Preparation and Membrane Separation Performances of Quarternized Ammonium Cationic Polyvinyl Alcohol

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ABSTRACT: The synthesis of quarternized ammonium cationic polyvinyl alcohol ($QPVA^+$) is studied in this article. The effect of synthesis conditions on the degree of substitution (DS) is studied to acquire the optimal synthesis conditions. Polyelectrolyte and polyelectrolyte complex (PEC) membranes of $QPVA^+$ and phosphatized anionic polyvinyl alcohol ($PPVA^-$) are made by solution casting method. It is found that the flux of polyelectrolyte and PEC membrane, consisting of $QPVA^+$ and $PPVA^-$ (1 : 1 in molar ratio), is 403 g/m^2 h, and its separation factor is 970 when the membrane is used in the pervaporation separation of ethanol/water. It is concluded that the hydrophilicity of the membrane and the rigidity of molecular chain segment are enhanced when the anionic and cationic groups are introduced in the PVA, and the membrane separation capability could be adjusted by changing polyelectrolyte material type and cation/anion mole ratio in the polyelectrolyte and PEC. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2584–2594, 2011

Key words: polyelectrolyte membrane; polyelectrolyte complex (PEC) membrane; pervaporation; $QPVA^+$; DS

INTRODUCTION

Polyelectrolyte and polyelectrolyte complex (PEC) membranes are ideal pervaporation membrane materials, owing to their excellent separation selectivity and permeation properties through strong hydration and salting-out effect to organic substances.[1–8] Polyelectrolyte membranes studied often include cationic polyelectrolyte membrane, anionic polyelectrolyte membrane, and PEC membrane prepared by cationic polyelectrolyte and anionic polyelectrolyte. Cationic polyelectrolyte adopted by Krasemann et al.[9] included poly(allylamine hydrochloride), PAH, poly-(diallyldimethylammonium chloride), PDADMAC, poly(4-vinylpyridine), P4VP, poly(ethylenimine), PEI,

and poly(3-alkylthiophene). Feldheim and Elliott[10] studied the pervaporation separation capability of polypyrrole to propanone/water, 2-butanol/water, and 2-butanol/heptane. Teng et al.[11] adopted a series of poly(3-alkylthiophene) membranes to separate ethanol/water solutions.

Zhao et al.[12] reported the preparation of polyelectrolyte and PEC membrane using polyelectrolyte and PECs of sodium carboxymethyl cellulose (CMCNa) and poly(diallyldimethylammonium chloride) (PDADMAC) onto polysulfone ultrafiltration membrane.

PEC membranes, based on two anionic polysaccharides, composed of sodium alginate (SA) and carrageenan (CG), are prepared by interaction with divalent calcium ions. These membranes showed approximately the following pervaporation performance: permeation flux of 94–253 g/m^2 h and ethanol concentration in the permeate of 0.26–0.52 wt % at 40°C when pervaporation separation for an 85/15 wt % ethanol/water mixture is carried out.[13]

However, there tends to be a compromise between the permeability and selectivity in pervaporation. A high permeability is often accompanied with a low selectivity, and vice versa. To realize ideal permeability and selectivity at the same time, it should be careful to choose the package of polyelectrolyte types, polyelectrolyte concentration in deposition, a single-sided coating process, and crosslinking.[14,15]

In this article, PVA is chosen as membrane material to prepare a novel $QPVA^+$ membrane. The effects of

etherifying synthesis temperature, synthesis time, the mole ratio of catalyst to etherifying agent, and the mass ratio of water to isopropanol in the synthesis medium on the DS of etherification are examined systematically, and the optimal synthesis conditions are obtained. The structure and thermal behavior of this material are characterized. Then, the polyelectrolyte and PEC membrane with QPVA$^+$ as polycation is prepared. This membrane is used in pervaporation separation of ethanol/water solution. The effects of cation/anion mole ratio in the membrane, feed concentration, and feed temperature on flux and separation factor are studied. It is obtained that QPVA$^+$/PPVA$^-$ complex membrane is of excellent permeation separation capability. The results will be described in the following sections.
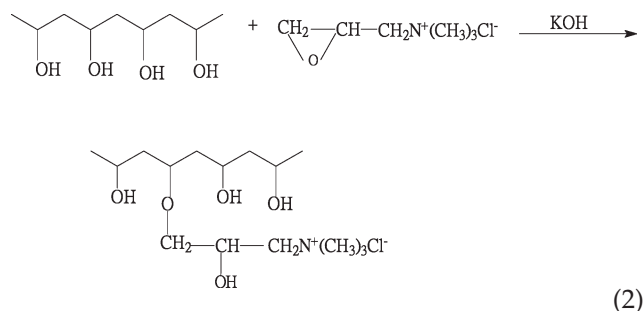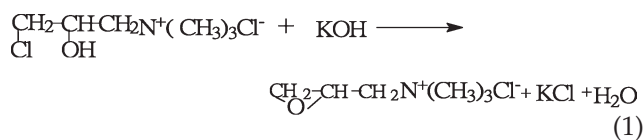
EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA, average degree of polymerization 1750) is purchased from Beijing Organic Chemical Plant. Cationic etherifying agent (3-chloro-2-hydroxypropyl trimethyl ammonium chloride, 60% water solution) is purchased from Japan Tokyo Asahi Kasei Corporation. Potassium hydroxide (KOH, analytically pure) is purchased from China Huamei Medical Fine Chemical Plant. Absolute ethyl alcohol (analytically pure) is purchased from China Beijing Chemical Reagents Company. Deionized water (ultrapure) is obtained from Institute of Microelectronics of Tsinghua University. Nonwoven fabric (90 g/m^2) is made in the USA. Polyacrylonitrile (PAN, molecular weight about 90,000) is purchased from Sinopec Shanghai Petrochemical Company. N,N-Dimethylformamide (chemically pure) is purchased from Korea Samsung Company.

Methods

Kjeldahl method is the standard method of nitrogen determination. Kjeldahl flasks (500 mL) including Kjeldahl digestion unit with fume removal manifold Kjeldahl distillation apparatus is used in the Kjeldahl method. Acid–base titration method is used to determine the DS of phosphatized polymer. Measurements of pH are made with Corning pH meter 445 using a combined glass electrode. The chemical structures of the resulting polymers are characterized by Fourier transform infrared (FTIR) spectroscopy (FTS-165; Rio-Rad company, USA). The DSC measurements are made using a Perkin-Elmer (USA) thermal analyzer with a heating rate of 10°C/min in the temperature range from 30 to 300°C.

Synthesis of QPVA$^+$

Etherification of etherifying agent 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and PVA is carried out in the presence of KOH. The synthesis equation[16] is as follows:

$$\text{CH}_2\text{-CH-CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^- + \text{KOH} \longrightarrow$$
$$\text{CH}_2\text{-CH-CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^- + \text{KCl} + \text{H}_2\text{O} \quad (1)$$
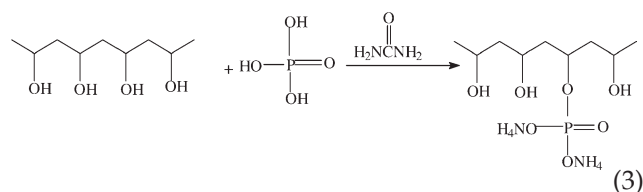

(2)

Synthesis method: After PVA is dissolved in isopropanol/water solution in the range of 5–10 wt % at 85–95°C with continuous stirring, the PVA solution is cooled naturally to the synthesis temperature, as shown in Table I. Then, certain amount of KOH and cationic etherifying agent are added, followed by 3–6 h synthesis with continuous stirring. After synthesis, absolute ethyl alcohol is added to precipitate the product. This product is washed repeatedly with absolute ethyl alcohol until its pH equals to 7. It is then vacuum dried at 58°C.

Synthesis conditions are shown in Table I.

Synthesis of PPVA$^-$

Esterification of phosphoric acid and PVA is carried out in the presence of catalyst urea. The synthesis equation is as follows:

(3)

Synthesis method: After PVA is dissolved in water in the range of 5–10 wt % at 85–95°C with continuous stirring, the PVA solution is cooled naturally to the synthesis temperature. Then certain amount of phosphoric acid and urea are added, followed by 2–5 h synthesis at 65–95°C with continuous stirring. After this synthesis, absolute ethyl alcohol is added

Time	Temperature	The PVA concentration	The mole ratio of KOH to cationic etherifying agent	The mass ratio of water to isopropanol
2–5 h	55–70°C	10 wt %	0.2–1.0	5–25

to precipitate the product. This product is washed repeatedly with absolute ethyl alcohol until its pH equals to 7. It is then vacuum dried at 58°C.

Calculation method of DS

Calculation method of QPVA$^+$ DS

Kjeldahl method is used to determine nitrogen content of samples, and then this nitrogen content is substituted into the substitution formula to calculate DS of sample. The calculation formula of nitrogen content is as follows:

$$x\% = \{[14.01 \times C \times (V - V_0) \times 10^{-3}]/W\} \times 100\%,\tag{4}$$

where V is the volume of standard hydrochloric acid solution consumed by sample (mL), V_0 is the volume of standard hydrochloric acid solution consumed in blank test (mL), C is the concentration of standard hydrochloric acid solution (mol/L), and W is the mass of examined sample (mg).

The calculation formula[17] of QPVA$^+$ DS is as follows:

$$DS = \frac{x/14}{(100 - 195.5x/14)/44 + x/14} \times 100\%,\tag{5}$$

where 14 is nitrogen atomic weight; 44 is molecular weight of PVA segment; and 195.5 is molecular weight of QPVA$^+$ segment.

Calculation method of PPVA$^-$ DS

Acid–base titration method is used to determine the PPVA$^-$ DS. PPVA$^-$ is dissolved in water with a concentration of 0.5 wt % at 85–95°C, and the PPVA$^-$ solution is added. After cooling to room temperature, the PPVA$^-$ in the solution is titrated with 0.05N aqueous NaOH solution to reach the neutral pH point (7.00), as monitored by a pH meter (Corning pH meter 445). The calculation formula[18] of PPVA$^-$ DS is as follows:

$$DS = \frac{\frac{CV}{2}}{\frac{(m-158CV/2)}{44} + \frac{CV}{2}} \times 100\%,\tag{6}$$

where m is the PPVA$^-$ mass (g); C is the concentration of standard sodium hydroxide solution (mol/L);

V is the volume of standard sodium hydroxide solution consumed by sample (mL); 44 is molecular weight of PVA segment; and 158 is molecular weight of PPVA$^-$ segment.

Structure characterization of QPVA$^+$

Infrared analysis is used in structure characterization. Specific method: PVA and cationic polyelectrolyte of different DS is heated to dissolve in water. Then, the solution is defoamed on standing. Afterward, it is then used to make membrane on a clean and horizontal glass plate by scrapping method. After drying in air, a cationic polyelectrolyte membrane of 10 μm is obtained, which is used for infrared analysis.

Thermal behavior of QPVA$^+$

PVA and QPVA$^+$ of different DS are sheared into small pieces, and their glass transition temperatures (T_g) are measured by a Perkin-Elmer (USA) thermal analyzer.

Preparation of polyelectrolyte and PEC membranes

Polyelectrolyte and PEC membranes are prepared by coating QPVA$^+$ or/and PPVA$^-$ solution on the support membrane with a home-made membrane coating machine. The support membrane of the polyelectrolyte and PEC membranes is an ultrafiltration membrane, which is prepared from PAN with the phase inversion method. Polyester nonwoven fabric is used as supporting material. QPVA$^+$ (DS = 10.5%) and PPVA$^-$ (DS = 10.7%) are used as separation material. A solution of the QPVA$^+$ (DS = 10.5%) or/and PPVA$^-$ (DS = 10.7%) is prepared with a concentration of 5–10 wt %. Polyelectrolyte and PEC membranes are prepared in the membrane coating machine, including QPVA$^+$/PAN membrane, PPVA$^-$/PAN membrane, QPVA$^+$, and PPVA$^-$/PAN membrane. The pervaporation separation capabilities of the membranes to ethanol/water solution are determined. The effects of cation/anion mole ratio, operating temperature, and feed concentration on the flux and separation factor of these membranes are studied. The mixture ratio of polyelectrolyte and PEC membranes liquid is shown in Table II.

TABLE II
The Composition of Polyelectrolyte and PEC Solution

| Number	Membrane material	Cation/anion mole ratio
#1	PPVA⁻	0/1
#2	QPVA⁺0.3 + PPVA⁻0.7	0.3/0.7
#3	QPVA⁺0.5 + PPVA⁻0.5	0.5/0.5
#4	QPVA⁺0.7 + PPVA⁻0.3	0.7/0.3
#5	QPVA⁺	1/0

QPVA⁺, quarternized ammonium cationic polyvinyl alcohol; PPVA⁻, phosphatized anionic polyvinyl alcohol.

Experimental apparatus

Figure 1 is the flow chart of the pervaporation performance setup. The system includes three parts: feed system, heating system, and vacuum system. In the feed system, the feed liquid flows from the feed tank, being delivered to the heater by the magnetic drive pump, heated to the specified temperature, and entered into the membrane module. The feed liquid can circulate in the system. The heating system mainly includes a heater and evaporator. In the vacuum system, the permeating vapor can be ventilated from the vacuum housing and then condensated by liquid nitrogen to liquid.

To operate the pervaporation performance setup, the feed system and the heating system are first run. After the feed is heated to the specified temperature and kept at it for 30 min, the vacuum system is switched on. The temperature of the feed is measured, and the feed is sampled at the inlet of membrane module. The volume flow is read from the float flow meter (L/h). Permeating liquid is obtained through the condensation of liquid nitrogen, and the membrane flux and separation factor can be calculated according to eqs. (1) and (2) after the weighing of permeating liquid.

$$J = W_{\text{permeate}}/(A \cdot t), \tag{7}$$
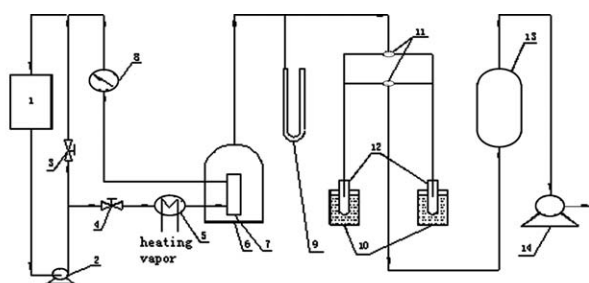
1-feed tank; 2-feed pump; 3-backflow valve; 4-mainpipe valve; 5-heater; 6-vacuum housing; 7-membrane module; 8-float flow meter; 9-mercury vacuum gauge; 10-cold trap; 11-triple valve; 12-sampler collector; 13-buffer tank; 14-vacuum pump

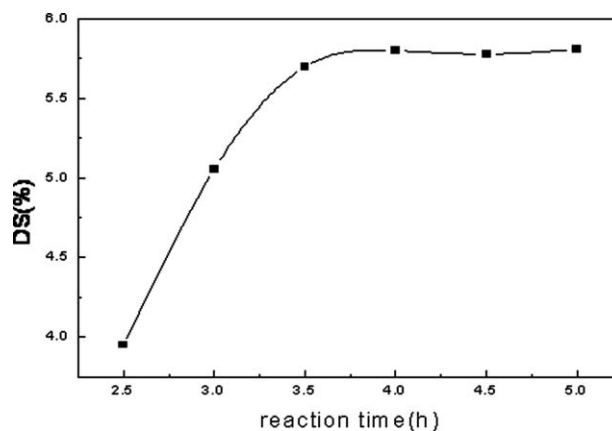**Figure 1** Flow chart of pervaporation performance setup.

Figure 2 The effect of reaction time on DS.

where W_{permeate} is the mass of permeating substances, A is membrane area (0.168 m²), and t is time (h).

$$\alpha_{w/a} = \frac{Y_{\text{feed}} \cdot X_{\text{perm}}}{X_{\text{feed}} \cdot Y_{\text{perm}}}, \tag{8}$$

where $\alpha_{w/a}$ is the separation factor, X is the water mass percentage, and Y is the ethanol mass percentage.

RESULTS AND DISCUSSION

The effect of synthesis conditions on DS of QPVA⁺

The following experiment conditions of QPVA⁺ are shown in Table I.

The effect of synthesis time on DS

The DS of QPVA⁺ produced in the synthesis is measured for different synthesis time frames with other synthesis conditions unchanged in Table I. The result is shown in Figure 2.

It is shown from Figure 2 that the product DS tends to increase with synthesis time because the etherification catalyzed by KOH is irreversible. After the synthesis is in the fourth hour, DS changes little with synthesis prolonging. Therefore, the optimal synthesis time is 4 h.

The effect of synthesis temperature on DS

The DS of QPVA⁺ produced in the synthesis is measured at different temperatures with other synthesis conditions unchanged in Table I. The results are shown in Figure 3.

It is shown from Figure 3 that DS is very sensitive to synthesis temperature. Because activation energy of molecule is low at low temperature, few molecules react. This leads to low DS. Consequently, the
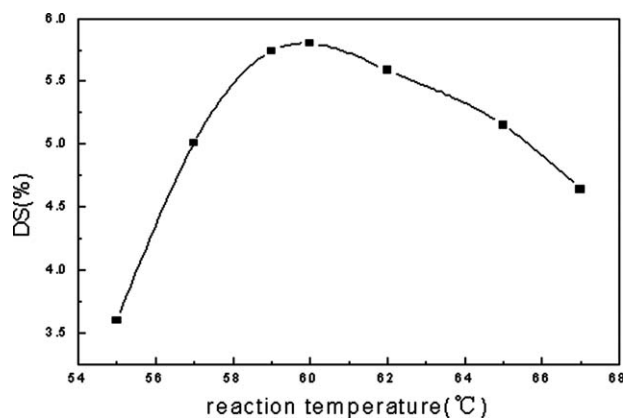
Figure 3 The effect of reaction temperature on DS.

Figure 5 The effect of the mass ratio of water to isopropanol on DS.

temperature is raised to accelerate synthesis. When the temperature is over 60°C, however, the probability of alkoxy anion contacting with etherifying agent molecule is decreased and DS is decreased. The reason is that alkoxy anion is very easy to be enclosed by circumjacent hydrones in drastic molecular motion considering the polarization of alkoxy anion to hydrones at the high temperature.[19] In addition, there is side reaction at high temperature. The optimal synthesis temperature is about 60°C.

The effect of the mole ratio of KOH to cationic etherifying agent on DS

The effect of the mole ratio of KOH to cationic etherifying agent on DS of the product is measured through alteration of the addition of KOH with other synthesis conditions unchanged in Table I. The result is shown in Figure 4.

It is shown from Figure 4 that DS tends to increase with increasing mole ratio of KOH to etherifying agent. However, when the mole ratio increases to about 0.6, DS tends to decrease. When KOH is
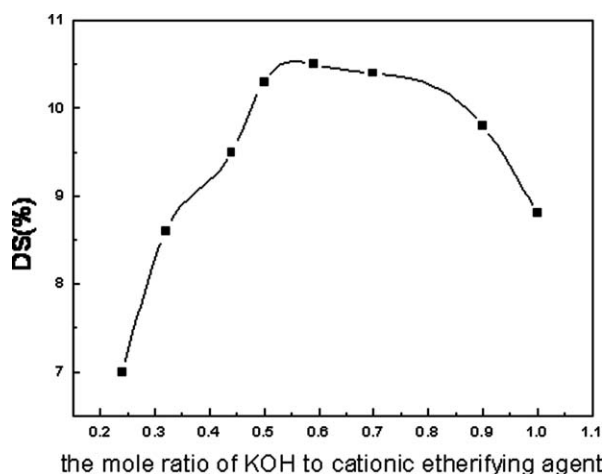
not enough, neither hydroxyl group of PVA can convert to alkoxy anion nor etherifying agent can change to epoxy compound. This leads to the decreasing of DS. When the mole ratio of KOH to cationic etherifying agent is larger than 0.6, PVA turns into gel to impede synthesis because of the crosslinking synthesis of PVA.[20] This leads to the decreasing of DS. The optimal mole ratio is about 0.6 if high DS is required.

The effect of the mass ratio of water to isopropanol on DS

The effect of the mass ratio of water to isopropanol in synthesis system on DS is measured with other synthesis conditions unchanged in Table I. The result is shown in Figure 5.

It is shown from Figure 5 that isopropanol alters the interaction between water and PVA favoring etherification. This is explained as that water suppresses alkoxy anion generating.

It is concluded from the experiments that the optimal synthesis conditions of QPVA$^+$ are shown in Table III.

Infrared analysis of QPVA$^+$

The infrared spectra of PVA and QPVA$^+$ of different DS are shown in Figure 6.

It is shown from Figure 6 that the distinction absorption peak of 1740 cm^{-1} disappears in the infrared spectrum of hydrolyzed PVA because of the hydrolysis of vinyl acetate in PVA. Furthermore, new absorption peak of 1640 cm^{-1} appears in the infrared spectrum of etherified PVA, and the strength of this absorption peak increases with increasing DS. This absorption peak is the characteristic absorption of quarternized ammonium cation.

Figure 4 The effect of the mole ratio of KOH to cationic etherifying agent on DS.

TABLE III
The Optimal Synthesis Conditions of QPVA$^+$

Time	Temperature	The PVA concentration	The mole ratio of KOH to cationic etherifying agent	The mass ratio of water to isopropanol
4 h	60°C	10 wt %	0.4–0.6	5

The thermal behavior of QPVA$^+$

The T_g curves of PVA and QPVA$^+$ of different DS are shown in Figures 7 and 8.

It is shown from Figures 7 and 8 that T_g of QPVA$^+$ increases obviously with increasing DS. Compared with $T_g = 89$°C of PVA, T_gs of QPVA$^+$ are 188.0, 210.53, and 221.53 when DSs of QPVA$^+$ are 2.00, 3.73, and 5.80, respectively. One reason is the reducing flexibility of polymer segment caused by that the regular arrangement of the original hydroxyl group in the PVA main chain is broken by substituting group of quarternized ammonium cation. The other reason is that the formation of ionic polymer has a great effect on T_g. For example, when polyacrylic acid is converted to sodium polyacrylate, T_g can increase to 280°C from 106°C. When polyacrylic acid is changed to copper polyacrylate,[21] T_g can increase to 500°C from 106°C.

The effect of cation/anion mole ratio in the polyelectrolyte and PEC on membrane separation capability

To observe the effect of cation/anion mole ratio in the polyelectrolyte and PEC on membrane flux and separation factor, polyelectrolyte and PEC are prepared by adjusting positive to negative charge ratio in the cationic and anionic polyelectrolyte using QPVA$^+$(DS = 10.5%) and PPVA$^-$(DS = 10.7%) as separation materials. Polyelectrolyte/PAN membranes are prepared when the polyelectrolyte and PEC are used as separation layer materials, and the flux and separation factor of the membrane to separate ethanol aqueous solution are measured. The

ethanol concentrations in the ethanol aqueous solution are 95, 90, and 80 wt %, and feed temperatures are 60 and 75°C.

The membrane flux and separation factor of the different cation/anion mole ratio are shown in Figures 9 and 10.

X_{PVA^+} is the mole fraction of cationic polyelectrolyte in the Figures 9 and 10.

It is indicated from the experimental results that the mole ratio of cationic PVA to anionic PVA is an important factor to separation capability in the polyelectrolyte and PEC membrane formed by QPVA$^+$ and PPVA$^-$. Flux and separation factor first increase and then decrease as the mole fraction of cationic group in the membrane material increases. Membrane flux is maximal when the mole fraction of cation in the polyelectrolyte membrane is 0.7. Membrane separation factor is maximal when the mole fraction of cation in the polyelectrolyte membrane is 0.5.

It is also obtained from the experimental results that the flux of pure PPVA$^-$ membrane is minimum, and the flux of pure QPVA$^+$ membrane is larger than that of pure PPVA$^-$ membrane.

The concept of pervaporation separation index (PSI)[22] is applied to understand the overall properties of these membranes. It is found from the experiment results that there is a trade-off between flux and separation factor in most cases. Flux of the membrane is small when separation factor of the membrane is large. Thus, the two parameters shall be considered jointly, not pursued their individual
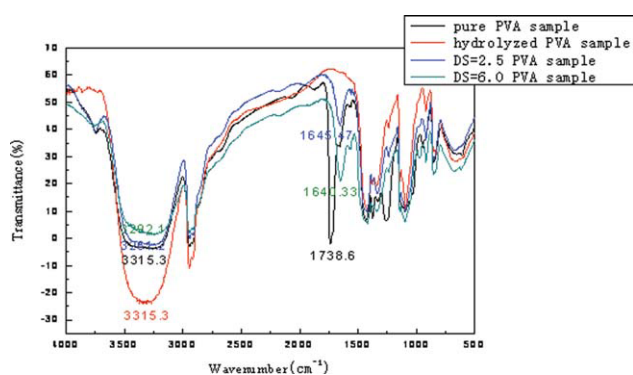

Figure 6 The infrared spectra of PVA and QPVA+ of different DS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
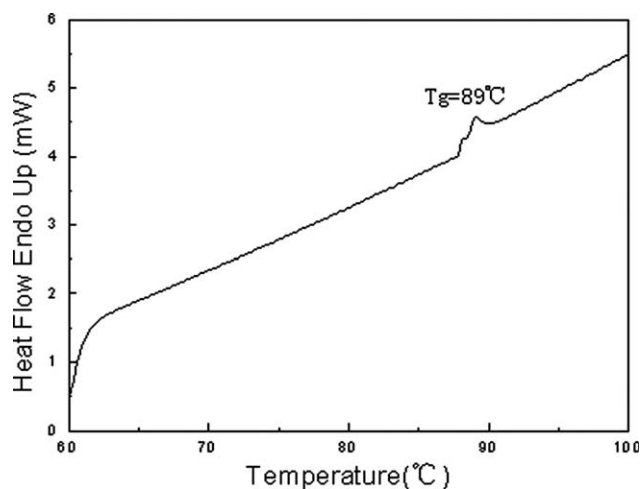
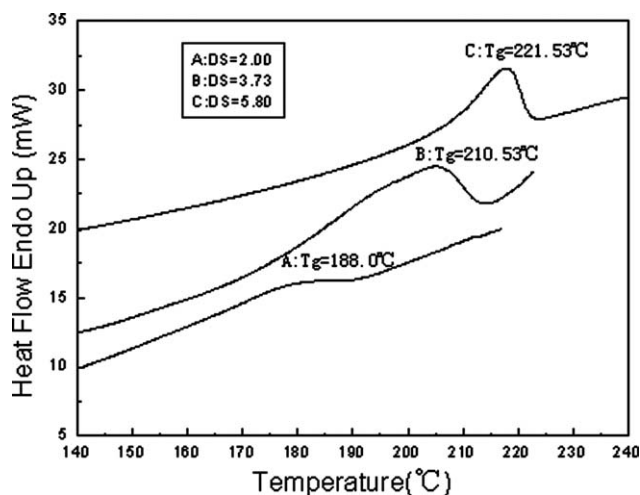

Figure 7 T_g curve of PVA.

Figure 8 T_g curve of QPVA+ of different DS.

optimal values in practical application. Huang and Yeom introduced that PSI is defined as the product of separation and flux:

$$PSI = J \times \alpha, \qquad (9)$$

where J is the membrane flux and α is the separation factor.

The dependence of PSI on the mole ratio of cation/anion is evaluated. The results are shown in Figures 11 and 12.

It is indicated from the above research results that the mole ratio of $QPVA^+$ to $PPVA^-$ is an important factor to influence the permeability and permselection of polyelectrolyte and PEC membrane.

With $QPVA^+$ and $PPVA^-$ in a proportion of one to one, the prepared #3 membrane is of the highest separation selectivity, high flux, and the largest PSI

that manifest the most excellent comprehensive property.

The structure and property of polyelectrolyte are strongly changed after cationic polyelectrolyte and anionic polyelectrolyte interact with each other to form polyelectrolyte. The properties of polyelectrolyte and PEC membrane are dependent on the strength of cationic or anionic groups, charge density, the positions of the cationic or anionic groups in the polymer segment, the mole ratio of the cationic or anionic groups, etc. In addition, the influence of the polymer main chain to polar charge distribution should also be considered.

The process of fabricating polyelectrolyte and PEC from $QPVA^+$ and $PPVA^-$ proposed in this article is the neutralization of the opposite charges in the polyelectrolyte chains. The equation of this process is as follows:
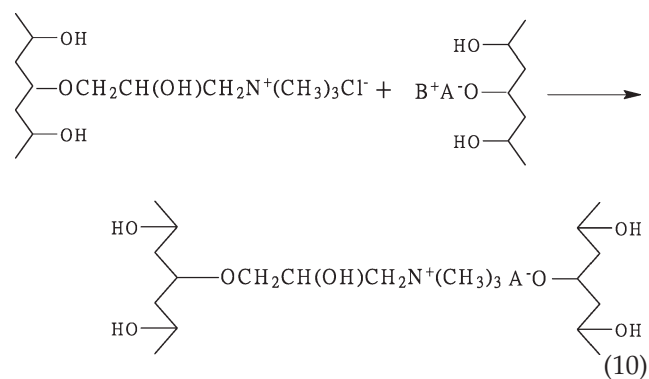
where A^- represents HPO_3^- and B^+ represents NH_4^+.

Quarternized ammonium and phosphate in the above equation are both strong hydrophilic groups, and these two groups combine into ion pairs
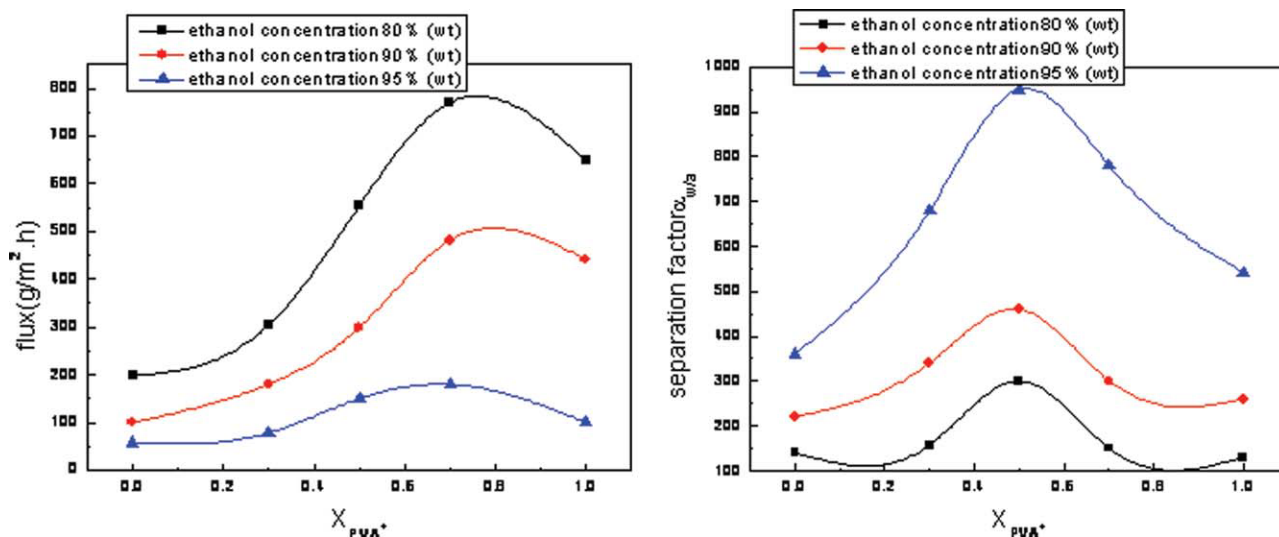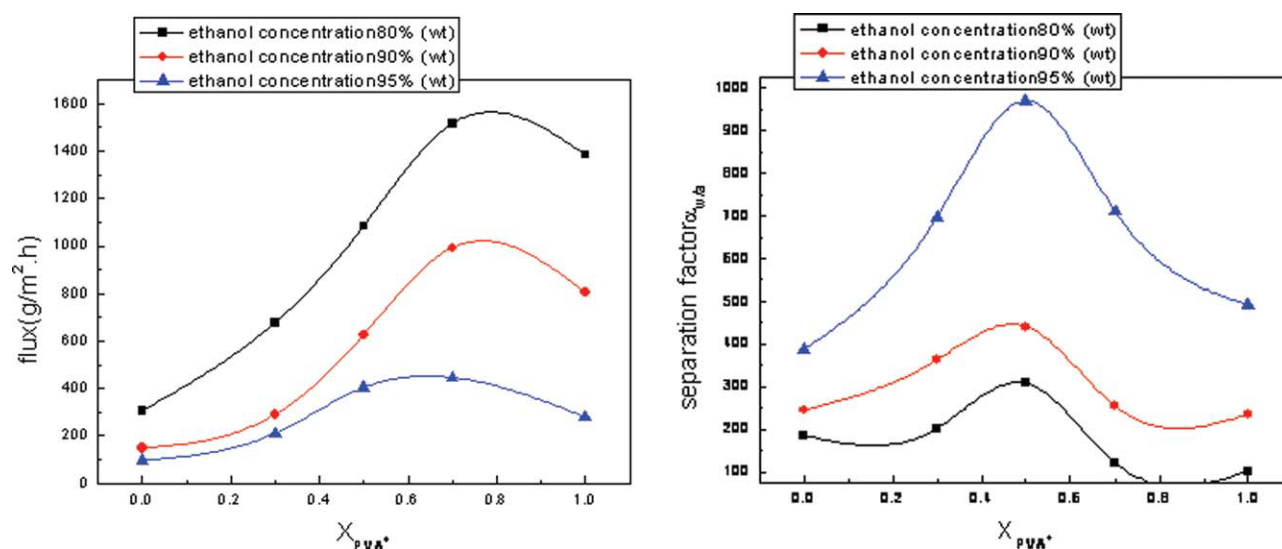

Figure 9 The relation of cationic mole ratio to flux and separation factor in polyelectrolyte membrane (60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10 The relation of cationic mole ratio to flux and separation factor in polyelectrolyte membrane (75°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

through electrostatic interaction. This electrostatic interaction in the polyelectrolyte and PEC is the strongest interaction in the material system, which is named as the dipole–dipole attraction. These ion pairs aggregate to become ionic polymer through the dipole–dipole attraction, which restricts the motion of molecular chain and raises T_g of the material.

The hydrophilicity of polymer chain aggregation structure is not reduced because of the limited screening of the Coulomb force. Additionally, the remained hydroxyl groups are of high hydrophilicity. Usually, polyelectrolyte and PEC deposit are of-

ten formed when polyelectrolyte aqueous solutions of opposite charges mix, but it is not precipitated as usual when $QPVA^+$ and $PPVA^-$ aqueous solution are used in the article. This confirms the structural uniqueness of the polyelectrolyte and PEC. About 10 hydroxyls per 100 hydroxyls are replaced because of the low DS of $QPVA^+$ and $PPVA^-$. The ratio of quarternized ammonium or phosphate in the molecular chain is 1/10, indicating the long average distance between cation and anion. The long distance leads to the small probability of cation and anion under the Coulomb force screened by other groups. Therefore, the hydrophilicity of polymer chain is not
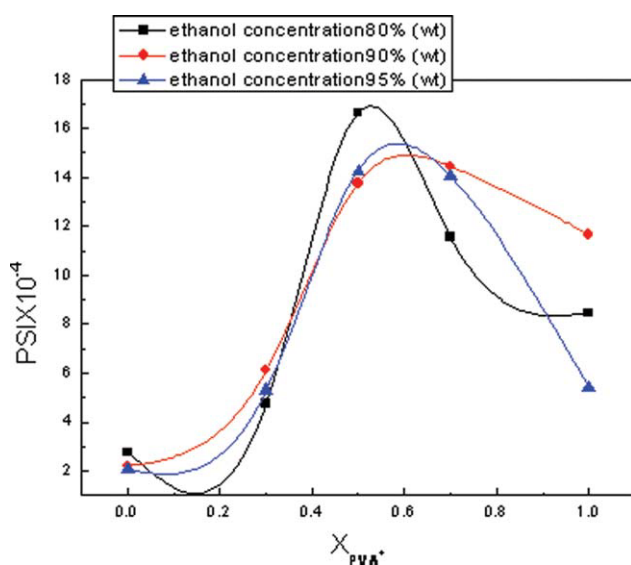

Figure 11 The relationship between PSI and the cationic mole ratio in the membrane (feed temperature 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
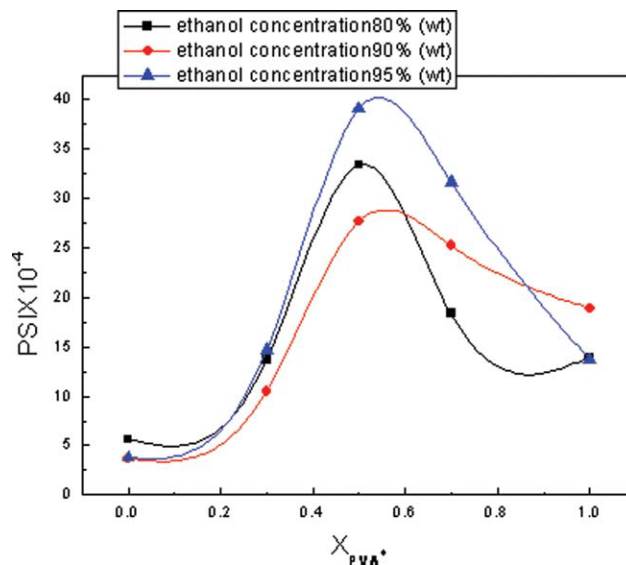

Figure 12 The relationship between PSI and the cationic mole ratio in the membrane (feed temperature 75°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
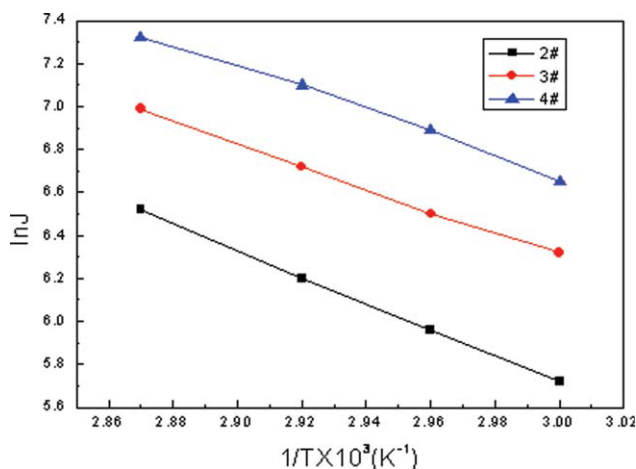
Figure 13 The relation between flux and feed temperature (Feed: water 20 wt %, ethanol 80 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduced after the formation of polyelectrolyte and PEC.

This structural characteristic leads to higher adsorption selectivity of the PEC to the highly polar hydrone than the original polyelectrolyte and the stronger salting-out effect to organic substances than polyelectrolyte that comprises of the $QPVA^+$ + $PPVA^-$ polyelectrolyte and PEC. Therefore, polyelectrolyte and PEC membrane is of higher flux and separation factor to ethanol aqueous solution. One reason is that the larger volume of cationic and anionic groups makes the arrangement of molecular chain looser to allow hydrone permeating. The other reason is that the excessive swelling of the membrane is restricted to make the ethanol molecules of larger volume difficult to permeate because the motion of molecular chain is restricted by the dipole–dipole attraction of ion pairs. The above two reasons result
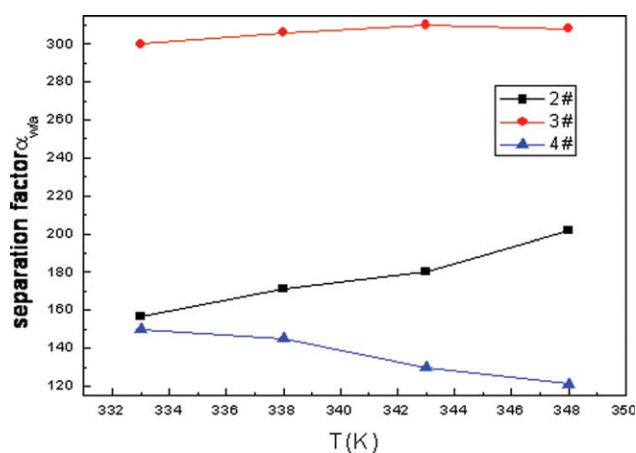

Figure 14 The relation between separation factor and feed temperature (Feed: water 20 wt %, ethanol 80 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
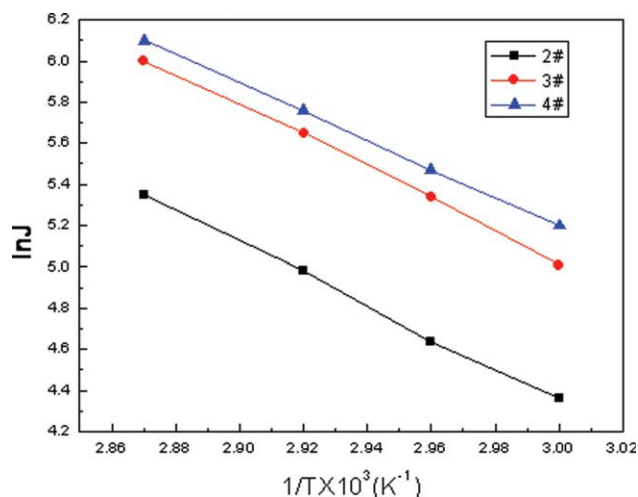

Figure 15 The relation between flux and feed temperature (Feed: water 5 wt %, ethanol 95 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in #3 membrane as shown in Table II of excellent separation capability to ethanol aqueous solution.

The effect of feed temperature on membrane separation capability

The relation between feed temperature and property of five polyelectrolyte and PEC membranes is studied in this work. The experiment results are shown in Figures 13–16. Membrane numbers are shown in Table II.

It is shown from Figures 13–16 that fluxes of three PEC membranes increase with increasing feed temperature, and the relation between flux and feed temperature is in accordance with the Arrhenius equation. This is because the dissolving rate of
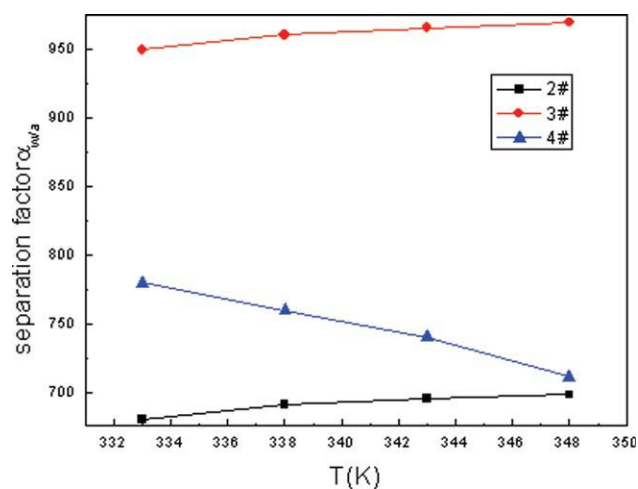

Figure 16 The relation between separation factor and feed temperature (Feed: water 5 wt %, ethanol 95 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
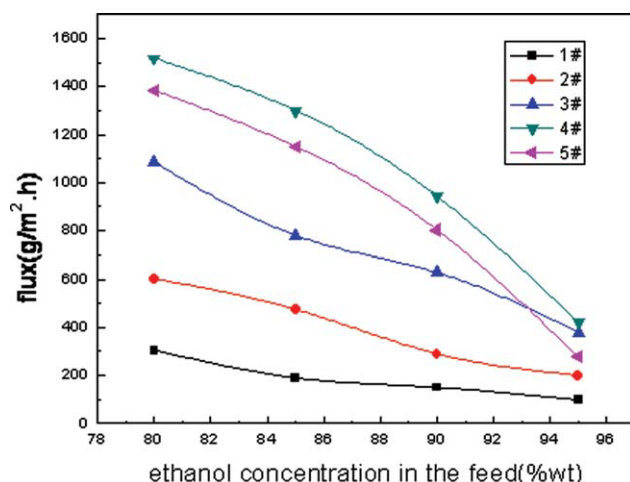
Figure 17 The effect of feed concentration on flux (feed temperature is 75°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

permeating substances on membrane surface and the diffusion rate of permeating substances within membrane are enhanced when temperature increases. At last, this leads to the increasing of flux.

The effect of temperature on separation factor is more complicated. In this study, the effect of temperature on separation factor of #3 membrane is small. Separation factor does not obviously increase with increasing temperature because the effect of temperature on membrane swelling is small by reason of stronger dipole–dipole attraction between cation and anion. Separation factor of #2 membrane increases with increasing temperature, and separation factor of #4 membrane decreases with increasing temperature. #4 membrane has greater flux meaning that membrane swelling is larger at higher temperature. Excessive membrane swelling leads to the decreasing of polymer network density, which contributes to increasing free volume of membrane. This leads to increasing ethanol-permeating quantity but decreasing separation selectivity.

The effect of feed concentration on membrane separation capability

The relationship between feed temperature and separation capability of five polyelectrolyte and PEC membranes is studied in this work. #1, #2, #3, #4, #5 membranes as shown in Table II are adopted, and ethanol concentrations are, respectively, 80, 85, 90, and 95 wt %. The relationships between feed concentration and flux and separation factor at a feed temperature of 75°C are shown in Figures 17 and 18.

It is shown from Figures 17 and 18 that feed concentration has obvious effect on membrane permeability and permselection. Flux of membrane increases and separation factor of membrane

decreases with increasing water content of ethanol aqueous solution. This is because increasing water content leads to excessive membrane swelling, which makes flux increase. Excessive membrane swelling also leads to decreasing of polymer network density, which makes increasing free volume of membrane. This leads to more ethanol dissolving, which makes separation factor decrease. It is also shown from the experimental results that flux of #4 membrane is maximal, and separation factor of #3 membrane is maximal.

CONCLUSIONS

$QPVA^+$ is synthesized, and the optimal synthesis conditions are determined to be: 20 g PVA dissolves into 180 g isopropanol/water solution, the mass ratio of water to isopropanol is 5, the mole proportion of KOH to cationic etherifying agent is 0.4–0.6, synthesis time is 4 h, and the synthesis temperature is 60°C.

When $QPVA^+/PPVA^-$ complex membrane is used to separate ethanol aqueous solution, flux and separation factor first increase and then decrease with increasing cation mole ratio in the membrane. Flux of the #4 membrane is maximal when mole ratio of $QPVA^+$ is 0.7. Separation factor of the #3 membrane is maximal when the mole ratio of cation/anion in the PEC is one to one.

It is indicated from the research results that cationic and anionic groups are introduced in the PVA to enhance hydrophilicity of this membrane material and rigidity of polymer chains. Alteration of polyelectrolyte species and the mole ratio of cation/anion in the polyelectrolyte and PEC can efficiently adjust separation capability of this membrane.
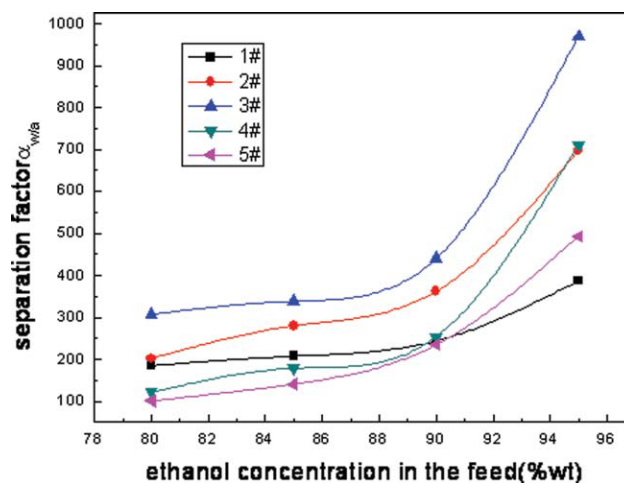

Figure 18 The effect of feed concentration on separation factor (feed temperature is 75°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The optimal conditions of membrane obtained from the research are that polyelectrolyte and PEC membrane is prepared from $QPVA^+(DS = 10.5\%)$ and $PPVA^-(DS = 10.7\%)$. Comprehensive properties of the #3 membrane are optimal when the mole ratio of cation/anion is one to one. Flux of this membrane is $403g/m^2$ h, and separation factor of this membrane is 970 when it is used to separate an ethanol aqueous solution containing 95% ethanol and feed temperature is 75°C.

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