane with a unipolar charge distribution. Indeed, anion selectivity can reach almost 200 which means that the flux of chloride ions through the bipolar membrane is 200 higher than that of sulfate ions.

The discrepancy between the bipolar membranes and the other membranes is even more important with the NaCl / $MgCl_2$ mixture since the selectivity between sodium and magnesium cations can be close to 60 while it is less than 1 for membranes that bear only negative surface groups (meaning that Mg^{2+} is transferred preferentially to Na⁺ through these membranes).



Fig. 8 Theoretical selectivity between Na⁺ and Mg²⁺ ions as a function of the permeate volume flux by membranes with different charge distributions (shown in the inset) for a NaCl / MgCl₂ mixture. The mixture is characterized by [Na⁺] = [Mg²⁺] = 0.001 eq/L.

5. CONCLUSIONS

A transport model allowing for the possibility of an inhomogeneous distribution of the fixed charge of NF membranes was used to investigate the effect of a non uniform distribution of charged surface groups on the separation properties of NF membranes. Both single-salt solutions and ternary mixtures with ions of different valences were considered.

For single-salt solutions with electrolytes of different stoechiometries, the sequence of salt rejection $Na_2SO_4 > MgCl_2 > NaCl$ was predicted for membranes with bipolar charge distributions. This sequence was confirmed experimentally with polyamide membranes while a different sequence was obtained for membranes having only one kind of charged surface groups.

For ternary mixtures, it was shown that the selectivity between monovalent and multivalent ions can be significantly improved for both cations and anions by using membranes with bipolar charge distributions.

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