

Preparation, Characterization, and Performance of Poly(acrylamidocaproic acid) Partially Neutralized with Calcium for Use in Nanofiltration

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SYNOPSIS

The preparation, characterization, and application to nanofiltration of a membrane made of poly(acrylamidocaproic acid) partially neutralized with calcium using the thin-film composite membrane technique are reported in this study. The long hydrophobic side substituent prevents excessive swelling with water and binds the chain. The neutralized ionic group is designed to enhance the affinity of the membrane to water. By controlling the degree of neutralization, the performance of the membrane could be adjusted. The amount of water molecules participating in the hydration shell surrounding an ionic group was increased with increasing ionic concentration in the membrane. The exponential increase of flux with increasing degree of neutralization is due to the increase of the number and size of the hydration shell. The effect of the pressure and molecular weight of the solute on performance was also investigated. The surface interaction between the solute and the membrane seemed to mainly affect the characteristics of performance.

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INTRODUCTION

Nanofiltration is a pressure-driven membrane process for selective separation of solvent from solvent and solute mixture with molecular weight range from 100 to 10,000. Nanofiltration is commonly used as a concentration step, particularly in the food, galvanic, and dairy industries.

Thin-film composite membrane, which is an asymmetric film having a dense surface layer and a porous underlayer, is regarded as a suitable membrane for nanofiltration as well as reverse osmosis. The advantage gained by using the composite approach is that each material used for the microporous support and the skin layer can be optimized separately to provide improved membrane performance. A comprehensive review of the thin-film composite membrane preparation and performance for reverse osmosis and nanofiltration appeared re-

cently in the literature.¹ Because performances such as flux and rejection are determined by the dense top layer, particular attention was given to the selection of this layer.^{1,2} For high permeability of water, which is usually solvent, the dense top layer is generally made of the polymers containing hydrophilic groups such as polyamide and poly(vinyl alcohol).^{1,2} Although the increase of flux is gained by addition of a hydrophilic group, the selectivity of the solute decreases due to the increase of physical pore size upon swelling. Thus, the excessive swelling should be avoided for high rejection, despite a flux decrease. In recent years,³⁻⁵ the modulation of performance, flux, and rejection was performed by adjusting the degree of crosslinking and/or chemical modification.

Ionomer membrane is one of the potential candidates for water permselective membrane because of its hydrophilic character. Nafion, a perfluorocarbon ionomer membrane, was tested for pervaporation of water and alcohol by other researchers.^{6,7} They found that the ionic group strongly interacts with water and contributes to the water permselectivity.

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In this work, application to nanofiltration of poly(acrylamidocaproic acid) partially neutralized with calcium and modulation of performance by changing the degree of neutralization were performed. The poly(acrylamidocaproic acid) has a carboxylic acid group at the end of the side substituent, an amide group at the linkage of main chain and side substituent, and five methylene groups between the amide and the carboxylic acid in a monomeric unit. The hydrophobic interaction between methylene groups prevents excess swelling of water. When the carboxylic acid remains as a protonated form, poly(acrylamidocaproic acid) is insoluble in water due to the hydrophobic interaction between the methylene groups. The hydrophilicity of this membrane can be varied with the degree of neutralization of the acid group. As increasing the neutralization, affinity to water increases due to the ion-dipole interaction between the ion pair and water. For a low degree of neutralization, hydrophobic interaction binds chains effectively, even in the presence of a hydration shell surrounding the neutralized ion pair. We expect that the flux of water and rejection of organic solute can be controlled by varying the ionic content in this membrane; in other words, the degree of neutralization can potentially offer a wide spectrum of properties.

The objectives of this study were to prepare the membrane composed of hydrophobic hydrocarbon chain and hydrophilic ionic group, and to investigate its characteristics on nanofiltration with varying the ionic content, solute molecular weight, and operating pressure. An attempt was also made to explain the observed data in terms of the interaction between the solute and the membrane surface, which is composed of the hydration shell surrounding the ionic pair and hydrophobic chains.

EXPERIMENTAL

Synthesis of Monomer and Polymer

The vinyl monomer, acrylamidocaproic acid, was prepared by condensation reaction of acryloyl chloride and 6-aminocaproic acid according to the method reported by Babucci et al.⁸ Acryloyl chloride and 6-aminocaproic acid were purchased from Aldrich.

The acrylamidocaproic acid was polymerized with radical initiator in water medium. Acrylamidocaproic acid (10 g) and sodium hydroxide (4 g) were dissolved in 200 mL water. The mixture of reactants was immersed in a temperature controlled water

bath, and then potassium persulfate (500 mg) and sodium bisulfate (200 mg) were injected. Polymerization was conducted for 3 h at 30°C under nitrogen atmosphere. The reacted solution was acidified by 2M HCl aqueous solution to precipitate poly(acrylamidocaproic acid). This precipitate was dissolved in ethanol and reprecipitated by pouring into the distilled water. The sample was dried under vacuum at 130°C for 24 h.

To prepare the calcium partially neutralized poly(acrylamidocaproic acid), the protonated polymer and the predetermined amount of calcium hydroxide were dissolved in water and ethanol mixture, and the solvents were evaporated in atmosphere and then dried under vacuum at 130°C for 2 days.

Characterization of Monomer and Polymer

The obtained monomer and polymer were characterized using ¹H-NMR, ¹³C-NMR, IR spectroscopy, and DSC (differential scanning calorimetry). Bruker AMX 500 and Bomem 102 spectra were used for obtaining NMR spectra and IR spectra, respectively. DSC thermograms were obtained by using a Dupont Thermal Analyst 2000. The heating rate was 10°C/min.

Membrane Preparation

The porous polysulfone membrane was used as a support. The solution of polysulfone/*N*-methyl-2-pyrrolidone (15/85, g/g) was cast onto nonwoven polyester (the backing material) by using a casting knife, and the cast membrane was immediately immersed into a water bath to produce the porous support. The prepared support was dipped into the ethanol/water solution of calcium partially neutralized poly(acrylamidocaproic acid) and poly(ethylene glycol) (molecular weight 200, PEG 200). The compositions of these solutions are summarized in Table I. PEG 200, ended with an OH group, acts as a crosslinking agent intended to physically stabilize the top layer. The OH group in PEG reacts with the acid moiety resulting in an ester linkage. The solution on the membrane surface was drained by holding the membrane vertically, leaving a thin layer of polymer solution. The dip coated membrane was then dried for 5 h at room temperature, and curing was conducted under vacuum at 130°C for 7 h.

Table I Composition of Casting Solution for Top Layer

Polymer DN	Composition of	
	Mixed Solvent Ethanol/Water (mL/mL)	Casting Solution Polymer/Solvent/PEG 200 (g/g/g)
0	100/0	5/95/0.134
4	90/10	5/95/0.134
6	85/15	5/95/0.134
10	78/22	5/95/0.133
12	75/25	5/95/0.133

DN, degree of neutralization.

Determination of Type and Amount of Water Swollen in Membrane

The equilibrium water content (degree of swelling) of the polymer was determined by the weight gain after immersion in water at room temperature for 1 day. The water molecules in the polymer membrane can be classified into three types: free water, freezing bound water, and nonfreezing water.^{9,10} Nonfreezing water directly hydrates to ions, forming a glassy state due to the interference of crystallization. Thus, the nonfreezing water adsorbed to the specific site of the polymer does not show its melting, although the freezing bound water and free water do. The amount of freezing water (freezing bound water and free water) was estimated by DSC. DSC curves were obtained in the temperature range from -80 to 70°C . Enthalpy of melting of water in the swollen polymer was calibrated using pure water as a standard. The total water content of the system, W_{tw} , is defined as

$$W_{tw} = \text{wt water absorbed/wt dried polymer (g/g)} \quad (1)$$

The freezing water content was estimated from the endothermic peak area of melting. The freezing water content, W_{fw} , can be also defined as

$$W_{fw} = \text{wt freezing water/wt dried polymer (g/g)} \quad (2)$$

and nonfreezing water content, W_{nw} , was calculated by

$$W_{nw} = W_{tw} - W_{fw} \quad (3)$$

Nanofiltration

The nanofiltration experiments were conducted using a high-pressure permeation cell with an effective membrane area of 19.63 cm^2 , schematically illustrated in Figure 1. The pressure of the feed side can be controlled by adjusting two valves shown in Figure 1. The pressure of the permeate side was atmospheric. The solute concentration of the feed was 2000 ppm, and the feed was circulated through the feed chamber of the permeation cell. The solute rejection R is defined as

$$R = (C_f - C_p)/C_f \quad (4)$$

where C_f and C_p is the concentration of the feed and the permeate, respectively. The concentration of the solute was determined by the peak area observed from liquid chromatography data.

RESULTS AND DISCUSSION

Characterization of Monomer, Polymer, and Membrane

Acrylamidocaproic acid obtained was characterized using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra, which showed that the resulting monomer was pure. The $^1\text{H-NMR}$ spectrum of acrylamidocaproic acid in this study was consistent with the one reported by Babucci et al.⁸ The melting point was 90.5°C examined from the DSC thermogram. The poly(acrylamidocaproic acid) was characterized using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy, indicating that the synthesized polymer was completely pure. The chemical shifts in the $^{13}\text{C-NMR}$ spectrum were found as follows:

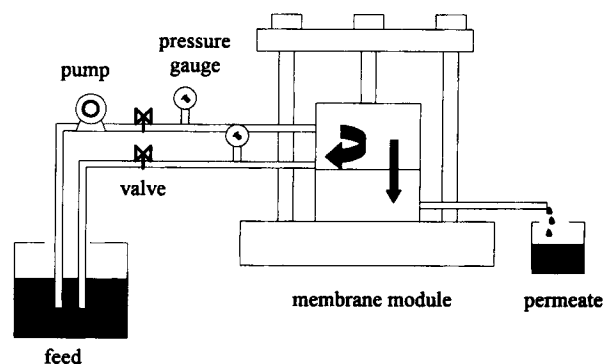


Figure 1 The schematic diagram of the nanofiltration process.

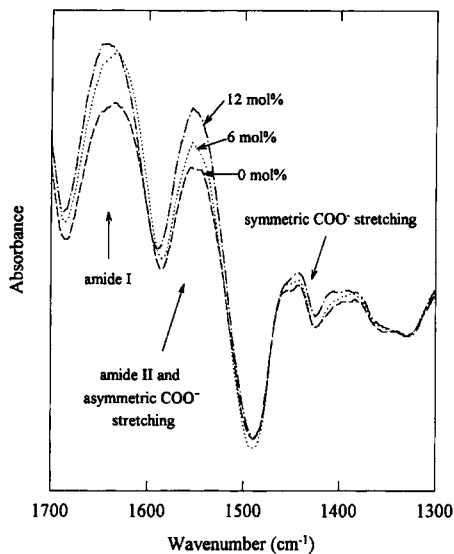
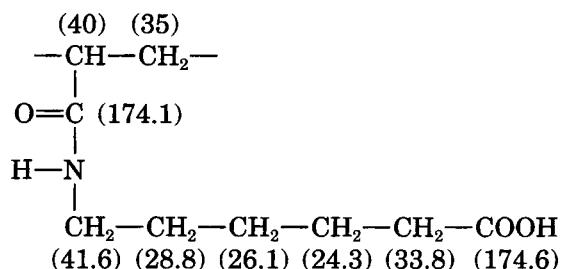


Figure 2 FTIR spectrum of calcium partially neutralized poly(acrylamidocaproic acid) in the range of 1300–1700 cm^{-1} .



solvent: $\text{DMSO-}d_6$

Neutralization was evidenced by the changes in IR spectra given in Figure 2. The neutralization of carboxylic acid is indicated by the characteristic bands at 1560 cm^{-1} (asymmetric COO^- stretching peak) and 1480 cm^{-1} (symmetric COO^- stretching peak). The asymmetric COO^- stretching peak is overlapped with the amide II band. The line at 2200 cm^{-1} , at which no peak was observed, was used as a baseline; and the heights of the peaks were normalized with the reference band at 1330 cm^{-1} , which seemed to be unchanged with neutralization. The intensities of asymmetric and symmetric COO^- stretching increased with neutralization. The glass transition temperatures of the partially neutralized polymers in the dry state are summarized in Table II, showing that the glass transition temperature was increased with increasing neutralization due to the ionic crosslinking formed by the divalent calcium cation. The crosslinking reaction of carboxylic acid and OH was evidenced by the ^{13}C -NMR spectra of the crosslinked polymer swollen in methanol- d_4 , in

Table II Glass Transition Temperature (T_g) and Equilibrium Water Content (W_{tw}) of Poly(acrylamidocaproic Acid) Partially Neutralized with Ca

Degree of Neutralization (mol %)	T_g ($^{\circ}\text{C}$)	W_{tw} (g/g)
0	68	1.5
4	73	3.3
6	76	5.4
10	80	8.7
12	81	12.0
16	85	16.1

which the peak corresponding to the carbon in the ester group was revealed at 177.5 ppm . A 2–3 mol % monomeric unit was found to participate in the crosslinking reaction. It should be noted that the calcium partially neutralized poly(acrylamidocaproic acid) used in this study is insoluble in water even when the crosslinking reaction is not conducted. The crosslinking is intended not to insolubilize the membrane in water but to enhance the mechanical stability.

The typical SEM image of the cross section of thin-film composite membrane (0 mol % neutralization) is given in Figure 3. The thickness of the polysulfone support was about $80 \mu\text{m}$, and the thin top layer was also resolved.

Type and Amount of Water Absorbed in Calcium Partially Neutralized Polymer

To investigate the type and amount of water absorbed in the top dense layer, the DSC thermograms of the water swollen calcium partially neutralized polymer with various water contents were obtained

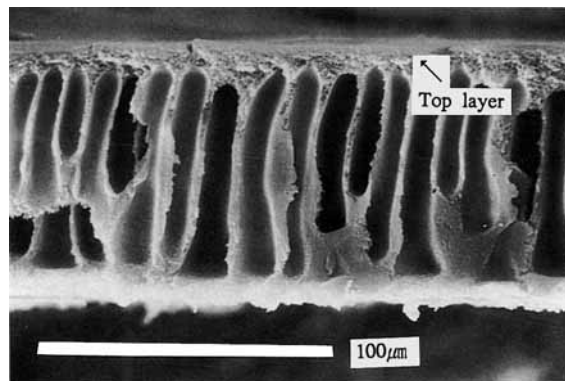


Figure 3 SEM image of the cross section of thin-film composite membrane (0 mol % neutralized).

and analyzed as explained in the Experimental section. The changes of the amount of nonfreezing water and freezing water are shown in Figure 4 as a function of the total water content for the four polymers having different ionic contents. In the case of the unneutralized one (0 mol %), the nonfreezing water content was leveled off with increasing total water content. At the equilibrium water content ($W_{tw, equilibrium} = 1.56$), the nonfreezing water content was about 0.2. The number of the nonfreezing water molecules at equilibrium swelling per monomeric unit can be calculated by the following equation:

$$N_{nw, equilibrium} = W_{nw, equilibrium} \times \text{MW of monomeric unit} / \text{MW of water} \quad (5)$$

where $W_{nw, equilibrium}$ is the nonfreezing water content at equilibrium swelling. $W_{nw, equilibrium}$ can be obtained from the extrapolated nonfreezing water content at the equilibrium water content. The value of $N_{nw, equilibrium}$ for the unneutralized polymer is calculated to be 2.06. This result suggests that each water molecule is strongly adsorbed on a carboxylic acid and an amide group individually, because these are the specific sites that can interact strongly with water. As with increasing the neutralization, more water can be drawn into the polymer matrix upon swelling. The equilibrium water contents are given in Table II. Accepting that each molecule of nonfreezing water adsorbed on the amide and carboxylic acid, even for the partially neutralized one, the number of the nonfreezing water molecules per ionic pair (one calcium cation and two carboxylate anions) can be calculated with the following equation:

$$N_{nw, ionic\ pair} = \{ W_{nw, equilibrium} \times (\text{MW of monomeric unit}) / (\text{MW of water}) - 1 - (1 - \text{DN}/100) \} \times 200/\text{DN}, \quad (6)$$

where DN is the degree of neutralization (mol %). The equilibrium nonfreezing water content was 0.44, 0.98, and 1.3 for the 6, 12, and 16 mol % neutralizations, respectively; and the corresponding number of nonfreezing water molecules per ionic pair was approximately 81, 121, and 147. These indicate that more water molecules are adsorbed on the ionic group with increasing neutralization.

A hydration shell is known to be composed of water molecules surrounding the ionic group. Near the ionic group, water molecules are strongly bound to the ionic group producing a primary hydration shell. Water molecules outside the primary hydra-

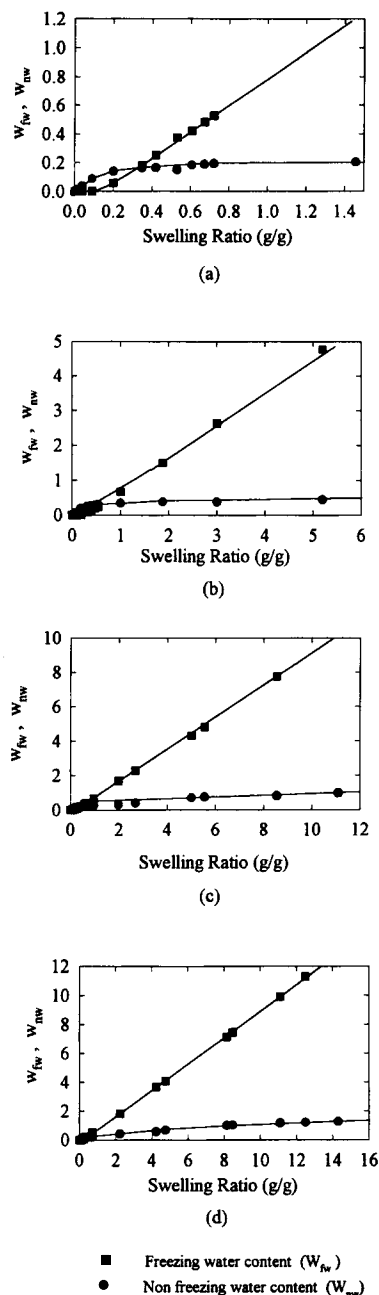


Figure 4 Change of nonfreezing and freezing water content versus total water content: (a) unneutralized, (b) 6 mol % neutralized, (c) 12 mol % neutralized, (d) 16 mol % neutralized.

tion shell, denoted as the secondary hydration shell, are relatively free compared to the water molecules in the primary shell. The amount of nonfreezing water per ionic pair can be an indicator of the size of the hydration shell, because the nonfreezing water molecules would be the major element in the primary and the secondary hydration shell. The increase in

the number of nonfreezing water molecules with increasing neutralization is indicative of the larger hydration shell. As the degree of neutralization increases, the number of hydrophobic chains per ionic pair decreases, resulting in the decrease of hydrophobic chain interaction. Because the retention of the chain dimension by hydrophobic interaction hinders the growth of the hydration shell upon swelling, the decrease of hydrophobic interaction causes the dimensional increase of the hydration shell.

Consequently, it is evident from the above results that: the ionic group acts as a strong hydrophilic site, there are a large amount of water molecules near the ionic group producing the hydration shell, and the dimension of the hydration shell increases with increasing the degree of neutralization.

Effect of Ionic Content on Performance

The flux and rejection data with change of the ionic content are shown in Figures 5 and 6, respectively. It was found that flux is increased and the rejection is decreased with increasing the ionic content for all the solutes studied. It is interesting to note that the flux varies in large degree with the ionic content, but the rejection of solutes, except for PEG 200, decreases a little. The exponential increase of flux with neutralization may be due to the increase of the number and dimension of the hydration shells surrounding the ionic groups. Because the free volume in the hydration shell is expected to be larger

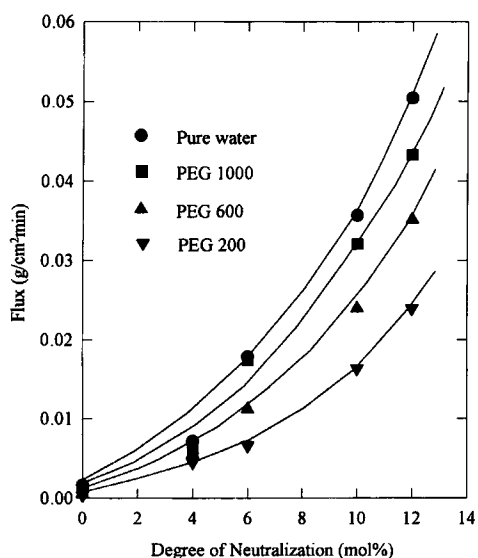


Figure 5 Change of the flux with degree of neutralization of the top layer; P , 400 psi; T , room temperature.

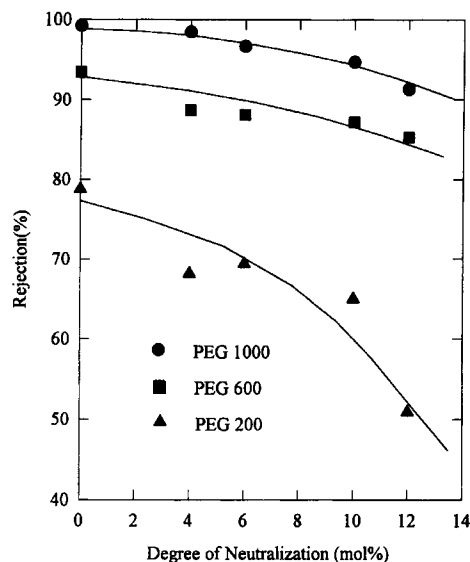


Figure 6 Change of the rejection with degree of neutralization of the top layer; P , 400 psi; T , room temperature.

than that of the swollen hydrophobic chains, the hydration shell could act as a tunnel for water transport.

The permeability of the permeate is generally expressed by the product of its solubility and diffusivity.² The ratio of water solubility between the two membranes can be replaced with the ratio of equilibrium water content between them. When we compare the 12 mol % neutralized polymer with unneutralized one, an eightfold increase is observed in the equilibrium water content (degree of swelling) as shown in Table II. Because the pure water flux is increased by 31 times as shown in Figure 5, the ratio of diffusivity between the two membranes would be 3.9, with the assumption that the thickness of the top layer is the same for both. The enhanced diffusivity with the addition of the ionic groups indicates that the hydration shell significantly contributes to the water transport.

The rejection was increased with increasing molecular weight of the solute as given in Figure 6. This fact is well understood in terms of the hydrodynamic volume of the solute. The larger the hydrodynamic volume, the slower the diffusion in the polymer matrix. In spite of the well-predicted trend of rejection with the molecular weight of the solute, the change of flux with molecular weight of the solute is somewhat strange. As given in Figure 5, the flux was increased with the increase in the molecular weight of the solute. Considering only the contribution of the steric factor of the solute, the flux

should be decreased as molecular weight of the solute is increased, because the retarded transport of the higher molecular weight solute can cause the production of a gel layer near the membrane surface, resulting in additional resistance for water transport, denoted concentration polarization. Thus, this behavior cannot be explained only in terms of the steric factor of the solute.

Effect of Pressure on Performance

To investigate the characteristics of solute transport in this system, the operating pressure was varied. The pressure dependency of flux and rejection can reveal the mechanism governing the transport characteristics. Two simple models, which were expected to be adequate for explaining the observed results, were considered in this study. The solution-diffusion model, which was suggested by Lonsdale and colleagues,¹¹ describes the diffusive transport of solute and solvent through the dense membrane that does not contain the defect. The solute rejection, R , is given for the solute-diffusion model as follows:

$$R = \frac{1}{1 + \frac{P_s}{P_w} \frac{1}{\Delta P - \pi}} \times 100 (\%) \quad (7)$$

where ΔP is the pressure difference between the feed and the permeate and P_s , solute permeability, P_w , solvent (water) permeability, and π , osmotic pressure due to the concentration difference between the two sides of the membrane. It should be noted from the above equation that the solute rejection increases when increasing the operating pressure. The other model considered is the solution-diffusion imperfection model.¹² In this model, the flow through the defect in the membrane was additionally considered. The rejection of the solute can be expressed as in eq. (8) for this model:

$$R = \frac{1}{1 + \frac{P_3 \Delta P + P_2}{P_w (\Delta P - \pi)}} \times 100 (\%) \quad (8)$$

where P_2 is the solute permeability in the dense matrix, P_3 is the permeability in defect, and P_w is the solvent permeability in the dense matrix. When the transport through the defect is dominant, $P_3 \Delta P > P_2$, the rejection is weakly dependent on pressure; and when most of the solute penetrates through the dense matrix, $P_3 \Delta P < P_2$, the same relation as eq. (7) resulted.

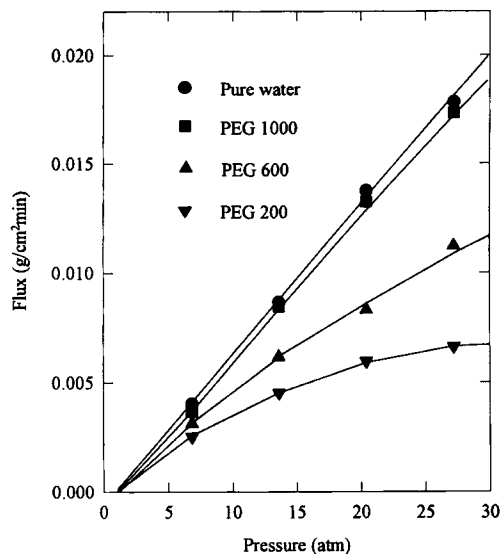


Figure 7 Change of flux with pressure for the 6 mol % neutralized membrane.

Figure 7 shows the dependency of flux on pressure for the 6 mol % neutralized membrane. The linear increase of the flux with pressure for pure water is a general tendency for pressure driven transport. When the solute is contained in the feed, the concentration polarization phenomena is frequently observed. The more deviation from the pure water flux with increasing the pressure indicates the formation of the layer of high solute concentration, frequently referred to as the gel layer, which is associated with the decrease of the flux. As shown in Figure 7, the concentration polarization was observed more evidently in the following order: PEG 200 > PEG 600 > PEG 1,000. The higher flux for the higher molecular-weight solute represents the lower concentration polarization and lower additional resistance to water transport by the gel layer. This means that more solute was adsorbed on the membrane surface for the lower molecular-weight solute. As previously mentioned, this behavior cannot be explained by the steric factor of the solute. A possible explanation can be drawn from the concept of surface interaction between the solute and the membrane. The PEG can be considered a hydrophilic solute, because it is soluble in water, but the polymer chain without the ionic group may be classified into the hydrophobic site. It should be noted that the unneutralized poly(acrylamidocaproic acid) is insoluble in water. Thus more attractive interaction acts between the solute and water than between the solute and polymer chain. The hydration shell surrounding the ionic group is the site at which the PEG and polymer interacts favorably. Al-

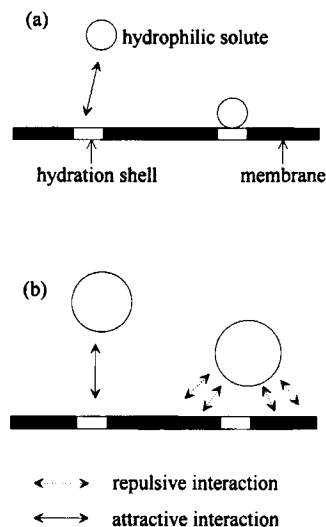


Figure 8 Schematic illustration of surface interaction of membrane with solute (a) when the dimension of solute is smaller than that of the hydration shell or (b) when the dimension of solute is larger than that of the hydration shell.

though the favorable interaction between the PEG and hydration shell would enhance the adsorption of the solute on the membrane surface, the repulsive force between the PEG and hydrophobic chain prohibits solute deposition. When the solute is so small that the hydration shell accommodates the solute, the surface concentration of the solute would be high. The surface concentration would be lower for the higher molecular-weight solute whose dimension is larger than that of the hydration shell, because the repulsive interaction between the solute and the hydrophobic chain occurs. This consideration is illustrated in Figure 8.

The change of rejection with pressure for the 6 mol % neutralized membrane shown in Figure 9 can support the above consideration. When the solute is effectively rejected by the repulsive interaction between the dense matrix of the membrane and the solute, the transport through the defect becomes important relative to the transport through the dense matrix, especially through the hydration shell. For the PEG 200, the rejection is increased with increasing pressure, which is well explained by the solution-diffusion model. For PEG 200, the transport through the dense polymer matrix, including the hydration shell and hydrophobic chain, seems to be the dominant mechanism for nanofiltration. Contrary to PEG 200, the rejection for PEG 600 and 1,000 are nearly independent of the pressure, clearly indicating that these solutes are predominantly per-

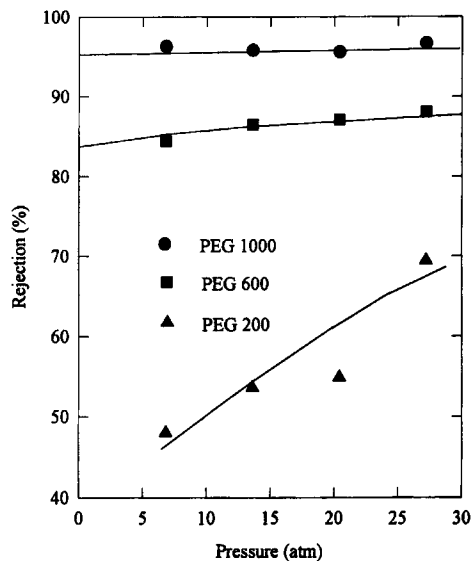


Figure 9 Change of the rejection with pressure for 6 mol % neutralized membrane.

meated through the defect in the membrane, not the dense polymer matrix.

As previously mentioned, the dimension of the hydration shell is increased with increasing the ionic content in the membrane. The larger dimension of the hydration shell could accommodate the larger hydrophilic solute. Figures 10 and 11 show the flux and rejection data for the membrane of 12 mol % neutralization. The concentration polarization was evidently found in PEG 1,000 as well as PEG 600 and 200, and increased with the following order:

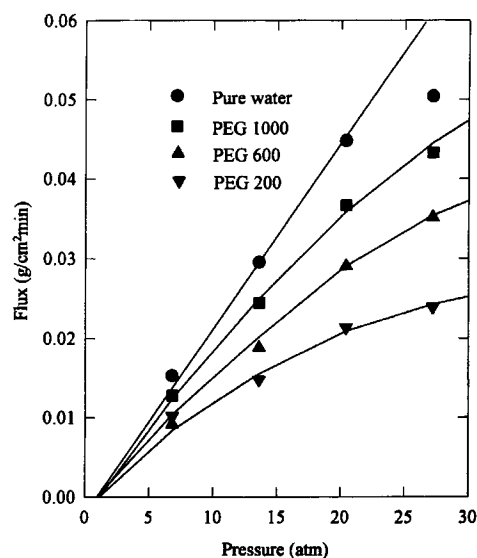


Figure 10 Change of the flux with pressure for 12 mol % neutralized membrane.

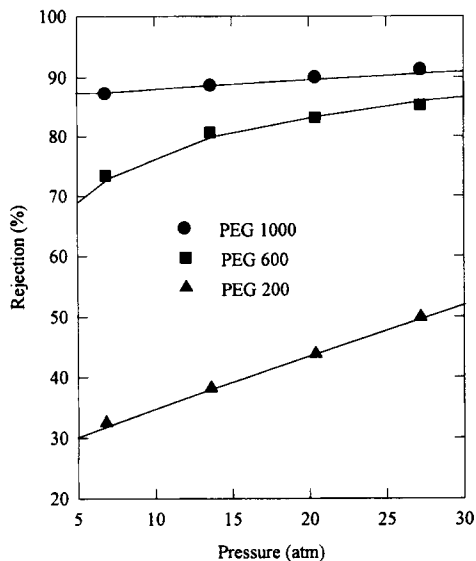


Figure 11 Change of the rejection with pressure for 12 mol % neutralized membrane.

PEG 1,000 < PEG 600 < PEG 200 (shown in Fig. 10). It is noted that the concentration polarization of PEG 1,000 was negligible for the 6 mol % neutralized membrane as shown in Figure 7. The surface adsorption occurs even for PEG 1,000 when the dimension of the hydration shell is increased. In the rejection data shown in Figure 11, a slight increase of the rejection with pressure can be found for PEG 600. This demonstrates that transport through the dense matrix via diffusion significantly contributes to the solute transport and the hydration shell effectively accommodates solute, resulting in concentration polarization, even for PEG 600.

CONCLUSIONS

Several conclusions can be drawn from this study. The amount of water molecules surrounding the ionic group is increased with increasing the neu-

tralization of the membrane, meaning that the larger hydration shell is formed at higher neutralization. The wide spectrum of flux can be obtained by varying the ionic concentration of the membrane. This can be one of the useful methods for tuning the properties of the membrane. All the membranes studied showed rejection of more than 90% for PEG 1,000 at operating pressure of 27.2 atm (400 psi). The higher flux with the higher solute molecular weight indicates that the surface interaction between the solute and membrane governs the characteristics of performance.

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