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Convective transport of boron through a brackish water reverse osmosis membrane

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ABSTRACT

In this work, cross-flow filtration experiments using a brackish water reverse osmosis polyamide membrane have been performed to gather boron rejection data as function of feed concentration, pressure, pH and salinity. Increasing transmembrane pressure increases the permeation of boron indicating that convective flow is important. This result is in contrast to the normal assumption that solution diffusion dominates in such systems. The extended Nernst–Planck equation with a Donnan-steric partition coefficient is used to analyse the transport mechanisms of both neutral boric acid and negatively charged borate ions through the RO membrane. The contribution of surface charge is experimentally determined by streaming potential measurements and the electrokinetic surface charge density is then calculated as a function of ionic strength and pH. It is found that a 0.380 nm pore radius and an effective membrane porosity of 0.05 shows good agreement with experimental data. Charge screening becomes more dominant with increasing ionic strength and this contribution is readily incorporated into the model. The study extends our understanding of the transport mechanism of boric acid and borate ions which can assist in predicting the performance of polyamide reverse osmosis membranes. It also raises questions as to the true mechanism of transport through such a membrane.

1. Introduction

Reverse osmosis is a versatile method that has been widely adopted in water treatment applications such as desalination. Nonetheless, it is often difficult to attain drinking water standards for neutral solutes such as boron using this technique. Boron is present in seawater with average concentrations of 4–6 mg/L [1–6]. Excessive boron consumption can result in health problems, thus, according to the World Health Organization (WHO), the maximum limit for boron in drinking water is 0.5 mg/L [7]. Extensive research has been conducted into boron removal using polyamide reverse osmosis membranes [1,2,5,6,8–13].

One widely-known mathematical model that has been employed to analyze the rejection of such neutral solutes is the Spielger–Kedem (Kedem–Katchalsky) model [10,14–16]. This model describes water flux and solute flux as follows:

$$J_v = -A\left(\frac{dP}{dx} - \sigma\frac{d\pi}{dx}\right) \tag{1}$$

$$J_s = -B\frac{dC}{dx} + (1-\sigma)J_w\overline{C} = J_vC_p \tag{2}$$

The permeate flux (J_v) is dictated by both the pressure (P) and osmotic pressure (π) gradient. The effect of the osmotic pressure difference is corrected by a theoretical reflection coefficient (Staverman reflection coefficient, σ) that represents the correction for non-ideality in a semi-permeable membrane ($\sigma \equiv (\Delta P/\Delta\pi)_{J_v=0}$). For an ideal semi-permeable membrane, which passes water but has 100% rejection of solutes, $\sigma = 1$; while for a completely non-selective porous membranes $\sigma = 0$ [17]. The solute flux (J_s) combines the contribution of a diffusion term (embedded in the solute permeance, B) as well as the convection of bulk solution.

For salt transport through a reverse osmosis membrane, it is generally assumed that $\sigma \sim 1$, due to the high rejection of ions [2,13,18–21]. It is argued that as RO membranes possess free volume elements (or pores) that are comparable or smaller in size to the rejected ions, and as these elements fluctuate in position and volume on the time scale of permeation, the active layer of the membrane should be considered as non-porous [22,23]. This assumption leads to the derivation of the solution-diffusion model [16,18,23] in which the flux of solute is independent of the applied pressure (or water flux) and the second term in Eq. (2) can be eliminated. This means that the solute flux is only governed by the diffusion (i.e. solute permeance $= B = DK^L/l$) and is no longer affected by the bulk convection. Wijmans and Baker [23] suggest that the transition from a pore flow model to a solution diffusion model occurs at a free volume element size of 5 to 10 Å.

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However, the solution diffusion approach has proved less successful in the modeling of boron rejection at lower pH values, and Eqs. (1) and (2) can better predict the rejection of boron [10,15]. In this case, $\sigma < 1$, indicating that solute and water transport are not independent and that some convective flow occurs. However, the approach is empirical and does not explain the transport mechanisms across the membrane. Further, it does not include contributions from Donnan exclusion and ion interactions [16,24]. Finally, the assumptions of a constant reflection coefficient and water permeability carry inaccuracies since these fitted parameters (σ and B) are greatly affected by experimental variables such as pH, pressure and ionic strength [16,24].

This study focuses on understanding the transport mechanisms across a reverse osmosis membrane by incorporating contributions of both pore size and surface charge. The surface charge of the membrane is experimentally determined by streaming potential measurements. Since the size and number of the free volume elements within a reverse osmosis membrane are not widely reported, the pore radius and the effective membrane porosity are both optimized to match the experimental data. The effects of pH, pressure and ionic strength toward rejection of boric acid and borate ion are investigated and analyzed using a model developed by Bowen and co-workers [25–27]. This model has been extensively used to represent the transport of charged solutes through nanofiltration membranes [28–33], yet to our knowledge, it has not been applied previously to dense thin-film reverse osmosis membranes. We show that this model can satisfactorily represent the transport of small molecules, both charged and uncharged, through a reverse osmosis membrane. The approach can provide a more sophisticated understanding than the solution diffusion model which is more commonly used.

2. Theoretical aspects

In seawater, boron commonly exists as the neutral boric acid (H_3BO_3). This is a Lewis acid that undergoes dissociation as well as hydrolysis following Reactions 1 and 2 [8,9,12,34,35]:

Reaction 1. $H_3BO_3 \leftrightarrow H_2BO_3^- + H^+$

Reaction 2. $H_3BO_3 + H_2O \leftrightarrow B(OH)_4^- + H^+$

However, boric acid is electron deficient and so Reaction 2 is favoured [12,36]. This electron deficiency also causes boric acid to have a large crystal radius that results in poor hydration [12]. As a consequence, boric acid has a small hydrated radius; reported to be between 0.244 and 0.261 nm [12,35].

The dissociation of boric acid through Reaction 2 is affected by pressure, temperature and ionic strength [12,37]. At a standard temperature of 20 °C, the apparent *p*Ka varies from 9.23 to 8.60 as the salinity varies from 0 to 400 g/L [5,12,36,38]:

$$p\mathrm{Ka} = \left[\mathrm{B(OH)}_4^-\right][H^+]$$

Fig. 1 presents the percentage of boric acid ionised with respect to pH and salinity based on this *p*Ka data. For concentrations of boron lower than 22 mg/L, the formation of poly-borate compounds is negligible, therefore only $B(OH)_4^-$ and H_3BO_3 primarily exist in the solution [12,39].

2.1. Rejection of uncharged solutes

At very dilute concentrations, where activity coefficients can be assumed equal to unity, the flux of an uncharged solute such as boric acid is given by the balance between diffusion and convective flow [25–27,40]:

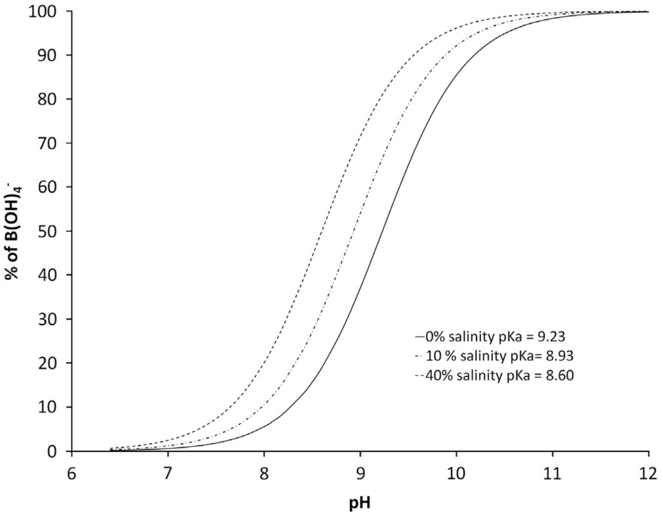

Fig. 1. Degree of dissociation of boric acid with respect to pH and salinity. The *p*Ka for boric acid as a function of salinity is obtained from Dyrssen and Hansson 1972 [58].

$$\frac{J_s}{A_k} = \frac{J_v C_{ip}}{A_k} = \frac{K_{ic} c_i J_v}{A_k} - D_{ip}\frac{dc_i}{dx} - \frac{c_i D_{ip}}{RT} V_{is}\frac{d(P-\pi)}{dx} \tag{3}$$

where the solute (j_s) and solution (J_v) fluxes are determined on a membrane area basis by accounting for the membrane effective porosity, (A_k). D_{ip} is the diffusion coefficient in the pore, K_{ic} the convective hindrance factor, V_{is} *is* the partial molar volume of the solute. C_{ip} represents the bulk permeate concentration of the solute i, while c_i is the concentration within the pore at any position x. The net pressure gradient across the membrane is given by the difference between the bulk pressure *(P)* and the osmotic pressure *(π)* as a function of the distance through the membrane (x).

This pressure gradient can be related to the volumetric solution flux if it is assumed that the membrane pores are cylinders and that flow through these cylinders can be described using the Hagen-Poiseulle equation:

$$J_v = \frac{r_p^2}{8\eta(\Delta x/A_k)}(\Delta P - \Delta\pi) \tag{4}$$

where η is the solvent viscosity, r_p is the pore radius and Δx is the thickness of the active layer of the membrane. This approach assumes that the entire pressure drop occurs across this active layer and there is no significant pressure drop across the support layer. It also assumes that concentration polarisation is insignificant. If the pressure drop is assumed to be linear across the membrane thickness:

$$\frac{d(P-\pi)}{dx} = \frac{8J_v\eta}{r_p^2 A_k} \tag{5}$$

Rearranging the equations above, the concentration gradient across the membrane is calculated

$$\frac{dc_i}{dx} = \frac{J_v}{D_{ip}A_k}\left[\left(K_{ic} - \frac{D_{ip}}{RT}V_{is}\frac{8\eta}{r_p^2}\right)c_i - C_{ip}\right] \tag{6}$$

K_{ic} and K_{id} can be calculated based on the ratio of solute to pore radius (Table 1). D_{ip} is then determined from the bulk diffusion coefficient as $D_{ip} = K_{id}D_\infty$.

For uncharged solutes, the boundary conditions for this equation are given by the steric partition coefficient Φ_i which is a function only of the ratio of the solute and pore radii ($\Phi_i = (1-\lambda)^2$):

$$\frac{c_{i\,x=0}}{C_{if}} = \frac{c_{i\,x=\Delta x}}{C_{ip}} = \Phi_i \tag{7}$$