Pore-filled Membranes Capable of Selective Negative Rejections

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Abstract: Pore-filled cation-exchange membranes containing poly(styrene-sulfonic acid) have been evaluated in pressure-driven separation of inorganic salts. The membranes are capable of separating single and mixed solutes at low pressures (low fluxes). The separation performance is affected significantly by salt concentration and concentration ratio of mixed salts. The observation of negative separation of counterions particularly at low operating pressures is unique. This type of separation may allow the selective removal of multivalent couterions and their replacement by monovalent couterions. [Nature and Science 2003;1(1):21-26].

Key words: pore-filled membranes; pore-filling; ion-exchange; polyelectrolyte; negative rejection; nanofiltration

Introduction

The phenomenon of negative rejection, a process in which a solute is found to be more concentrated in the permeate than in the feed in pressure driven membrane separation processes is possible but not normally observed, equation 1.

$$\text{Rejction (\%)} = \frac{C_f - C_p}{C_f} \times 100\% \qquad (1)$$

where C_f and C_p are the concentrations of the solute in the feed and permeate, respectively. There are a limited number of reports of the phenomenon in the literature (Mika, 1995; Hoffer, 1968; Hayashita, 1983). The negative rejections of acids (Mika, 1995) has been observed experimentally in membrane nanofiltration processes and calculated negative rejections of anions (Hoffer, 1967) or anion complexes (Hayashita, 1983) have been reported in multi-anion systems in reverse osmosis. The membranes used were collodion membranes, which have little practical significance in modern water treatment. The early work of Hoffer and Kedem (1968) briefly reported the experimental finding of negative cation rejection using a negatively charged membrane. Recently, Nielsen and Jonsson (1994) have reported modelling studies of negative rejections in multi-anionic solutions. We are not aware of modelling and experimental studies of negative cation rejections.

The work described here makes use of negative cation rejection, which has been found with pore-filled cation-exchange membranes. The "Pore-filling" concept was developed by Childs and coworkers (Mika, 1995). This concept is illustrated in Figure 1. The pores of substrate membranes are filled with a wide range of polymers followed by functionalization of the incorporated polymers. These stable, robust membranes with new functionality have shown exceptional performance in desalination, organic substance removal, and gas separation. Patent protection has been sought for this type of membrane and its uses by Childs and coworkers (Mika, 1999; Rilling, 1999; Komkova, 2003). These include specifically the preparation of the membranes, the use of membranes for ultra-low pressure water softening and gas separation device. The present work adds a new dimension to the already pore-filled membranes.
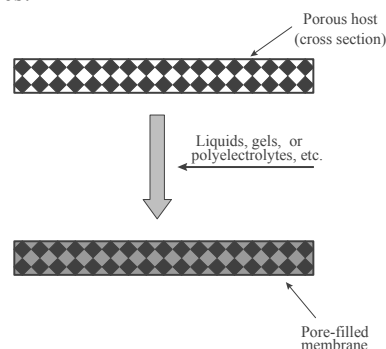
Figure 1. Pore-filling Concept. Functionality such as polyelectrolyte or hydrogel is incorporated into the pores of the substrate membrane to form a stable, robust, and high performance membrane.

Experiments
Material

The membranes used in this work were cation-exchange membranes containing poly(styrene-divinylbenzene sulfonic acid)-filled in a polyethylene membrane. The substrate membrane fabricated by the 3M Company was a polyethylene microfiltration membrane and its properties are listed in Table 1. The preparation and characterization of pore-filled ion-exchange membranes have been described in elsewhere (Jiang 1999, 2003). Inorganic reagents used, NaOH, NaCl, HCl, MgCl$_2$, and Na$_2$SO$_4$ (Aldrich), were all AR grades. Pure water used in this study was RO permeate water that was further deionized and carbon filtered. The pH of feed solutions in this work was adjusted to be neutral using NaOH and

HCl.

Pressure-driven Measurement
The pressure-driven system used in this study was a 6-cell nanofiltration/reverse osmosis (NF/RO) testing system (Mehdizadeh, 1990). The system consisted of an 8-liter feed tank and was running continuously. The effective membrane area was 15.08 cm². The flow rate of the feed solution was controlled at 1.00±0.05 L/min throughout the experiments. The temperature of the NF/RO system was controlled between 22 and 26°C and the results of fluxes were corrected to 25°C. The rejection of inorganic solutes or ionic species were calculated by the following equation 1. The flux was calculated from the following equation:

$$\text{Flux (kg/m}^2\text{s)} = \frac{\alpha_T \, m}{\tau \, A_m} \qquad (2)$$

where m was the mass of permeate collected over the time τ, A_m was the active membrane area, and α_T was the temperature correction factor calculated by the following empirical equation (Sourirajan, 1970):

$$\alpha_T = -0.575 \ln T + 2.85 \qquad (3)$$

where T was the temperature in Celsius (°C).

Results and Discussion
Our previous work (Jiang, 2003) reported fabrication and characterization of pore-filled cation-exchange membranes containing poly(styrene-sulfonic acid). Thus, a typical pore-filled membrane was selected for this study and its properties are list in Table 2. The experiments were carried out by using pure water, single solute (NaCl or MgCl₂), mixed solute (NaCl and MgCl₂), and tap water as the feed. Both the feed and permeate were collected and the concentrations of the

**Table 2. Properties of the Pore-filled Membrane Used in the NF/RO System**

Degree of crosslinking	2.5%
Mass of polystyrene incorporated	83%
Thickness (μm, wet)	67 [a]
Ion-exchange capacity (eq/g)	1.92 [a]
Water content (%)	67 [a]
Water permeability (kg/m²kPa)	0.66 [a]

[a] Reference (Jiang, 2003)

solutes were measured. The experimental error in salt concentration measurement was less than 2.5% (Jiang, 1999).

Single Solute System
The rejection and flux results for single solute system are given in Figure 2. The solution flux, for single salt,
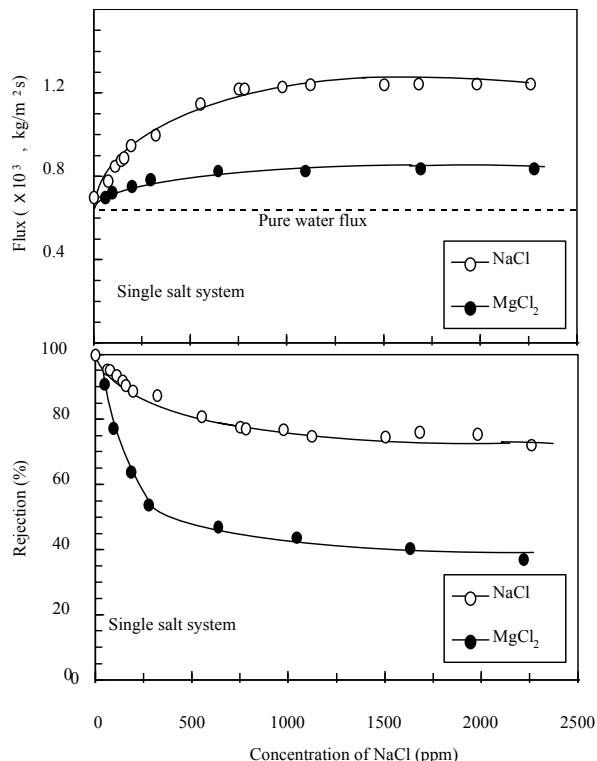
Figure 2. Rejection and flux as a function of concentration for single solutes; single salt systems were NaCl and MgCl₂; 2000 kPa pressure at 25°C.

is greater than the pure water flux (the dotted curve). As can be seen, a significant increase in flux was observed between 0 and approximately 500 ppm but the flux did not change dramatically in a wide concentration rage, i.e., from approximately 500 to 2500 ppm. The solution flux decreases with increasing valency of the counter-ion. This is not often seen for RO/NF thin film composite membranes. The confirmation of the crosslinked polyelectrolyte gels of the pore-filled membrane strongly depends upon ionic strength of the contacting solution and the nature of the salt. For example, besides higher effect of charge screening than the monovalent counter-ions (Na⁺), the bivalent counter-ions (Mg²⁺) in the membrane interact with two fixed charges, resulting in "ionic crosslinking". This kind of "ionic crosslinking" may lead to a decrease in pore size. Hence, the flux of single MgCl₂ is expected to be lower than that of single NaCl. Another effect (steric effect) may add to the ionic crosslinking effect. Another

possible explanation is that the ion size of the hydrated, bivalent Mg^{2+} is larger than that of Na^+. Thus, a hydrated bivalent Mg^{2+} ion is more difficult to go through pores of the membrane than a monovalent Na^+ ion.

It is known that usually Donnan exclusion, size exclusion, and the requirement of charge neutrality all contribute to the mechanism of the salt rejection in nanofiltration/reverse osmosis processes. From Donnan exclusion considerations, the co-ions dominate the rejection of salts. However, size exclusion is of minor importance for these pore-filled membranes as evidenced by the reported low rejections of sucrose. Strathmann and co-workers (Peeters, 1998) pointed out that the permeation of ions through charged membranes in nanofiltration processes depended primarily on the Donnan exclusion but the size effect also played an important role. For single salts, the rejection was observed to decrease with increasing valency of the counter-ion. Similar to the concentration effect presented in previous work (Jiang, 1999), bivalent ions (Mg^{2+}), compared to monovalent ions (Na^+), provides higher shielding to the fixed negative charges on the membrane and make it easier for co-ions (Cl^-) to pass through the membrane. As a result, the rejection of Mg^{2+} is expected to be lower than that of Na^+.

The difference in free solution diffusivity between Na^+ and Mg^{2+} could be a factor affecting their rejections. The diffusion coefficient is 1.33×10^{-9} m^2/s for Na^+ and 0.71×10^{-9} m^2/s for Mg^{2+} (Lide, 1996). These numbers are applicable in free solution. The ion diffusivity in a membrane is generally different due to hindrance and electrostatic interactions between the mobile ions and the fixed charges of the membrane. The difference in diffusion coefficient suggests that Na^+ diffuses faster than Mg^{2+} in dilute solution. However, for the polyelectrolyte highly filled membranes in this work, this effect should be smaller than the Donnan exclusion effect. For example, if the difference in diffusivity were the main effect, the net effect should have led to a lower rejection of single NaCl than single $MgCl_2$. This is not observed in Figure 2.

Mixed solute system
The rejection and flux results for mix solute systems are given in Figure 3. In the mixed salt system, NaCl and $MgCl_2$, with a co-ion in common, the difference in separation performance between Na^+ and Mg^{2+} is related to the change in valence of the competing cations, i.e., the selectivity of one ion is affected by the presence of the other competing ion (Xu, 1997). The rejection results with mixed solutes stand in marked contrast to the behavior of these membranes with single salts, Figure 2. For the mixed salt solutions containing Na^+ and Mg^{2+}, the rejection of Na^+ is lower than that of Mg^{2+}, Figure 3. The permeability of the monovalent

ions (Na^+) through the cation-exchange membrane is higher than Mg^{2+}. This can be understood in terms of the charge neutrality and Donnan exclusion. Because of the higher interactions between the bivalent ions (Mg^{2+}) and fixed charges, the Donnan exclusion prefers to attract Mg^{2+} into the membrane from solution but to repel co-ions (Cl^-). Due to the charge neutrality, the transport of counter-ions through the membrane must be accompanied by co-ions (Cl^-). The transport of the bivalent Mg^{2+} requires twice amount of the co-ions (Cl^-) than the monovalent Na^+. However, the Donnan exclusion restricts the transport of Cl^-. Thus, the monovalent counter-ions (Na^+) are forced to permeate preferentially comparing to the bivalent counter-ions (Mg^{2+}). Hence, a lower rejection is observed for monovalent Na^+ than bivalent Mg^{2+} in the mixed salt system.
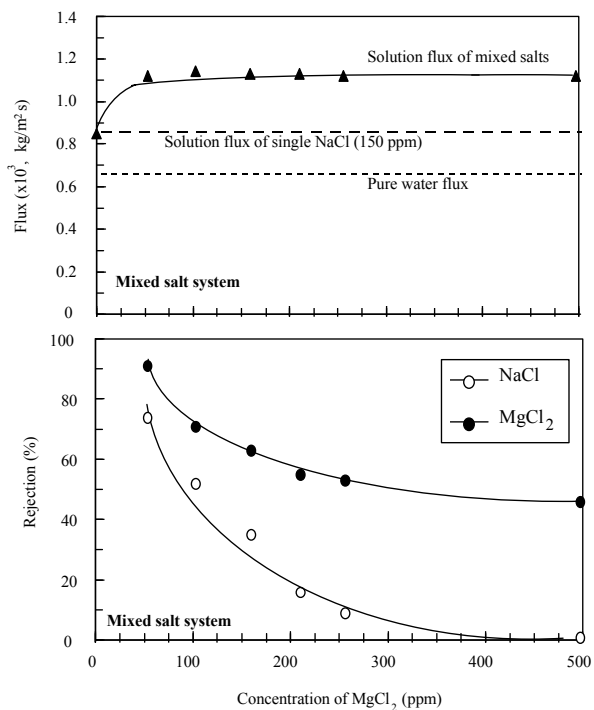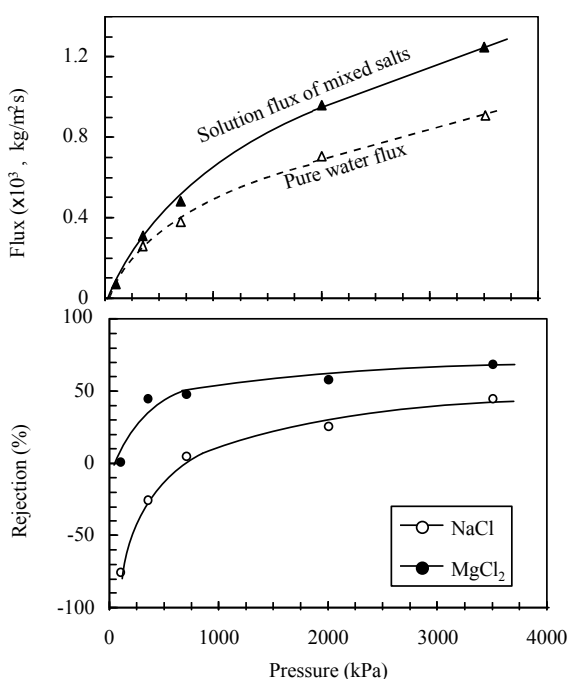

Figure 3. Flux and rejection as a function of concentration of $MgCl_2$ the mixed salt system was NaCl/$MgCl_2$; the concentration of NaCl was kept at 150 ppm; 2000 kPa pressure at 25°C.

Pressure effect
The results of flux and rejection as a function of applied pressure for a mixed solute system are given in Figure 4. The observed relationship of flux *versus* Pressure was not linear through the origin. A linear relationship is common in RO/NF membranes. Similar to the finding of Mika et al. (1995, 1999), who reported the results of pressure effect on separating salts in NF using polyvinylpyridine-filled membranes, a non-linear relationship was observed. The non-linear relationship

is likely due to that the highly swollen crosslinked polyelectrolyte gels are deformable by the ion flow through the membrane. When a solution flows through pores filled with swollen polyelectrolyte gels, the solution penetrates into a certain depth limit of the gel and perturbs the equilibrium. An increase in solution flow forces the polyelectrolyte chains to realign along the flow field. This alignment forces charged neighboring chains closer together resulting in an increase in excluded volume interactions and a lower solution flux (Kim, 1991; Levie, 1996). For example, Levie (1996) used a simplified polyelectrolyte-grafted brush model to developed mathematical equations that were in good agreement with the experimental nanofiltration results obtained by Mika (1995).

Figure 4. Flux and rejection as a function of pressure for a mixed solute system; the feed contains 110 ppm of NaCl and 55 ppm of $MgCl_2$.

Negative rejection
From Figure 3, the rejection of Na^+ was found to decrease with increasing the concentration ratio of Mg^{2+}/Na^+. Negative rejections of Na^+ were found in the mixed $NaCl/MgCl_2$ system, Figure 4. A negative rejection, calculated by equation 1, means that the ion is more concentrated in the permeate than in the feed. In the literature, negative rejections were observed and various reasonable explanations had been used to understand this phenomenon. Recently, Tsuru (1991) and Bardot (1995) had reported similar findings to the results shown in Figure 2 and Figure 3 for the same system of mixed salts using a sulfonated poly(2,6-dimethylphenylene ether) ion-exchange membrane and

using negatively charged, commercial membranes, respectively. Tsuru's explanation was based on partial association of the counter-ion (Mg^{2+}) of the higher valency within the fixed charges in the membrane. Bardot interpreted ion separation by the convective and diffusive fluxes caused by the addition of counter-ions of different mobilities.

In this study, negative cation rejection has been observed with multi-cationic solutions using the pore-filled cation-exchange membranes. For instance, for in the mixed ion system, Figure 3, when the pressure was decreased from 3500 kPa to 100 kPa, the rejection of decreased from 43% to -75% for Na^+. But at the time, the rejection of Mg^{2+} did not go negative, ie., from 70% to nearly 0%. Tap water and a synthetic mixed solute solution containing 2.0×10^{-3} M of NaCl and 1.0×10^{-3} M of $MgCl_2$ were used as the feed with two similar pore-filled cation-exchange membranes prepared previously (Jiang, 1999) under the conditions (350 kPa, 25°C). The results are presented in Table 3. As can be seen, the results obtained from the two pore-filled membranes are consistent. Negative rejections were observed with both tap water and the synthetic solution. For instance, with tap water, the rejection of Na^+ was negative (-29%) while the rejections for Mg^{2+} and Ca^{2+} were positive. Tap water is a complex system and concentration of all ionic species present was not measured. Thus, a simple synthetic mixture ($NaCl/MgCl_2$) was also examined and again the rejection was negative for Na^+ (-25%) and positive for Mg^{2+}. When a single cationic solution was used in the experiments, only positive rejections for the cation were observed irrespective of the charge of the cation due to electroneutrality. The rejection of a monovalent cation (Na^+) could be negative only in the presence of ions with competing ions, such as multi-valent cations (Mg^{2+} or Ca^{2+}). This is good for water softening, eg., Na^+ is concentrated in the permeate while most of hard Mg^{2+} and Ca^{2+} ions are removed. The pressure affected the negative rejection significantly in pressure-driven separation processes. As can be seen in Figure 4, negative rejections of Na^+ were observed when the pressure was low (low flux), ie., at 100 kPa and 350 kPa. This was probably due to the Donnan exclusion and charge neutrality.

Modelling studies are helpful to understand the membrane performances. For example, Nielson et al. (1994) found in their data that computed negative rejections up to 1000% could be obtained at low pressures. The results of the reductions in negative rejections (more negative) obtained from modelling studies seemed to be consistent with the experimental results in this work. However, the model developed by Yaroshchuk (1995) based on irreversible thermodynamics had failed to analyze the transport properties of macroscopically homogeneous gels. Though some mathematical model successfully fitted

the performance of the commercial nanofiltration membranes, these models failed to fit the performance of the pore-filled cation-exchange membranes prepared in this study. Some models could qualitatively but not quantitatively describe the salt rejections as a function of the salt concentrations, based on the data shown in Figures 2, 3 and 4.

Table 3. Rejection of Inorganic Ions Using Pore-filled Cation-exchange Membranes [a]

Ion	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
Tap water [b]					
Ion concentration in feed (ppm)	23	7	30	21	30
Rejection (%)	-29	21	23	16	26
Synthetic solution [c]					
Ion concentration in feed, ppm ($\times 10^3$, M)	42 (*2.0*)	23 (*1.0*)	-	140 (*4.0*)	-
Rejection (%)	-25	45	-	58	-

[a] Pressure = 350 kPa at 25°C.

[b] Membrane #1: ion-exchange capacity = 2.2 meq/g, mass increase = 83%, crosslinking = 2.5%, ion-exchange concentration = 3.3 eq/kg, flux = 0.31×10^{-3} kg/m^{2}s.

[c] Membrane #2: ion-exchange capacity = 1.9 meq/g, mass increase = 80%, crosslinking = 2.5%, ion-exchange concentration = 3.3 eq/kg, flux = 0.33×10^{-3} kg/m^{2}s.

Conclusion

This paper has presented the results of evaluation of pore-filled cation-exchange membranes using a pressure-driven separation process. These membranes were found to be capable of rejecting single and mixed solute systems in pressure-driven processes. The flux and rejection were studied. Negative rejections for counterions were observed in mixed salt solutions in this study. The degree of negative rejection is affected by concentration ratio of the competing mobile ions, primarily depending on membrane ion-exchange concentration (Donnan exclusion). As we have previously shown the new class of pore-filled ion-exchange membranes are unique in that they can function effectively under pressure-driven pressures. The observation of negative separations of counterions is very important in the context of this study. The pore-filled cation-exchange membranes are able to concentrate mono-valent ion and reject bivalent ions. Thus, this allows the treatment of a water stream by removing bi-valent ions, e.g., Ca^{2+} and Mg^{2+}, and replacing them by mono-valent ions, such as Na^+.

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