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## **Ion Rejection in Single and Binary Mixed Electrolyte Systems by Nanofiltration: Effect of Feed Concentration**

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**Abstract:** The objectives of this work were to investigate and compare the separation behavior of ions in single and binary mixed electrolyte systems by NF70, with emphasis on the effect of feed concentration. Experimental results showed that the anion rejection is lower in the binary mixed system compared to the single salt system. Anion rejection decreases with the enhancement of feed concentration of co-existing electrolyte. As for cation rejection,  $\text{Na}^+$  rejection in the mixed electrolyte system is generally greater than that in the single NaCl system; whereas the separation performance of  $\text{Ca}^{2+}$  at high feed concentrations shows the opposite trend, and cannot be explained by the Donnan theory. Several possible mechanisms have been evaluated. Finally, the Spiegler-Kedem equation was used and parameters were calculated.

**Keywords:** Nanofiltration, Donnan exclusion, membrane separation, feed concentration, ion rejection

### **INTRODUCTION**

Nanofiltration (NF) is a pressure-driven separation technique used for the removal of ions and small organic compounds. The solute rejection is mainly determined by the solution compositions, operating conditions, and physico-chemical properties of both the solute and membrane (1). Several

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mechanisms are involved in the explanation of the rejection behavior of solutes in NF, including sieving effects, electrostatic repulsions, dielectric interactions, degree of hydration, and differences in diffusivity and solubility, or a combination of these. As for the transport of charged species, the electrostatic interaction between the membrane and solutes is more important and is usually explained by the well-known Donnan exclusion theory.

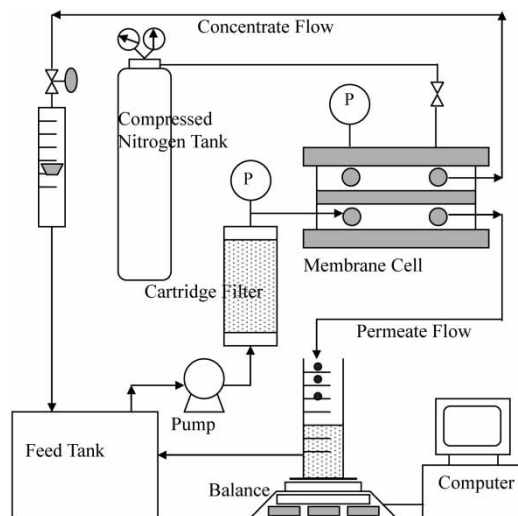
The separation performance of a NF membrane for single salts has been extensively investigated and the prediction of salt rejection has also been documented in the literature (2–5). The rejection to most single salt solutions by NF usually decreases with the growth of salt concentration (3–9). According to the elucidation of Wang et al. (6), the electrostatic effect is the major factor involved at low salt concentrations, whereas the steric-hindrance effect is the major factor at high salt concentrations.

Recently, more attention has been paid to the separation performance of a NF membrane for the mixed salts solution (8, 10–15). As a result of the interaction forces among various ions, the rejection properties in the mixed salt solutions become complex, and are different from those in the single salt solutions. Wang et al. (12) reviewed the prediction models in the mixed salts solution. However, the separation mechanisms for mixed salts solutions are not clearly understood and still need further investigation. Therefore, the objectives of this work were to investigate and compare the separation behavior of ions in single and binary mixed electrolyte systems by NF70, with the emphasis on the effect of feed concentration. The Spiegler-Kedem equation was used to modelize experimental data, and model parameters were calculated. Additionally, mechanisms responsible for the salt retention were evaluated and the limitations of the Donnan exclusion theory were discussed.

## MATERIALS AND METHODS

The Filmtec NF70, manufactured by Dow Chemical, was used. This membrane is a cross-linked aromatic polyamide thin film composite (TFC) membrane with molecular weight cut-off (MWCO) of about 200 Daltons. According to the literature data, NF70 is negatively charged at neutral pH (10, 16, 17). The water permeability coefficient of NF70 was reported to be 72.0 L/m<sup>2</sup>-h-MPa, and its retention of NaCl (0.2%) and MgSO<sub>4</sub> (0.2%) are 70% and 98%, respectively (16). Chemicals used in this experiment were reagent grade, and were used without further purification. Test solutions were prepared using deionized water (Milli-Q SP). Three salts, including NaCl, Na<sub>2</sub>SO<sub>4</sub>, and CaCl<sub>2</sub>, were chosen. Experiments with single electrolyte and binary mixed-electrolyte solutions (or called ternary electrolyte solutions), NaCl/Na<sub>2</sub>SO<sub>4</sub> and NaCl/CaCl<sub>2</sub> (common counter-ions and common co-ions) were performed.

Figure 1 is a schematic diagram of the membrane system used in this work. Experiments were carried out with the Osmonics Sepa CF cell made



**Figure 1.** Schematic diagram of the experimental setup.

of SS316 stainless steel. The operating pressure was provided by a pump and controlled by a backpressure regulator. The flat NF70 membrane sheet contained in the cell is 14.6 cm of length and 9.5 cm of width (the effective area is  $1.39 \times 10^{-2} \text{ m}^2$ ). The thickness of the spacer is 1.73 cm and was used to calculate the cross-sectional area of the membrane ( $9.5 \text{ cm} \times 1.73 \text{ cm}$ ). A 1- $\mu\text{m}$  paper cartridge filter was installed upstream of the membrane cell in order to eliminate potential dirtiness. The feed stream was pumped from a 20 L feed tank, kept at  $25^\circ\text{C}$ , into the membrane cell and flowed tangentially to the membrane. After the flow-rate measurement, both permeate and concentrate streams were recycled into the feed tank in order to work at constant feed concentration. Experiments were performed at applied pressures ranging from 414 to 1103 kPa and the cross-flow velocity was fixed at 0.15 m/s. The solution pH was not controlled or adjusted to a specific level in this study. It ranged between 5.5 and 6.5 throughout the course of each experiment.

At the beginning of each experiment, the membrane was pre-conditioned by deionized water at the specified operating pressure until it reached a constant permeation flux. Subsequently, the feed solution, containing predetermined concentrations of various electrolytes, was instantaneously introduced into the system. The run time required for the membrane system to reach steady state was usually about 24 h. After the system reached steady state, samples of permeate and concentrate solutions were collected and concentrations were measured. As for ion concentration measurements, an inductively-coupled plasma atomic emission spectrophotometer (ICP-AES,

Perkin Elmer, Optima 2000DV) and a Dionex-120 ionic chromatograph using a IonPac® AS4A-SC column and a conductivity detector were used to measure the cation ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) and anion ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) concentrations, respectively. For the single-electrolyte solution, conductivity was also measured (Mettler Toledo, MC 266) to represent the salt concentration. The permeate flux was determined by measuring the volume of permeate collected during a given time interval. Rejection rate is derived from the following relation:

$$R \text{ (\%)} = \left(1 - \frac{C_p}{C_o}\right) \times 100 \tag{1}$$

where  $C_p$  and  $C_o$  are the concentrations in permeate and the feed solution, respectively. Since the operating conditions of this study were adjusted to prevent the formation of concentration polarization layer, the concentration of feed solution at the entering surface of membrane ( $C_o$  in equation (1)) can be assumed to be the feed concentration in the bulk.

RESULTS AND DISCUSSION

Effect of Operating Conditions in the Single Electrolyte System

The effect of applied pressure on rejection and permeate flux for three single electrolyte solutions, is shown in Fig. 2. The permeate flux increases linearly with the enhancement of applied pressure. It reveals that the increase of applied pressure would promote the transport of solvent (water) molecules through the NF70 membrane. If the effective pressure difference ( $\Delta P_e$ ) is calculated by deducting the osmotic pressure difference across the membrane  $\Delta \pi$  from the values of applied pressure  $\Delta P$  (that is,  $\Delta P_e = \Delta P - \Delta \pi$ ) the

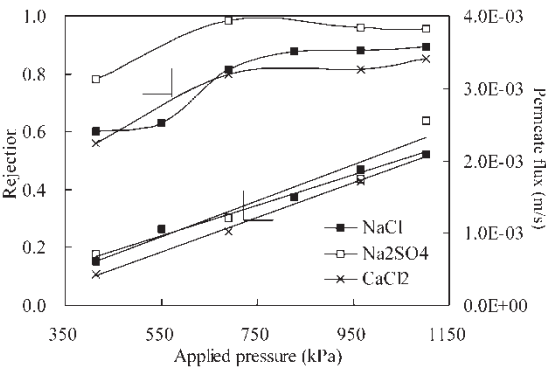
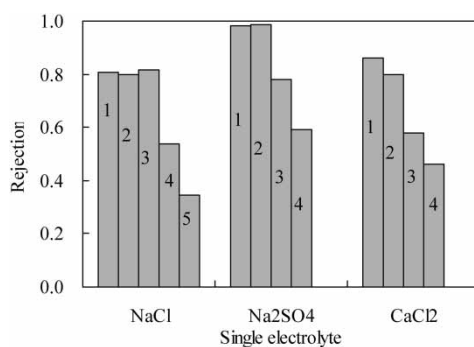


Figure 2. Effect of applied pressure on rejection and permeate flux of the single electrolytes (NaCl: 0.0278 M; Na<sub>2</sub>SO<sub>4</sub>: 0.0139 M; CaCl<sub>2</sub>: 0.0139 M).

linear dependency of the permeate volume flux on the effective pressure difference can still be observed. It is also noted that the permeate flux of three electrolytes has similar levels. On the other hand, rejection of the single salt solution first increases as the applied pressure increases, and then reaches a steady state. When the applied pressure rises from 414 to 689 kPa, the increase of permeate flux is greater than that of the solute flux. The corresponding rejection consequently increases. For experiments conducted with higher applied pressure, both solute and solvent passing through the membrane have the similar increments, resulting in a generally steady value of rejection. Similar experimental results were reported by several researchers (2, 8, 18, 19). Some attributed the phenomena to the counteracting contributions of both convective transport and concentration polarization. However, the linearity between permeate flux and applied pressure shown in Fig. 2 indicates an absence of concentration polarization. On the other hand, Paugam et al. (8) interpreted the result as the relative magnitude of membrane surface forces (including the friction and electrostatic forces) and convective forces. Surface forces remain constant as the applied pressure increases; whereas convective forces increase with the applied pressure. At low pressure, surface forces are stronger than convective forces. Therefore, the solute flux remains steady, while the solvent flux still increases with the pressure, which leads to an increase in the rejection rate (8). Above a certain pressure, the convective forces become comparable to or even greater than the surface forces. Consequently, the solute flux grows and the rejection rate reaches a steady state.

Rejection of three single salt solutions is depicted with different feed concentrations, as shown in Fig. 3. Figure 3 shows that rejection is generally decreased with the growth of feed concentration for all three electrolytes tested. Similar experimental observations were reported by several researchers (3–9). Peeters et al. (3) interpreted the result by the Donnan exclusion model,



**Figure 3.** Rejection of single electrolyte (NaCl, Na<sub>2</sub>SO<sub>4</sub>, and CaCl<sub>2</sub>) under various feed concentrations (1: 0.00556 M; 2: 0.0139 M; 3: 0.0278 M; 4: 0.0556 M; 5: 0.139 M) ( $\Delta P = 689$  kPa).

because the effect of Donnan exclusion reduces with increasing feed electrolyte concentrations. In the case of a higher ionic strength, the membrane charge will be extensively shielded, resulting in a lower effective charge and, consequently the retention is decreased. The results of  $\Delta P_e$ , the permeate, and the solute flux were calculated to elucidate the mechanism, as shown in Table 1. The permeate flux usually decreases with the increase of feed concentration; while solute flux reveals an opposite trend and increases accordingly. Table 1 also indicates the increase of solute flux with increasing feed concentration is more pronounced than the decrease of permeate flux. The reduction of  $\Delta P_e$  with the increase of feed concentration ought to have a contribution to the decrease of permeate flux and rejection, based on the findings shown in Fig. 2. On the other hand, the increase of the solute flux might be explained by the Donnan theory, as suggested by Peeters et al. (3). It can also be attributed to the greater concentration driving force across the membrane as the feed concentration increases, which promotes the passage of solutes through the membrane.

Besides, Wang et al. (6) explained that the increase of feed concentration compresses the thickness of electrical double layer and, consequently, the effective area of the membrane pore becomes larger. However, this interpretation is inconsistent with the experimental observations shown in Table 1. Both the solute and solvent flux would show comparable increments in case that the membrane pore becomes larger.

The rejection sequence is discussed based on the results shown in Fig. 3. It generally reveals the following sequence:  $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{CaCl}_2$ . NF70 is generally considered as the negatively charged membrane (10, 16, 17), the

**Table 1.** Effect of feed concentration on the permeate and solute flux for the single electrolyte systems ( $\Delta P = 689$  kPa)

System	Feed conc. (M)	$\Delta P_e$ (kPa)	Permeate flux (m/s)	Solute flux (mol/m <sup>2</sup> -s)
NaCl	$5.56 \times 10^{-3}$	667	$1.78 \times 10^{-3}$	$2.28 \times 10^{-5}$
	$1.39 \times 10^{-2}$	634	$1.53 \times 10^{-3}$	$5.02 \times 10^{-5}$
	$2.78 \times 10^{-2}$	577	$1.23 \times 10^{-3}$	$7.44 \times 10^{-5}$
	$5.56 \times 10^{-2}$	541	$1.32 \times 10^{-3}$	$3.98 \times 10^{-4}$
	$1.39 \times 10^{-1}$	452	$5.78 \times 10^{-4}$	$6.22 \times 10^{-4}$
$\text{Na}_2\text{SO}_4$	$5.56 \times 10^{-3}$	649	$1.72 \times 10^{-3}$	$2.26 \times 10^{-6}$
	$1.39 \times 10^{-2}$	588	$1.20 \times 10^{-3}$	$2.96 \times 10^{-6}$
	$2.78 \times 10^{-2}$	528	$1.29 \times 10^{-3}$	$9.30 \times 10^{-5}$
	$5.56 \times 10^{-2}$	446	$1.03 \times 10^{-3}$	$2.78 \times 10^{-4}$
	$5.56 \times 10^{-3}$	654	$1.30 \times 10^{-3}$	$1.19 \times 10^{-5}$
$\text{CaCl}_2$	$1.39 \times 10^{-2}$	607	$1.02 \times 10^{-3}$	$3.34 \times 10^{-5}$
	$2.78 \times 10^{-2}$	570	$8.75 \times 10^{-4}$	$1.21 \times 10^{-4}$
	$5.56 \times 10^{-2}$	499	$4.96 \times 10^{-4}$	$1.76 \times 10^{-4}$

higher rejection for  $\text{Na}_2\text{SO}_4$  (bivalent co-ion, monovalent counter-ion) and the lower rejection for  $\text{CaCl}_2$  (bivalent counter-ion, monovalent co-ion), and  $\text{NaCl}$  (both monovalent ions) are in accordance with the Donnan exclusion theory. The  $\text{Na}_2\text{SO}_4$  system with a more negative anion valence will create a higher electrostatic repulsion from the negatively charged NF membrane, and therefore a higher removal of ions is observed.

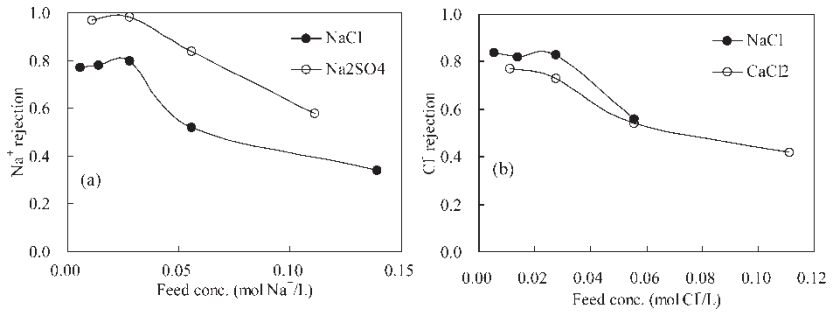
Additionally, based on the Donnan exclusion model, the permeation for salts with a bivalent counter-ion ( $\text{CaCl}_2$ ) should be higher than those with monovalent counter-ion ( $\text{NaCl}$ ), because  $\text{CaCl}_2$  has a greater attraction force with the negatively charged membrane.

It is also worth noting from Fig. 3 that at lower feed concentrations rejection of  $\text{NaCl}$  is roughly equal to that of  $\text{CaCl}_2$ . Peeters et al. (3) and Schaep et al. (4) have reported the effect of diffusion coefficient on rejection. Diffusion coefficients for  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{Na}_2\text{SO}_4$  are  $1.61 \times 10^{-9}$ ,  $1.45 \times 10^{-9}$ ,  $1.23 \times 10^{-9} \text{ m}^2/\text{s}$ , respectively (3, 4). The salt with the lower diffusion coefficient is supposed to possess the higher retention rate. In comparison with the explanation of the Donnan theory, the influence of the diffusion coefficient on the rejection of  $\text{NaCl}$  and  $\text{CaCl}_2$  makes the opposite contribution. Consequently, the similar rejection results for  $\text{NaCl}$  and  $\text{CaCl}_2$  solution at lower feed solutions might be explained by the counter-contributions of both the Donnan exclusion phenomena and the effect of the diffusion coefficient.

Figure 4 shows the rejection behavior of the common ion in the individual single electrolyte solution. It indicates that the  $\text{Na}^+$  rejection is significantly higher in a solution containing sulfate ion than that containing chloride ion (Figure 4(a)). Several other researchers reported similar experimental results (2, 4, 7, 18). The fact that the  $\text{Na}^+$  rejection is enhanced with the presence of bivalent anion can be explained by the Donnan exclusion theory. Anions are excluded as the membrane is negatively charged, and cations are also rejected together with anions due to the condition of electroneutrality at both sides of the membrane. Rejection is enhanced with more negative anion valence (i.e. the  $\text{Na}_2\text{SO}_4$  system) owing to increased electrostatic repulsion by the membrane.

In comparison with the rejection behavior of  $\text{Na}^+$ , the difference between  $\text{Cl}^-$  rejection in the  $\text{NaCl}$  and  $\text{CaCl}_2$  solutions is not so significant, as demonstrated in Fig. 4(b). According to the Donnan exclusion theory, co-ions (anions in this study) play a more important role. In other words, membrane selectivity is usually determined by the valence of the co-ion, and to a lesser extent by the valence of the counter-ion (13). Therefore, the differences of selectivity between solutions of common co-ion ( $\text{Cl}^-$  rejection in Fig. 4(b)) are not large.

In addition to the qualitative discussion, experimental findings were also explained quantitatively. Figure 5 shows that the rejection of NF70 membrane to three single electrolytes, increases with the growth of permeate flux. The relationship of rejection and flux for the permeation of three single salts



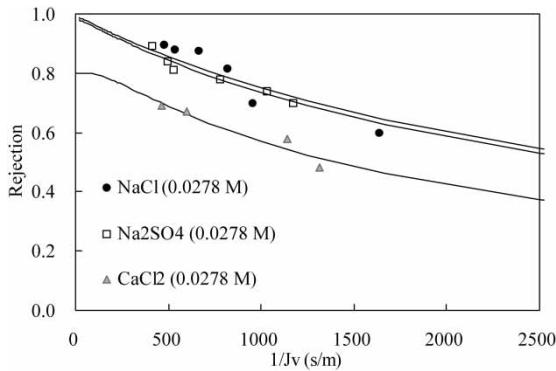
**Figure 4.** (a) Na<sup>+</sup> rejection in NaCl and Na<sub>2</sub>SO<sub>4</sub> single electrolyte solution; (b) Cl<sup>-</sup> rejection in NaCl and CaCl<sub>2</sub> single electrolyte solution, as a function of feed concentrations ( $\Delta P = 689$  kPa).

was fitted based on the Spiegler-Kedem equation (4, 20):

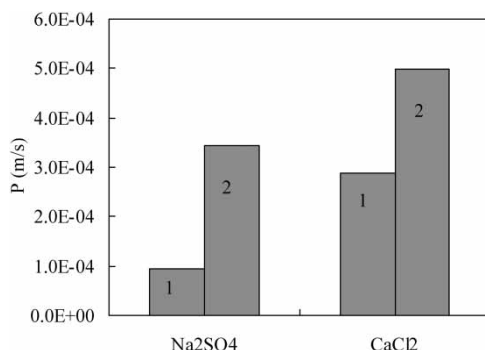
$$R = \frac{\sigma(1 - F)}{1 - \sigma F} \quad \text{with} \quad F = \exp\left(-\frac{1 - \sigma}{P} J_v\right) \quad (2)$$

where  $R$  is rejection;  $J_v$  is the permeate flux;  $\sigma$  is the reflection coefficient; and  $P$  is the solute permeability.

The Spiegler-Kedem equation can be applied to explain the separation performances of a NF system when the mechanisms of the solute transport processes are not fully understood. Calculations of rejection results were performed using the Spiegler-Kedem equation and fitted curves are demonstrated in Fig. 5.  $\sigma$  corresponds to the maximum rejection at infinite permeate flux. Data pairs of  $R$  and  $J_v$  were substituted into equation (1) and  $\sigma$  and  $P$  were iteratively determined by a best-fit method. Except for CaCl<sub>2</sub> at the concentration of  $2.78 \times 10^{-2}$  M, the reflection coefficients to three



**Figure 5.** Rejection of NF70 membrane to three single electrolytes as a function of the permeate flux. The curves were fitted by the Spiegler-Kedem equation.



**Figure 6.** The solute permeability of NF70 to Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> at various feed concentrations (1: 0.0139 M; 2: 0.0278 M).

salts are larger than 0.95. Figure 6 shows the dependency of the solute permeability for Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub>, on feed concentration. The solute permeability increases with increasing feed concentration, which is consistent with the findings in Fig. 3. The reason has been discussed previously.

### Rejection in the Binary Mixed Electrolyte Systems

Two binary mixed electrolyte solutions (that is, ternary electrolyte solutions), NaCl/Na<sub>2</sub>SO<sub>4</sub> and NaCl/CaCl<sub>2</sub> (common counter-ions and common co-ions), with various feed concentrations were studied. Rejection results and a comparison with the single electrolyte system are shown in Tables 2–4.

As for the anion rejection, Cl<sup>−</sup> rejection in the binary electrolyte NaCl/Na<sub>2</sub>SO<sub>4</sub> solution is less than that in the single NaCl solution under identical feed concentration, as shown in Table 2. For example, at the NaCl feed concentration of  $2.78 \times 10^{-2}$  M, Cl<sup>−</sup> rejection in the NaCl solution is 0.83; whereas Cl<sup>−</sup> rejection drops to the range of 0.53 to 0.66 with the presence of Na<sub>2</sub>SO<sub>4</sub>. Moreover, Cl<sup>−</sup> rejection decreases accordingly as the feed concentration of co-existing Na<sub>2</sub>SO<sub>4</sub> increases. The results for SO<sub>4</sub><sup>2−</sup> rejection exhibit the similar trends. SO<sub>4</sub><sup>2−</sup> rejection in the binary electrolytes is less than that in the single electrolyte. Also, SO<sub>4</sub><sup>2−</sup> rejection decreases with the enhancement of the feed concentration of co-existing NaCl. Similar results were found in other works (8, 10, 15, 18). Overall, the anion rejection is lower in the binary mixed system compared to the single salt system. Anion rejection decreases with the enhancement of feed concentration of co-existing electrolyte. The increase in osmotic pressure, due to the presence of other electrolyte, yields a lower  $\Delta P_e$  and will also affect anion rejection. One of the other possible explanations is assuming that the role of co-existing electrolyte is similar to the target electrolyte itself. That is, the

**Table 2.** Comparison of anion rejection in the single and binary mixed electrolyte systems ( $\Delta P = 689$  kPa)

System	Feed conc. (M)	Anion rejection in the single solution	Anion rejection in NaCl + Na <sub>2</sub> SO <sub>4</sub> (feed conc. of the co-existing electrolyte, M)
NaCl	$2.78 \times 10^{-2}$	0.83	0.53 ( $2.78 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.83	0.56 ( $1.39 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.83	0.66 ( $5.56 \times 10^{-3}$ )
	$5.56 \times 10^{-3}$	0.84	0.81 ( $2.78 \times 10^{-2}$ )
Na <sub>2</sub> SO <sub>4</sub>	$5.56 \times 10^{-3}$	0.99	0.80 ( $2.78 \times 10^{-2}$ )
	$1.39 \times 10^{-2}$	0.99	0.58 ( $2.78 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.90	0.54 ( $2.78 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.90	0.62 ( $5.56 \times 10^{-3}$ )

**Table 3.** Comparison of cation rejection in the single and binary mixed electrolyte systems ( $\Delta P = 689$  kPa)

System	Feed conc. (M)	Cation rejection in the single solution	Cation rejection in NaCl + CaCl <sub>2</sub> (feed conc. of the co-existing electrolyte, M)
NaCl	$2.78 \times 10^{-2}$	0.80	0.79 ( $2.78 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.80	0.85 ( $1.39 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.80	0.94 ( $5.56 \times 10^{-3}$ )
	$5.56 \times 10^{-3}$	0.77	0.81 ( $2.78 \times 10^{-2}$ )
CaCl <sub>2</sub>	$5.56 \times 10^{-3}$	0.95	0.90 ( $2.78 \times 10^{-2}$ )
	$1.39 \times 10^{-2}$	0.87	0.94 ( $2.78 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.62	0.95 ( $2.78 \times 10^{-2}$ )
	$2.78 \times 10^{-2}$	0.62	0.99 ( $5.56 \times 10^{-3}$ )

**Table 4.** The solute permeability (P) of Cl<sup>−</sup> and SO<sub>4</sub><sup>2−</sup> in the single and binary mixed electrolyte systems

Feed conc. of NaCl (M)	Feed conc. of Na <sub>2</sub> SO <sub>4</sub> (M)	Solute permeability of Cl <sup>−</sup> (m/s)	Solute permeability of SO <sub>4</sub> <sup>2−</sup> (m/s)
$2.78 \times 10^{-2}$	0	$3.26 \times 10^{-4}$	—
0	$2.78 \times 10^{-2}$	—	$3.44 \times 10^{-4}$
$2.78 \times 10^{-2}$	$2.78 \times 10^{-2}$	$7.52 \times 10^{-4}$	$6.39 \times 10^{-4}$
$2.78 \times 10^{-2}$	$5.56 \times 10^{-3}$	$4.05 \times 10^{-4}$	$5.78 \times 10^{-4}$
$5.56 \times 10^{-3}$	$2.78 \times 10^{-2}$	$1.29 \times 10^{-4}$	$1.76 \times 10^{-4}$

existence of the co-existing electrolyte and the increase of its feed concentration might have a similar effect to that of the increase of feed concentration of the target electrolyte. Increasing of electrolyte concentration would compress the thickness of the electrical double layers at the interface of the membrane and the influent solution, resulting in the destabilized condition around the membrane. Therefore, the charge effect becomes less effective and more salts permeate through NF70. Consequently, the rejection rate for ions is reduced.

Garcia-Aleman and Dickson (13) explained the results based on Donnan exclusion theory.  $\text{Cl}^-$  permeates preferentially compared to  $\text{SO}_4^{2-}$  because the former has a lower valence. Consequently, the  $\text{Cl}^-$  rejection decreases as more  $\text{SO}_4^{2-}$  is added to the feed solution. However, this mechanism cannot explain the separation behavior of  $\text{SO}_4^{2-}$  when  $\text{Cl}^-$  ions appear in the solution.

As for cation rejection, results of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  rejection display different patterns from anions, as shown in Table 3.  $\text{Na}^+$  rejection in the mixed-electrolyte system is generally greater than that in the single NaCl system. Except for the case at  $\text{CaCl}_2$  feed concentration of  $5.56 \times 10^{-3}$  M,  $\text{Ca}^{2+}$  rejection in the mixed electrolyte system is also greater than that in the single  $\text{CaCl}_2$  system. According to the Donnan exclusion theory, the negatively charged membrane has a greater attraction for a divalent counter-ion ( $\text{Ca}^{2+}$ ). Therefore,  $\text{Ca}^{2+}$  should permeate preferentially through the membrane along with the co-ion. The monovalent counter-ion ( $\text{Na}^+$ ) would be rejected preferentially by the membrane. The experimental observation for  $\text{Na}^+$  can be explained by this mechanism. For example, at NaCl feed concentration of  $2.78 \times 10^{-2}$  M,  $\text{Na}^+$  rejection in the single NaCl solution is 0.80; whereas  $\text{Na}^+$  rejection increases to the range of 0.85 to 0.94 with the addition of  $\text{CaCl}_2$ . However, the separation performance of  $\text{Ca}^{2+}$  at the higher feed concentration was opposite to the mechanism, as shown in Table 3. At  $\text{CaCl}_2$  feed concentration of  $1.39 \times 10^{-2}$  M and  $2.78 \times 10^{-2}$  M,  $\text{Ca}^{2+}$  rejection in the NaCl +  $\text{CaCl}_2$  mixed solution is greater than that in the single  $\text{CaCl}_2$  solution.

Other researchers have attributed the discrepancy to the phenomena of ion adsorption and charge inversion (4, 13). Garcia-Aleman and Dickson (13) reported that permeating ions of higher valences have a stronger tendency to adsorb on the surface of a charged membrane. If the amount of adsorbed ions is large enough, then the charge of the membrane may be neutralized or it may even experience a change of sign. According to this explanation, once  $\text{Ca}^{2+}$  ions are adsorbed and the membrane becomes positively charged,  $\text{Na}^+$  ions will permeate preferentially compared to  $\text{Ca}^{2+}$  ions. This is partly consistent with the experimental observation in our study. Both  $\text{Na}^+$  and  $\text{Ca}^{2+}$  rejection increase in the binary electrolyte solution and in most cases, the latter possesses a greater rejection. Another possible explanation is that the adsorption of  $\text{Ca}^{2+}$  ions may block the openings of the membrane. The permeation of both  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations

are consequently reduced and a higher rejection obtained. However, the phenomenon of counter-ion adsorption is not found in the results of single electrolyte systems. It seems to suggest that the presence of the divalent counter-ions and its high concentration are not the only causes of the charge inversion.

The Spiegler-Kedem equation was also used to examine the relationship between rejection and permeate flux of the binary mixed electrolyte systems. The solute permeability of anions was evaluated and compared with results of the single electrolyte system, shown in Table 4. The trend in the solute permeability is generally consistent with the experimental data shown in Table 2. The solute permeability for anions in the single salt solution is usually less than that in the binary electrolyte solution. Furthermore, anion permeation increases with the increase of the feed concentration of co-existing salts. Data on the solute permeability demonstrates again the effect of a co-existing electrolyte, and the possible explanations have been discussed previously.

## CONCLUSIONS

Effects of feed concentration and operating pressure on the rejection of three single electrolytes, as well as the corresponding rejection mechanisms, are discussed in this investigation. Rejection was generally decreased with the growth of feed concentration for all three electrolytes tested, which can be explained by the Donnan exclusion model. The effective pressure difference and solute flux were also calculated to elucidate the mechanism. As for the rejection sequence, the similar levels of rejection of  $\text{CaCl}_2$  and  $\text{NaCl}$  at lower feed concentrations cannot be described solely by the Donnan exclusion theory. The effect of diffusion coefficients should also be taken into consideration.

In the binary mixed electrolyte systems, the anion rejection is lower compared to that in the single salt system. The findings reveal that anion rejection decreases with the enhancement of feed concentration of co-existing electrolyte. As for cation rejection,  $\text{Na}^+$  rejection in the mixed electrolyte system, is generally greater than that in the single  $\text{NaCl}$  system; whereas the separation performance of  $\text{Ca}^{2+}$  at higher feed concentrations showed the opposite trend and cannot be explained by the Donnan theory. Several possible mechanisms have been evaluated.

The Spiegler-Kedem equation was also used to examine the relationship between rejection and permeate flux for both single and binary mixed electrolyte systems. The solute permeability for anions in the single salt solution is usually less than that in the binary electrolyte solution. Furthermore, anion permeation increases with the increase of the feed concentration of co-existing salts.

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