

## The application of polyethyleneimine draw solution in a combined forward osmosis/nanofiltration system

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**ABSTRACT:** The objective of this study is to investigate the effect of solution chemistry of branched polyethyleneimine (PEI) draw solute and to evaluate the PEI draw solute in a combined forward osmosis (FO)/nanofiltration (NF) system. Pure water was extracted from feed solution using the FO process, and the separation of pure water was achieved by the NF process. Lower molecular weight PEI showed higher water flux than higher molecular weight PEI, due to the lower internal concentration polarization caused by a higher diffusion rate and the easy permeation of pure water by lower viscosity of the draw solution (DS). The FO water flux was determined by the osmotic pressure induced by protonation/deprotonation of PEI, and the reverse draw solute flux was determined by the combination of PEI size due to the speciation and electrostatic interaction between the membrane and PEI. This study shows that the  $J/J_w$  value of PEI at pH 7 was smaller than those of sodium chloride and magnesium sulfate. The recovery of PEI DS using NF has a higher value (99.4%) than of sodium chloride (20.6%) and magnesium sulfate (97.0%); this means that PEI would be a promising draw solute in an FO–NF combined system for the saline water desalination. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42198.

**KEYWORDS:** membranes; polyelectrolytes; separation techniques

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### INTRODUCTION

Water is essential for humans and other lifeforms, but many places on earth are in danger of running out of potable water. The traditional hazard has been the lack of access to drinking water; but modern hazards include the loss of safe drinking water resources due to water pollution resulting from extensive industrial and intensive farming activities.<sup>1</sup> There are plentiful methods that have been developed and applied to supply water. OH radical oxidation is an effective technology that can be applied to water-treatment<sup>2</sup>; aeration can be applied to water contaminated with volatile hydrogen sulfide and ammonia gas<sup>3</sup>; and membrane technology is one of the promising methods to supply drinking water from the desalination of seawater and brackish water.<sup>4</sup> Membrane technology requires lower capital cost, due to less land space requirement, and lower maintenance/operation costs, resulting from advances in membrane technology.<sup>5</sup>

Forward osmosis (FO) causes the net flow of water from feed solution (FS) of low concentration to draw solution (DS) of high concentration through a semi-permeable membrane. The

FO process uses an osmotic force between FS and DS, so as to allow pure water to transport through the membrane but exclude most of the solutes or macromolecules in the solution.<sup>6</sup> The water flux across the FO membrane depends on the osmotic pressure which is dominantly determined by concentration of solute.<sup>7,8</sup> Unlike reverse osmosis (RO), hydraulic pressure is not required to operate the FO process, and thus the FO process has economic benefits over other membrane technologies in the field of seawater desalination, wastewater treatment, water purification, food concentration, and pharmaceutical production.<sup>6</sup> The FO process has further advantages over pressure-driven membrane processes; for example, lower scaling/fouling/energy consumption, high rejection of various materials, and easy cleaning of the membranes due to its low compaction of retained materials during operation.<sup>9–13</sup>

Many researches have been reported on the relationship between polymer properties and membrane performance for the understanding of appropriate FO membranes materials.<sup>14–18</sup> Hydrophilic property of the polymers is known as one of main factors which determines membrane performance. Natalia *et al.* showed that higher degree of substrate hydrophilicity improved the

**Table I.** Specifications of FO and NF Membranes

Membrane	Manufacturer	Water permeation	Monovalent ion rejection	Test condition	Operating pH range
HTI-TFC FO	Hydration technology innovations	20 L/m <sup>2</sup> h	<99.3%	Feed: DI water Draw: 1M NaCl FO mode	2-12
NE 70	Toray Chemical Korea	28.3 L/m <sup>2</sup> h	40.0-70.0%	FS: 2000 mg/L NaCl Applied pressure: 75psi Effective membrane area: 2.5m <sup>2</sup>	2-11

water flux in FO tests.<sup>19</sup> Han *et al.* reported that TFC FO membrane consisting of polydopamine-modified polysulfone substrates showed enhanced water flux and salt rejection.<sup>20</sup> Furthermore, the hydrophilicity improved fouling resistance, thus reducing performance decline caused by hydrophobic foulants such as organic pollutants and bovine serum albumin.<sup>21</sup> Castrillón *et al.* functionalized FO membrane surface with poly(ethylene glycol) for the treatment of alginate solution.<sup>18</sup> More hydrophilic membrane surface with enthalpic barrier improved fouling propensity.<sup>18</sup> Furthermore, hydrogen bonding interaction between hydrophilic membrane surface and water molecules prevented the approach of hydrophobic foulants on membrane surface.<sup>22</sup> Surface charge of the membrane surface has, also, an effect on the separation process. Alturki *et al.* researched removal of trace organic contaminants using FO membrane and showed the rejection of charged organic contaminants was governed by both size of contaminants and electrostatic interaction between organic contaminants and membrane surface.<sup>23</sup> Several efforts have been made to understand the properties of appropriate FO membrane materials.

However, the application of FO technology has been limited by the absence of suitable draw solutes. The review papers introduced general draw solutes such as MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaCl, KCl, MgSO<sub>4</sub>, KNO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>, sucrose, and albumin.<sup>6,25,28,29</sup> In addition, the specialized solutes such as inorganic salts,<sup>30-32</sup> hydrophilic nanoparticles,<sup>33</sup> stimuli-responsive polymer hydrogels,<sup>34,35</sup> hexavalent phosphazene salts,<sup>36</sup> have been evaluated as draw solute to the FO process. An ideal draw solute should be highly soluble, be charged to generate high osmotic pressure by effective ions, and have proper molecular weight to be efficiently recovered and recycled without loss during the operation. The important characteristics of draw solute are easy recovery, minimal reverse solute flux, high osmotic pressure, and high solubility.<sup>7</sup> McCutcheon *et al.*<sup>37</sup> proposed the use of ammonium bicarbonate as a candidate for draw solute. Ammonium bicarbonate is highly soluble in water to generate high osmotic pressure, and can be recovered by ammonia and carbon dioxide gases over 58°C. However, it needs a distillation process to evaporate into gases which consumes electrical and thermal energy.<sup>38</sup> Several polyelectrolytes have been evaluated as a draw solute in the FO/RO hybrid system to mitigate energy consumption. Ge *et al.*<sup>39</sup> introduced PAA-Na (polyacrylic acid sodium salts) polyelectrolyte which has a structurally expanded configuration and high solubility in water. The PAA-Na showed better

performance than other ionic salts since PAA-Na not only resulted in much lower reverse salt fluxes but also produced comparable water fluxes.<sup>39</sup> However, PAA-Na still had a relatively high value of  $J/J_w$  value ( $>0.005$  g/L). Li *et al.*<sup>40</sup> introduced poly(vinylsulfonic sodium) (PVS) and poly(sodium acrylate) (PSA) polyelectrolytes as draw solutes in FO accompanied by separation of draw solutes and water by various membrane types [e.g., Ultrafiltration (UF) and Nanofiltration (NF)]. But, PVS and PSA showed quite low recovery rates ( $<30\%$ ).

Branched PEI polyelectrolyte with proper molecular weight can be used as osmosis-inducing solutes since PEI is highly soluble in water, has diverse charged species according to solution pH, and can easily be recovered by pressure-driven NF process due to its relatively large size. The objective of this study is to investigate the performance of the branched PEI at various solution chemistries in the FO/NF combined system to evaluate it as a draw solute. The effects of PEI molecular weight and pH condition of the DS were investigated using thin film composite (TFC) HTI membrane. The performance was compared with ionic draw solutes such as sodium chloride and magnesium sulfate in terms of  $J/J_w$ ; and then the recovery of the draw solutes from diluted DS was evaluated in NF filtration tests to investigate the potential of PEI for desalinating saline water.

## MATERIALS AND METHOD

### Chemicals and Materials

Commercially available TFC membrane was purchased from Hydration Technology Innovations<sup>®</sup> and used as a representative FO membrane. A nanofiltration membrane (NE 70) supplied by Toray Chemical Korea was used to recover and recycle the draw solute from diluted DS of the FO process. Specifications of the membranes are given in Table I.<sup>41,42</sup> Milli-Q water (Millipore<sup>®</sup>, USA) was used for FS of FO process. Branched polyethyleneimine (PEI,  $M_w \sim 800$  and 1200), magnesium sulfate (MgSO<sub>4</sub>,  $\geq 99.5\%$  purity), hydrochloric acid (36.5–38.0% assay), and isopropyl alcohol (IPA) ( $\geq 99.7\%$  purity) were purchased from Sigma-Aldrich (St. Louis, MO). The PEI, magnesium sulfate, and sodium chloride (NaCl,  $\geq 99\%$  purity, Bioshop, Canada) were evaluated as draw solutes to extract pure water from FS in the FO process. IPA was used to investigate the swelling effect of the membrane.

### Preparation and Characterization of the Draw Solution

5 wt % of PEI, sodium chloride, and magnesium sulfate solution were prepared as DSs. The pH value of 5 wt % PEI was

about 11.5. The pH of PEI solutions was adjusted by spiking concentrated hydrochloric acid to have a target pH in the range from 3 to 11. The prepared DSs were evaluated in the FO/NF combined system under various pH conditions in terms of water flux and reverse solute flux (solute loss) through FO membrane and rejection (recovery) of the solute by the NF process.

The speciation of PEI at various pH values was evaluated by its  $pK_a$  values determined by buffer intensity measurement ( $\beta$ ) using an auto-titration system (888 Titrando, Metrohm). Buffer intensity, which is highest at  $pK_w$ , was calculated based on the following equation:<sup>43</sup>

$$\beta = -\frac{d C_A}{d pH} \quad (1)$$

where,  $\beta$  is the buffer intensity, and  $C_A$  is the molar concentration of hydrochloric acid added. The buffer intensity is the moles/liter of acid added to change one unit of solution pH. For the measurement of buffer intensity, aqueous solution of 0.1 g PEI ( $M_w = 800$ ) was titrated using 2M HCl.

Viscosities of the 5 wt % PEI solutions were measured using a Bop and Cup Rheometer (Haake Mars III Rheometer, Thermo Fisher Scientific, MA) at applied shear rates of 10–100 (L/s) at 25°C. Three measurement of viscosities were averaged for each representative data point. Osmolality of the 5 wt % PEI solution was measured using a Wescor VAPRO 5520 osmometer. 10  $\mu$ L of the PEI solution was dropped on a filter paper (6.5 mm in diameter), and the osmolality of the PEI solution was evaluated by measuring vapor pressure at room temperature. The osmolality is defined as the concentration of a solution in terms of solute per kilogram of solvent. The average hydration sizes of 5 wt % PEI solution at various pH values were measured using Zetasizer (Nano-ZS, Malvern Instruments, UK). Both the refractive index (1.5240) and the viscosities of PEI solutions in the range from pH 3 to pH 11 were used for the calculation of the hydration size. The zeta potential of membranes was measured by Surpass (Anton Paar, Austria), and the detailed description of analyzing method is given elsewhere.<sup>44</sup>

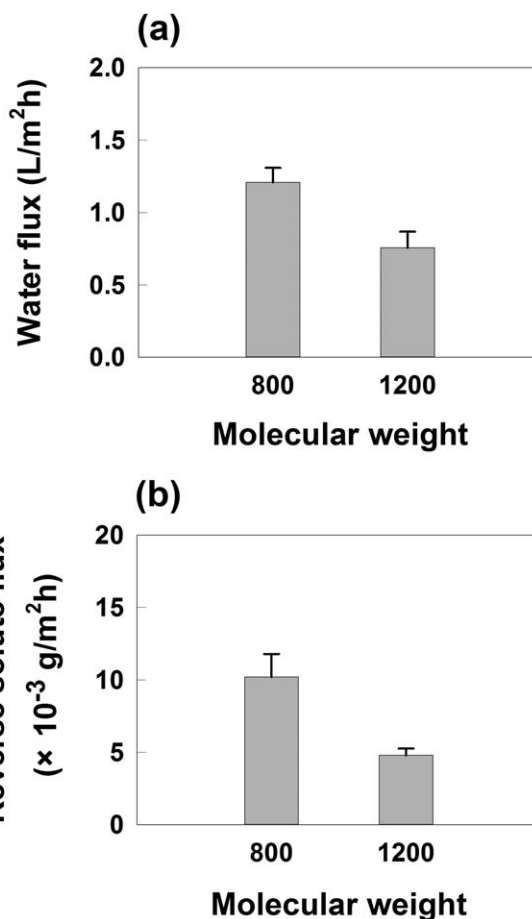
#### Forward Osmosis and Reverse Osmosis Experiment

The performance of FO membrane was investigated using a FO test cell with 27 cm<sup>2</sup> effective area.<sup>44</sup> The volume flow rates of feed and DS along the membranes were 1 L/min maintained by two gear pumps (81808, Cole-Parmer). The temperature of both feed and DSs was maintained at 25  $\pm$  1°C. The permeate water flux,  $J_w$  (L/m<sup>2</sup>h), was calculated by measuring the weight change of DS during 2 h after 30 min conditioning operation for the stabilization of water flux.

$$J_w = \frac{\Delta W}{\Delta t \times A \times \rho} \quad (2)$$

where  $\Delta W$  (g) is the weight change of the FS over a predetermined time  $\Delta t$  (h),  $A$  (m<sup>2</sup>) is the effective area of FO membrane, and  $\rho$  (g/L) is the density of the FS.

The reverse solute flux,  $J_s$  (g/m<sup>2</sup>h), of sodium chloride and magnesium sulfate DS was measured using a calibrated conductivity meter (Thermo Scientific, USA) immersed in FS and con-



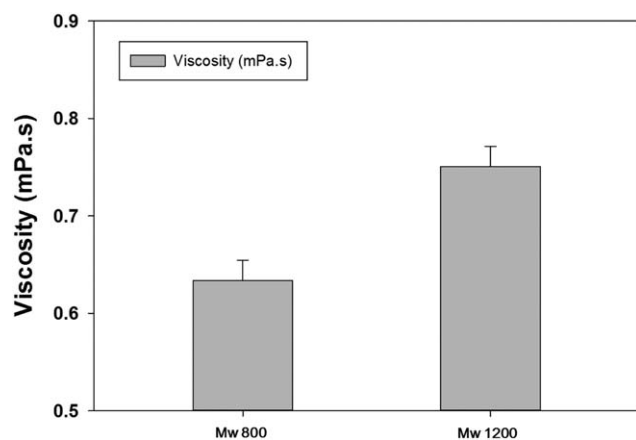
**Figure 1.** FO performance using 5 wt % PEI solution with molecular weight 800 and 1200.

verting the conductivity to weight of draw solutes. A total organic carbon analyzer (Shimadzu, Japan) was used to measure the reverse solute flux of the PEI. The reverse solute flux was defined as the weight change of the PEI passing from DS to FS per unit membrane area and unit time.

$$J_s = \frac{\Delta G}{\Delta t \times A} \quad (3)$$

where  $\Delta G$  (g) is the weight change of the draw solutes over a predetermined time  $\Delta t$  (h) and  $A$  (m<sup>2</sup>) is the effective FO membrane area.

The TFC HTI membrane and NE70 were tested in RO mode using a test cell of which a similar schematic diagram has been elsewhere described.<sup>45</sup> Two 19.635 cm<sup>2</sup> effective area membrane coupons and 1 L/min flow rates were used for the RO performance test. The FS was 500 ppm IPA solution for the membrane swelling test, and 2000 ppm diluted DSs for the recovery test at room temperature. The operating pressure for the recovery test was set to 150 psi for compaction during 1 h, and then 75 psi for the performance test. The water flux of the NF process was calculated using the same as eq. (2). The rejection,  $R$  (%), for each diluted DS containing sodium chloride, magnesium sulfate, and the PEI was calculated from the following equation.



**Figure 2.** Viscosity of 5 wt % PEI solution with molecular weight 800 and 1200.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (\%) \quad (4)$$

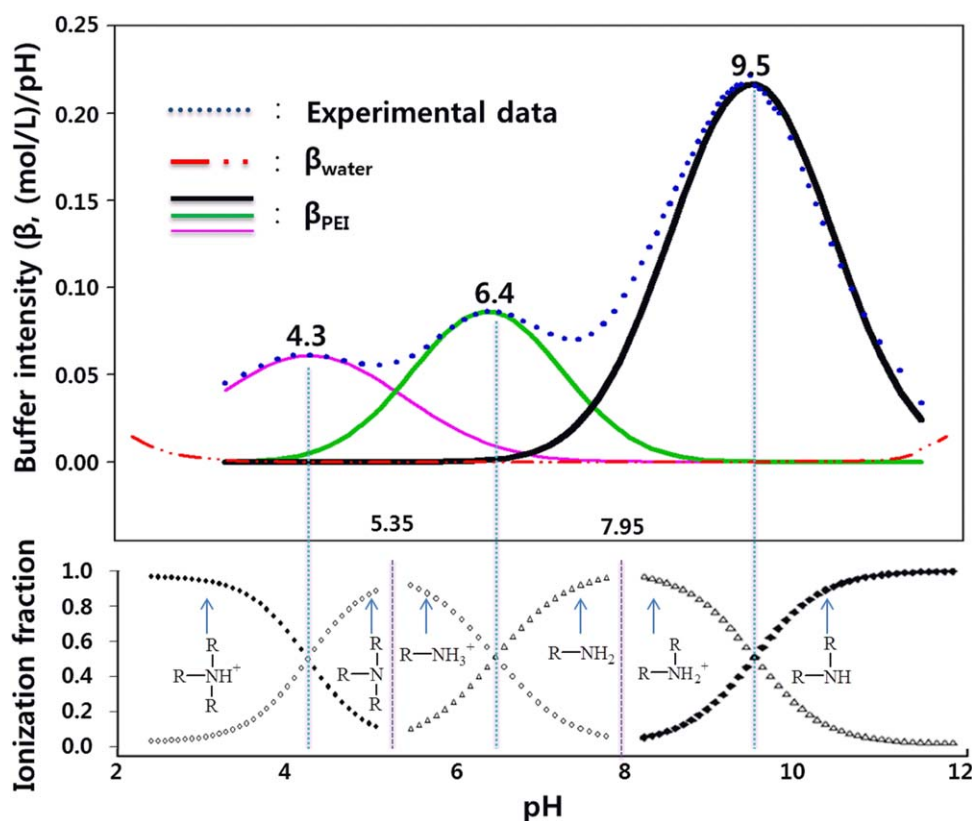
where,  $C_p$  and  $C_f$  are concentration of draw solutes in permeate and FSs, respectively.

## RESULTS AND DISCUSSION

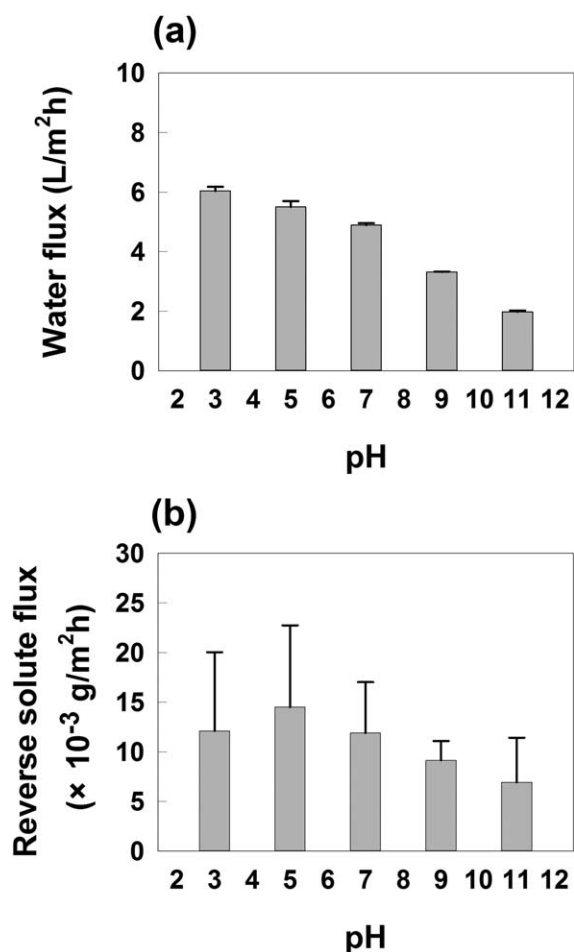
### Effect of Molecular Weight of PEI DS on FO Performance

PEI is a polymer with aliphatic spacer ( $\text{CH}_2\text{CH}_2$ ) and repeating unit of nitrogen-containing groups including primary, second-

ary, and tertiary amine. Amines are easily protonated when protons are available, since the presence of lone pair electrons and the relatively low electronegativity of nitrogen make it share its free electron pair to form a bond with a proton. Due to the protonating capability of the three different amines and subsequent increase of osmotic pressure, the 5 wt % PEI solution was evaluated as a DS. The effect of the molecular weight of PEI was investigated and its performance is shown in Figure 1. The PEI with lower molecular weight ( $M_w = 800$ ) showed a higher water flux than the PEI with higher molecular weight ( $M_w = 1200$ ). This is likely due to the higher diffusion rate of lower molecular weight PEI and both the lower viscosity and higher osmolality of lower  $M_w$  PEI solution. According to Hancock *et al.*<sup>46</sup> magnesium chloride ( $\text{MgCl}_2$ ) has a lower diffusion coefficient than sodium chloride ( $\text{NaCl}$ ), causing the increased severity of internal concentration polarization. Likewise, the PEI with higher molecular weight has a lower diffusion coefficient through the sublayer of the FO membrane, causing more severe internal concentration polarization and thus declined driving force for the water permeation. Viscosities of PEI solution with molecular weight 800 and 1200 were  $0.63 \pm 0.02$  mPa s and  $0.75 \pm 0.02$  mPa s, respectively (Figure 2). The higher viscosity of larger molecular weight PEI solution as a DS could obstruct the water transport from the feed to the DS. The PEI with higher molecular weight showed lower reverse solute flux through the membrane since larger molecules can easily be retained by the membrane due to the size exclusion effect.<sup>23</sup>



**Figure 3.**  $pK_a$  values (4.3, 6.4, 9.5) and ionization fraction of PEI at various pH values. ( $\beta_{\text{water}}$  is the contribution of  $\text{H}_2\text{O}$  to the total buffer intensity,  $\beta_{\text{PEI}}$  is the contribution of PEI to the total buffer intensity). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 4.** FO performance using 5 wt % PEI solution at various pH values from pH 3 to pH 11.

The osmolality of 5 wt % lower and higher molecular weight PEI ( $M_w = 800$  and  $1200$ ) were  $125.7 \pm 2.3$ ,  $88.3 \pm 1.5$  mmol/kg, respectively. It seems that the higher osmolality of molecular weight PEI ( $M_w = 800$ ), also, caused the higher permeation of water from FS to DS. Lower molecular weight PEI ( $M_w = 800$ ) showed higher water and reverse solute flux compared with higher molecular weight PEI ( $M_w = 1200$ ); and lower molecular weight PEI ( $M_w = 800$ ) was chosen for further research to get the higher flux of FO process.

#### Effect of DS pH on PEI Speciation

Amines in PEI draw solute can be protonated or deprotonated as a function of pH and the permeability of the PEI through the membrane depends on the protonation or deprotonation (so called speciation) of the draw solute. When the pH is less than  $pK_a$ , the protonating speciation is predominant; but when the pH is higher than  $pK_a$ , the deprotonating speciation is predominant. The concentration of protonated and deprotonated amines becomes equal when the pH is the same as  $pK_a$ . The protonated and deprotonated species can be simply converted by proton exchange, and the ratio depends on the pH condition. PEI is a kind of a base that can be protonated at lower pH than  $pK_a$ , since the PEI has three different types of amine: primary amine, secondary amine, and tertiary amine. Each type of

amine has its own  $pK_a$  value, and the structural/chemical properties set by the speciation determine the performance of the FO process. The effect of PEI speciation at various pH values was investigated first, and then the effect of the DS's pH on the FO performance was evaluated based on the speciation of the PEI.

The buffer intensity of PEI solution is shown in Figure 3, and peak fitting of the graph was carried out to estimate the  $pK_a$  of each type of amine since the buffer intensity becomes maximum at a pH that is equal to  $pK_a$ . The  $pK_a$  values of the PEI with molecular weight 800 were at about 4.3, 6.4, and 9.5, respectively. The ratio of primary : secondary : tertiary amines of the PEI (average  $M_w \sim 800$  by LS, average  $M_n \sim 600$  by GPC) are 1 : 2 : 1, according to the supplier of the chemical. Based on both the dominant presence of secondary amine and relationship between amine center structure and molecular weight, the values at 4.3, 6.4, and 9.5 are likely the  $pK_a$  of tertiary, primary, and secondary amines, respectively.

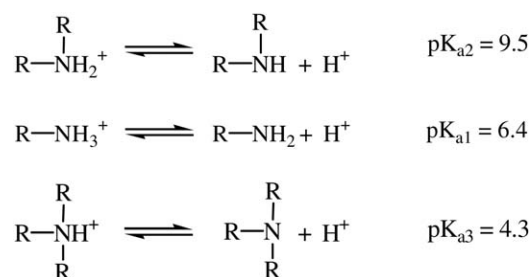
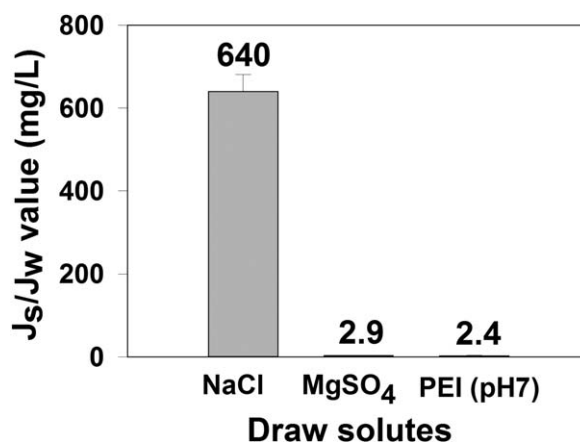


Figure 3 also shows a distribution diagram of the species as a function of pH. When the pH of PEI solution is above 9.5, the dominant species of PEI is a neutral one. Also, with decreasing pH, the dominant species becomes secondary, primary, and tertiary amine in sequence.

#### Effect of DS pH on FO Performance

Figure 4 shows the water flux and reverse solute flux through the FO membrane at various pH values of DS. With decrease in pH from pH 11 to pH 3, the water flux monotonically increased from  $1.98 \text{ L/m}^2\text{h}$  to  $6.04 \text{ L/m}^2\text{h}$ . This resulted from both the enhanced protonation of the PEI, as shown in Figure



**Figure 5.** Osmolality of 5 wt % PEI solution at various pH values from pH 3 to pH 11.

**Table II.** Viscosity of PEI Using at Various pH Conditions from pH 3–11

pH condition	pH 3	pH 5	pH 7	pH 9	pH 11
Viscosity (mPa.s)	$0.572 \pm 0.014$	$0.597 \pm 0.021$	$0.596 \pm 0.012$	$0.673 \pm 0.005$	$0.661 \pm 0.011$

**Table III.** Zeta Potential of the HTI TFC Membrane

pH	3	4	5	6	7	8	9
Zeta potential (mV)	~0	$-13.1 \pm 0.6$	$-24.1 \pm 0.5$	$-32.1 \pm 0.9$	$-34.4 \pm 3.5$	$-37.0 \pm 2.3$	$-39.4 \pm 2.7$

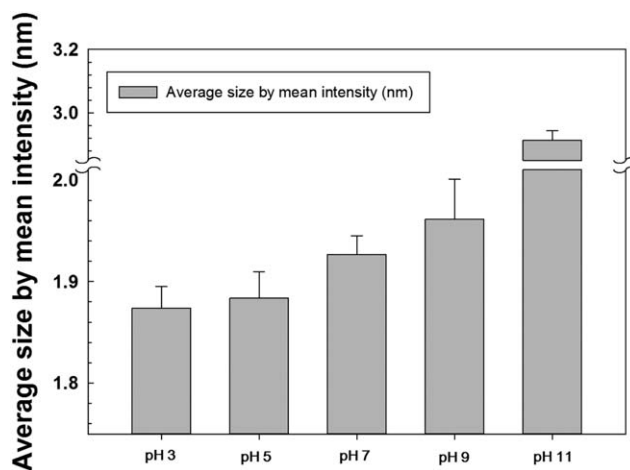
3, and the increased number of counterions balancing the DS in charge, enhancing osmotic pressure of the DS, and subsequent increasing driving force of water permeation from FS to DS. The enhanced driving force of water permeation at lower pH condition was evaluated by measuring osmolality of the DS. The osmolality of DS monotonically increased as shown in Figure 5 with decrease in pH from pH 11 to pH 3. Furthermore, the slightly declined viscosity of the DS at lower pH could help the pure water pass through the membrane more easily (Table II).

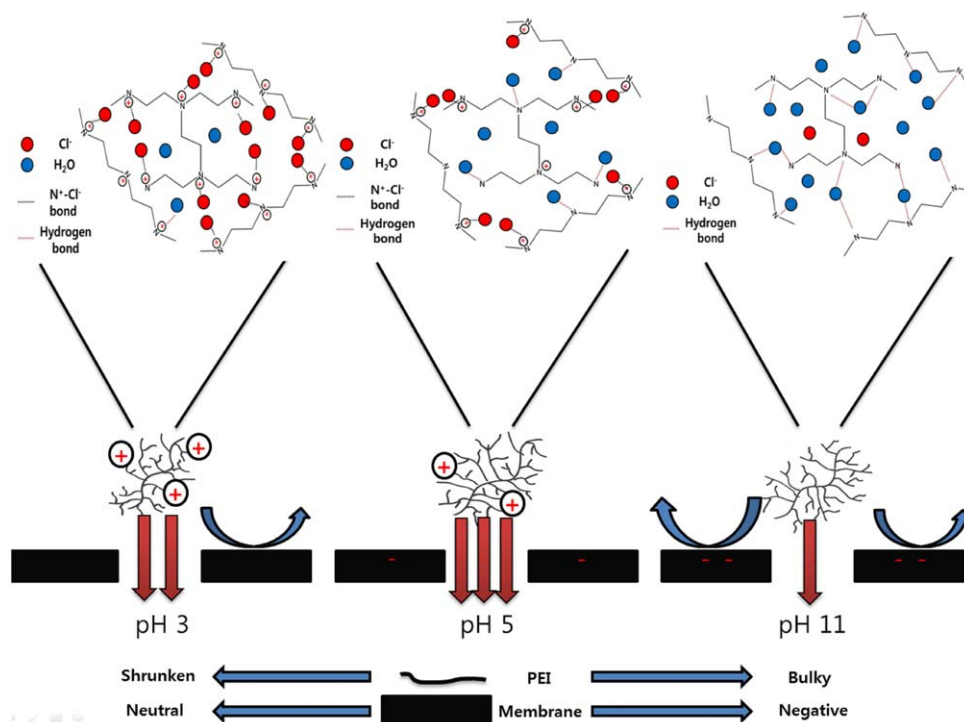
However, with decreasing pH, the reverse solute flux increased from  $6.92 \times 10^{-3} \text{ g/m}^2\text{h}$  at pH 11 to  $14.5 \times 10^{-3} \text{ g/m}^2\text{h}$  at pH 5, and then decreased to  $12.1 \times 10^{-3} \text{ g/m}^2\text{h}$  at pH 3. A polyamide membrane has amine and the carboxylic functional groups, and the protonation of the amine at low pH and deprotonation of carboxylic group at high pH can have the membrane more charged above or below the isoelectric point (Table III) and cause the swollen membrane due to the electrostatic repulsion interaction between membrane polymers at the low and high pH. The swelling effect of the FO membrane was investigated using 500 ppm IPA solution at various pH values, since IPA is a good indicator to evaluate the extent of membrane swelling due to its small and neutral characteristics along different pH conditions. Table IV presents the performance of the TFC HTI FO membrane operated in a pressure-driven mode using IPA solution. The rejection of IPA was maximum at neutral pH, and then decreased with both decreasing and increasing pH. If the swelling is the main factor that determines the PEI reverse solute flux through the FO membrane, the PEI loss should be higher at low and high pH. However, the experimental results in Figure 4 showed the opposite results. The swelling of PA membrane did not dominantly contribute to the water flux and reverse solute flux of PEI DS in the FO process.

**Table IV.** RO Performances at Various pH Values: Water Flux and Rejection (Tested at 225 psi, Using 500 ppm Isopropyl Alcohol)

pH	Flux (L/m <sup>2</sup> h)	Rejection (%)
3	$27.2 \pm 1.9$	$88.2 \pm 0.6$
5	$25.7 \pm 1.0$	$88.7 \pm 0.8$
7	$25.8 \pm 0.6$	$89.4 \pm 1.8$
9	$25.7 \pm 0.6$	$89.2 \pm 1.0$
11	$28.8 \pm 1.6$	$86.7 \pm 2.0$

The maximum reverse solute flux at pH 5 and then decreasing reverse solute flux with increasing and decreasing DS pH seems to be due to the structural change of PEI and electrostatic interaction between the PEI and membrane surface at the operating pH. The PEI can have a swollen structure at high pH since the deprotonated amines form strong hydrogen bonding with water molecules in the DS. However, at low pH, the PEI have a shrunken structure, because the protonated amines and large amount of counterions present to satisfy the charge balance of DS prevent the hydrogen bonding of the amines with water molecules and make the PEI have smaller size due to the van der Waals interaction between  $-\text{CH}_2\text{CH}_2-$  spacers of the PEI. Figure 6 shows the size of the hydrated PEI at various pH conditions. The small size of the PEI might increase the passage through the FO membrane with decreasing pH from 11 to 5. Furthermore, the zeta potential of the FO membrane in Table III shows the membrane surface became less negative with decreasing pH and had an isoelectric point at about pH 3. The positively charged amine and negatively charged membrane surface can have attractive electrostatic interaction and assist the permeation of the PEI through the membrane. Therefore, the increasing reverse solute flux could be explained with decreasing pH to 5. However, at pH 3, the membrane had almost no negative charges, causing loss of electrostatic driving force to move the positively charged PEI through the membrane. Those would be the reasons why the reverse solute flux of PEI increased from pH 11 to pH 5, and then decreased from pH 5 to pH 3. The

**Figure 6.** Average size of 5 wt % PEI solution at various pH values from pH 3 to pH 11.

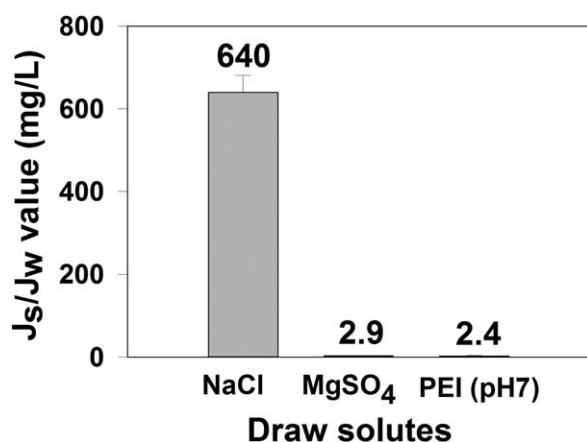


**Figure 7.** Schematic diagram of PEI structure and membrane surface at various pH conditions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

conceptual model is summarized in Figure 7 to show the effect of change of both PEI structure and surface charge on performance at various pH conditions. The optimum operation pH condition of PEI DS in the FO process was obtained at pH 7 considering the relatively lower loss of draw solute with high flux, and lesser amount of acid added to decrease the pH of DS to the target operating pH.

#### Specific Reverse Solute Flux and Recovery of Draw Solutes

The efficiency of draw solutes was evaluated in terms of the specific reverse solute flux ( $J_s/J_w$ ) and recovery of the solute. The



**Figure 8.** Specific reverse solute flux ( $J_s/J_w$ ) of 2000ppm NaCl, MgSO<sub>4</sub>, and PEI draw solutions.

specific reverse solute flux is a ratio of reverse solute flux to water flux, and represents the amount of lost solute per unit volume of pure water produced during the operation of the FO process. The specific reverse solute flux of PEI at pH 7 was compared with those of sodium chloride and magnesium sulfate in FO condition (Figure 8). The  $J_s/J_w$  value of the PEI was about 270 times smaller than that of sodium chloride, and the parameter is slightly lower than that of magnesium sulfate. The lower  $J_s/J_w$  value of PEI shows that PEI is a proper reagent to use in the FO process, because of the small amounts of solutes diffused from draw to feed side (small lost solute during operation) and, because it maintained high osmotic pressure during the FO operation.

Besides the lower loss rate and subsequent maintenance of osmotic pressure, the recovery efficiency of the draw solutes is an important factor to be applied to the FO process. In this study, a pressure-driven recovery process (nanofiltration) was combined with the FO process, and the recovery of the draw solutes was evaluated in terms of its rejection. NF membranes can be operated in a wide range of pressure and salt concentration. NE70 membrane was used for the recovery of the DS

**Table V.** Recovery Test of Draw Solutes with NE 70 Membrane (Tested at 75 psi, using 2000 ppm Concentration)

Draw solutes	NaCl	MgSO <sub>4</sub>	PEI (pH 7)
Flux (L/m <sup>2</sup> h)	25.5 ± 0.8	28.1 ± 1.2	25.8 ± 0.5
Rejection (%)	20.6 ± 0.9	97.0 ± 0.2	99.4 ± 0.1

under the condition of 2000 ppm at 75 psi, of which was used as a standard operating condition of the membrane for the product specification of a manufacturer. Table V shows the water flux and rejection when the diluted DS (2000 ppm DS) is used as the FS of the NF process. Magnesium sulfate showed higher water flux than sodium chloride due to its lower molar concentration. The lower concentration corresponded to lower osmotic pressure and thus reduction in flux. However, PEI showed the highest recovery rate of the draw solute (99.4% rejection). The specific reverse solute values in the FO process and rejection of the draw solute in the recovery process (NF) show PEI is a promising solute in an energy efficient FO-NF combined system in terms of low  $J/J_w$  value and high rejection.

## CONCLUSIONS

The effect of the solution pH of branched PEI draw solute was investigated, and the PEI was evaluated as a draw solute in an FO/NF combined system in comparison with sodium chloride and magnesium sulfate. The PEI with lower molecular weight ( $M_w = 800$ ) showed higher water flux than the PEI with higher molecular weight ( $M_w = 1200$ ) due to the declined internal concentration polarization and lower viscosity of the DS. Furthermore, the reverse solute flux of higher molecular weight PEI was lower due to the size exclusion effect. Operation at pH 7 of DS showed relatively high water flux and low reverse solute flux. The  $J/J_w$  value of PEI at pH 7 ( $\sim 2.4$  mg/L) was smaller than that of the other draw solutes of sodium chloride and magnesium sulfate. Furthermore, when NE 70 membrane was used for recovery process, PEI had a higher rejection (99.4%) than sodium chloride (20.7%) and magnesium sulfate (97.0%). In conclusion, FO operation with NF recovery and PEI DS is a promising method for the preparation of sustainable water resources.

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