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Removal of boric acid, monoborate and boron complexes with polyols by reverse osmosis membranes

Piotr Dydo *, Marian Turek [1], Andrzej Milewski [1]

Silesian University of Technology, Faculty of Chemistry, B. Krzywoustego 6, 44–100 Gliwice, Poland

HIGHLIGHTS

- The effects of RO membrane type on boron species rejection were evaluated.
- The species considered were: boric acid, monoborate and complexes with polyols.
- The rejection efficiency was found to be predetermined by boric acid transport.
- Boric acid rejection decreased as follows: SW-30 > BW-30 > TW-30 > XLE.

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ABSTRACT

The effects of reverse osmosis (RO) membrane type on the rejection efficiency of boric acid, monoborate and boron complexes with D-mannitol, sodium D-gluconate and *N*-methyl D-glucamine was revealed. The membranes examined included: XLE, TW-30, BW-30 and SW-30, supplied by DOW™ FILMTEC™. The mass transport coefficients: permeability and reflection coefficient were determined for each species in boric acid–polyol aqueous system. The influence of the membrane type upon these coefficients was evaluated and quantitative, comparative analysis of the efficacy of boron rejection at varying permeate flux, the feedwater boron content, the alcohol/boron molar ratio and the pH was conducted. It was found that boron rejection in the above systems was determined by the extent of boric acid transport, even when boric acid constituted only a minor component of the feedwater. At high permeate flux the effectiveness in boric acid rejection decreased in the following descending membrane order: SW-30 > BW-30 > TW-30 > XLE. The results presented here enable the selection of the best membrane, the most suitable operating conditions for boron separation by RO in the presence or absence of polyols, and for quantitative prediction of the efficiency of boron removal with various RO membranes.

1. Introduction

Boron and its compounds need to be removed from waters with high concentrations. The necessity for boron removal and the methods applied to accomplish this goal have been thoroughly discussed in recent review papers [1]–[4]. The boron concentration should be reduced to at least below a concentration of 2.4 mg/L, which is the guideline drinking water limit proposed by the World Health Organization (WHO). Among the suggested methods for boron removal are reverse osmosis-based methods for water purification. However, these methods face serious limitation in boron rejection due to the aqueous chemistry of boron-containing species [1–4]. In the majority of boron containing waters, boron is present as boric acid. In this form, it permeates through most of the RO membranes with ease, and its rejection is very limited.

Boric acid is a weak acid (pK_a of approximately 9.2), that ionizes to a significant extent only at a pH higher than 9. Upon ionization of H_3BO_3, mono-, tri- and tetra-borates are produced. These borates have been shown to be rejected by RO membranes more effectively than boric acid, as summarized in the above-mentioned reviews. Effective boron removal from waters with high boron content, however, requires RO operation under high pH conditions (most likely a pH of 10 or greater), at which serious risk of membrane scaling with insoluble carbonates, hydroxides or mixed salts occurs. To eliminate the necessity for high pH conditions, a method that involves binding borate with polyols that contain 1,2-diol functional groups was proposed [5]. The mono- and dichelate complexes produced by that process are schematically presented in Fig. 1. These complexes are much more stable than monoborate and are produced under lower pH conditions. These complexes are also rejected more effectively than boric acid and monoborate, not only by RO but also by nanofiltration membranes [5–7]. It was anticipated that with this modification, a significant reduction would be achieved in feedwater pH required to maintain

* Corresponding author. Tel.: +48 32 237 10 52; fax: +48 32 237 22 77.
E-mail address: Piotr.Dydo@polsl.pl (P. Dydo).
[1] Tel.: +48 32 237 10 52; fax: +48 32 237 22 77.

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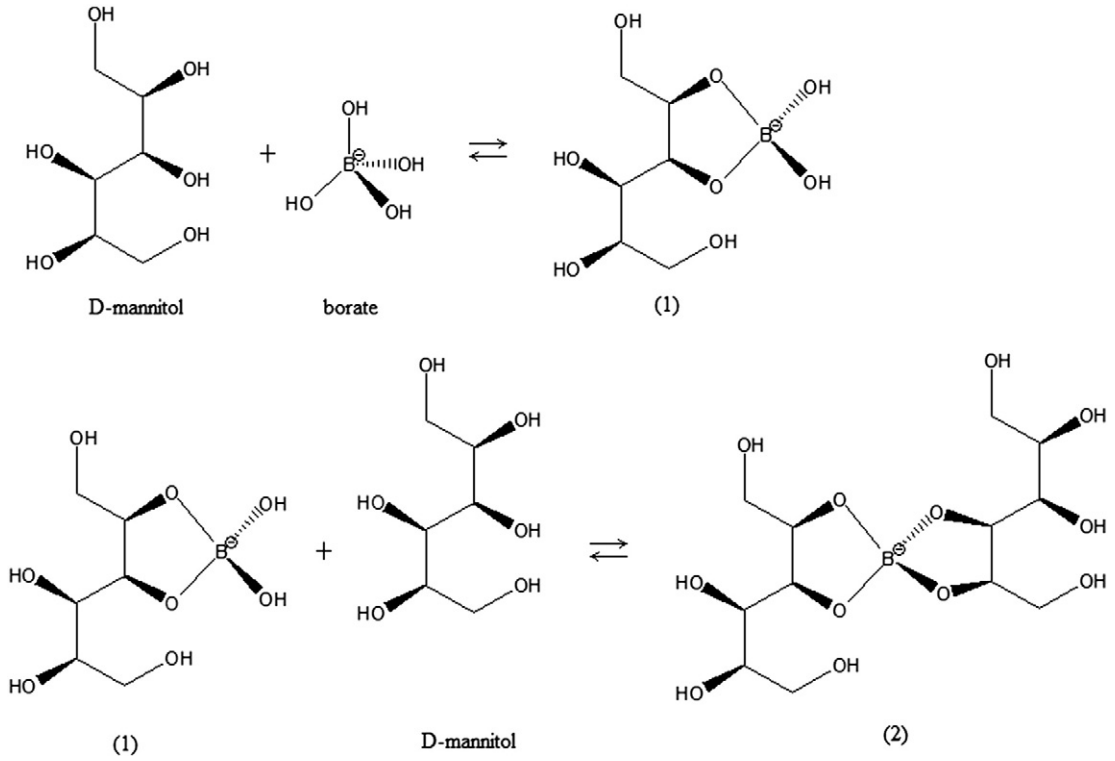

Fig. 1. Scheme of the reaction between monoborate and D-mannitol. Structures (1) and (2) represent monochelate and dichelate complexes, respectively.

sufficiently high boron rejection efficiency. However, an in-depth analysis of the underlying mechanisms of transport across RO membranes was necessary. Mechanistic studies on the rejection of boric acid and monoborate by various RO membranes have been reported previously [8–11]. Recently, a model for mass transport of boric acid, monoborate and boron complexes with D-mannitol, sodium D-gluconate and *N*-methyl D-glucamine across a thin-film composite membrane was described [12]. This model combines an equilibrium model for monoborate and complex formation with a model of solvent–solute coupled transport for the prediction of boron mass transport across a RO membrane.

2. The objective

The objective of this work was to determine the effects of RO membrane type on the rejection efficiency for boric acid, monoborate and boron complexes with D-mannitol, sodium D-gluconate as well as *N*-methyl D-glucamine. This objective was achieved via determination of mass transport coefficients: permeability and reflection coefficients for each species and for each type of membrane. These coefficients were determined by using an existing methodology and a mass transport model that was proposed previously [12]. The influence of the membrane type on these coefficients was determined, and quantitative analyses were conducted to compare the effectiveness of the tested membranes for boron separation with varied permeate flux, boron concentrations in the feedwater, alcohol/boron molar ratios and pH conditions. The discussion presented here should enable the selection of the most appropriate membrane and operating conditions for boron separation by RO in the presence or absence of polyols.

3. Methods and apparatus

The efficiency of boron species removal was tested using the following DOW™ FILMTEC™ RO membranes: TW-30, XLE, BW-30 and SW-30. The characteristics of these membranes differ greatly and make them suitable for different applications. According to data supplied by the manufacturer [13], the TW-30 membrane is designed for purification of low salinity waters (tap water) by small commercial systems. In contrast, the BW-30 and XLE membranes are designed for desalination of brackish waters, with the XLE membrane demonstrating greater efficiency at low permeate flux (low pressures). Finally, the SW-30 membrane should be applied for desalination of high salinity waters, such as seawater, as this membrane has demonstrated excellent rejection properties. These membranes were selected to represent a range of membranes designed to handle different salinity levels that boron containing waters and wastewaters can possess.

The apparatus and methodology for prediction of transport coefficients of boric acid, monoborate and borate complexes have been described in great detail [12]. Filtration experiments were conducted in a stirred cell, the HP4570 supplied by Sterlitech, USA. Feedwater volume and active membrane area equaled to 300 mL and 14.6 cm^2 respectively. The experiments were conducted at 1200 rpm. It was demonstrated previously that at this high stirring intensity, the extent of concentration polarization was negligible. The water samples tested contained 5–100 mol/m^3 of boron as well as polyol at molar ratio of 2:1 for alcohol: boron. The pH values of the samples varied from 4 to 11. These samples were filtered at an excess pressure of 10 to 40 atm. The permeate and retentate boron contents, alcohol content and pH values were determined. Quantitative analyses of individual species (boric acid, monoborate, mono- and dichelate complex) in the retentate and permeate were evaluated using a mathematical model that includes the equilibrium constants for monoborate–polyol complex formation and boric acid dissociation, along with the alcohol and boron mass balance. The mathematical methodology behind the above evaluation was described previously [12]. Based on the predicted concentrations of individual species in the retentate and permeate, and the volumetric flux of permeate, the permeability coefficients (P_i) and reflection coefficients (σ_i) specific for boric acid, monoborate and mono- and dichelate complexes were estimated. This estimation was based on the model equation specific for solvent–solute coupled mass transport:

$$j_i = -P_i \Delta C_i + (1-\sigma_i) J_v \overline{C}_i \quad (1)$$