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ANALYSIS OF THE PERMEATION AND SEPARATION OF ELECTROLYTE SOLUTIONS THROUGH REVERSE OSMOSIS CHARGED MEMBRANES

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ABSTRACT

Various charged homogeneous 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. Swelling ratios of the charged membranes were measured in water and the electrolyte solutions of Na_2SO_4, $MgSO_4$, NaCl, and $CaCl_2$. The permeation and separation behaviors of the salt aqueous solutions have been investigated through the charged membranes with various charge densities. As

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the content of the ionic polymer increased in the membrane, the hydrophilicity of the membrane increased and pure water flux as well as solution flux increased correspondingly, indicating that the permeation performance through the membrane is determined mainly by its hydrophilicity. When the membrane was charged strongly, electrostatic interactions between the charged membrane and the ionic solute molecules were observed to be attributed to salt rejection to a great extent; attraction between counter-ions and repulsion between co-ions. Molecular sieve mechanism was effective for the separation of the salt solution when the membrane was nonionic or weakly charged.

Key Words: Charged membrane; Reverse osmosis; Electrolyte solution; Donnan exclusion; Sieving

INTRODUCTION

One of the most important features of charged membranes in reverse osmosis process is their ability to separate ions from electrolyte solutions. Possible mechanisms for the separation of electrolytes are based on both sieving effect and charge effect associated with the electrostatic interactions between the membrane and the ions or between the ions mutually (1–3). Thus, the transport of the ions across the charged membrane, as a result of concentration and electrical potential gradients is well described by the extended Nernst–Planck flux equation in terms of diffusion and migration terms (2,3). In general, when the charged membrane is in contact with an electrolyte solution, co-ions in the membrane are distributed less densely than in the solution, whereas the counter-ions have a higher concentration in the membrane than in the solution. The distribution of the ions generates a potential difference at the interface between the membrane and the solution to maintain electrochemical equilibrium between the two phases. By this potential, which is called Donnan potential, co-ions are repelled by the membrane, whereas counter-ions are attracted. The Donnan equilibrium is dependent on the feed concentration, fixed charge-density in the membrane, and valence of the co-ion or the counter-ion.

In a previous work (4), in order to separate an anionic surfactant from the residual aqueous solution in poly(tetrafluoroethylene) (PTFE) emulsion polymerization, reverse osmosis process was carried out using three kinds of charged membranes, i.e., anionic, cationic, and nonionic membranes. The permeation and separation were affected significantly by the charge characteristics of the membranes. Especially, for the cationic membrane, membrane performance deteriorated seriously with time due to membrane fouling and concentration polarization of the anionic surfactant. For the separation of the anionic surfactant, the selection of an anionic polymer as the membrane material could be rationalized in terms of minimizing the concentration polarization and membrane fouling. Also, it was observed that the separation of the ionic compound could be affected by the intrinsic characteristics of the membranes as well as the electrostatic interaction between permeant molecules and the charged membrane.

In the case of an uncharged membrane or a membrane with low fixed charge-density, the separation of salts is affected mainly by the salt's size or its diffusion coefficient through the membrane (1). The salt with lower diffusion coefficient or smaller molecular size shows a lower rejection. In addition, the structure of the membrane in contact with an electrolyte solution will be another crucial factor influencing the separation. The swollen structure of the membrane formed by absorbing the solution yields unfavorable results with respect to separation.

In this paper, homogeneous charged membranes with a wide spectrum of charge densities were prepared by blending an ionic polymer and a nonionic polymer in different ratios, and permeation experiments of single salt solutions were carried out with the charged membranes. The permeation and separation behaviors of the electrolyte solution will be discussed with respect to membrane swelling ratio, membrane charge density, and the valence type of electrolyte.

EXPERIMENTAL METHODS

Materials

Sodium alginate (SA) and chitosan (CS) (extrapure grades) were purchased from Showa Chemical Inc. (Tokyo, Japan) and calcium chloride (extrapure grade) from Oriental Chemical Ind. (Seoul, Korea). Poly(vinyl alcohol) (PVA), hydrochloric acid (35% content guaranteed reagent), and Glutaraldehyde (GA) (25% content in water, pure grade) were purchased from Junsei Chemical Co. (Tokyo, Japan). The average molecular weight and saponification of the PVA were 65,000 and 99%, respectively. H_2SO_4, Na_2SO_4, $MgSO_4$, NaCl, and $CaCl_2$ were obtained from Junsei Chemical Co. (Tokyo, Japan) and all of them were of extra pure grades. Calcium chloride and GA were used as crosslinking agents of SA and PVA, respectively, and HCl was used as a catalyst in the crosslinking reaction between GA and PVA. Glutaraldehyde and H_2SO_4 were used as crosslinking agents of CS. Ultrapure deionized water was used.

Membrane Preparation

Poly(vinyl alcohol) of 10 wt%, 2.5 wt% of SA, and 5 wt% CS solutions were prepared by dissolving the respective polymer in distilled water. All solutions were filtered before use to remove undissolved particles. Casting solutions for anionic membranes were prepared by blending PVA and SA solutions with various weight ratios of PVA and SA, 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, and 0/100. The casting solutions were cast onto a glass plate with the aid of a Gardner casting knife and then dried at room temperature in a fume hood for 1 day. The dry membrane was peeled off the glass plate and immersed at 30°C for 48 hr in the first reaction solution that contained 5 and 0.05 vol% of GA and HCl in acetone, respectively. After the crosslinking reaction, the membranes were taken out of the reaction solution, washed out several times with pure methanol to eliminate any possible residual HCl and GA, and then dried under vacuum for 24 hr. The dry films were immersed again in the second reaction solution containing $CaCl_2$ and CS for crosslinking the SA part for 30 min. The concentrations of $CaCl_2$ and CS in the reaction solution were fixed at 1.5 and 0.1 wt% in water, respectively, as suggested in a previous work (4). For the fabrication of the cationic membrane, preparing casting solutions, casting them, and treating them with the first reaction solution after drying were made subsequently in the same way as in fabricating the anionic membranes, with the exception of using CS instead of SA in the casting solutions. The membranes were soaked in the second reaction solution containing 7 and 0.5 vol% of GA and H_2SO_4 in acetone, respectively, for 1 hr and then washed with distilled water several times.

For the preparation of pure PVA membrane, the cast film was treated with only the first reaction solution while pure ionic membranes were fabricated by treating them with only the respective second solution (5). All the dry membranes fabricated were 11–13 μm in thickness. A detailed procedure of the preparation of the SA and CS membranes is described elsewhere (6).

Measurements of PH of Electrolyte Solutions and the Swelling Ratio of Membrane in the Electrolyte Solutions

The pH of the respective electrolyte solution was measured by a pH meter (Corning Inc., Model 340, New York). In all the measurements, measuring temperature and salt concentration in the solution were 30°C and 10^{-2} mol/L, respectively.

The swelling measurements in the electrolyte solutions were performed to determine the amount of the aqueous solution absorbed onto the ionic membranes in electrochemical equilibrium between the solution and the membranes. Dry membrane strips were immersed in the aqueous solutions thermostated at 30°C for 48 hr to allow the strips to reach equilibrium sorption. The dimension of a strip was about $7 \times 1.5\,\mathrm{cm}^2$. After measuring the swollen length, l of a strip at equilibrium sorption, the strip was dried for 30 hr at room temperature under vacuum and then the dry length, l_o was measured. The swelling ratio, R for an isotropic material is defined as

$$R = \frac{l - l_o}{l_o} \tag{1}$$

All measurements were repeated four or five times and the resulting data had standard deviation of ± 6%. In all the measurements, salt concentrations in the solutions were 10^{-2} mol/L.

Reverse Osmosis Experiments

A schematic representation of the reverse osmosis 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 pressure. The membrane cell was designed to allow high fluid velocity parallel to the membrane surface. The effective membrane area in the membrane cell was 19.63 cm^2. The feed from the feed tank was passed through a heat exchanger and the four membrane cells subsequently 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 was 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 4 hr before any of the measurements of the membrane performances were made 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 10^{-2} mol/L. 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 measured by a Conductance–Resistance Meter (YSI Model 34, YSI Scientific, Ohio). The rejection exhibited on a membrane was defined as

$$\text{Rejection}\,(\%) = 1 - \frac{C_P}{C_F} \tag{2}$$

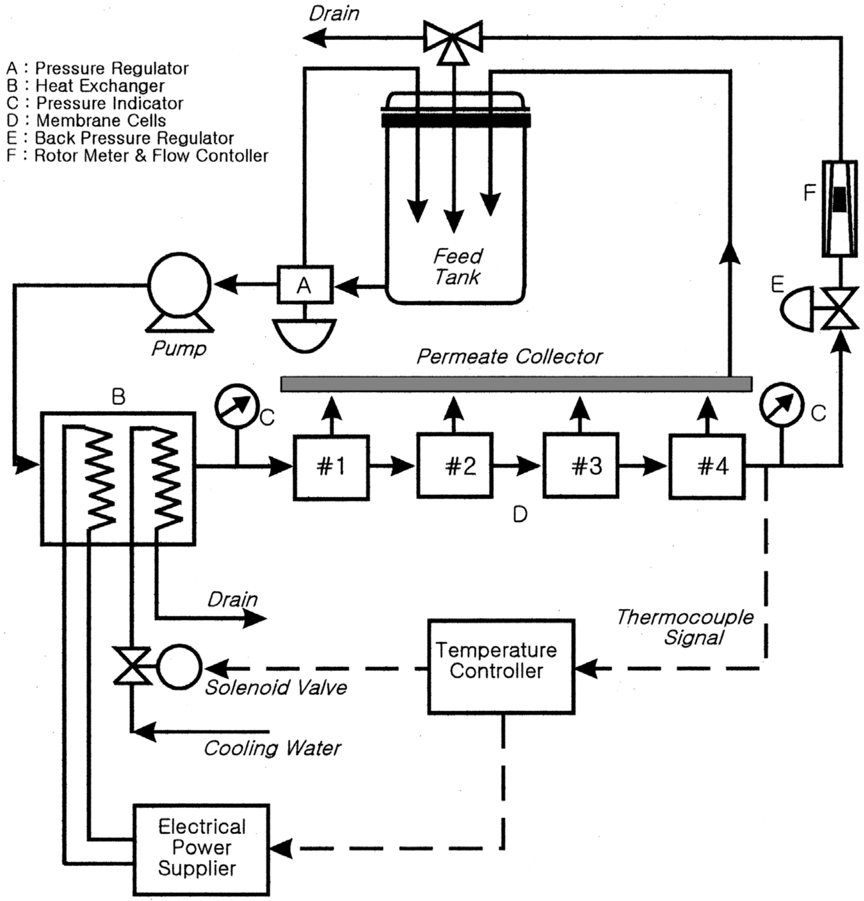

Figure 1. A schematic representation of a reverse osmosis test apparatus.

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

RESULTS 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 having SO_4^{2-}. The difference in pH between the electrolyte solutions will affect presumably the swelling behavior of an ionic

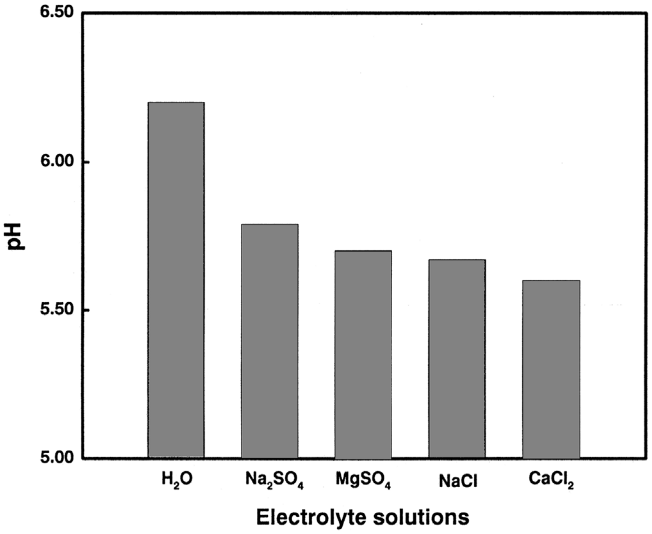

Figure 2. pH of electrolyte solutions at 30°C and 2000 ppm of solute content.

membrane as well as its membrane performance, depending on the charged ionic property of the membrane.

It is reported (7,8) that, on blending the nonionic polymer PVA and the ionic polymer, since these polymers are not completely miscible, a phase separation occurs to some extent and a heterogeneous structure is formed, depending on the blend composition. As the ionic polymer content in the blend increases from pure PVA, the ionic polymer is dispersed in a continuous phase of PVA, and the dispersed domain becomes bigger. As the ionic polymer increases further beyond 50 wt%, the phase is reversed; PVA becomes a dispersed domain while the ionic polymer, a continuous phase, and then the domain size decreases. Looking at the swelling ratio of the blend membranes in water in Figs. 3 and 4, the swelling ratios of both the anionic and the cationic blend membranes increase monotonously with the increase in ionic polymer content. It indicates that the sorption property of the blend membrane is a function of the blend composition rather than the membrane structure.

Figure 3 also presents the swelling ratio of anionic membrane with PVA/SA ratio, i.e., ionic polymer SA content in membrane in the different electrolyte solutions. The swelling ratio of the membrane with a given PVA/SA ratio increased with increase in solution acidity because the anionic membrane tends to be more ionized and thereby more hydrophilic under more acidic circumstances (4). However, the swelling of the membrane in NaCl solution gave

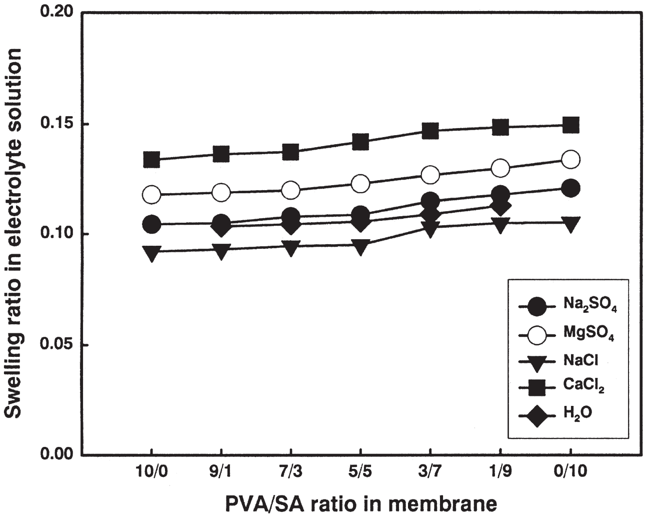

Figure 3. Swelling ratios of anionic membranes in various electrolyte solutions with PVA/SA ratio in membrane at 30°C.

a result that deviated from this tendency. The pH value of NaCl solution was in the middle among the electrolyte solutions but the swelling ratio of the membrane in it was the lowest, even lower than that of pure water. The reason for that is not clear and hence more systematic work is needed to explain the observation. The swelling ratio of the membrane increased with the SA content, because the membrane with higher SA content had more ionic moieties in it, and it would be more hydrophilic and swollen in the solutions.

The swelling ratio of cationic membrane in the different electrolyte solutions was plotted against the content of the cationic polymer, CS in the membrane as shown in Fig. 4. On the contrary, to the anionic membranes, the cationic membranes in the electrolyte solutions were found to have a lower swelling ratio than in water. It could be explained in terms of the neutralization by ionic complexation between solute molecules having an acidic characteristic and cationic sites in the membrane by which the resulting membrane loses its hydrophilicity and then is less swollen in the solution than in pure water. As explained previously with the anionic membranes, however, the membrane with more ionic moieties has characteristically more hydrophilicity. Therefore, the cationic membrane has a slight increase in the swelling ratio with increase in ionic polymer content in membrane even though the increase is not as significant as that found in the anionic membrane. As a result, the sorption property of the cationic membrane in the electrolyte solutions may be affected by the

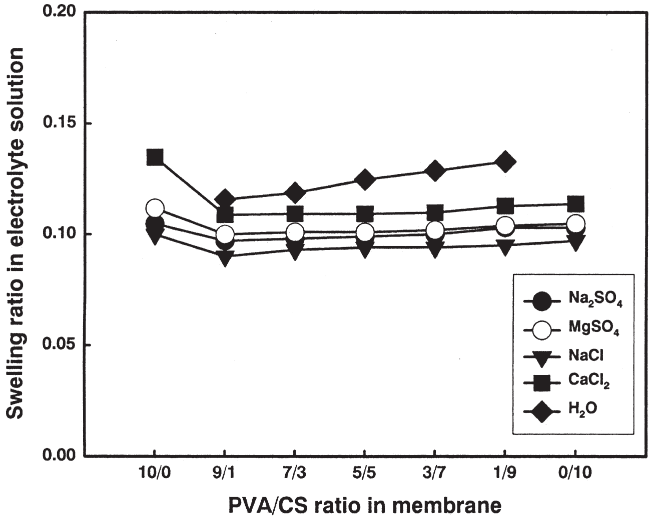

Figure 4. Swelling ratios of cationic membranes in various electrolyte solutions with PVA/CS ratio in membrane at 30°C.

complexation reaction and the content of the ionic polymer in membrane in an opposite way. Such sorption behaviors of the ionic membranes will affect differently the permeation performance of the electrolyte solutions through the respective membrane, which will be discussed later.

Figures 5 and 6 show the plots of PWF (J_o) through anionic and cationic membrane against the content of ionic polymer in the membrane at 30°C, respectively. Both the membranes had an increase in PWF with increase in ionic polymer content in them. As mentioned before, as the ionic polymer content in the membrane increased, the resulting membrane was more hydrophilic and more swollen in water. So the higher PWF in pure water permeation is attributed obviously to the increased hydrophilic property of the membrane.

The fluxes of the electrolyte solutions through the membranes were normalized by dividing them by their PWFs to explain the flux change relative to PWF. The flux normalized with respect to J_o, i.e., flux ratios of solution flux to PWF were plotted against the SA content in the membrane in Fig. 7. On the whole, the solution flux through the anionic membrane was enhanced in comparison to PWF, depending on the type of salt and the ionic polymer content in the membrane. The flux sequence with the type of salt is exactly the same as the swelling ratio sequence; the lower the pH value of a salt solution, the higher the flux of the solution through the membrane, and also, although NaCl solution does not possess the highest value of pH, its flux

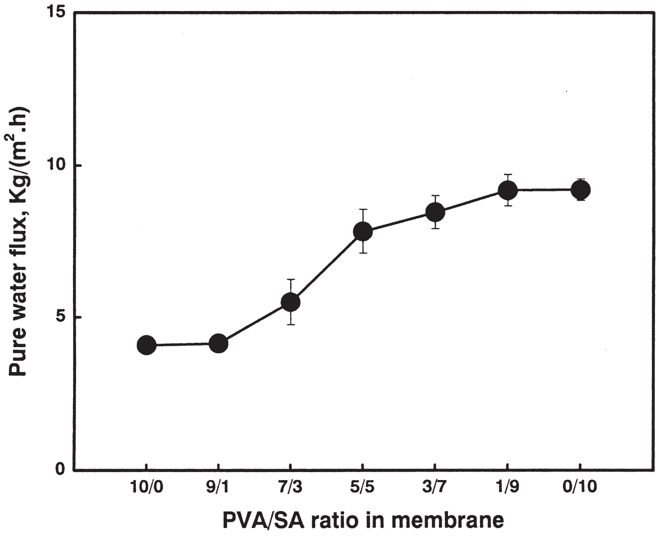

Figure 5. Pure water flux of anionic membranes with PVA/SA ratio in membrane at 30°C and a feed pressure of 3 MPa.

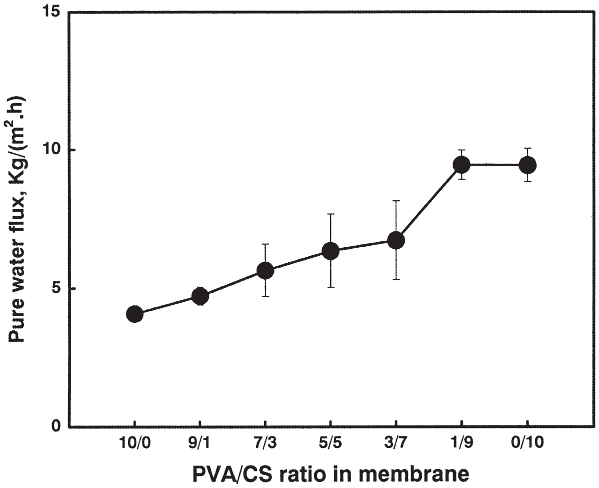

Figure 6. Pure water flux of cationic membranes with PVA/CS ratio in membrane at 30°C and a feed pressure of 3 MPa.

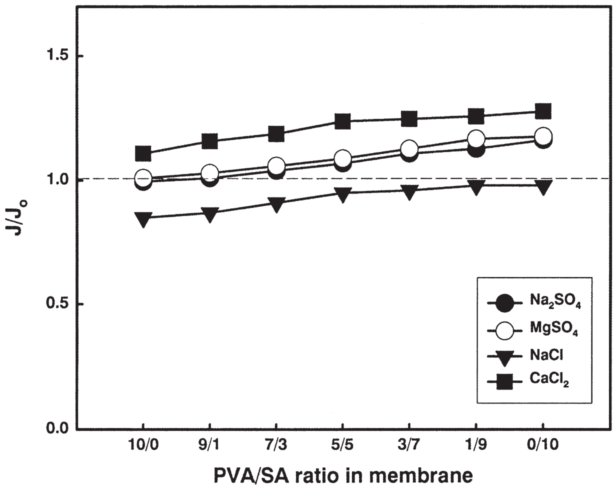

Figure 7. Flux ratios of anionic membranes with PVA/SA ratio in membrane at 30°C, a feed pressure of 3 MPa, and a feed concentration of 10^{-2} mol/L : J = solution flux, J_o = pure water flux (PWF).

was the lowest among the solutions used in this study, exceptionally, and also lower than the PWF. With increase in ionic polymer content in the membrane, the fluxes of all salt solutions were observed to increase. The increase in the solution flux with the SA content could be associated with the increase in the swelling ratio of the membrane, which is due to the increase in the hydrophilicity of the membrane. In the case of the cationic membrane, all of the solution fluxes were lower than the PWF as shown in Fig. 8. The permeation sequence is also similar to the swelling ratio sequence for the cationic membrane. Like the anionic membrane, the permeation of electrolyte solutions through the cationic membrane could be explained by the sorption behaviors. Therefore, it is summarized that the tendency of flux with the ionic polymer content in membrane exhibits a similarity to that of swelling ratio, indicating that the permeation is controlled mainly by the sorption properties of the membrane.

Figure 9 shows rejection against the ionic polymer content in the anionic membrane. It was mentioned that the separation mechanism of the charged membrane could be the 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 bivalent co-ion is higher than that of the electrolytes having monovalent co-ion because the charged membrane repels the bivalent co-ion more. Conversely, electrolytes having bivalent counter-ion show

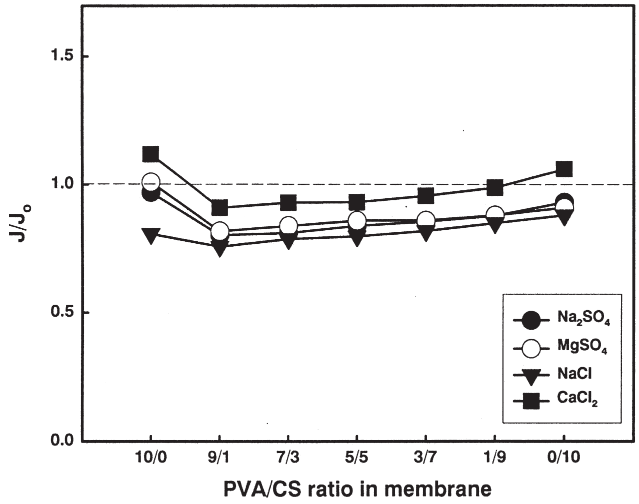

Figure 8. Flux ratios of cationic membranes with PVA/CS ratio in membrane at 30°C, a feed pressure of 3 MPa, and a feed concentration of $10^{-2}\,\mathrm{mol/L}$: J = solution flux, J_o = pure water flux (PWF).

lower rejection than those having monovalent counter-ion. Therefore the rejection is dependent upon the valence types of electrolytes as well as the ionic polymer content in the membrane as shown in Fig. 9. The rejection sequence changed with the ionic polymer content in membrane. When the ionic polymer content is zero, the resulting membrane showed a rejection sequence: $Na_2SO_4 \geq MgSO_4 > CaCl_2 > NaCl$, which is in the order of electrolyte diffusion coefficient in water as shown in Table 1. This order of diffusion coefficients is reflected inversely in the rejection sequence. The membrane with zero ionic polymer content has a nonionic characteristic, so that the diffusion coefficient or molecular size of the salt seems to play an important role rather than the charge

Table 1. Diffusion Coefficient of Different Electrolytes in Water (9)

Electrolyte	D ($10^{-9}\,\mathrm{m^2/sec}$)
NaCl	1.61
$CaCl_2$	1.45
$MgSO_4$	—
Na_2SO_4	1.23

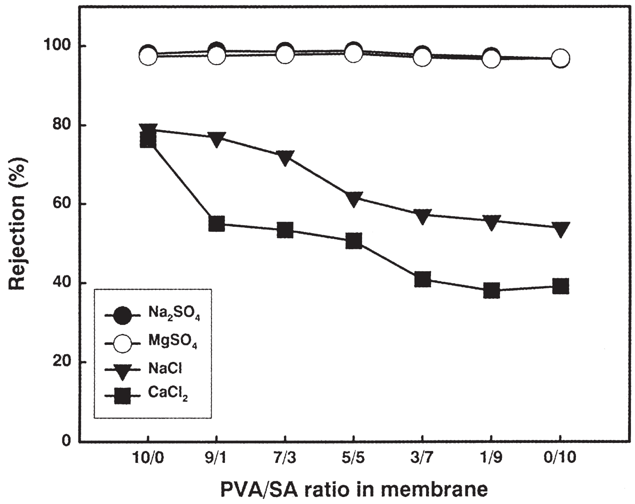

Figure 9. Rejection (%) of various salt solutions through anionic membrane with PVA/SA ratio in membrane at 30°C, a feed pressure of 3 MPa, and a feed concentration of 10^{-2} mol/L.

effect. So, the separation could be explained by the sieve effect. When the ionic polymer content was increased, the resulting membrane was characterized as more anionic and the separation could be determined more by the charge effect rather than the sieve effect, finally showing a rejection sequence: $Na_2SO_4 \geq MgSO_4 > NaCl > CaCl_2$, which is the typical rejection sequence of the negatively charged membrane.

Looking at the salt rejection of positively charged membranes in Fig. 10, the rejection sequence is also observed as a function of the ionic polymer content. When the ionic polymer content in the membrane was low, the size exclusion was predominant over the charge effect: bigger ions were rejected largely by the membrane. However, as the membrane was more positively charged, the charge effect could contribute to the salt rejection to a greater extent. Thus with the increase in ion polymer content in the membrane, the electrolyte having bivalent co-ion and monovalent counter-ion ($CaCl_2$) showed an increase in the rejection, whereas the electrolyte having bivalent counter-ion and monovalent co-ion (Na_2SO_4) showed a rapid decrease in the rejection. The rejection of the salt having bivalent co-ion and bivalent counter-ion ($MgSO_4$) also decreased significantly but not as much as that of Na_2SO_4, as expected from the principle of the charge effect. Finally, the membrane with 0/10 PVA/CS ratio had a salt rejection sequence: $CaCl_2 > NaCl > MgSO_4 > Na_2SO_4$, which was coincident

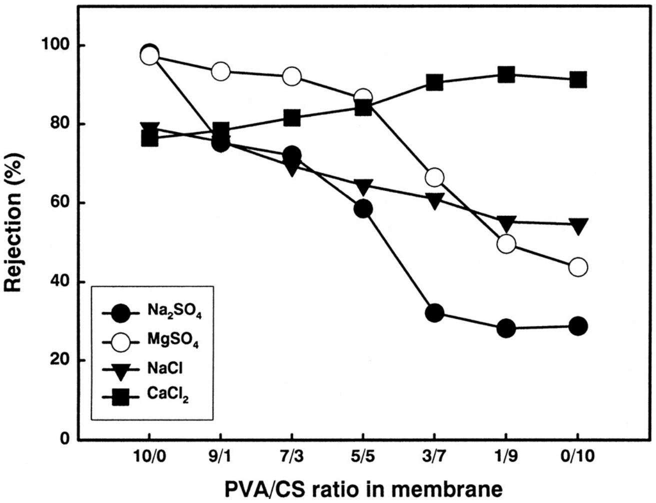

Figure 10. Rejections (%) of various salt solutions through cationic membrane with PVA/CS ratio in membrane at 30°C, a feed pressure of 3 MPa, and a feed concentration of 10^{-2} mol/L.

with that predicted from the principle of the charge effect mentioned above. From these observations, it could be seen that when ionic polymer content in the membrane is low, salt separation is determined mainly by the sieve effect, and as the ionic content in membrane increases, the separation by the charge effect becomes more important. Briefly, the separation through the charged membranes results from the combined effects of the sieve mechanism and the Donnan exclusion, depending on the charge density of the membrane and the salt nature.

CONCLUSIONS

Various charged homogeneous membranes were fabricated by blending an ionic polymer with a nonionic polymer in different ratios. In this study, SA, CS, and PVA were employed as anionic, cationic, and nonionic polymers, respectively. The permeation rate was affected mainly by the sorption property, and salt separation was controlled by the combined effects of the molecular sieve mechanism and the Donnan exclusion, depending on the membrane charge density and the salt nature. As the hydrophilicity of the membrane increases, PWF as well as solution flux increases correspondingly, indicating that the permeation performance through the membrane is determined mainly by its swollen state. When the membrane was strongly charged, electrostatic interaction between the charged membrane and the ionic solute molecules, i.e., the Donnan exclusion was observed to a great extent, while when the membrane is uncharged or weakly charged, molecular sieve mechanism was found to be effective for the separation of the salt solution.

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