

Porous Nylon-6 Membranes with Dimethylamino Groups for Low Pressure Desalination

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ABSTRACT: Porous Nylon-6 membranes with dimethylamino groups were prepared by coagulating the polymer-formic acid solution into water. The effect of LiCl addition in the polymer cast solution on filtration characteristics of the resultant membranes was examined. It was found that resultant membranes have porous structure and show molecular size exclusion property under 0.025–0.1 MPa of applied pressure. Desalination property of the porous membranes was investigated using NaCl solution containing 0.05–0.85 mM concentration. The porous membranes showed effective rejection to saline at lower than 0.2 mM NaCl concentration. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1546–1553, 2000

Key words: Nylon-6; dimethylamino Nylon; porous membrane; desalination membrane

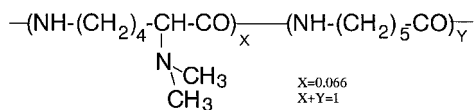
INTRODUCTION

Porous membranes have an advantage of low resistance to mass transfer of solutes in solution because the presence of the pores in the membrane results in an increase of permeation rate.^{1,2} Therefore, porous membranes have been employed in membrane filtration systems³ for separation of proteins and macromolecules mixture and for salt concentration. In membrane filtration, there are mainly four developed processes: microfiltration, ultrafiltration, reverse osmosis (RO), and electrodialysis. The first three processes are related filtration techniques that are used for filtrating dissolved or suspended solutes with membrane. In such filtration processes, porous membrane used differs principally in average pore diameter. Polymeric materials have been used as conventional materials for porous membrane preparation.¹ For polyamide, which are characterized by the amide group (—CO—NH—),

it is very interesting to show good chemical stability. It was reported that aliphatic polyamides (Nylon) are of greater interest for microfiltration and ultrafiltration applications.¹ In another applications of Nylon membranes, previous studies were concerned mainly with RO and dialysis.^{4–7} Furthermore, to improve the performance of Nylon membranes, heat,⁸ plasma,⁹ and γ -radiation^{5,10–12} treatments for grafting hydrophilic vinyl monomer on the Nylon membranes were utilized. However, RO filtration process needs to be operated at very high pressure. Thus, several composite nanofiltration membranes have been developed, recently, in order to separate and concentrate small size solute and inorganic salt.^{13–15} In the nanofiltration process, which can be operated by low hydraulic pressure resulting in low energy consumption, composite polyamide membranes are suitable for use in desalination membrane system. Here, the composite membranes contain very thin polyamide layer on the membrane support, because charged groups such as —NH₂ and —COOH groups affect rejection of ionic solutes. Therefore, these approaches give us the possibility on porous Nylon membranes, if the

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Scheme 1

Nylon polymeric chains contain a functional charged groups. In addition, little is known about porous Nylon membranes having such charged side groups. For application of charged Nylon-6 with dimethylamino group (DN) (Scheme 1), we previously developed enzyme immobilization materials.^{16,17} In the present study, to develop novel type of desalination membranes, porous DN membranes were prepared by phase inversion method.^{1,2} Because the resulting membranes have a porous nature, the saline desalination would be studied under low applied pressure. The DN membrane properties were discussed from the viewpoint of membrane preparation condition. In order to control the permeability of DN membrane, LiCl additive was added into the cast solution. Further, the DN membrane characteristics for desalination were compared with those of Nylon-6 membrane having no dimethylamino groups.

EXPERIMENTAL

Materials

DN having 6.8 mol % dimethylamino groups was produced by Toray Industries (Tokyo, Japan). Preparation methods for DN were reported previously.^{18–20} Nylon-6 was of Mitsubishi Kagaku Co. (Tokyo, Japan). All reagents used in the present experiments were of reagent grade unless otherwise described. Water used for permeation experiments was distilled and purified using ion-exchange resin before uses. For molecular weight (MW) of DN and Nylon-6, viscosity of the polymer-formic acid was measured at 25°C using Ubbelohde viscometer. The MW values obtained for DN and Nylon-6 were calculated as 9800 and 19 000, respectively, according to literature²¹ by using the following equation, $MW = 1.16 \times 10^4 [\eta]^{1.49}$.

Membrane Preparation

Preparation of DN and Nylon-6 membranes was performed by the phase inversion method^{1,2} as follows. In 100 ml of formic acid (99%) including 0–12 g LiCl, 20 g DN, and 12.5 g Nylon-6 were

dissolved overnight at 40°C, respectively. The mixture solution was cast on a glass plate (150 × 200 mm²) with a pair of 100 μm thick spacers and then coagulated into water at 25°C. The coagulated membranes were immersed in water overnight. The resultant membrane was washed with a large quantity of water to remove formic acid and LiCl additive from the membrane.

Permeation Experiments

The resultant membranes sheet having 70–140 μm thickness were cut into disks with 43 mm diameter before filtration uses. The apparatus for filtration experiment was similar to that used in the previous reports using ultrafiltration (UF) cell (Amicon Co., LTD, Danvers, USA, type 8050).^{22–24} All experiments were performed mainly at 25°C and 0.1 MPa applied pressure. The hydraulic applied pressure was measured with a pressure gauge. Volume flux (m³/(m²s)) of water and saline solution was calculated from permeating volume (m³) per filtration time (s) per unit area (m²) of the membrane. To evaluate molecular size exclusion property of the resultant membrane, 0.02 wt % polyethylene glycol (PEG) aqueous solution was permeated through the membranes under the driven pressure condition with a stirring rate of 200 rpm. For desalination characteristics of the membranes, NaCl aqueous solutions over the concentration range of 0.05–0.85 mM were used and filtrated under the similar condition to that of PEG permeation. The concentrations of PEG and NaCl in feed and permeate solution were estimated from the area of high-pressure liquid chromatography (HPLC) curves. The experimentally obtained rejection, R , is defined as $R = (1 - C_p / C_f) \times 100$, where C_f and C_p denote the solute concentrations in the feed and the permeate solution, respectively. Using a gel permeation chromatography (type CCPD UV8000, Toyo soda Co., Tokyo, Japan) with a 30-cm column (TSK_{gel} G5000 PW_{xc}), the detection of PEG and NaCl was carried out with a differential refractometer (UV 8010) and conductivity measurements (CM 8010), respectively.

Membrane Characterization

Morphology of the cross-section of the membrane was observed by scanning electron micrograph (SEM), JXA-733 (JEOL). The sample preparation for SEM measurements was similar to that reported previously.²⁵ IR spectra of DN and Nylon-6

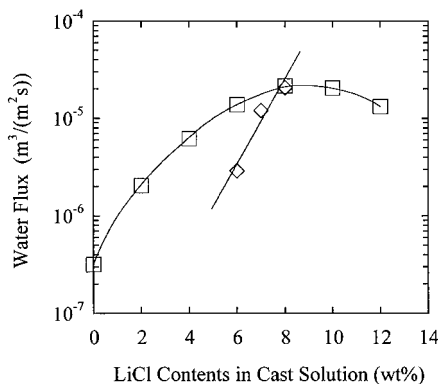


Figure 1 Relationship between water volume flux of DN and Nylon-6 membranes and amount of LiCl concentration in formic acid-polymer cast solution. □, DN membrane; ◇, Nylon-6 membrane. Applied pressure was 0.1 MPa.

membranes were measured with Shimadzu Fourier transform infrared spectroscopy (FTIR) 8100 spectrometer by transmittance set up using KBr pellet.

RESULTS AND DISCUSSION

Effect of LiCl Additive on Membrane Characteristics

Figure 1 shows the effect of LiCl addition to formic acid-polymer cast solution on water flux of resultant DN and Nylon-6 membranes. For DN membranes prepared without LiCl, the resultant membrane shows very low flux ranging of 10^{-7} ($\text{m}^3/\text{m}^2\text{s}$). As the LiCl concentration in the cast solution increased from 0 to 8 wt %, the values of water permeation flux through the resultant membranes increased from about 10^{-7} to 10^{-5} ($\text{m}^3/\text{m}^2\text{s}$). This fact indicates that the filtration properties can be controlled by the addition of LiCl into the cast solution. At 8 wt % LiCl concentration, the values of water flux for DN membrane are shown to be maximum. But at higher than 6 wt % LiCl concentration, the resulting volume flux was in the range from 1×10^{-5} to 2×10^{-5} ($\text{m}^3/\text{m}^2\text{s}$). For Nylon-6 membrane prepared by changing LiCl concentration, the value of water flux increased with increasing the LiCl concentration in the range of 6–8 wt %. However, to control the permeability of Nylon-6 membrane by the addition of LiCl was very difficult at lower LiCl content than 6 wt %. In particular, Nylon-6

membrane prepared without LiCl additive has no permeability of water at 0.1 MPa.

Figure 2 shows SEM photographs of the cross-section of DN membranes prepared from the cast solutions containing different LiCl additive concentration, 0, 6, and 12 wt % and Nylon-6 membrane prepared with 6 wt % LiCl concentration. It is obvious from the photographs that their membranes have porous structures. The SEM photographs show that the addition of LiCl to the cast solution influences the resultant membrane morphology. When the LiCl concentration was increased, the membrane thickness of the cross-section increased as shown in Figure 2a–c, corresponding to 0, 6, and 12 wt % LiCl concentration. Table I lists the thickness of membrane cross-section and pore size estimated from the SEM photographs. As the cast solution without LiCl was used, the resultant membrane has about 70 μm thickness and the pore size observed in the cross-section is about 2–5 μm diameter. The DN membrane, as shown in Figure 2a, looks dense through the cross-section. With the increase of LiCl concentration in the cast solution, as shown in Figure 2b and c, the membrane thickness increases to 80–140 μm . There is also an obvious gradient in the pore size across the membrane thickness. These membranes were prepared by phase inversion method. Here, water, which is nonsolvent for the Nylon polymer, was used as coagulation medium. When the polymer was coagulated in water, the solidification process of the polymer was influenced by the concentration of formic acid, which is a good solvent for the polymer. If formic acid was effectively removed from the cast solution in the phase inversion process, the polymer is coagulated quickly in water medium. In the SEM pictures for the resulting membrane, water was penetrated from top to bottom of the membrane as the phase inversion proceeded. At the top surface of the membrane, the strong coagulation was occurred because Nylon was quickly coagulated at the interface of Nylon-formic acid solution and water medium. In an excess of water the solvent removal from the polymer solution to water was easily occurred. However, in the middle and bottom area of the membrane, the polymer coagulation was lowered because the solvent exchange between formic acid and water was also lowered. This may result in the pore size gradient across the membrane.

As shown in Figure 1, results for water flux of each membrane indicate the porosity increase in a high LiCl concentration, because the perme-

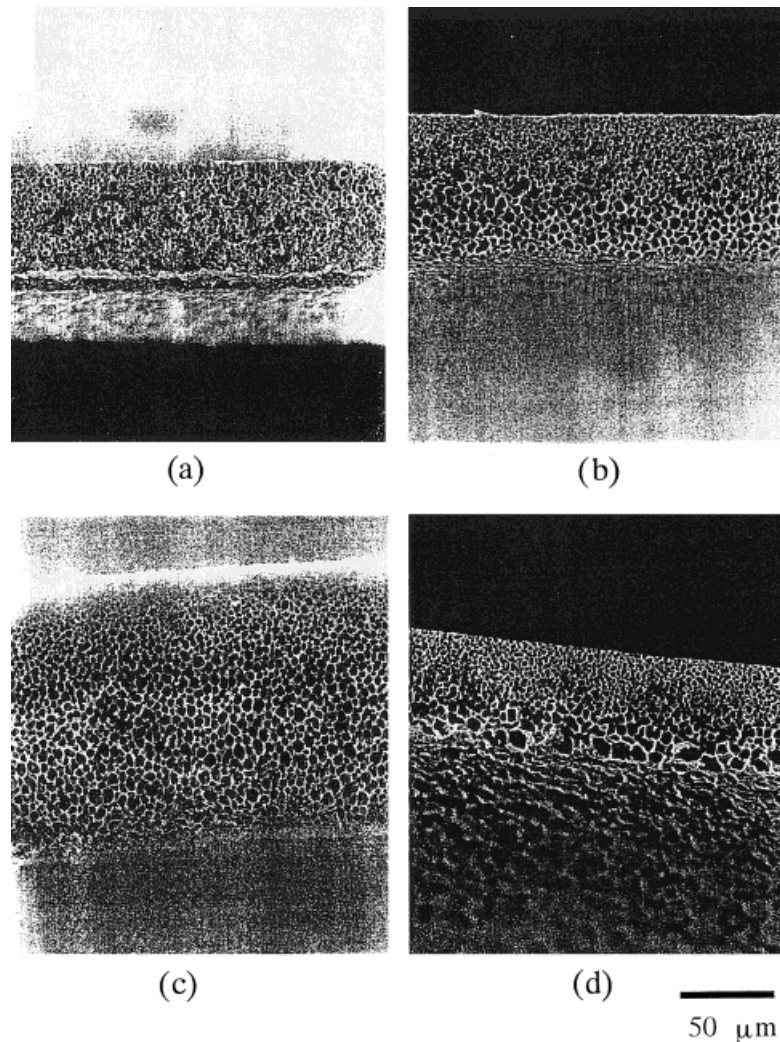


Figure 2 SEM photographs of the cross-section of DN membrane prepared from formic acid cast solutions (a) without and with (b) 6 wt % and (c) 12 wt % LiCl additive; (d) Nylon-6 membrane prepared with 6 wt % LiCl.

ation rate increases in the membrane prepared with high LiCl concentration. Also, the data of water content (WC) of the porous membrane in Table I support the increase of porosity in high LiCl concentration. For Nylon-6 membranes, the SEM photographs show similar morphology to that of DN membrane. As shown in Table I, in the Nylon-6 membrane prepared with 6 wt % LiCl concentration, the membrane thickness and pore size are about $55 \mu\text{m}$ and $2\text{--}6 \mu\text{m}$, respectively. It is noted for Nylon-6 membrane that the value of WC, 77.3%, is smaller than those observed in DN membranes, which have WC in the range of 81–88%. This means that the porosity of Nylon-6 membrane is slightly smaller than that of DN membrane.

In order to estimate permeability of macromolecule solutes through porous DN membranes, various PEGs having MW in the range of $2 \times 10^2\text{--}7 \times 10^5$ were used as a solute. Figure 3 shows rejection of PEG for the DN membranes prepared from different cast solution containing LiCl additive in the range of 0, 6, and 12 wt % concentration. The molecular weight cutoff (MWCO) curves obtained indicate that the resultant membranes show different molecular size exclusion properties, because the rejection of PEG is dependent upon MW of the solute. The MWCO curves show a diffuse cutoff of PEG. In addition, the MWCO curves shift toward high MW side of PEG, when LiCl concentration in the cast solution increases. This means that

Table I Properties of Porous DN and Nylon-6 Membranes Prepared from Formic Acid Cast Solution Without and With LiCl Additive

Polymer	LiCl Concentration (wt %)	Thickness (μm)	Pore Size ^a (μm)	WC ^b (%)
DN	0	70	2–5	81.6
DN	6	80	2–7	84.5
DM	12	140	2–7	88.4
Nylon-6	6	55	2–6	77.3

^a The values of pore size were estimated from SEM photographs of the cross-section of membranes.

^b Water content (WC) was calculated from the following equation: $\text{WC} = ((w_w - w_d)/w_d) \times 100$, where w_w and w_d were weight of wet membrane and dried membrane, respectively.

pore size for the PEG rejection increases by the addition of LiCl.

It is shown in SEM data that a thin dense layer can be observed at in the top surface of the membranes. The resistance to permeation of PEG is determined by size of pores in the dense top layer as well as for typical UF membranes.^{23–25} Therefore, porous structure shown by Figure 2 acts as support layer under high applied pressure for high permeate flux.¹ The SEM morphology indicates that the LiCl addition influences the DN coagulation in water nonsolvent. Because porosity and thickness of the DN membranes increase in high LiCl concentration, the LiCl addition enhances the water nonsolvent penetration into the polymer-formic acid layer in the polymer coagulation. For a typical phase inversion membranes with asymmetric structure, finger-like macrovoids formation in membrane is believed to be instantaneous demixing of the cast polymer-water nonsolvent.^{1,26,27} Relative to the asymmetric structure of common UF membranes, the DN membranes prepared in the present study have no finger-like macrovoids. This may be due to a hydrophilic nature of Nylon segments with amide groups.

Figure 4 shows IR spectra of DN membranes prepared by cast solution without (Fig. 4a) and with 12 wt % of LiCl (Fig. 4b). We can find the characteristic peaks of amide group at 700, 1270, 1540, and 1650 cm^{-1} and those of $-\text{NH}$ stretching near 3300 and 3500 cm^{-1} .^{28,29} Table II summarizes IR absorption bands observed in DN and Nylon-6 membranes. It is noted that IR spectrum for DN membrane prepared without LiCl additive shows broadening IR bands for amide I (1650

cm^{-1}) and II (1540 cm^{-1}) relative to that for the membrane prepared with LiCl additive. In addition, for the spectrum (a), the broadening of the IR absorption band for $-\text{NH}$ group near 3300 cm^{-1} is observed relative to that for (b) spectrum. The finding suggests that the LiCl addition causes the increase in distance between amide groups ($-\text{NH}-\text{O}=\text{C}$) of the coagulated Nylon membrane. This result is supported by the SEM morphology of DN membranes, whose structure depends on LiCl concentration in the cast solution.

Desalination Property of Porous Nylon Membranes

Under 0.1 MPa of applied pressure, various NaCl solutions in the range of 0.05–0.85 mM concentration were permeated through DN and Nylon-6 membranes. Figure 5 shows volume flux of each saline solution for these membranes. Here, the DN membranes used were prepared from cast solution without and with 6 and 12 wt % LiCl. For Nylon-6 membrane prepared with 6 wt % LiCl concentration was used in the desalination experiments because the permeabilities of PEG through the Nylon-6 membrane was almost same as that for DN membrane prepared with 12 wt % LiCl concentration. In all of the membranes used, the values of volume flux of saline solution are slightly decreased by the increase of the salt concentration in the range of 0–0.1 mM. At higher concentration than 0.1 mM the values of flux become constant. For DN membranes prepared with 6 and 12 wt % LiCl concentration, the values of flux are about 1×10^{-5} ($\text{m}^3/\text{m}^2\text{s}$). The data of the volume flux for NaCl solutions are almost same as

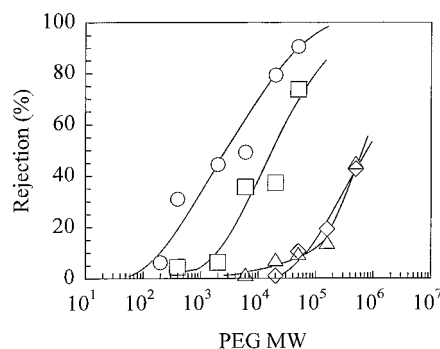


Figure 3 MWCO curves of DN and Nylon membranes: DN membranes prepared without LiCl (○) and with 6 wt % (□) and 12 wt % (◇) of LiCl concentration in the cast solution. △, Nylon-6 membrane prepared from the cast solution with 6 wt % LiCl additive.

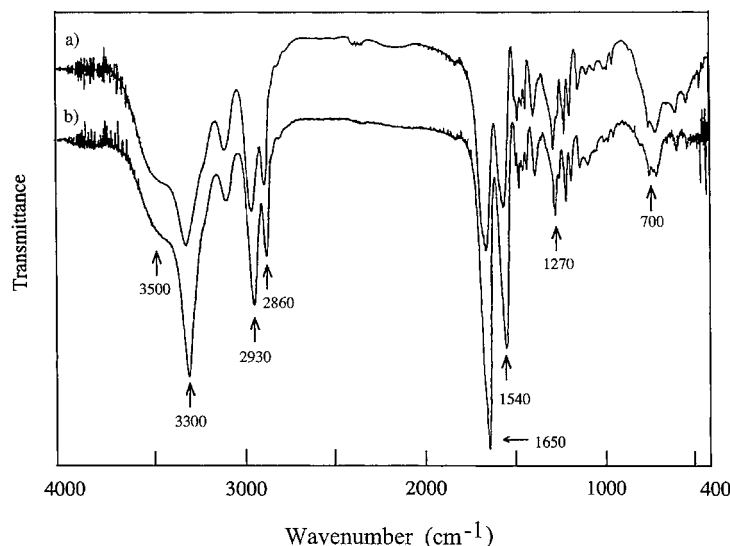


Figure 4 FTIR spectra of DN membranes prepared from the cast solution (a) without and (b) with 12 wt % LiCl additive.

those shown in Figure 1 for water. When the LiCl concentration increased from 6 to 12 wt %, the membrane thickness was increased (Fig. 2 and Table I). The increase of the membrane thickness leads to the increase of permeation resistance. On the other hand, it was shown that high LiCl concentration caused a high porosity of the resulting membrane, resulting in increase of permeability of solute solution. Hence, the effect of LiCl concentration on permeability may be little in the range of 6–12 wt % concentration, as shown in Figure 5 (represented by \square and \triangle).

For Nylon-6 membrane, which has similar molecular size exclusion effect to that of DN membrane prepared with 12 wt % of LiCl addition (Fig. 3), the permeation rate of saline solution is slower than that of the DN membrane and shows an analogous salt effect to that of DN membrane.

Figure 6 shows the desalination characteristics of the DN and Nylon-6 membranes for different

NaCl solution. The values of NaCl rejection by the membranes are plotted as a function of the NaCl concentration of feed solution. As the concentration of NaCl increased, the rejection of salt decreased in the range of $[\text{NaCl}] = 0.05\text{--}0.15$ mM. The tendency was almost same as the membrane prepared by different LiCl concentration. In cases of DN membranes the salt rejection behavior was similar with the membranes prepared by the addition of 6 and 12 wt % LiCl. It is noted that the value of salt rejection for 0.05 mM saline solution was 100% for the DN membrane prepared without LiCl addition. However, the values of the rejection decreased with an increase in NaCl concentration. At higher NaCl concentration than 0.4 mM the rejection of saline became almost constant for all of the membranes. As indicated in Figures 1 and 3, the LiCl addition resulted in high permeabilities of water and PEG through the membranes. From the data of MWCO curves in

Table II IR Absorption Bands Observed in DN and Nylon-6 Membranes

	Wave Number (cm^{-1})	Assignment ^{19,26,27}
Amide	700, 1270	NH
Amide	1540	Amide II
	1650	Amide I
—CH stretching	2860, 2930	—CH ₂ —
NH-stretching	3300	Hydrogen bonding
NH-stretching	3500	Free(nin hydrogen bond)

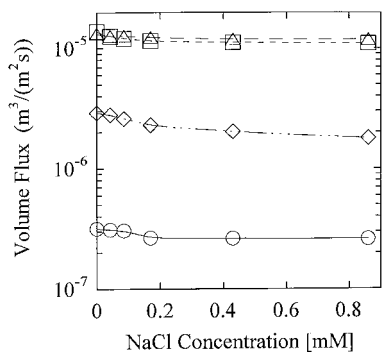


Figure 5 Volume flux of NaCl solutions for DN and Nylon-6 membranes prepared by LiCl additions. DN membrane prepared without LiCl addition (\circ) and with 6 wt % (Δ) and 12 wt % (\square) and Nylon-6 membrane (\diamond) prepared with 6 wt % LiCl addition.

Figure 3, the MWCO for DN membrane prepared without LiCl additive was estimated as about 5×10^4 . Here, the value of MWCO was defined as MW of solute, which was rejected with 90%. For the membranes prepared with 6 and 12 wt % LiCl addition, the values estimated were about 1×10^5 and 3×10^6 , respectively. Approximate effective ionic radius of Na^+ and Cl^- in aqueous solution was 4 and 3 Å, respectively.³⁰ It is obvious that the porous membranes have much larger pore size than the size of NaCl, because these membranes have no rejection to the 2×10^3 MW PEG, whose molecular size is much larger than the ion size of NaCl. Our data indicated that high rejection was appeared in a dense structure membranes prepared without LiCl addition. In other words, the membranes with high permeability of the solution have a tendency to behave low performance on salt rejection.

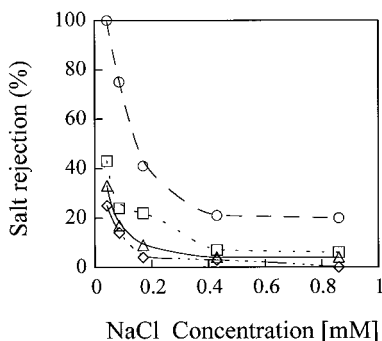


Figure 6 Rejection of salt for DN and Nylon-6 membranes prepared by different LiCl addition to the cast solution. The symbols were same as those in Figure 5.

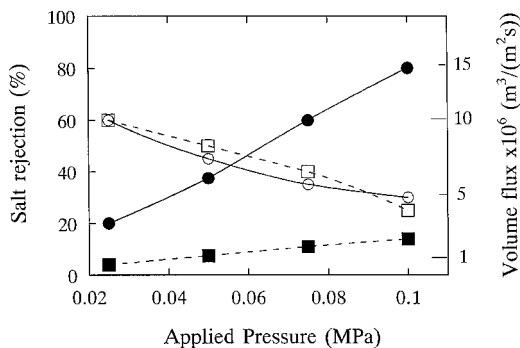


Figure 7 Salt rejection and volume flux of 0.05 mM NaCl solution for DN and Nylon-6 membranes operated with different applied pressure. Open symbols represent salt rejection of DN (\circ) and Nylon-6 (\square) membranes and closed symbols represent volume flux for DN (\bullet) and Nylon-6 (\blacksquare) membranes.

It is very interesting to note that the decrease of NaCl rejection depends upon salt concentration of feed solution. This is a characteristic of charged membranes,^{3,31} because the change of the rejection is caused by binding salt ions to the membrane. In Nylon membranes, the dissociation of weak acid and base may depend on the salt concentration. In the present experiment of DN and Nylon-6 membranes, when the salt was added, the electrical shielding of the dissociated $-\text{COOH}$ and $-\text{NH}_2$ groups for polymer ends may act as a driving force to reject the salt. In a low NaCl concentration, thus, the high salt rejection by the membrane may result from electrostatic effects of residual $-\text{COO}^-$ and $-\text{NH}_3^+$ groups dissociated. The COO^- end should interact with Na^+ and the NH_3^+ end should do with Cl^- ion and the added salt electrostatically shields $-\text{NH}_3^+$ and $-\text{COO}^-$ groups.³²⁻³⁴

Figure 7 shows salt rejection and volume flux of 0.05 mM NaCl solution for DN and Nylon-6 membranes prepared with 6 and 12 wt % LiCl addition. The rejection and volume flux are plotted versus applied pressure. At higher pressure than 0.12 MPa, the DN membrane was broken. This results from the DN membrane having porous structure. As the pressure increased, the volume flux increased, whereas the salt rejection by the membrane decreased. For both membranes the values of rejection obtained at 0.025 MPa were about 60%. Note that the volume flux of DN membrane was about one order higher than that of Nylon-6 membrane, although both membranes shows behavior of the salt rejection at each applied pressure. At 0.025 MPa, the values of the

volume flux for DN and Nylon-6 membranes were 4×10^{-6} and 6×10^{-7} ($\text{m}^3/(\text{m}^2\text{s})$), respectively. The results for salt rejection with higher flux suggest the possibility of application of DN membrane to extreme low pressure desalination process.

CONCLUSION

Novel porous Nylon membranes having dimethylamino group were prepared by phase inversion method. The effect of LiCl addition in the formic acid cast solution on filtration properties of the porous membranes was examined. The effectiveness of the porous Nylon membranes for low pressure desalination was demonstrated in UF filtration system with high permeation under applied pressure of 0.025–0.1 MPa.

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