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## Coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes

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# **Coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes**

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## Abstract

The coupling effects of solution pH and ionic strength on boron rejection by nanofiltration (NF) and reverse osmosis (RO) membranes were investigated. Two NF membranes (namely NF270 and NF90) and three RO membranes (namely BW30, SW30 and UTC80) were used to provide a full spectrum of NF/RO membranes. The rejection of boron by all five membranes was pH-dependent. The dependency of boron rejection on the feed solution pH became much more substantial as the nominal salt (sodium or calcium) rejection value of the membrane decreased. At pH 11, boron rejections by the NF90 and the NF270 membranes were only 10% and 30% lower than those by the other three RO membranes, respectively. On the other hand, the permeabilities of the two NF membranes investigated here were 3 to 11 times higher than those of the RO membranes. The reported data suggest a possibility of using NF membranes for the second pass in seawater desalination applications to avoid over-demineralisation of the final product water. The reported results also reveal an intricate interplay among the feed solution pH, ionic strength and their effects on the rejection of boron by NF/RO membranes. At pH 10, which is immediately above the intrinsic pK<sub>a</sub> value (9.23) of boric acid, as the feed solution ionic strength increased up to 42.5 mM, a considerable increase in boron rejection by both the NF270 and the BW30 membranes was observed. This phenomenon could be attributed to the reduction in the apparent pK<sub>a</sub> of boric acid as the ionic strength increased, which possibly resulted in the observed increase in boron rejection at pH 10. Results reported here suggest that the rejection of boron in the second pass could be further optimised by increasing the feed solution pH and allowing for a marginally higher salt passage in the first pass.

*Keywords:* boron, seawater desalination, ionic strength, pH, nanofiltration, reverse osmosis.

## 1. Introduction

Boron is a common element and can be found in the aquatic environment primarily in the form of boric acid. In seawater, the average boron concentration is approximately 4.6 mg/L. The boron concentration in confined ocean bodies can be substantially higher than this average value. For example, boron concentration in the Mediterranean Sea can be as high as 9.6 mg/L [although this is rather uncommon in other marine water bodies](#) [1]. The typical concentration of boron in other natural water bodies is relatively low, and the average concentration in freshwater is commonly less than 0.1 mg/L. Boron concentration in groundwater is generally location-specific, and values based on existing data are commonly below 2 mg/L [1]. Water with a high boron concentration is not suitable for consumption by humans and animals nor for the irrigation of many plant species. Until very recently, because freshwater or groundwater have been the dominant sources of drinking water supply, boron has not been given much attention by water authorities. However, the dramatic and recent growth in seawater desalination using reverse osmosis technology has reinstated boron as a major contaminant of concern in water supply [2].

The possible health and ecological effects of boron contamination has been known for many years. Although a minute amount of boron plays a necessary role in human diet [3], excessive ingestion of boron can be toxic to human beings and other animals. Symptoms of boron toxicity in human include nausea, vomiting, diarrhoea, dermatitis, lethargy, poor appetite, weight loss, and decreased sexual activity [4]. Although boron is an essential micro-nutrient for some plants, there is a certain level of tolerance. Excessive concentrations of boron in soil and in irrigation water can be harmful to plants. Boron toxicity has been reported to limit crop yield in Australia, North Africa, and West Asia where alkaline and saline soils are present together with low rainfall and very limited leaching, and where plants are irrigated with water containing high boron level [5].

Standards or guideline values for boron concentration in drinking water vary widely around the world, ranging from 0.5 to 5.0 mg/L [6]. These standard or guideline values of boron in drinking water seem to be based on the tolerance of plants which can be assumed to be most sensitive to boron contents. For instance, Israel has a very stringent boron standard because citrus – a boron sensitive plant species - is agriculturally important [7]. Available boron removal technologies can also affect the regulations. In 1990, the World Health Organisation (WHO) established a

guideline of 0.3 mg/L for boron content in drinking water. This level was raised to 0.5 mg/L in 1998 due to a lack of financially viable boron removal technologies. In 2009, the WHO revised the recommended boron level in drinking water to 2.4 mg/L in accordance with the latest data from the UK and US on dietary intakes. It is noteworthy that the WHO guideline has been formulated based exclusively on human health consideration. Because drinking water may also be used for gardening and landscaping purposes, it is expected that boron standards in drinking water set by water authorities will be more stringent than that of the recent WHO guideline. In fact, most current seawater desalination plants using RO technology have proactively set very low boron targets, typically at 1 mg/L or lower [6].

Seawater desalination can be achieved by either thermal distillation or reverse osmosis (RO) separation. Thermal distillation is generally more energy intensive than RO desalination [2, 8]. The elevating cost of energy in recent years together with the significant development of membrane technology have led to a dramatic shift from thermal distillation to RO technology. However, the rejection of boron by RO membranes under a typical seawater desalination condition is somewhat limited. In recent years, several membrane manufacturers have developed novel boron-specific RO membranes which are able to remove up to 91-93% boron [9] at natural pH conditions (pH 6-8). Nevertheless, somewhat lower boron rejection is commonly observed in actual RO desalination plants. In general, typical seawater RO membranes **may not be able** to reduce boron to below a desirable level using a single pass [10]. Therefore, most full-scale RO desalination plants have utilised a multi-pass system configuration in order to produce permeate with an acceptable boron level. Such a configuration leads to a burden on energy consumption and operating cost, and high chemical consumption to re-mineralise the desalinated water. Consequently, there has been a growing body of dedicated research work aiming to optimise the rejection of boron during seawater desalination using RO technology [6, 11]. Most of the previous research examined the effects of operating conditions (such as feed solution pH [9, 12], temperature [13], and recovery [10, 14]) on boron rejection by RO membranes in attempts to optimise the removal of boron in an RO seawater desalination process. In a recent study, the effects of biofouling on the rejection of boron have also been investigated [15]. However, it is noteworthy that previous research elucidating the effects of ionic strength on boron rejection by NF/RO membranes remains very limited. To date, the intricate interplay between the feed solution pH and ionic strength and their effects on boron rejection have not

been systematically investigated. Oo and Song [13] reported a decrease in boron rejection by three RO membranes (ESPA1, LFC1, and CPA2) as the feed solution salinity increased up to 15,000 mg/L of NaCl (corresponding to an ionic strength of approximately 260 mM). In their subsequent study, Oo and Ong [16] attributed the decrease in boron rejection by these three RO membranes to a shift in zeta potential of the membrane surface from negative to positive values as the feed solution salinity increased beyond 2,000 mg/L of NaCl (or an ionic strength of approximately 35 mM). Nevertheless, in this study, Oo and Ong [16] also reported an increase in boron rejection by two other RO membranes (ESPA-B and SWC4+) as the feed solution salinity increased over the same range.

This study aimed to elucidate the coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes. Five commercially available membranes were selected for this investigation to span the complete NF/RO membrane spectrum, thus allowing for a systematic investigation of the mechanisms involved. Key physiochemical properties of the selected membranes were characterised in detail. Boron rejection was evaluated at different pH and ionic strength values. The obtained rejection data were delineated with respect to physiochemical properties of boric acid and the selected membranes.

## **2. Physiochemical properties of boric acid**

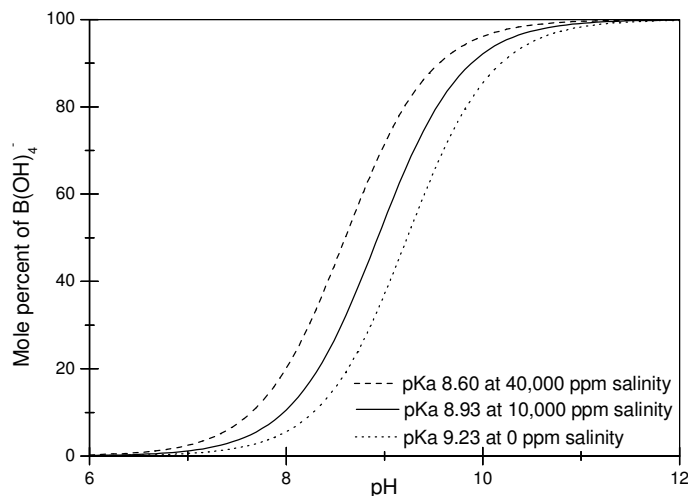
In seawater, boron exists primarily in the form of boric acid. Boric acid is a weak Lewis acid. However, with only 3 electrons in the valence shell, boron cannot comply with the Octet rule and therefore boric acid is not a proton donor. Instead, the dissociation of boric acid can only occur via a hydrolysis process:



The dissociation constant ( $\text{pK}_a$ ) of this reaction is 9.23 [6]. At pH below this  $\text{pK}_a$  value, boric acid mostly exists in an undissociated form. Since boron is an electron deficient element, the crystal radius of boric acid is quite large, which is reported in the range of 0.244-0.261 nm [17]. As a result, boric acid is poorly hydrated and is therefore expected to have a small hydrated radius.

It is noteworthy that the above mentioned  $\text{pK}_a$  value of boric acid corresponds to the standard condition (i.e., dilute solution, at 20°C and atmospheric pressure). Being a weak acid, the

apparent (actual)  $pK_a$  value of boric acid can deviate considerably from this intrinsic value depending on several factors including ionic strength, pressure, and temperature. It was reported that the  $pK_a$  of boric acid would decrease approximately 1 unit, from 9.23 to 8.60, when the feed salinity increased from 0 ppm to 40,000 ppm (Figure 1) [18]. The shift in  $pK_a$  of the boric acid in response to the solution ionic strength is expected to exert some influence on the rejection of boron by NF/RO membranes. This premise will be examined in a later section.



**Figure 1.** The speciation of boric acid in an aqueous solution at different salinity [18].

### 3. Materials and methods

#### 3.1. Nanofiltration and reverse osmosis membranes

Two nanofiltration membranes, namely NF270 and NF90, and three reverse osmosis membranes, namely BW30, SW30 and UTC80, were used in this study. The UTC80 membrane was supplied by Toray<sup>TM</sup> Industries (Tokyo, Japan). All other membranes were supplied by Dow FilmTec<sup>TM</sup> (Minneapolis, MN, USA).

#### 3.2. Contact angle measurement

Contact angle measurement were conducted by a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) using the standard sessile drop method. Milli-Q water was used as the reference solvent. The membranes were dried in the air before the measurements. Contact angles

on both sides of the droplet were measured. At least 5 droplets on each membrane sample were measured, and twenty counts of each droplet were recorded.

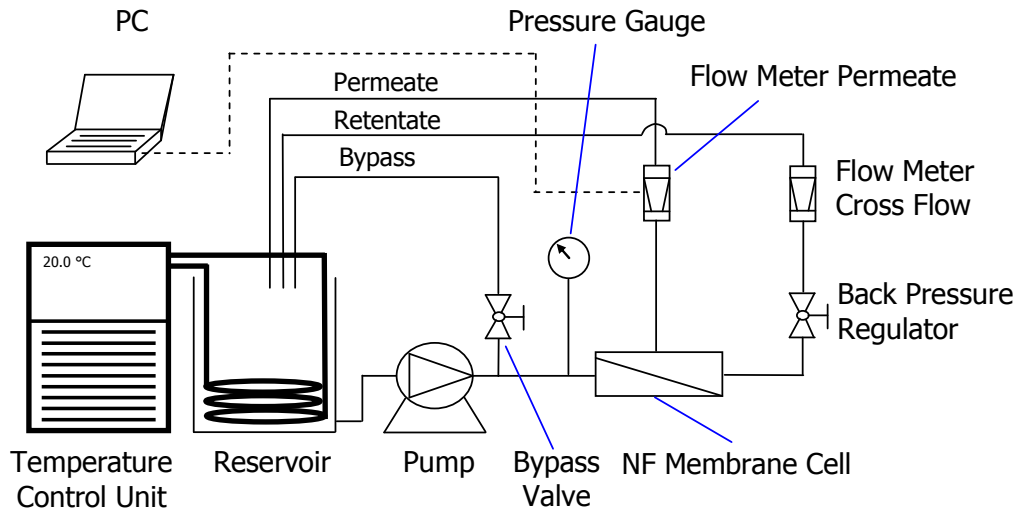
### *3.3. Zeta potential measurement*

Zeta potential of the membrane surface was measured by a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria). The zeta potential of each membrane surface was calculated from the measured streaming potential using the Fairbrother-Mastin approach. All streaming potential measurements were conducted in a background electrolyte solution containing 10 mM KCl. Hydrochloric acid and potassium hydroxide were used to adjust pH by means of manual titration. The test solution was used to thoroughly flush the cell prior to the pH adjustment for each measurement. All streaming potential measurements were performed at room temperature of approximately 25 °C, which was monitored by the temperature probe of the instrument.

### *3.4. Cross-flow membrane filtration system and experimental protocol*

A laboratory-scale, cross-flow membrane filtration test unit with a rectangular stainless steel cross-flow cell was used in this study (Figure 2). This cell has an effective membrane area of 40 cm<sup>2</sup> (4 cm x 10 cm) with a channel height of 2 mm. The unit utilizes a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN) capable of providing pressures up to 6800 kPa and a flow rate of 4.21 L/min. Feed pressure and cross-flow velocity were controlled by a bypass valve and a back-pressure regulator. The temperature of the test solution was kept constant using a chiller/heater (Neslab RTE 7) equipped with a stainless steel heat exchanger coil, which was submerged directly into a stainless steel reservoir. Permeate flow was measured by a digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA) connected to a PC, and the cross-flow rate was monitored by a rotameter. Permeate and retentate flows were recycled back to the feed reservoir.





**Figure 2.** Schematic diagram of the NF/RO filtration system.

At beginning of each experiment, the membrane was compacted using 9 L deionized water at a pressure of approximately 500 kPa higher than the normal operating pressure of each membrane. Membrane compaction was conducted for at least 1 hour until a stable baseline flux was obtained. The electrolyte solution was then added to the feed reservoir, and made up to the total feed volume of 10 L. For all experiments, the cross-flow velocity and permeate flux were adjusted to be 30.4 cm/s and 40 L/m<sup>2</sup>h, respectively. The temperature of the feed solution was kept constant at  $20 \pm 0.1$  °C during the experiment. To assess the impact of solution pH on the rejection of boron, the solution pH was raised to 11 by adding an appropriate volume of 1M NaOH, and then the pH was incrementally dropped to pH 6 by adding an appropriate volume of 1M HCl. To investigate the impact of ionic strength on the rejection of boron, a predetermined volume of 0.1 M CaCl<sub>2</sub> or 1 M NaCl was added to the feed solution to create a stepwise increase in the concentration of either CaCl<sub>2</sub> or NaCl in the feed solution, respectively. Feed and permeate samples were collected for analysis after the filtration system had been stabilised for 1 hour at each investigated condition. The system was operated under a recirculation mode, where both permeate and concentrate were recirculated to the feed tank, except for permeate sample collection. Permeate flux was kept constant during the experiment to minimize the effect of flux on rejection.

Unless otherwise stated, all experiments were conducted based on an electrolyte background that includes NaCl, CaCl<sub>2</sub>, and NaHCO<sub>3</sub> at concentrations of 10 mM, 1 mM, and 1 mM, respectively.

Boron in the form of boric acid was spiked into the feed solution at a level of 0.43 mM (or 4.6 mg/L as boron), which is the average boron concentration in seawater. Trace analytical grade Suprapur nitric acid from Merck Co. (Darmstadt, Germany) was used for dilution and sample preparation prior to ICP-MS analysis. All other chemicals used in this investigation are of analytical grade.

### *3.5. Analytical methods*

The concentrations of boron, sodium and calcium were analysed using an Agilent 7500CS (Agilent Technologies, Wilmington, DE, USA) inductively-coupled plasma mass spectrometer (ICP-MS). Lithium internal standard (BDH Spectrosol, Poole, UK) was spiked to all samples at the concentration of 40 µg/L. Sample dilution was carried out with 5% Suprapur nitric acid with a dilution factor of up to 20. To avoid contamination, all apparatus used for sample preparation was of plastic materials, and were soaked in 5% Suprapur nitric acid for at least 24 hours before being used. Calibration was conducted prior to each batch of analysis. The linear regression coefficients of all calibration curves were more than 0.99 for all elements. Prior to each analysis batch, the ICP-MS was tuned by a multi-element tuning solution that contained 10 µg/L of Li, Y, Ce, Tl and Co. Each analysis was conducted in triplicate and the variation was always less than 5%. Conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Beverly, MA, USA).

## **4. Results and discussion**

### *4.1. Membrane characterization*

According to the manufacturers, all five membranes used in this study are made of an ultra thin polyamide skin layer on top of a microporous supporting layer. The former governs the separation characteristics of the membrane whereas the latter provides mechanical strength to the membrane. These membranes are selected to span the spectrum of NF/RO membranes with regard to their nominal salt (such as sodium) rejection values. The NF270 is a loose NF membrane with low sodium rejection whereas NF90 is a tight NF membrane with moderate sodium rejection (Table 1) [19]. The BW30 is a brackish water RO membrane which can be used in the second pass of a standard seawater RO desalination plant whereas both the SW30 and

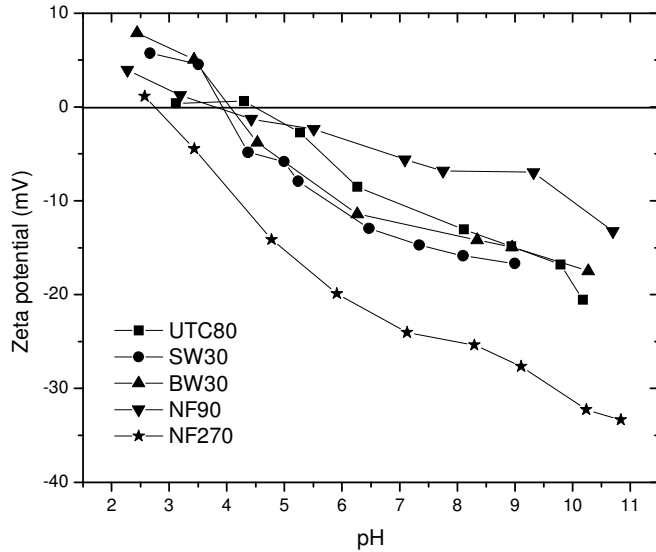
UTC80 are seawater RO membranes commonly used in the first pass. The three RO membranes used in this study are considered to have a non-porous active skin layer and the nominal values of their pore size are not available. The membranes are listed in Table 1 in the order of decreasing pure water permeability, which is also consistent to the order of increasing salt rejection value with respect to both sodium and calcium. Although contact angle (which measures the hydrophobicity of the membrane surface) does not directly affect the rejection of solute, these parameters can determine the transport of water through membranes which governs the overall rejection of a membrane system [20]. However, contact angle does not correlate to salt rejection nor the pure water permeability (Table 1). Because the polyamide layer that forms the membrane active skin contains both carboxylic and amine functional groups that can ionize in an aqueous solution [21], the membrane surface zeta potential can vary as a function of the solution chemistry, such as pH and ionic strength. Schäfer et al. reported that the more negative membrane zeta potential could lead to a higher salt rejection due to an enhanced electrostatic interaction between the negatively charged membrane surface and a charged solute [22]. All five membranes selected in this study are negatively charged in the pH range between 6 and 11 (Figure 3). In addition, their negative surface charge density increases as the solution pH increases (Figure 3). Results reported in Figure 3 suggest that electrostatic interaction can be an important rejection mechanism of charged solutes, particularly for the two NF membranes.

Table 1. Properties of the membranes used in this study.

Membrane	Average pore diameter <sup>a</sup> (nm)	Na <sup>+</sup> rejection <sup>b</sup> (%)	Ca <sup>2+</sup> rejection <sup>b</sup> (%)	Pure water permeability (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Contact angle (°)
NF270	0.84	35.8	57.5	14.0	28.8 ± 2.4
NF90	0.68	87.2	88.6	10.5	50.9 ± 4.9
BW30	not available	96.2	97.7	3.5	54.6 ± 3.0
UTC80	not available	97.9	98.2	1.75	48.5 ± 5.4
SW30	not available	97.9	98.5	1.23	62.0 ± 7.2

<sup>a</sup> Ref [19].

<sup>b</sup> Rejection data were recorded at pH 8.



**Figure 3.** Zeta potential of the selected membranes (measured at 25 °C, in a background electrolyte solution containing 10 mM KCl; pH was adjusted using HCl and KOH).

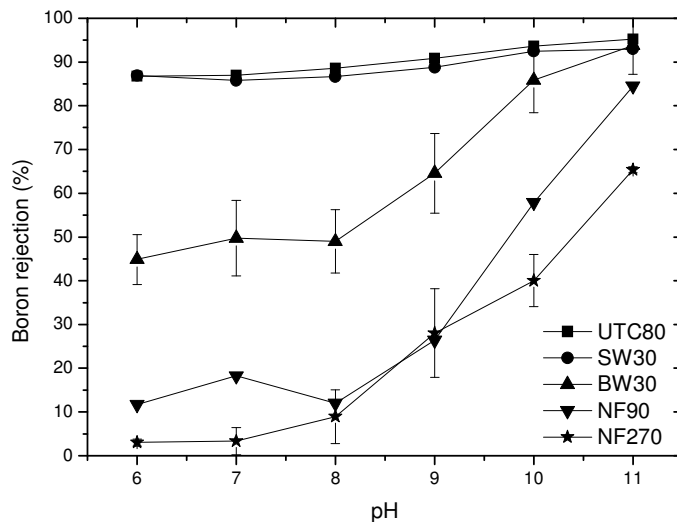
#### 4.2. Effects of pH

The solution pH appears to be a major parameter governing the rejection of boron by the five NF/RO membranes selected in this study (Figure 4). Results presented in Figure 4 are consistent with the literature and can be explained by the intricate relationship among the speciation of boric acid, membrane surface charge, and solution pH. Boric acid (which is the dominant form of boron in environmental water) can speciate from a neutral species to a negatively charged borate ion as the solution pH increases beyond its  $pK_a$  value of 9.23. In addition, as previously discussed in Section 2, when existing as a neutral form, boric acid is poorly hydrated. On the other hand, the borate ion is well hydrated and therefore the speciation of boric acid to borate not only represents the change in charge interaction, but also an increase in the apparent hydrated size of the boron solute. In addition, an increase in the solution pH can also increase the membrane negative surface charge density (Figure 3), leading to an enhanced electrostatic interaction with charged solute [21].

Previous studies investigating the effects of solution pH on boron rejection have focused almost exclusively on RO membranes [13, 16, 23-29]. By assessing a full NF/RO membrane spectrum, results reported in Figure 4 systematically demonstrate the significance of electrostatic interaction and a major boron rejection by NF membranes. The two seawater RO membranes

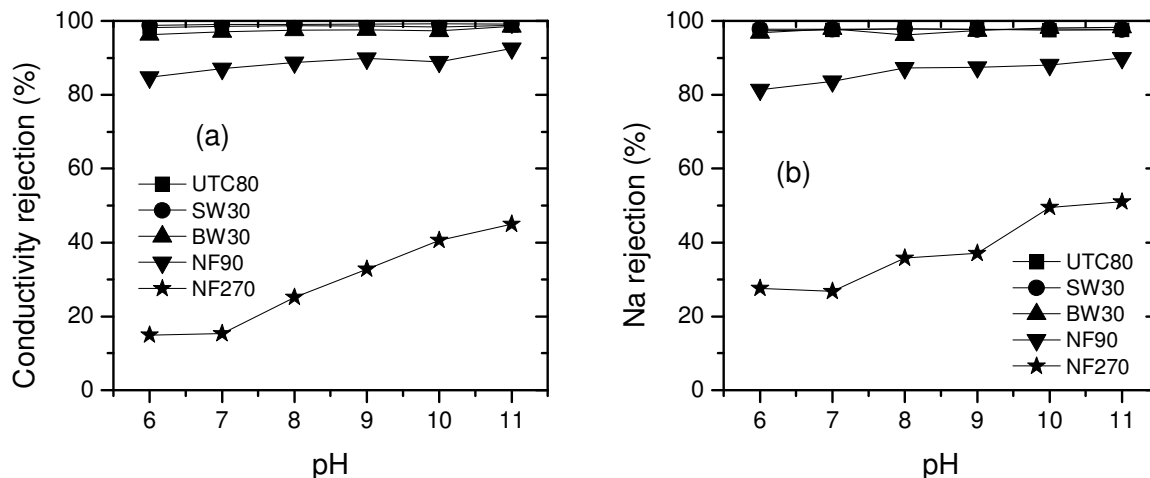
(SW30 and UTC80) show a small increase (less than 10%) in boron rejection as the solution pH increases from 6 to 11 (Figure 4). In contrast, a much more dramatic increase in boron rejection can be observed with the NF270 and NF90 membranes, whereas the BW30 shows an intermediate behaviour (Figure 4). As a result, the differences in boron rejection by all five selected membranes decrease substantially as the feed solution pH increases. Results reported in Figure 4 suggest that charged repulsion is a predominant boron rejection mechanism of NF membranes at high pH. Furthermore, there is considerable scope for the use of NF rather than RO membranes in the second pass. At pH 11, boron rejection by the NF90 is only approximately 10% lower than that by the three RO membranes. Similarly, at pH 11, the NF270 can achieve a boron rejection value of 65%, which is approximately 30% lower than that by the three RO membranes. On the other hand, these NF membranes can offer much higher permeabilities (from 3 to 11 times) than those of the RO membranes and do not lead to over-demineralisation of the product water due to their low sodium and calcium rejection values (Table 1). The latter can also reduce the risk of membrane scaling involved in membrane filtration operation at high pH.

It is noteworthy that size exclusion is always an underlying rejection mechanism of boron by NF/RO membrane under most if not all conditions. The importance of size exclusion exhibits through the differences in boron rejection at a certain pH. At any given pH value, boron rejection by five membranes generally increases in the order of decreasing membrane pore size (Figure 4 and Table 1). At a high pH value (pH 11), this order is still maintained although the differences become smaller. This implies that boron rejection by size exclusion mechanism is important at all pH conditions.



**Figure 4.** Boron rejection by different membranes as a function of solution pH. Feed solution contained 10 mM NaCl, 1 mM CaCl<sub>2</sub>, 1 mM NaHCO<sub>3</sub>, and 0.43 mM B(OH)<sub>3</sub> (or 4.6 mg/L as B). Feed temperature = 20 °C; permeate flux = 40 L/m<sup>2</sup>h; cross flow velocity = 30.4 cm/s. The error bars show the standard deviations of four repetitive experiments.

The rejection of conductivity or common cations such as sodium does not appear to be a good surrogate for the removal of boron by NF/RO membranes. Conductivity rejections by most of the membranes remain largely constant despite any changes in the feed solution pH (Figure 5). An exception is the NF270 membrane, which shows a considerable increase in conductivity rejection as the feed solution pH increases. This observation can be attributed to the large pore size of this membrane which encourages the impact of increasing electrical double layer on the membrane surface in high pH conditions [30, 31]. The result implies that the rejection mechanisms of boron differ substantially from that of the basic cations such as sodium.

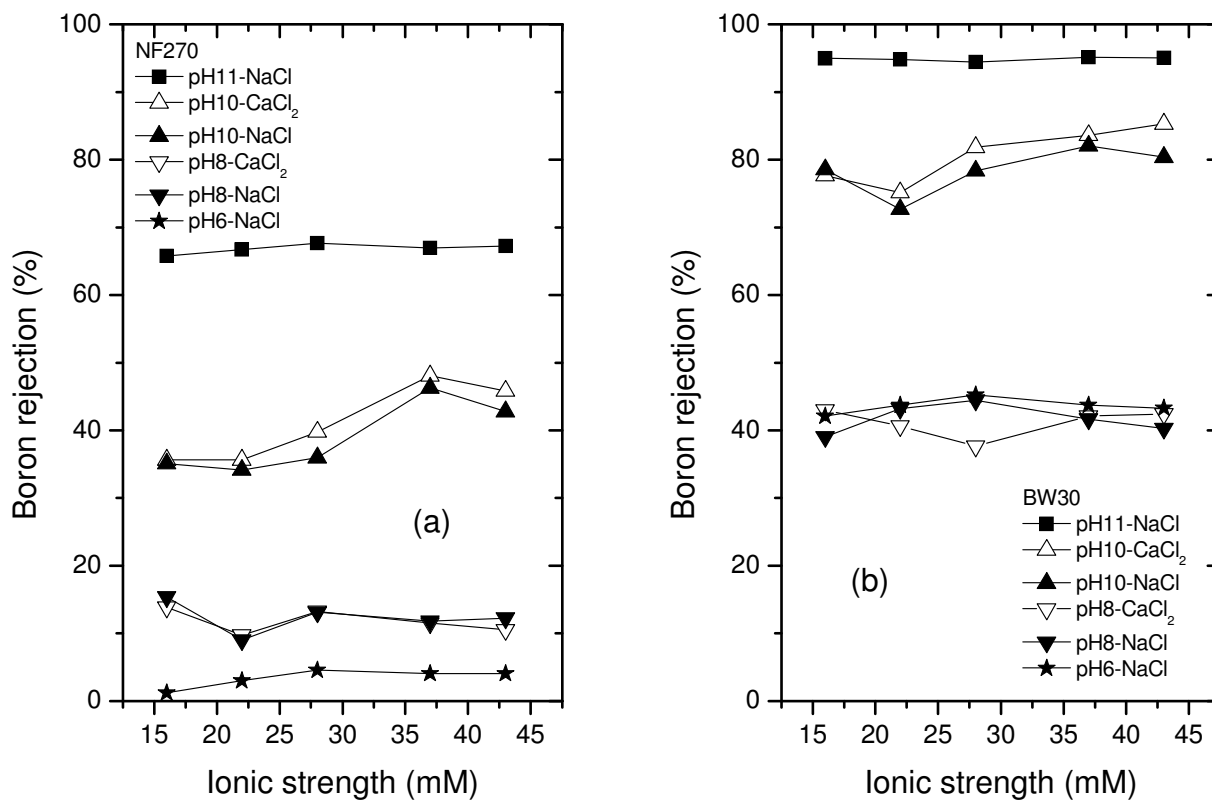


**Figure 5.** The rejection of conductivity (a) and sodium (b) as a function of solution pH. Feed solution contained 10 mM NaCl, 1 mM CaCl<sub>2</sub>, 1 mM NaHCO<sub>3</sub>, and 0.43 mM B(OH)<sub>3</sub> (or 4.6 mg/L as B). Feed temperature = 20 °C; permeate flux = 40 L/m<sup>2</sup>h; cross flow velocity = 30.4 cm/s.

#### 4.3. Effects of ionic strength

It is well established that an increase in the solution ionic strength can compress the double layer of a charged solute or a charged membrane surface, resulting in a reduced electrostatic interaction between these two entities [21]. On the other hand, as previously discussed in Section 2, an increase in the solution ionic strength may also reduce the apparent pK<sub>a</sub> value of boric acid, leading to a change in the speciation of boric acid particularly at pH in the vicinity of its intrinsic pK<sub>a</sub> value of 9.23. This interesting interplay between pH and ionic strength and their effects on boron rejection by NF/RO membranes are systematically demonstrated in Figure 6. At pH 10, there was a considerable increase in boron rejection by the NF270 membrane as the feed solution ionic strength increased from 15 mM to 42.5 mM. This behaviour was consistently observed when either CaCl<sub>2</sub> or NaCl was used to increase the feed solution ionic strength. At pH 10, boron exists in both negatively charged and neutral forms, which the former being the more abundant species (Figure 1). A reduction in the apparent pK<sub>a</sub> value (in response to the increasing ionic strength) can increase in the fraction of the negatively charged borate ions, possibly resulting in the subtle increase in boron rejection observed in Figure 6a. Boron rejection by the BW30 also

increased slightly as the feed solution ionic strength increased (Figure 6a). Nevertheless, such an increase was quite marginal and in fact there was a slight decrease in boron rejection by the BW30 as the ionic strength increased from 15 mM to 22.5 mM. This is possibly because the BW30 is a RO membrane and the charge repulsion rejection mechanism is not as significant as that of the loose nanofiltration NF270 membrane. In contrast, at pH 6, 8, and 11, boron rejection by both the NF270 and BW30 remained constant despite the changes in the feed solution ionic strength. At pH 6 and 8, boron exists predominantly in the neutral boric acid form, charge repulsion is not a major rejection mechanism and the feed solution ionic strength is not expected to have any substantial influence on boron rejection. On the other hand, since pH 11 is almost 2 units above the  $pK_a$  value of boric acid, any reduction in the apparent  $pK_a$  value of boric acid would only result in a minor redistribution between the borate and boric acid species (Figure 1).

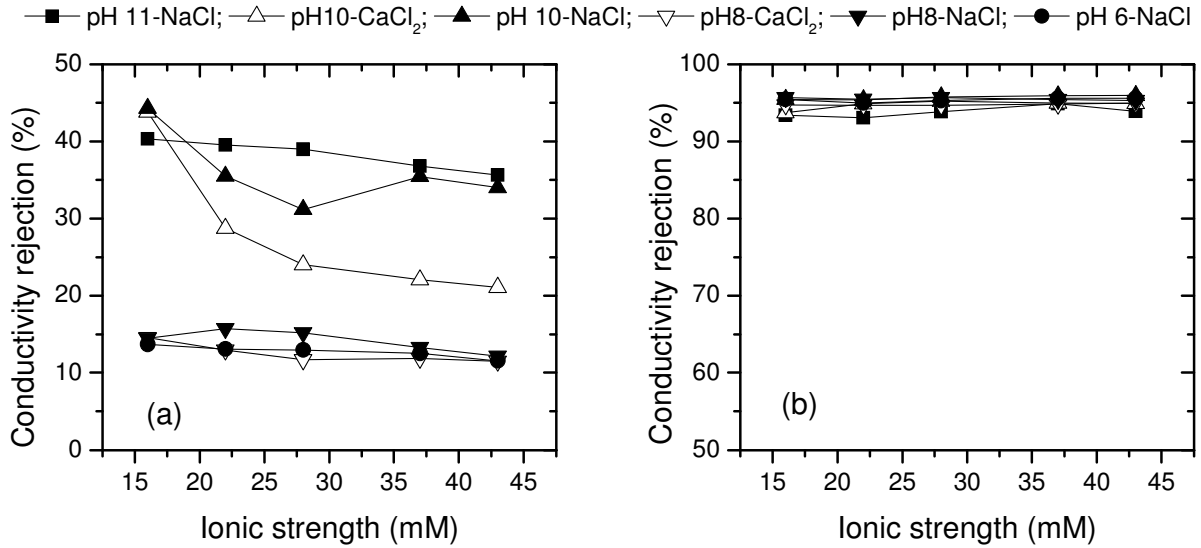


**Figure 6.** Boron rejection as a function of ionic strength at pH 11, 10, 8 and 6 by (a) the NF270 membrane (b) the BW30 membrane. Either  $CaCl_2$  or  $NaCl$  was used to increase the feed solution ionic strength. Feed solution also contained 0.43 mM  $B(OH)_3$  (or 4.6 mg/L as B); feed temperature = 20 °C; permeate flux = 40 L/m<sup>2</sup>h; cross flow velocity = 30.4 cm/s.



Results reported in Figure 7 further highlight the differences between the separations of boron and common inorganic salts, which can be readily determined by conductivity measurement. In fact, conductivity rejection by the NF270 membrane decreased considerably with increasing solution ionic strength (Figure 7a). The effect of increasing ionic strength on conductivity rejection appears to be more prominent at high pH (10 and 11) than that at pH 6 and 8. As can be seen in Figure 3, an increase in the solution pH would result in an increase in the surface charge of the NF270, which would subsequently lead to a stronger electrostatic interaction at high pH conditions. This observation has been widely reported in the literature [21, 30], and was attributed to the compaction of the electrical double layer of both the membrane surface and the charged solute as a result of an increase in the feed solution ionic strength. However, the decrease in conductivity rejection in response to an increase in the feed solution ionic strength was not observed with the BW30 membrane (Figure 7b). This is because salt rejection by the BW30 membrane is dominated mostly by size exclusion and the impact of a compacted double layer on conductivity rejection is expected to be negligible.

It is noteworthy that the impact on conductivity rejection by the NF270 membrane caused by  $\text{CaCl}_2$  was more severe than that by  $\text{NaCl}$  at the same ionic strength (Figure 7a). This is in good agreement with a previous study reported by Braghetta et al. [30] who found that the divalent cation  $\text{Ca}^{2+}$  is more effective than the monovalent cation  $\text{Na}^+$  in compressing the membrane electrical double layer. In addition, the divalent cation  $\text{Ca}^{2+}$  can readily adsorb to the membrane surface leading to a decrease in the membrane negative charge [21].



**Figure 7.** Conductivity rejection as a function of ionic strength at pH 11, 10, 8, and 6 by (a) the NF270 membrane and (b) the BW30 membrane. Either CaCl<sub>2</sub> or NaCl was used to increase the feed solution ionic strength. Feed solution also contained 0.43 mM B(OH)<sub>3</sub> (or 4.6 mg/L as B); feed temperature = 20 °C; permeate flux = 40 L/m<sup>2</sup>h; cross flow velocity = 30.4 cm/s.

The range of ionic strength investigated in this study is comparable to that of the first pass permeate. Results reported here suggest a possibility to increase boron rejection in the second pass by allowing for a marginally higher salt passage in the first pass, [which can be achieved by deploying high flux RO membranes with slightly higher salt passage](#). This will not only increase the rejection of boron but also prevent the over-demineralisation of the final product water.

## 5. Conclusion

This study investigated the coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes. Boron rejection by the five NF/RO membranes investigated in this study was pH-dependent. The dependency of boron rejection on the feed solution pH became much more significant as the nominal salt (sodium or calcium) rejection capacity of the membrane decreased. The reported results suggest a possibility of using NF membranes at high feed solution pH for the second pass in double-pass membrane seawater desalination plants to avoid over-demineralisation of the final product water and to reduce energy consumption. The results also reveal an intricate interplay among the feed solution pH, ionic strength and their effects on the rejection of boron by NF/RO membranes. At pH 10, an

increase in ionic strength up to 42.5 mM resulted in a considerable increase in boron rejection. This phenomenon was explained by the reduction in the apparent  $pK_a$  of boric acid as the ionic strength increased, which possibly led to the observed increase in boron rejection [at pH in the vicinity \(within one pH unit\) of the intrinsic  \$pK\_a\$  value \(9.23\) of boric acid](#). The effect of ionic strength on conductivity rejection was consistent with data previously reported in the literature. Results reported here also suggest that the rejection of boron in the second pass could be further optimised by operating at a high pH and allowing for a marginally higher salt passage in the first pass.

## 6. Acknowledgements

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