Nanofiltration of Electrolytes with Charged Composite Membranes

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Abstract: A characterization of the permeation and separation using single salt solution was carried out with charged composite membranes. Various charged composite membranes were fabricated by blending an ionic polymer with a nonionic polymer in different ratios. In this study, sodium alginate, chitosan and poly(vinyl alcohol) were employed as anionic, cationic and nonionic polymers, respectively. The permeation and separation behaviors of the aqueous salt solutions have been investigated through the charged composite membranes with various charge densities. As the content of the ionic polymer increased in the membrane, the hydrophilicity of the membrane increased, and pure water flux and the solution flux increased correspondingly, indicating that the permeation performance through the membrane is determined mainly by its hydrophilicity. Electrostatic interaction between the charged membrane and ionic solute molecules, that is, Donnan exclusion, was observed to be attributed to salt rejection to a greater extent, and molecular sieve mechanism was effective for the separation of salts under a similar electrostatic circumstance of solutes.

Keywords: ionic polymer, charged composite membrane, charge effect

1. Introduction

Nanofiltration (NF) is a relatively new membrane process located between Ultrafiltration(UF) and Reverse osmosis(RO), and its application is rapidly growing in water treatment for removal of natural organic matter, salts, dyes and organic molecules.

The process has the advantage of low operating pressure compared to RO and a high rejection of salts compared to UF. One of the most important features of NF membranes is their ability to separate ions from water. Possible mechanisms for the separation of electrolytes are (i) sieving, (ii) electrostatic interactions between the ions and (iii) differences in diffusivity and solubility or a combination of those. Their separation potentials for ionic solutes in aqueous solutions can be explained with the chemical potential gradient and the

electrical potential gradient as driving force. Thus, the transport of the ions across the charged membranes is well described by the extended Nernst-Planck flux equation(1) in terms of diffusion and migration terms, as a result of concentration and electrical potential gradient. In the charged membrane in contact with an electrolyte solution, the concentration of co-ions, i.e, ions with the same charge as the membrane, in the membrane will be lower than that in solution, whereas the counter-ions, which have the opposite charge, have a higher concentration in the membrane than in the solution. On account of this concentration difference of the ions, a potential difference is generated at the interface between the membrane and the solution to maintain electrochemical equilibrium between solution and membrane. By this potential, which is called the Donnan potential, co-ions are repelled by the membrane, whereas counter-ions are attracted. Therefore, the separation mechanism of charged membranes can

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be based upon not only the "sieve effect"but also the "charge effect". The charge effect on ion separation depends upon the valence type of the ion, and thus there is a possibility of ion separation according to valence type(1~8).

$$J_i = -D_i \frac{d c_i}{dx} - \frac{z_i \, c_i \, d_i}{RT} F \frac{d\phi}{dx} \qquad (1)$$

2. Experimental Methods

Materials

· PVA(Poly(vinyl alcohol) was purchased from Aldrich. The average molecular weight and saponification of the PVA were 30,000 and 99%.

SA(Sodium alginate) and CS(Chitosan) were purchased from Showa Chemical(Tokyo, Japan), glutaraldehyde (GA) (25% content in water, pure grade) and hydrochloric acid (35% content guaranteed reagent), sulfonic acid from Junsei Chemical(Tokyo, Japan).

Calcium chloride(extrapure grade) from Oriental Chemical (Seoul, Korea) and sodium dodecylbenzenesu lfonate (SDS) was purchased from Aldrich.

GA and calcium chloride were used as cross-linking agents of PVA and SA, respectively, and HCl was used as a catalyst in the cross-linking reation between PVA and GA. Sulfonic acid was used as cross-linking agents of CS. SDS was used as surfactant. A commercial polysulfone (PSU) ultrafiltration membrane was used as a support membrane.

The support membrane was generously provided by Saehan(Seoul, Korea). The membrane has an asymmetric structure supported by nonwoven polyester fabric. The molecular cut-off of the Saehan membraen was 30,000. Ultrapure deionized water was used. All chemicals were used without further purification

Membrane Preparation
Anionic composite membranes

To fabricate thin film anionic composite membrane, hydrophilic polymers(PVA,SA) were coated in thin film on hydrophobic support membrane. 1 wt% PVA,

SA solutions were prepared by dissolving in deionized water. First, the PSU support membrane was pretreated with 1.5 wt% GA solution in water for 30 min to increase its surface energy or to increase its wettability by dipping in its aqueous solution. Thereby, the reactant molecules were dispersed in the pores and the surface of support so that the polymers could be coated uniformly thin on the support surface by an interfacial reaction between the reactant and the hydrophilic polymers. And then the PSU support membrane was dipped in blending an ionic polymer (SA) with a nonionic polymer(PVA) in different ratios and 0.1 wt% surfactant(SDS) for 5 min. And then coating layer was crosslinked for 10 min with an aqueous solution containing 7 wt% GA, 0.15 wt% HCl, and 1.5 wt% CaCl$_2$ in water. After the cross-linking reation, the membranes were taken out of the reaction solution, and then dried under vaccum for 24 hr. The dried membranes were washed out several times with pure water to eliminate any possible residual HCl and GA

Cationic Composite Membranes

The cationic composite membranes were made subsequently in the same way as in fabricating the anionic membranes, with the exception of using CS instead of SA in the hydrophilic polymers. The membranes were soaked in the crosslinking solution containing 7 wt% GA and 0.5 wt% H$_2$SO$_4$ in water for 10min. The procedure for the preparation of pure PVA, SA, and CS membranes is described elsewhere (9,10).

Permeation and Separation Experiments

The schematic nanofiltration test apparatus is shown in Fig. 1. It consists of four flat sheet membrane cells, and a closed loop recycle system in which the piping, fittings, and the cells were made of SS-316. A diaphragm pump (Hydro-cell Model-13, Wanner Engineering Inc, Minnesota) equipped with a pressure regulating valve(Model C46), was used for recycling the electrolyte solution through the system under
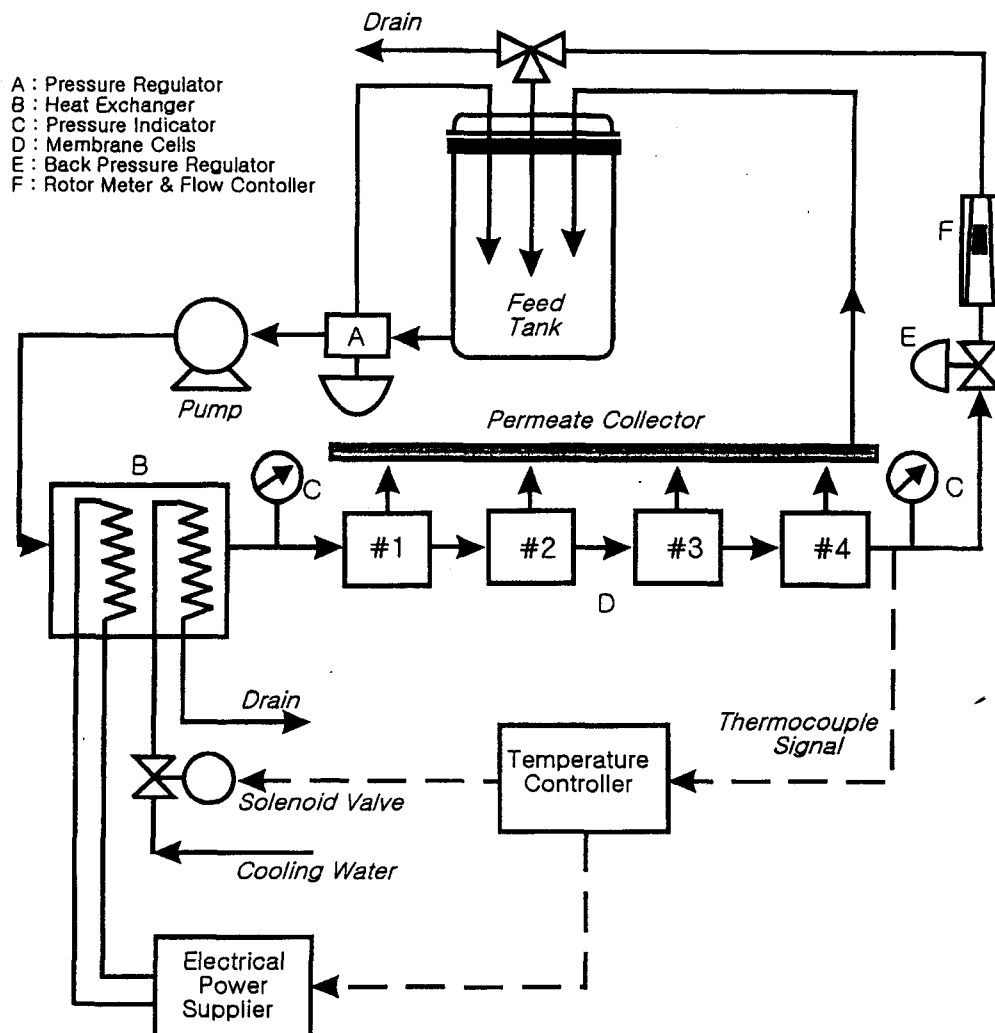
Fig. 1. A schematic representation of a nanofiltration test apparatus.

pressure. The membrane cell was designed to allow a high fluid velocity parallel to the membrane cell was 19.63 cm². The feed solution from the tank was pumped through a heat exchanger and the four membrane cells in series and into a back-pressure regulator (TESCOM Corporation, Minnesota) through stainless steel tubing. The low-pressure retentate circulated from the back-pressure regulator through a rotameter (Brooks Instrument Division, Emerson Electric Co, Minnesota) and returned to the feed tank. Temperature was monitored in the feed line and in the retentate line by K-type thermocouples using a digital thermometer (Han Young Model DX7, Seoul, Korea).

The membranes were rinsed with deionized water

before using. Pure water was pressurized and circulated over the surface of the membranes at 50 bar for at least 4hr before any measurements to minimize any effect of membrane compacting.

After pressurizing the membrane and then adjusting the feed pressure to a desired value, pure water fluxes(PWFs) were measured. The feed solutions were the electrolyte solutions with a solute content of 5, 10, 15 mmol. The feed flow through the system was maintained at 1.0 L/min and the feed temperature was kept constant at 30±0.1°C. Samples of the permeate were collected at various time intervals to determine the permeate flux through the membrane. The conductivities of the permeate and feed solutions were
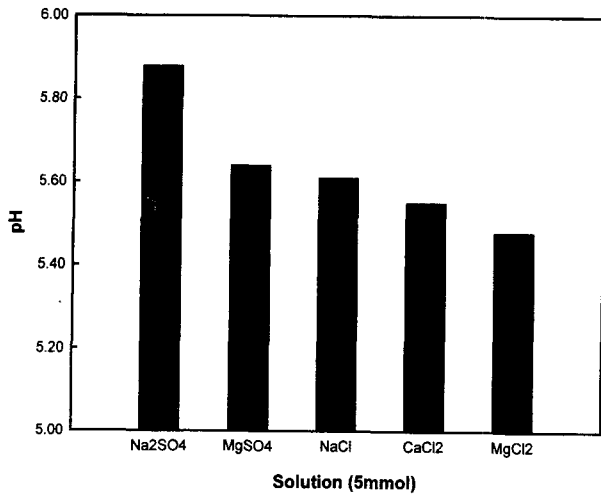
Fig. 2. pH of electrolyte solutions at 30°C and 500 ppm of solute content (Na_2SO_4, $MgSO_4$, NaCl, $MgCl_2$, $CaCl_2$).

measured by a Conductance-Resistance Meter (YSI Mode 34, YSI Scientific, Ohio). The rejection exhibited on a membrane was defined as

$$Rejection\ (\%) = 1 - \frac{C_P}{C_F}$$

where C_P and C_F are salt concentrations in bulk permeate and feed, respectively. The fluxes and rejections were determined by multiple replication.

3. Result and Discussion

Figure 2 presents the pH values of the electrolyte solutions used in this study. All of them show a weak acidic characteristic. Electrolytes with Cl^- were more acidic than those with SO_4^{2-}. The difference in pH between the electrolyte solutions would presumably affect the swelling behavior of an ionic membrane as well as its membrane performance, depending on the charged ionic property of the membrane.

Figures 3 and 4 show the plots of pure water flux(PWF) through anionic and cationic membranes against the content of ionic polymer in membranes at 30°C, respectively. Both membranes had an increase in pure water flux with increasing ionic polymer content in them. As mentioned before, as ionic polymer
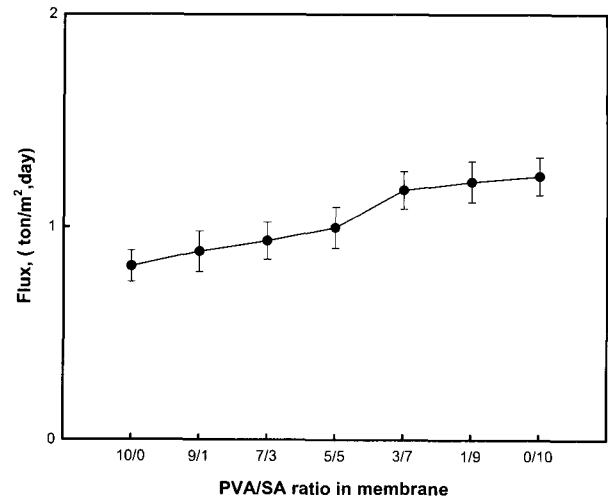

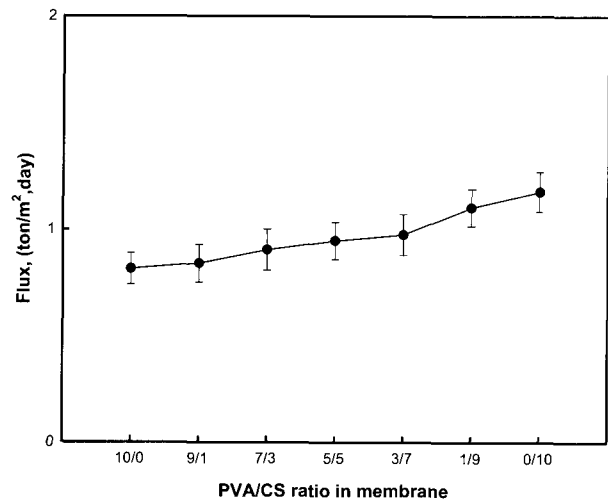Fig. 3. Pure water flux of anionic membranes with PVA/SA ratio in membranes at 30°C and a feed pressure of a 20 kgf/cm^2.

Fig. 4. Pure water flux of cationic membranes with PVA/CS ratio in membranes at 30°C and a feed pressure of a 20 kgf/cm^2.

content in membranes increased, the resulting membrane became more hydrophilic(9,10).

Figures 5 and 6 and 7 show the fluxes of electrolyte solutions through the membranes which were normalized by dividing them by their PWFs to explain the flux change relative to PWF at different feed concentration.

The fluxes normalized with respect to PWF, that is, ratios of solution flux to PWF, were plotted against the SA content in the membranes in Figures 5, 6 and 7.
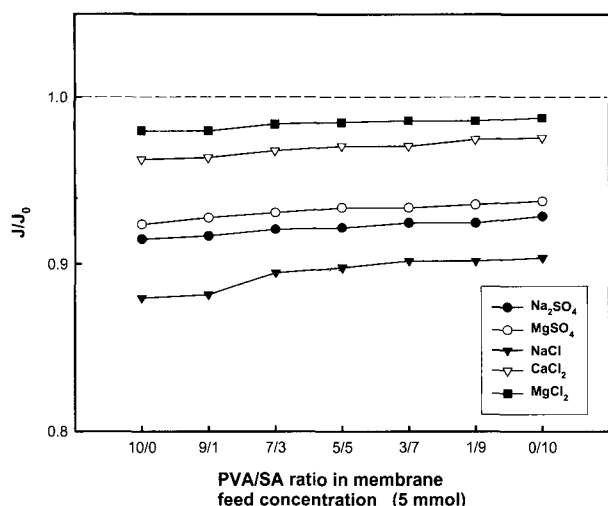
Fig 5. Flux ratios of PVA/SA membrane at 30°C and a feed pressure of 20 kgf/cm² ; J= solution flux, J₀= pure water flux, solute concentration in feed= 5 mmol.
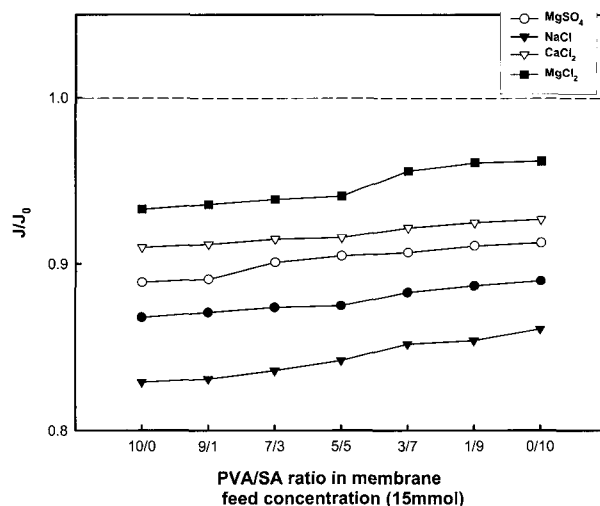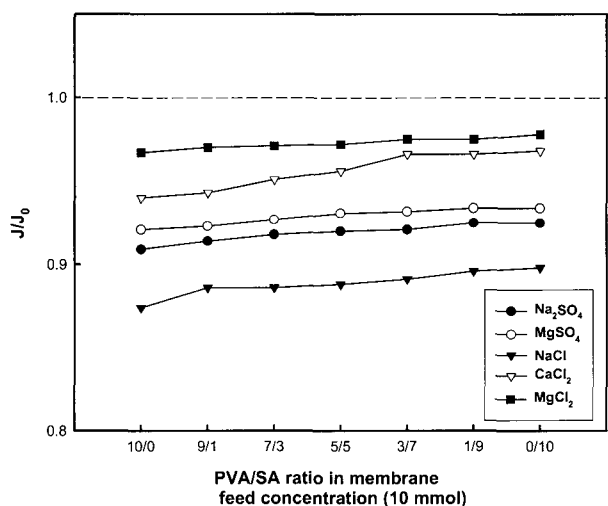

Fig 7. Flux ratios of PVA/SA membrane at 30°C and a feed pressure of 20 kgf/cm² ; J= solution flux, J₀= pure water flux, solute concentration in feed= 15 mmol.

Fig 6. Flux ratios of PVA/SA membrane at 30°C and a feed pressure of 20 kgf/cm² ; J= solution flux, J₀=pure water flux, solute concentration in feed= 10 mmol.

At first, the solution flux through the anionic membrane decreased in comparison to PWF, dependence on the type of salt is exactly the same as the swelling ratio sequence in the previous work(9). The lower pH value of a salt solution, lead to the higher the flux of the solution through the membrane. A although NaCl solution had not the highest value of pH, exceptionally its flux was the lowest among the solutions used in this study. The lowest flux of NaCl solution is much likely to be due to the remarkable

osmotic pressure developed in the opposite direction to the driving force for the permeation. With increasing the ionic polymer content in membrane , the fluxes of all salt solutions were observed to increase. The increase in solution flux with SA content could be associated with the increase in the swelling ratio of the membrane, which is due to the increasing of the hydrophilicity of the membrane. Then as feed concentration increased, the ratio of solution flux to PWF decreased. The change of solution flux as a function of feed concentration is due to osmotic pressure. With increasing the feed concentration, the osmotic pressure increased. As a result, the driving force decreased. The decrease in the driving force is associated with the decrease in the solution flux. In the case of cationic membrane, the permeation sequence is also similar to the swelling ratio sequence for the cationic membrane as shown in Figs 8, 9 and 10. Like the anionic membrane, the permeation of electrolyte solutions through the cationic membrane could be explained by the sorption behaviors. As the feed concentration increased, the ratio of the solution flux to PWF decreased. Therefore, it is summarized that the tendency of flux with ionic polymer content in membrane exhibits a similarity to that of swelling ratio, indicating that the permeation is controlled
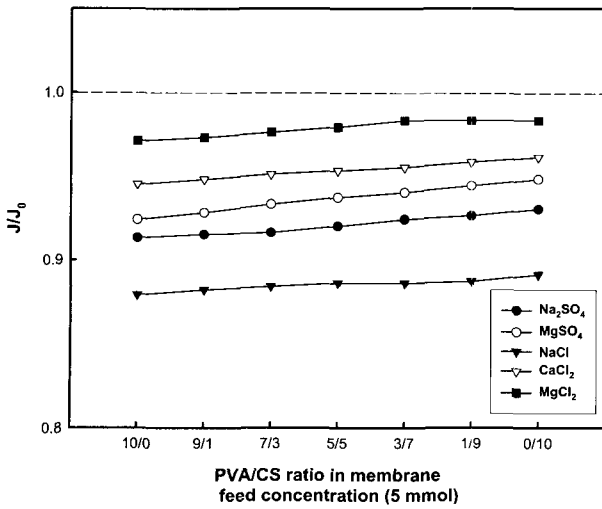
Fig 8. Flux ratios of PVA/CS membrane at 30°C and a feed pressure of 20 kgf/cm² ; J= solution flux, J₀= pure water flux, solute concentration in feed= 5 mmol.
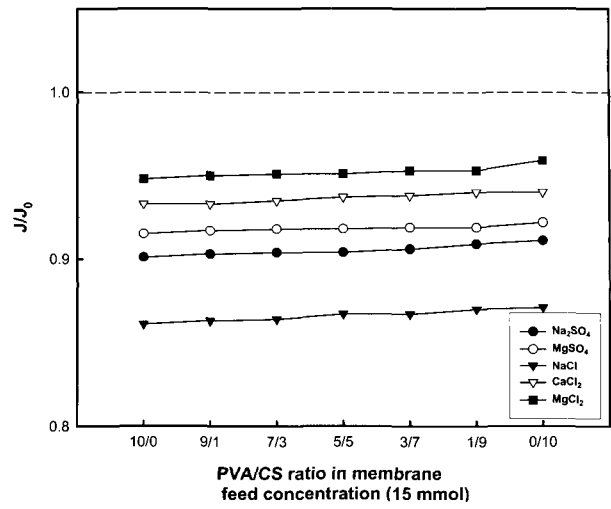

Fig 10. Flux ratios of PVA/CS membrane at 30°C and a feed pressure of 20 kgf/cm² ; J= solution flux, J₀= pure water flux, solute concentration in feed= 15 mmol
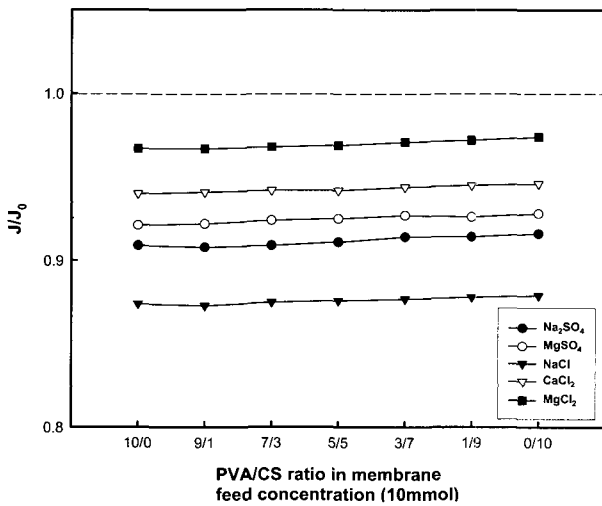

Fig 9. Flux ratios of PVA/CS membrane at 30°C and a feed pressure of 20 kgf/cm² ; J= solution flux, J₀= pure water flux, solute concentration in feed= 10 mmol.
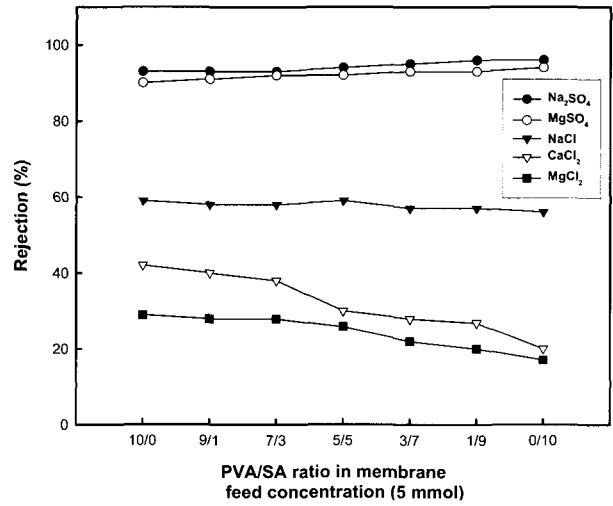

Fig 11. Rejection of various salt solution through anionic membrane with the composition of the membrane at 30°C and a teed pressure of 20 kgf/cm²

mainly by the sorption properties of the membrane (9,10).

Fig 11 shows rejection against ionic polymer content in the anionic membrane. It was mentioned that the separation mechanism of charged membrane could be explained by Donnan exclusion, which is based on the "charge effect". According to the charge effect, in the permeation through ionic membrane, the rejection of electrolytes having divalent co-ion is higher than that of electrolytes having monovalent co-ion because the

charged membrane repels more than the divalent co-ion. Conversely, electrolytes having divalent counter-ion show lower rejection than those having monovalent counter-ion. Therefore the rejection could be dependent upon the valence types of electrolytes as well as the ionic polymer content in membrane as shown in Fig 11. Also molecular sieve mechanism was effective for the separation of the salt solution under a similar electrostatic circumstance of solutes. When the ionic polymer content in membrane was low, the size
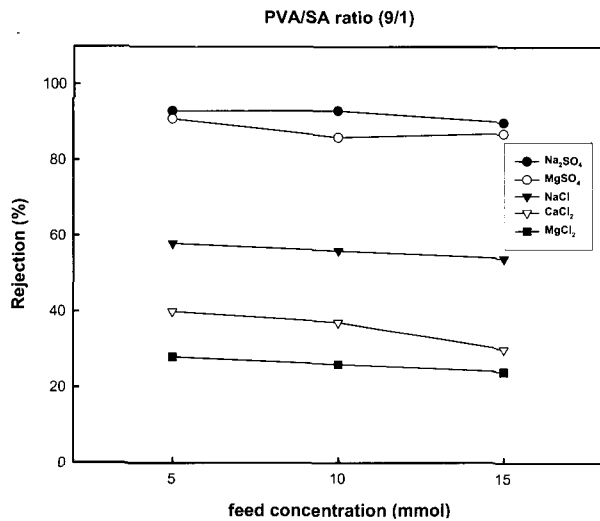
Fig 12. Rejection of various feed concentration through anionic membrane at 30°C and a teed pressure of 20 kgf/cm².
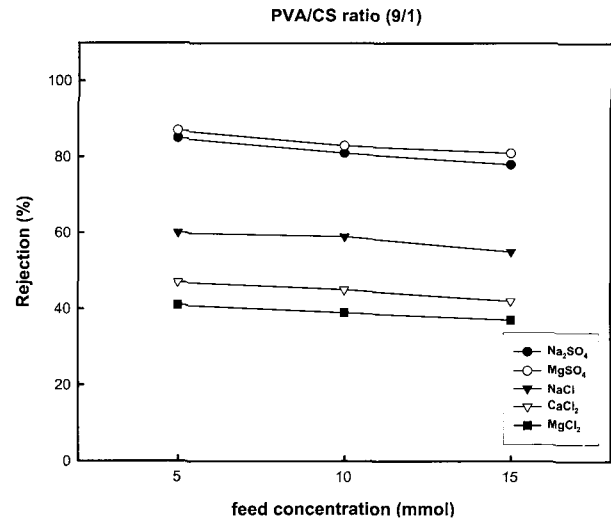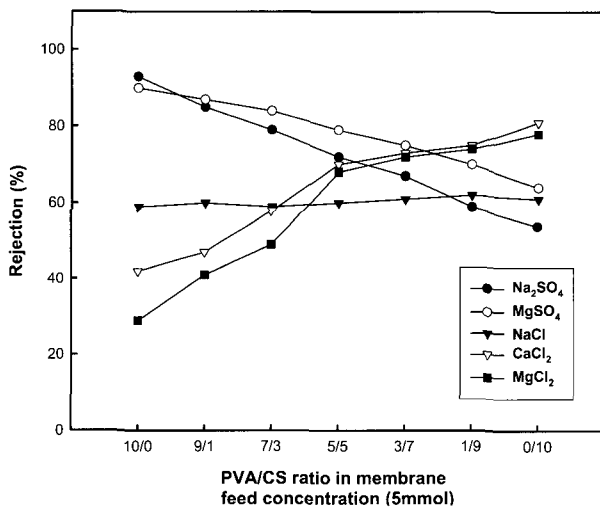

Fig 13. Rejection of various salt solution through cationic membrane with the composition of the membrane at 30°C and a teed pressure of 20 kgf/cm².

Fig 14. Rejection of various feed concentration through anionic membrane at 30°C and a teed pressure of 20 kgf/cm².

exclusion was predominant over the charge effect: bigger molecules or ions more rejected by the membrane. However, as the membrane was more charged, the charge effect could contribute to the salt rejection to a greater extent.

The anionic membrane showed a rejection sequence: $Na_2SO_4 \geq MgSO_4 > NaCl > CaCl_2 \geq MgCl_2$.

Fig 12 shows the rejection against feed concentration. As feed concentration increased, the rejection decreased. The reason is the fact that as the feed

concentration increased, more solutes existed around the membrane, and the solutes permeated well through the ionic membrane.

Observing the salt rejection of positively charged membranes in Fig 13, the rejection sequence is also observed as expected.

With the increasing cationic polymer content in the membrane, the electrolyte having divalent co-ion showed a rapid increase in the rejection, whereas the electrolyte having divalent counter-ion showed a rapid decrease in the rejection. Thus with the increase in an ion polymer content in the membrane, the electrolyte having divalent co-ion and monovalent counter-ion ($CaCl_2$, $MgCl_2$) showed a rapid increase in the rejection, whereas the electrolyte having divalent counter-ion and monovalent co-ion(Na_2SO_4) showed a rapid decrease in the rejection. The rejection of the salt having divalent co-ion and divalent counter-ion ($MgSO_4$) also decreased significantly but not as much as that of Na_2SO_4. We presume that SO_4^{2-} ion display stronger charge effect than Mg^{2+} ion. With the increasing cationic polymer content in the membrane, the electrolyte having monovalent co-ion and monovalent counter-ion(NaCl) is not changed in the rejection significantly. And then Fig 14 shows rejection against the feed concentration. As the feed concen-

tration increased, the rejection decreased. It is explained by the fact that as feed concentration increased, more solutes existed around membrane, and the solutes permeated well through the ionic membrane(9-12).

4. Conclusion

Various charged composite membranes were made by blending ionic polymer with a non-ionic polymer with different ratios. In this study, sodium alginate, chitosan and poly(vinyl alcohol) were employed as anionic, cationic, and non-ionic polymers, respectively. The permeation rate was affected mainly by the sorption property, and the salt separation was controlled by the combined effects of molecular sieve mechanism and Donnan exclusion, depending on the membrane charge density.

As the hydrophilicity of the membrane increases, pure water flux as well as solution flux increases correspondingly, indicating that the permeation performance through the membrane is determined mainly by its swollen state(10). When the membrane was strongly charged, electrostatic interaction between the charged membrane and ionic solute molecules, that is, Donnan exclusion was observed to be attributed to salt rejection to a great extent, while the molecular sieve mechanism was more effective for the separation of the salt solution, when the membrane was non-charged or weakly charged.

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