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A. L. Ahmad[a]; B. S. Ooi[a]; J. P. Choudhury[a]
[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia

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Effect of Hydrophilization Additive and Reaction Time on Separation Properties of Polyamide Nanofiltration Membrane

A. L. Ahmad,*[*] B. S. Ooi, and J. P. Choudhury

School of Chemical Engineering, Engineering Campus, Universiti Sains
Malaysia, Seri Ampangan, Nibong Tebal, Penang, Malaysia

ABSTRACT

Thin film composite (TFC) nanofiltration membrane can be optimized in terms of flux and rejection by controlling the hydrophilization additive [3,5-diaminobenzoic acid (BA)] content and reaction time in the interfacial polymerization (IP) process. By using the Donnan steric pore flow model (DSPFM), uncharged solute was passed through the membrane to determine the pore size (r_{p}) as well as the effective thickness/porosity ($\Delta x/A_k$). The coating condition was related to the performance of NaCl permeation using the fitted r_{p} and $\Delta x/A_k$ data. It was found that the pore size was reduced as reaction time was increased. Cross-linking reduced the porosity of polypiperazinamide membrane but it was noticed that by adding a small amount of BA, the porosity was increased at

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[*] Correspondence: A. L. Ahmad, School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia; Fax: 604-5941013; E-mail: chlatif@eng.usm.my.

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longer reaction time. A small amount of BA could increase both the flux and rejection especially at higher pressure.

Key Words: Hydrophilization additive; Reaction time; Polyamide; Nanofiltration.

INTRODUCTION

Nanofiltration membranes have been recognized as membranes with pore size between reverse osmosis and ultrafiltration membrane. The advantages of nanofiltration over reverse osmosis are low operating pressure, high flux, high retention of multivalent anion salt and organic molecules of molecular weight above 300, relatively low investment, and low operation and maintenance cost.[1] Nanofiltration has attracted worldwide attention in various applications in the wastewater treatment,[2−11] water treatment,[12,13] and bioprocess[14,15] industries.

Interfacial polymerization (IP) technique can be utilized for the preparation of composite nanofiltration membrane. The membranes produced are characterized by high water permeation flux and salt rejection properties. There are several advantages in making membrane using the IP process. The IP film, which forms the selective permeable barrier layer, can be made quite thin to less than 0.1 μm.[16] The TFC membranes made by the IP process also offers good selectivity and high permeation rates. Besides that, IP technique also allows the properties of the permselective barrier layer to be optimized independently from the supporting layer. The IP process permits creation of barrier layers that are highly resistant to degradation from exposure to harsh environments.[17]

The separation performance of composite polyamide membranes prepared by IP method depends on several variables, such as concentration of reactant in the aqueous and organic phase, additive content, and reaction time. The preparation condition for different thin film composite (TFC) nanofiltration membrane still requires further investigation.[18] Rao et al. found a method using attenuated total reflectance infrared (ATR-IR) spectroscopy to study the structure-performance correlation of polyamide TFC membranes.[19] From this study, it was clear that the critical parameters for thin film coating were reaction time, relative humidity, and coating temperature, which played an important role in determining the structure of the interfacially polymerized surface film and, subsequently, the membrane performance.[19]

Lu et al. also pointed out that the key of the IP method was to select the right partition coefficient of the reactants in the two-phase solution and to set the appropriate diffusion speed of the reactants to achieve the ideal degree of densification of the membrane surface.[1]

The objective of this paper is to study the effect of additive and reaction time of the IP process on the performance of the membrane. The characteristics of the membrane, like pore size and porosity, are to be determined using the Donnan steric pore flow model (DSPFM) by pass through uncharged solute. The salt rejection and flux values of polyamide membrane are to be reported under various operating pressures and preparation conditions. The membrane properties are to be related to the membrane performance.

METHODOLOGY

Material

The polysulfone Udel P-1700 (M_n: 17,000) is a product of Union Carbide Corporation. Piperazine (PIP), 3,5-diaminobenzoic acid (BA), *n*-hexane, sodium chloride, and glucose were supplied by Merck Corporation. *N*-methylpyrrolidone and trimesoyl chloride (TMC) were purchased from Fluka, and polyvinylpyrrolidone from Sigma–Aldrich Corporation. The nonwoven polyester was kindly supplied by Ahlstrom, LLC, USA.

Preparation of Polysulfone Support Layer

The polysulfone support was prepared by dissolving 18% polysulfone (Udel P-1700) in *N*-methylpyrrolidone with 15% polyvinylpyrrolidone as pore-former. The solution was casted onto a nonwoven polyester fabric with a thickness of 200 μm under ambient temperature of 24–26°C and relative humidity of 60–65%. Then, the membrane was immersed in a water bath and kept in the water bath for 24 hr until most of the solvent and water-soluble polymer were removed.[20]

Fabrication of TFC Membranes

The support layer was taped onto a glass plate, then immediately dipped into an aqueous diamine solution containing PIP with/without BA for 5 min at ambient temperature of 24–26°C and relative humidity of 60–65%. The excess solution was removed by draining for 1 and 4 min, or with rubber roller from the impregnated membrane surface. The membrane was then dipped into *n*-hexane solution, which consisted of TMC. The reaction was carried out at the predetermined time. The formulation and coating condition are tabulated in Table 1. The group "A" membranes were produced under different reaction times, whereas group "B" membranes were made for comparison between pure polypiperazinamide and BA added polyamide.

Table 1. Thin film formulation and coating conditions for composite membrane development.

Code	Draining/rolled	PIP (%)	BA (%)	TMC (%)	Reaction time (sec)
A1-I	4 min	2	—	0.15	45
A1-II	4 min	2	—	0.15	60
A2-I	Rolled	2	0.20	0.10	45
A2-II	Rolled	2	0.20	0.10	60
A3-I	1 min	2	0.10	0.10	60
A3-II	1 min	2	0.10	0.10	75
B1-I	1 min	2	—	0.10	60
B1-II	1 min	2	0.10	0.10	60

Membrane Testing and Characterization

Membrane testing was carried out in the Amicon 8200 stirred cell, which was supplied by Millipore Asia Ltd., at five different pressures: 150, 250, 350, 400, and 450 kPa. Nitrogen gas was used to pressurize the cell and a membrane with an effective area of 28.27 cm^2 was used in the experiment. The membrane was mounted at the bottom of cell and the solution was stirred at 350 rpm to prevent concentration polarization. Pure water, 0.01 M NaCl solution and 300 ppm glucose solution were fed continuously from a reservoir. Concentration of NaCl in permeate solution was measured using a conductivity meter (Hanna Instruments, Model: HI8633). Glucose in permeate solution was analyzed using a spectrophotometer (Thermo Spectronic, Model: GENESYS 20) at 485 nm.

Each membrane was subjected to pressure pretreatment operations at 450 kPa for 1 hr and it was equilibrated under each operating pressure for the passage of the first 20 mL of permeate. The product rate reading and rejection reading were obtained from the next 10 mL. Each point is an average of data of three permeation test from newly fabricated membranes.

DSPFM

In order to determine the pore size and effective thickness/porosity, the DSPFM was used.[21,22] Below are the assumptions applied to the derivation of the DSPFM:

- The membrane consists of a bundle of identical straight cylindrical pores of radius pore size (r_p) and length Δx.
- A very diluted system was used, which enable the coupling effect between the components in the solution to be neglected.

- For porous membranes, the fluxes, concentrations, potentials, and velocity were all defined in terms of radially averaged quantities.
- The pore radii are very small, thus, the solute velocity was not fully developed and a homogeneous velocity for transport across the membrane was assumed.

Equation (1) is integrated across the membrane with the solute concentration in the membrane at the upper ($x = 0$) and lower ($x = \Delta x$) expressed in terms of the external concentrations ($C_{i,\mathrm{m}}$ and $C_{i,\mathrm{p}}$) using the equilibrium partition coefficient, Φ

$$j_{\mathrm{i}} = -D_{i,\mathrm{p}} \frac{dc_i}{dx} + K_{i,\mathrm{c}} c_i v \tag{1}$$

$$\Phi = \frac{c_{i,x=0}}{c_{i,\mathrm{m}}} = \frac{c_{i,x=\Delta x}}{C_{i,\mathrm{p}}} \tag{2}$$

For purely steric interactions between the solute and the pore wall, Φ is the steric terms relate the finite size of the solute and pore size.

$$\Phi = (1 - \lambda)^2 \tag{3}$$

where λ is a ratio of solute to pore size. In terms of real rejection, Eq. (1) becomes

$$R_{\mathrm{real}} = 1 - \frac{C_{i,\mathrm{p}}}{C_{i,\mathrm{m}}} = 1 - \frac{K_{i,\mathrm{c}}\Phi}{1 - \exp(-Pe_m)[1 - \Phi K_{i,\mathrm{c}}]} \tag{4}$$

where the Peclet number, Pe_m is defined as

$$Pe_m = \frac{K_{i,\mathrm{c}}}{K_{i,\mathrm{d}}} \frac{V\Delta x}{D_{i,\infty} A_k} \tag{5}$$

Since the pore radii are very small, a homogeneous velocity for transport of solute across the membrane was assumed. $K_{i,\mathrm{d}}$ and $K_{i,\mathrm{c}}$ are related to the hydrodynamic coefficients as

$$K_{i,\mathrm{d}} = K^{-1}(\lambda,\ 0) = 1.0 - 2.30\lambda + 1.154\lambda^2 + 0.224\lambda^3 \tag{6}$$

$$K_{i,\mathrm{c}} = G(\lambda,\ 0) = 1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3 \tag{7}$$

To find the film layer concentration, the concentration polarization equation was employed. The observed rejection was related to the real rejection by volume flux, J_{v}, and mass transfer coefficient, k, as follows:[21]

$$\ln\left(\frac{1 - R_{\mathrm{obs}}}{R_{\mathrm{obs}}}\right) = \ln\left(\frac{1 - R_{\mathrm{real}}}{R_{\mathrm{real}}}\right) + \frac{J_{\mathrm{v}}}{k} \tag{8}$$

$$k = k'\omega^{0.567} \tag{9}$$

where

$$k' = 0.23\left(\frac{r^2}{v}\right)^{0.567}\left(\frac{v}{D_\infty}\right)^{0.33}\frac{D_\infty}{r} \qquad (10)$$

RESULTS AND DISCUSSION

Membrane Characterization (r_p and $\Delta x/A_k$)

The curve fitting for real rejection vs. volumetric flux of glucose was done using curve fitting software (Sigma Plot 5.0), which utilized the Levenberg–Marquardt method. Through the fitted curve, r_p and the effective thickness porosity ($\Delta x/A_k$) were obtained using the DSPFM. The variant of the fitting is good, which is more than 0.95. The results of the r_p and $\Delta x/A_k$ for each membrane are shown in Table 2. The average pore size of the nanofiltration membrane was around 0.5 nm with the effective thickness/porosity ranged from 1 to 10 μm.

Effect of Reaction Time on Flux and Rejection of NaCl

Comparison was done on the group A membrane to study the effect of the reaction time on the performance of the skin layer. Each group was studied using a different preparation method. Impregnated A1 group membranes, which did not contain BA additive, were dried by draining for 4 min. The reaction time for A1-I membrane was 45 sec, while the reaction time for A1-II membrane was 60 sec. The other group of membranes, A2 membranes, were

Table 2. Properties of various membranes.

Membrane	Code	Pore size, r_p (nm)	Effective thickness/ porosity, $\Delta x/A_k$ (μm)
1	A1-I	0.468	3.32
2	A1-II	0.474	1.09
3	A2-I	0.562	9.06
4	A2-II	0.499	2.85
5	A3-I	0.514	8.37
6	A3-II	0.473	1.10
7	B1-I	0.427	1.13
8	B1-II	0.514	8.37

dried by the rolling method. The BA in the amount of 0.2% was mixed into the aqueous solution. The reaction time for A2-I membrane was 45 sec, while the reaction time for A2-II membrane was 60 sec. For the third group of membranes, A3 membranes, the aqueous solution mixed with 0.1% of BA, were drained for 1 min. The reaction time for A3-I membrane was 60 sec, while the reaction time for A3-II membrane was 75 sec. All the data are the average of three readings obtained from three newly fabricated membranes. The differences in flux and rejection within the membranes are below 10%.

The flux and rejection data under different pressures for membranes A1, A2, and A3 are shown in Figs. 1–6. Figure 1 (pure PIP) shows not much changes (only 4.5% at 450 kPa) of the volumetric flux between membrane A1-I (45 sec) and A1-II (60 sec) over the pressure range. The reaction time from 45 to 60 sec showed that they did not affect the flux of the membrane. Figure 2 (pure PIP) shows only a slight increase of 2.9% rejection at 450 kPa for the A1-II (60 sec) membrane over the A1-I (45 sec) membrane.

Contrary to membranes A1, Figs. 3 and 4 show that the flux was comparatively higher at a shorter reaction time (no matter the preparation method of rolled or drained). Figure 3 shows that the flux of A2-I (45 sec) was about

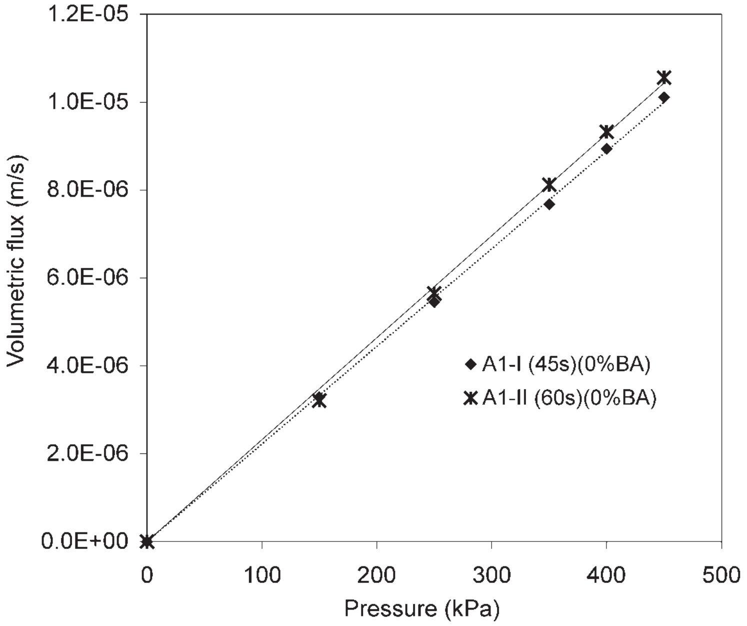

Figure 1. Effect of pressure on volumetric flux for Group A1 membrane at different reaction times.

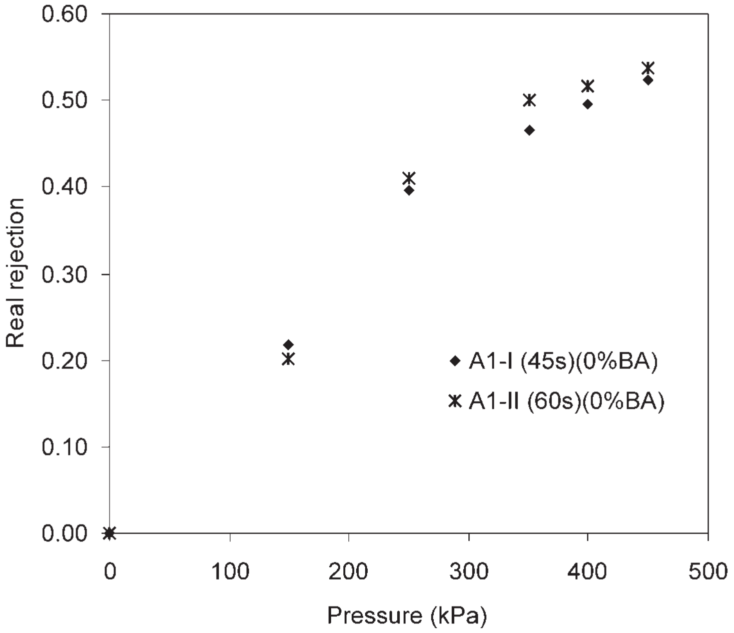

Figure 2. Effect of pressure on real rejection for Group A1 membrane at different reaction times.

19% higher than the flux of membrane A2-II (60 sec) at 450 kPa while Fig. 4 shows that the flux of A3-I (60 sec) was about 38% higher than the flux of membrane A3-II (75 sec) at 450 kPa. For shorter reaction time, thinner effective layer was produced. A thinner layer allows water to pass at higher rate because of reducing resistance. This observation was in agreement with Chai and Krantz, Chen et al., and Ji et al.[17,18,23] Figures 3 and 4 also show that all the membranes obeyed a linear relationship between the volumetric flux and pressure, such that with increase of pressure, flux was increased. The flux difference between A2-I (45 sec) and A2-II (60 sec) was higher at higher pressure. A more significant increase of flux at high pressure was observed between A3-I (60 sec) and A3-II (75 sec) as shown in Fig. 4.

At longer reaction time, extended cross-linking occurred, which produced a denser/tighter effective layer. As a result, the rejection was expected to be higher. However, Figs. 5 and 6 show an adverse trend. The rejection at lower reaction time was better than the rejection at higher reaction time. This phenomenon could be explained by looking at the slower reactivity of BA compared to PIP. The electron-drawing carboxylic group in BA made the

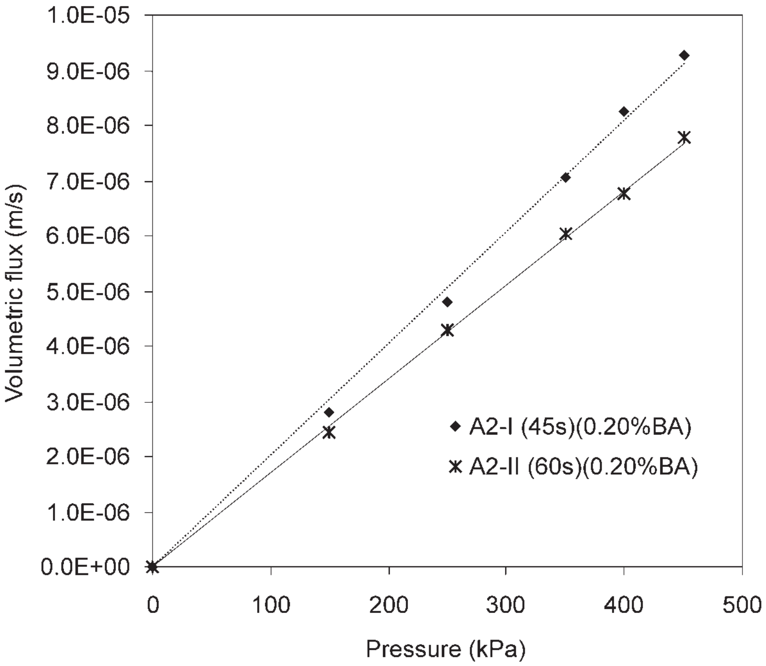

Figure 3. Effect of pressure on volumetric flux for Group A2 membrane at different reaction times.

diamine functional group less nucleophilic, therefore its reactivity was reduced. At a longer reaction time, the content of BA in the polyamide skin layer was increased. Higher content of BA contributed a higher ratio of hydrophilic group in the membrane. Consequently, exceeding water uptake produces a loose skin structure compared to the pure polypiperazinamide membrane.

The characteristic of the skin structure can be proved from the r_p and $\Delta x/A_k$ fitted data in Table 2. The r_p of membranes A2-I (45 sec) and A2-II (60 sec) were 0.562 and 0.499 nm, respectively. The pore size was reduced at higher reaction time. The $\Delta x/A_k$ for A2-I (45 sec) was 9.06 μm while the A2-II (60 sec) was 2.85 μm.

$$\left(\frac{\Delta x}{A_k}\right)_{\text{A2-I,45sec}} = 9.06 \tag{11}$$

$$\left(\frac{\Delta x}{A_k}\right)_{\text{A2-II,60sec}} = 2.85 \tag{12}$$

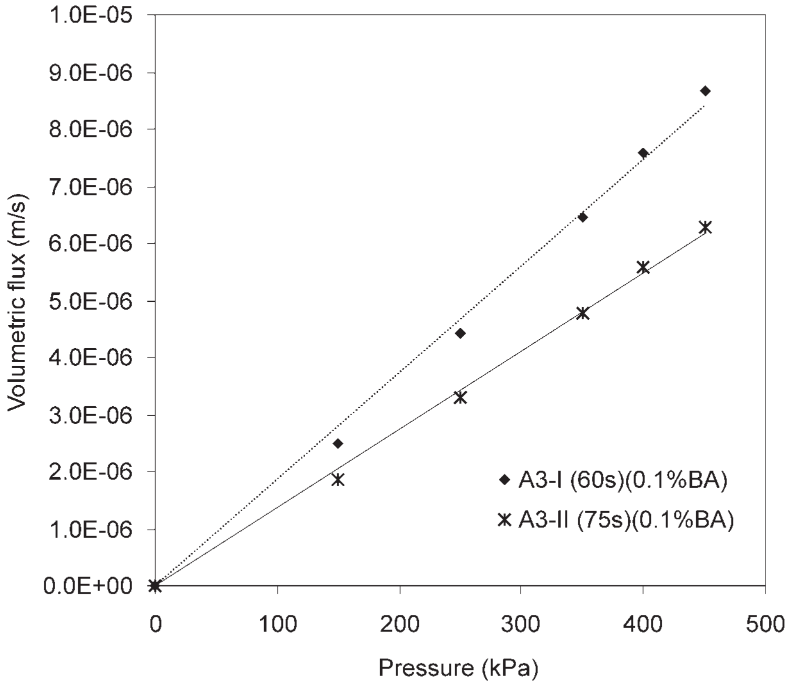

Figure 4. Effect of pressure on volumetric flux for Group A3 membrane at different reaction times.

By assuming $(\Delta\, x_{A2-II,60sec}/\Delta\, x_{A2-I,45sec}) \geq 1$, which is acceptable because the effective layer will not be reduced at longer reaction time, then the following relationship can be valid

$$\frac{A_{k,\text{A2-II,60sec}}}{A_{k,\text{A2-I,45sec}}} = \frac{9.06}{2.85} \times \frac{\Delta x_{\text{A2-II,60sec}}}{\Delta x_{\text{A2-I,45sec}}} \geq 3.1789 \tag{13}$$

This means that A2-II (60 sec) membrane was at least three times higher in porosity compared to A2-I (45 sec) membrane.

The same trend was observed in A3 group membrane. The r_p of membrane A3-I (60 sec) and A3-II (75 sec) were 0.514 and 0.473 nm, respectively. The pore size was reduced at a higher reaction time. The $\Delta x/A_k$ for A3-I (60 sec) is 8.37 μm while the A3-II (75 sec) was 1.10 μm, which indicated that A3-II (75 sec) membrane was at least seven times higher in porosity compared to A3-I (60 sec) membrane.

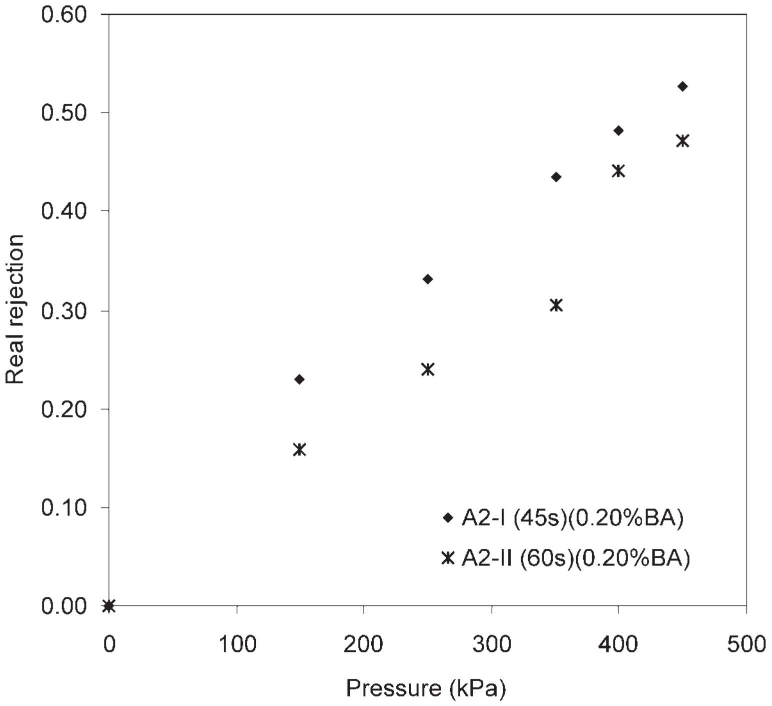

Figure 5. Effect of pressure on real rejection for Group A2 membrane at different reaction times.

There is a slight difference of flux and rejection for Group A1 membranes compared to Group A2 and A3 membranes. This phenomenon can be explained by looking at the r_{p} and $\Delta x/A_k$ data. The r_{p} and $\Delta x/A_k$ for A1 membranes are close to each other compared to A2 and A3 membranes. The A1 membranes are free of any BA contents thus, their performance is merely affected by reaction time but for A2 and A3 membranes, the performance depends not only on reaction time but also the effect from hydrophilization additive (BA) content. Effect of hydrophilization additive will be further discussed in the following section.

Figures 3–6 unambiguously agree that membrane with BA additive had better rejection and flux at shorter reaction time. The skin layer thickness was increased with the reaction time, however, the porosity also was increased at longer reaction time if BA was introduced.

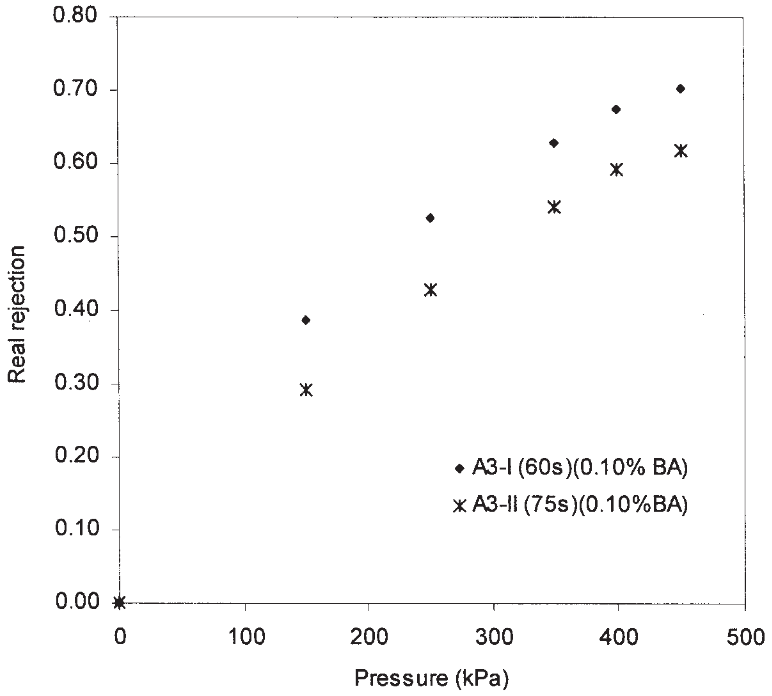

Figure 6. Effect of pressure on real rejection for Group A3 membrane at different reaction times.

Effect of Hydrophilization Additive (BA) on Flux and Rejection of NaCl

Our previous study on the effect of BA on the performance of NaCl retention showed that, by incorporating this hydrophilic additive to the polypiperazinamide backbone, the water flux could be increased.[24] However, the rejection ability did drop as the ratio of additive to PIP was increased. In the current study, a lower additive concentration was introduced, namely 0.1%.

Figure 7 shows a flux comparison between membranes B1-I (0% BA) and B1-II (0.1% BA) under the same 60 sec reaction time. It was found that both membranes also showed linear increase in flux over the pressure range. By mixing a 0.1% of BA in the aqueous solution, the flux of membrane B1-II (0.1% BA) could be increased as much as 38% compared to membrane B1-I (0% BA) at 450 kPa. The increase in flux was attributed to the hydrophilic effect of the carboxyl group as well as the increase of porosity.

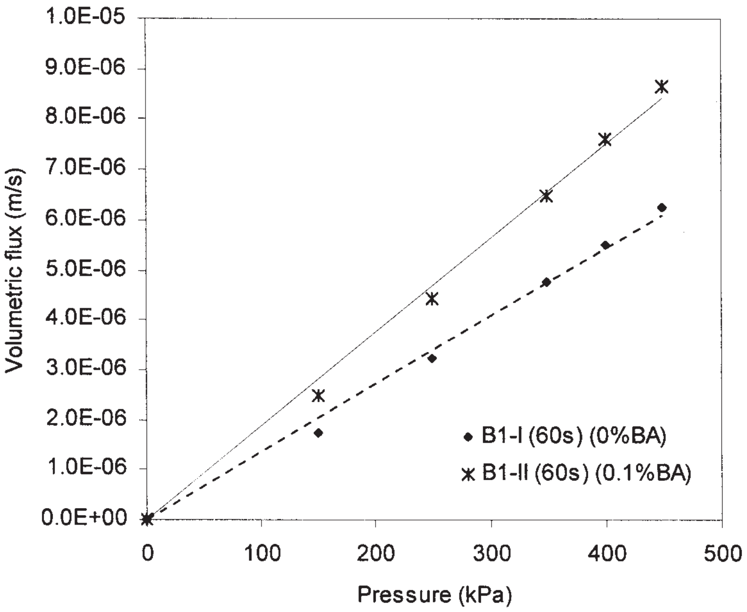

Figure 7. Effect of pressure on volumetric flux for BA added membrane.

Figure 8 shows that, basically, the addition of 0.1% BA did not impair the rejection ability of the membrane. In fact, membrane with 0.1% BA (B1-I) had better rejection ability compared to that of the pure polypiperazinamide membrane (B1-II) at higher operating pressure (450 kPa). From the molecular viewpoint, BA is in planar conformation while PIP is in chair conformation. Aromatic polyamide membranes based on PIP (chair conformation) showed higher compaction on use at high pressure.[25] This compaction might impair rejection ability of the thin rejection layer. This was the reason for better rejection performance of BA-added membrane at higher pressure. Rejection profiles from Fig. 8 showed that, polypiperazinamide membrane (B1-I) leveled off at about 450 kPa but for membrane B1-II (0.1% BA), the rejection still increased with the pressure.

An addition of a small amount of BA, not only helped to hydrophilize the polyamide but also made the membranes more porous in structure. According to Kim et al., hydrophilicity is very important for improvement of water flux.[20] Hence, the reason for the higher flux might be due to the higher porosity as well as the hydrophilization effect.

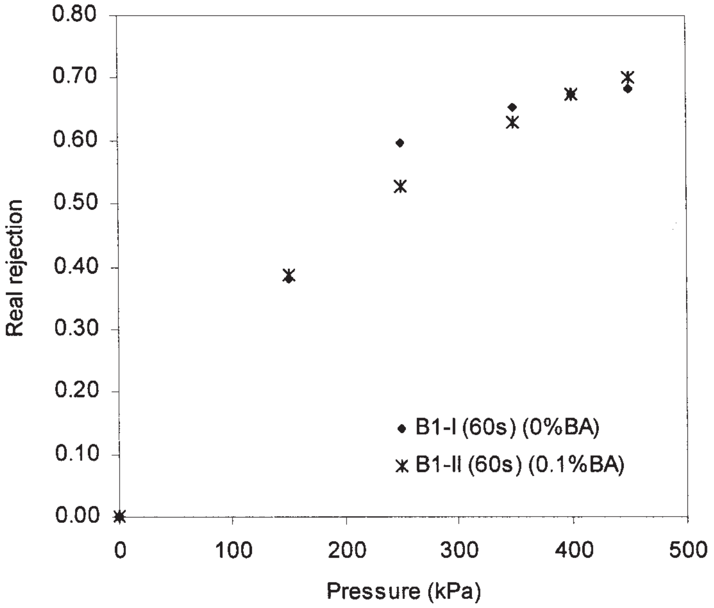

Figure 8. Effect of pressure on real rejection for BA added membrane.

CONCLUSION

Reaction time is an important parameter to be considered in skin layer optimization. When reaction time was changed, the effective thickness, pore size, porosity, and degree of cross-linking were affected. Longer reaction time could extend the cross-linking process, which produced a dense effective layer. However, by addition of BA, the hydrophilic property, was improved and at the same time, when reaction time was increased, the porosity was also increased. A small quantity of hydrophilization additive (BA), which was incorporated into the polyamide layer, could have improved the flux and the rejection of the membrane ability, especially at higher pressure. The effective thickness layer, degree of porosity, and hydrophilicity should be controlled by both the additive content and reaction time so that an optimum membrane could be produced.

NOMENCLATURE

A_k	porosity of the membrane
c_i	concentration in the membrane (mol m^{-3})

$C_{i,\mathrm{m}}$	concentration on the feed side of membrane ($\mathrm{mol\,m^{-3}}$)
$C_{i,\mathrm{p}}$	concentration in permeate ($\mathrm{mol\,m^{-3}}$)
$D_{i,\mathrm{p}}$	hindered diffusivity ($\mathrm{m^2\,sec^{-1}}$)
$D_{i,\infty}$	bulk diffusivity ($\mathrm{m^2\,sec^{-1}}$)
j_i	ion flux (based on membrane area) ($\mathrm{mol\,m^{-2}\,sec^{-1}}$)
j_v	volume flux (based on membrane area) ($\mathrm{mol\,m^{-2}\,sec^{-1}}$)
k	mass transfer constant ($\mathrm{m\,sec^{-1}}$)
k'	mass transfer constant defined by Eq. (9)
K^{-1}	hydrodynamic enhanced drag coefficient
$K_{i,\mathrm{c}}$	hindrance factor for convection
$K_{i,\mathrm{d}}$	hindrance factor for diffusion
Pe_m	Peclet number
r	radius of stirrer
r_p	effective pore radius (m)
r_s	Stokes radius of solutes (m)
R_obs	observed rejection
R_real	real rejection
V	solute velocity
x	distance normal to membrane (m)
Δx	effective membrane thickness (m)
Φ	steric partition term
λ	ratio of solute radius/pore radius
ω	stirring speed

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