



Permeation mechanism and interplay between ions in nanofiltration

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ABSTRACT

Nanofiltration (NF) is widely used today for water purification, however, governing physical mechanisms are still largely unclear and predictive modeling remains a challenge, especially, for mixed ionic solutions. The current study systematically investigates NF of binary mixtures of NaCl and CaCl₂ with the purpose to understand the mechanisms and interplay between different ions in the membrane. Using extensive filtration data and the Nernst-Planck relations, the paper concludes that (a) the standard mean-field models based on an average Donnan potential are unsuitable for describing ion permeation in NF; (b) the observed ranking of ion permeabilities ($\text{Na}^+ > \text{Cl}^- > \text{Ca}^{2+}$) points to the solvation (Born) energy rather than interaction with fixed charges as the main factor controlling ion permeation; (c) the fixed charges are largely neutralized by pairing with counterions, which reduces their role in ion permeation; (d) saturation of Ca²⁺ uptake and its competition with Na⁺ for pairing with fixed charges may explain the unusual decrease of Ca²⁺ permeability with Ca²⁺ concentration and its strong effect on Na⁺ permeability. These conclusions, inconsistent with the commonly used mean-field picture, strongly suggest the need to revise the current approach to NF modeling.

1. Introduction

Nanofiltration (NF) is a membrane separation process used in a variety of applications, mainly for removal of ions or low molecular weight solutes from water [1–3]. NF offers a high flux, high rejection for multivalent ions and low rejection for monovalent ions [2,4,5]. These characteristics enable the use of NF in many areas including water and wastewater treatment, pharmaceutical industry, biotechnology, food engineering etc. [2].

Unfortunately, predictive modeling desired for design of new NF processes and optimization of existing membrane applications is still a challenge [6–8]. This is especially true for mixed feeds containing both mono- and divalent ions [9,10]. Additional complication arises from the effects of the solution chemistry, in particular, pH, on the membrane permeability to ionic solutes [7–9,11–19].

The extended Nernst-planck (ENP) equation is a common framework for NF modeling. ENP relations link the permeation of all ions through the membrane matrix or pores by diffusion, electromigration and convection to electroneutrality conditions [10,11]. However, computing ion permeabilities requires accurate knowledge of the membrane thickness and morphology and appropriate relations for ion mobility and exclusion. The latter usually combines in a mean-field manner the steric, Donnan and dielectric exclusion mechanisms (SDE) and may include non-ideality corrections and account for radial variations of the potential within the pores. However, such an approach has failed so far

to yield a consistent predictive description for different salts and salt mixtures using the same set of physical parameters. In addition, fitted model parameters, such as dielectric constant and fixed charges density, disagree with the independently measured physical characteristics of the active layer. Moreover, the models often fail to predict even the observed trends [5,6,10,20–25].

An alternative, more “engineering” approach to modeling is to use constant ion permeabilities as the appropriate set of measurable phenomenological parameters for ENP modeling of ion mixtures [13,15,26,27]. In the simplest case ion transport is computed using average value of ion partitioning and mobility across the entire membrane [28], which may still be allowed to vary with the feed composition, when such variation is significant [5,14]. The model can be simplified by neglecting the coupling between the ions and water due to the low membrane thickness [15,29]. In addition, since ions are dilute, direct frictional coupling between ions may be neglected as well. However, note that fluxes of ions do couple strongly through electric potential gradient imposed by electroneutrality. The main advantage of this approach is that it employs only the most general assumption of the linearity between fluxes and forces, without assuming any physical mechanism, such as the SDE relations. Nevertheless, such a simple model with measurable phenomenological coefficients, allows reasonable accurate modeling of ion mixtures [13], including complex ones such as sea water [5], and transparent test of trends, e.g., concentration dependence of permeabilities as a fingerprint of specific physical

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mechanisms [23].

Many reports observed that for NF membranes the permeability of NaCl as a single salt increases with salt concentration while CaCl₂ permeability decreases [23,30–32]. The effect of Ca²⁺ on membrane NF separations in mixed feeds was also reported by several groups [7,13,17,18,30,33]. Yaroshchuk et al. demonstrated that in mixtures of CaCl₂ and NaCl, when Ca²⁺ was the dominant cation in the mixture, its permeability was significantly lower compared to the case when it was a trace ion, while chloride permeability showed little variation [13]. Yang et al. also showed that a small Ca²⁺ concentration can significantly affect rejection of charged species in NF [18]. A possible charged reversal or complexation with Ca²⁺ was suggested; still it could not fully explain all findings, emphasizing the need for further investigations.

Deon et al. and Escoda et al. examined rejection of several combination of MgCl₂ or CaCl₂ and NaCl [8,11,34]. They showed that increase in the divalent ion fraction enhanced divalent cation rejection while monovalent ion rejection decreased. The model used by these authors required readjustment of the effective dielectric properties and fixed charge density of the membrane to fit the data. However, the fitted values were quite different from the direct measurements of these characteristics [25,35–37]. The above studies highlight the intriguing interplay between Na⁺ and Ca²⁺ ions within NF membranes, but the amount of data has been relatively limited for unequivocal conclusions. They mainly included cases when one salt was present at a tracer level relative to the main salt, and important effects, such as pH, were not considered. To fill the gap and understand the underlying mechanism, here we systematically investigate NF separation of binary mixtures of NaCl and CaCl₂ at different pH values. The results provide an insight into the actual physics of ion exclusion, permeation and competition in NF of multi-ion mixtures.

2. Model

The general modeling approach was described previously [5]. In brief, ion permeation is described using a set of Nernst-Planck (NP) equations for Na⁺, Ca²⁺ and Cl⁻ coupled via local electroneutrality. Equations are written and permeabilities defined in terms of virtual ion concentrations, which are defined as those of a hypothetical solution in equilibrium with the membrane at a specific location and essentially gauge the chemical potentials of the respective ions. Each ion *i* is assigned a permeability ω_{*i*} [5,13,15,16,38], which is assumed to have a single average value across the membrane for a given feed, but could vary with feed compositions. Ion convection is neglected, as it was shown to be negligible in NF membranes compared to diffusion and electromigration [23,29,39–41]. The resulting model equations are as follows

$$J_i = -\omega_i \left(\frac{dC_i}{d\bar{x}} + \frac{Fz_i C_i}{RT} \frac{d\psi}{d\bar{x}} \right) \quad (1)$$

$$\sum_i z_i C_i = 0, \quad \sum_i z_i J_i = 0 \quad (2)$$

where *J_i* is the ion flux, ω_{*i*} is the ion permeability, *C_i* is the local "virtual" concentration of ion *i*, \bar{x} is the thickness coordinate scaled to the total thickness varying from 0 at the feed side to 1 at the permeate side, *F* is Faraday constant, *R* is the gas constant, *T* is the solution temperature and ψ is the local electric potential.

For a ternary mixture of Na⁺, Ca²⁺ and Cl⁻, not too far from pH 7, H⁺ and OH⁻ ions may be ignored, and Eq. (2) (local electroneutrality and zero current conditions) becomes

$$C_{Cl} = C_{Na} + 2C_{Ca}, \quad J_{Cl} = J_{Na} + 2J_{Ca} \quad (3)$$

After substituting Eq. (3) to NP equation for Cl⁻ and eliminating the electric potential ψ form the NP equations for Na⁺, Ca²⁺ and Cl⁻, the following equation is obtained

$$J_{Na} \left(\frac{1}{\omega_{Na}} + \frac{1}{\omega_{Cl}} \right) + J_{Ca} \left(\frac{1}{\omega_{Ca}} + \frac{2}{\omega_{Cl}} \right) = -2 \frac{dC_{Na}}{d\bar{x}} - 3 \frac{dC_{Ca}}{d\bar{x}}. \quad (4)$$

Integration of Eq. (4) across the membrane for constant ω's yields two equivalent linear relations

$$\frac{1}{\hat{\omega}_{NaCl}} + \left[\frac{3C''_{Ca}}{2C''_{Na}} \right] \frac{1}{\hat{\omega}_{CaCl_2}} = \left[\frac{2(C'_{Na} - C''_{Na}) + 3(C'_{Ca} - C''_{Ca})}{2J_V C''_{Na}} \right], \quad (5a)$$

$$\frac{1}{\hat{\omega}_{CaCl_2}} + \left[\frac{2C''_{Na}}{3C''_{Ca}} \right] \frac{1}{\hat{\omega}_{NaCl}} = \left[\frac{2(C'_{Na} - C''_{Na}) + 3(C'_{Ca} - C''_{Ca})}{3J_V C''_{Na}} \right]. \quad (5b)$$

Here the single and double primes designate the feed and permeate values, respectively, *J_V* is the volume flux, and ω's are pseudo salt permeabilities, defined in the same way as the permeabilities of pure single salts, but for ions in a ternary mixture, i.e.,

$$\frac{2}{\hat{\omega}_{NaCl}} = \frac{1}{\omega_{Na}} + \frac{1}{\omega_{Cl}}, \quad \frac{3}{\hat{\omega}_{CaCl_2}} = \frac{1}{\omega_{Ca}} + \frac{2}{\omega_{Cl}}. \quad (6)$$

Obviously, for single salts Eq. (5a) and (b) are reduced to (and are generalization of) the corresponding relations for the genuine salt permeabilities ω_{*s*}, *s* = NaCl or CaCl₂, measured in experiments with single salts.

Note that all quantities in square brackets in Eq. (5) are measurable. If they are defined as follows

$$X_1 = \frac{3C''_{Ca}}{2C''_{Na}}, \quad Y_1 = \frac{2(C'_{Na} - C''_{Na}) + 3(C'_{Ca} - C''_{Ca})}{2J_V C''_{Na}}, \quad X_2 = \frac{2C''_{Na}}{3C''_{Ca}}, \quad Y_2 = \frac{2(C'_{Na} - C''_{Na}) + 3(C'_{Ca} - C''_{Ca})}{3J_V C''_{Na}}, \quad (7)$$

Y's may be plotted versus respective *X*'s, thus the intercepts and slopes yield the corresponding ω's, while deviations from linearity indicate variations of ion permeabilities with composition. The plot of *Y*₁ versus *X*₁ suits the cases when [Na⁺] is non-zero, i.e., *X*₁ is finite, while *Y*₂ versus *X*₂ applies when [Ca²⁺] is non-zero, i.e., *X*₂ is finite.

3. Experimental

Filtration tests were performed in a laboratory system containing two cross-flow cells mounted in series. Each cell contained a flat sheet of NF270 membrane of 15.6 cm² wet area with a spacer mesh from a Toray TMS20R-440 membrane module mounted in the cross-flow channel. Prior to filtration, membranes were soaked in 50% water-ethanol solution in ultrasonic bath for 15 min to ensure complete pore wetting, afterwards membranes were washed with deionizer water (DW). After passing both cells in series the retentate was circulated back to the feed tank, which initially contained 10 L of feed solution. Since permeate flow rates (5·10⁻¹⁰ to 1·10⁻⁷ m³/s) were much lower than feed flow rates (2.5·10⁻⁵ m³/s), feed and retentate concentrations and cross-flow velocities differed negligibly. Feed temperature was maintained at 25 ± 1 °C using a water bath and heat exchanger. Feed tank was continuously purged with N₂ gas in order to minimize dissolution of CO₂ that could alter pH. pH was monitored using a Medidor BASIC 20 pH meter and adjusted using NaOH or HCl. The total amount of Na⁺ and Cl⁻ added to the feed solution upon pH adjustments was negligible compared to the feed concentrations.

The feed solution included a combination of NaCl and CaCl₂ of analytical grade in DW with pH adjusted by adding HCl or NaOH. Experiments included four sets of feed solutions, defined as follows

- (a) Total chloride concentration of 0.1 M and pH 5.5
- (b) Total chloride concentration of 0.1 M and pH 8.0
- (c) Total chloride concentration of 0.5 M and pH 5.5
- (d) Total chloride concentration of 0.5 M and pH 8.0

In each set the equivalent Na fraction, defined as follows

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