



CHAPTER V

HIGH PERFORMANCE OF POLYBENZOXAZINE MEMBRANES FOR ETHANOL–WATER SEPARATION VIA PERVAPORATION TECHNIQUE

5.1 Abstract

Pervaporation process is used to separate ethanol-water mixture by partial vaporization through a non-porous selectively permeable polybenzoxazine membrane synthesized by using bisphenol-A, formaldehyde, and two different types of diamine, 1,6-hexanediamine (hda) and ethylenediamine (eda), denoted as poly(BA-hda) and poly(BA-eda), respectively. It is found that both membranes with a thickness of 200 μm are suitable for the ethanol–water separation via pervaporation process at a feed temperature of 70 °C. However, poly(BA-eda) membrane provides higher permeation flux and separation factor with increasing ethanol concentration.

Keywords: Pervaporation; Polybenzoxazine; Permeation flux; Separation factor

5.2 Introduction

Pervaporation process using membranes has become of great interest in the past decade since it not only saves both energy and cost in separation of azeotropic mixtures or similar boiling-point mixtures but can also be used in many applications, such as the removal of polluting compounds and volatile organic compounds from the feed solution, dehydration of organic solvents [1], recovery of ethanol from fermentation broths [2, 3], etc. In the pervaporation process, permeate is passed through a non-porous or porous membrane via partial vaporization. When a liquid mixture is in contact with a membrane, one of the components is preferentially eliminated from the mixture because of its higher attraction to, and/or faster diffusivity in, the membrane. Many polymeric membranes, such as poly(dimethylsiloxane) (PDMS) [4], polyimide [5] and polyurethane [6], have been widely used for separation of the water and ethanol mixture via pervaporation because the selectivity and permeability of the membranes can be tailored to effectively separate all kinds of chemicals [7].

Recently, we have developed polybenzoxazine (PBZ) membrane for ethanol-water separation using pervaporation technique [8]. PBZ is a phenolic resin type that offers a number of outstanding properties, including a high glass-transition temperature (T_g), high thermal stability, good mechanical properties, low shrinkage upon polymerization, and excellent molecular design flexibility [9].

In this study, the new PBZ membrane, called poly(BA-eda) membrane, was successfully synthesized and studied with regard to its efficiency in separating water from ethanol when compared with a poly(BA-hda) membrane. The effects of aliphatic chain length, feed temperature, feed concentration, and membrane thickness on the pervaporation performance were also investigated.

5.3 Experimental

5.3.1 Materials

1,4-Dioxane (analytical grade, Labscan, Ireland), bisphenol-A (BPA, 97% purity, Aldrich, Germany), hda (98% purity, Aldrich, Germany), ethanol (99.9% purity, J.T. Baker; White Group, Malaysia), formaldehyde (analytical grade, 37%wt. in water, Merck, Germany), and eda (99% purity, Fluka, Switzerland) were all used as received.

5.3.2 Methodology

5.3.2.1 *Synthesis of Polybenzoxazine Precursors*

Polybenzoxazine precursors were prepared using BPA, formaldehyde, and eda or hda with a mole ratio of 1:1:4, respectively [8, 10-11]. BPA (6.84 g, 30 mmol) was first dissolved in 15 mL of 1,4-dioxane in a 50 mL glass bottle and stirred until clear solution was obtained, followed by adding formaldehyde solution (9.73 g, 324 mmol). The temperature was kept at 10 °C, using an ice bath. Diamine (eda or hda) was then added dropwise into the mixture while continuously stirring for approximately 1 h until transparent viscous liquid was obtained. A heat treatment at 100 °C was required to accelerate the reaction to obtain the PBZ precursors, abbreviated as poly(BA-eda) and poly(BA-hda), for PBZ membrane preparation. The PBZ precursors were purified by washing with 200 mL of 0.1 M NaHCO₃ solution before solvent removal by evaporation and drying under vacuum. The characterization was analyzed by proton nuclear magnetic resonance spectroscopy (¹H-NMR, Varian Mercury 300) using deuterated chloroform (CDCl₃) as a solvent.

5.3.2.2 *Preparation of Polybenzoxazine Membranes*

PBZ precursors were cast on a glass plate at room temperature using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membranes were dried at room temperature in air for one day and further dried at 80 °C in an air-circulating oven for one day to

remove excess solvent, yielding the yellow transparent membranes. The PBZ membranes were prepared with thicknesses of 100, 200, and 300 μm to study the effect of the thickness. An attenuated total reflectance infrared spectrometer (ATR-IR, Thermo Nicolet Nexus 670) was used to analyze the chemical structure of PBZ membranes, using ZnSe 45° (flat plate) with a scanning resolution of 4 cm^{-1} . The membrane morphology was also investigated on a scanning electron microscope (SEM, hitachi/s-4800).

5.3.3 Pervaporation Study

A pervaporation experiment schematic drawing is shown in Figure 5.1. The membranes with various thicknesses (100, 200, and 300 μm), were placed in a stainless steel reactor. A flow rate of 900 mL/min was used to circulate the ethanol-water mixture in which the concentration was varied (5, 10, 15, and 20% ethanol) from the feed reservoir to a permeation unit. The temperature of the feeding mixture was also varied at 40°, 50°, 60°, and 70 °C. The performances of the membranes were determined by measuring % ethanol and water in the permeate side to calculate the permeate flux ($\text{kg}/\text{m}^2\text{h}$) and the separation factor. The quantities of the ethanol and the water were determined using gas chromatography (GC, Agilent GC-6890). Samples of 0.5 μL were injected under the following conditions: helium as carrier gas, thermal conductivity detector (TCD) with pressure setting at 55 kPa, oven temperature set at 200 °C, injector and detector temperatures set at 200 ° and 250 °C, respectively. The separation factor and the permeate flux ($\text{kg}/\text{m}^2\text{h}$) were determined by using the following equations:

$$\text{Permeation flux (J, kg/m}^2\text{h)} = \frac{M}{At} \quad , \quad (5.1)$$

where

M = permeate weight (kg),

A = effective membrane surface area (m^2), and

t = pervaporation time (h).

$$\text{Separation Factor } (\alpha_{\text{water/ethanol}}) = \frac{Y_{\text{water}}/Y_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}} \quad , \quad (5.2)$$

where

Y_{water} = mole fraction of water in the permeate,

Y_{ethanol} = mole fraction of ethanol in the permeate,

X_{water} = mole fraction of water in the the feed, and

X_{ethanol} = mole fraction of ethanol in the feed.

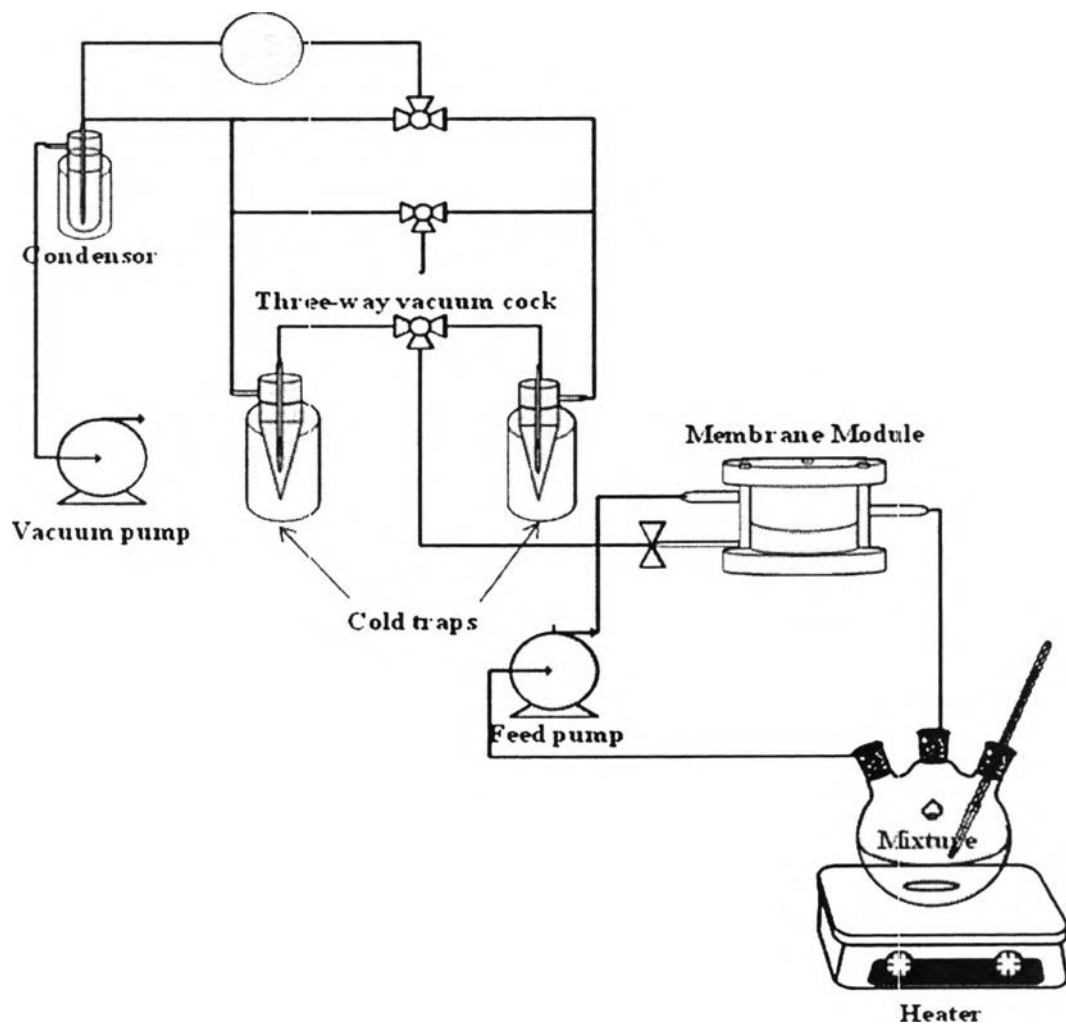


Figure 5.1 Experimental set up for the pervaporation apparatus.

5.4 Results and Discussion

5.4.1 Characterization of PBZ Precursors and membranes

Unlike the traditional solvent method, in which more solvent, more heat, and longer reaction time are required [12], both poly(BA-eda) and poly(BA-hda) were synthesized via quasi-solventless within one hour at low temperature. The resulting Poly(BA-eda) and poly(BA-hda) were confirmed by $^1\text{H-NMR}$ measurement. $^1\text{H-NMR}$ spectra (Figure 5.2) show that the characteristic peaks assigned to the methylene protons of $\text{O-CH}_2\text{-N}$ were found around 4.80 to 4.82 ppm. The methylene protons of $\text{Ar-CH}_2\text{-N}$ of the ring-closed benzoxazine were observed around 3.90 to 3.94 ppm. The peaks at approximately 2.85 to 2.92 represent the methylene protons of the ring-opened benzoxazine. Moreover, the characteristic peaks of the methyl protons of BPA were observed around 1.55 to 1.57 ppm. These results agree with those reported by Takeichi *et al.* [12] and Ning *et al.* [13].

The chemical structure of poly(BA-eda) and poly(BA-hda) were also confirmed using ATR-IR (not shown). The out-of-plane bending vibration of C-H was observed at 932 cm^{-1} . The band assigned to asymmetric stretching of C-O-C and C-N-C were found at 1233 and 1128 cm^{-1} , respectively. Furthermore, the CH_2 wagging of oxazine ring was observed at 1378 cm^{-1} . In addition, the band at 1502 cm^{-1} represents the stretching of trisubstituted benzene ring. These results are in agreement with the study of Ning and Ishida [13].

The SEM micrographs (Figure 5.3) show that the resulting PBZ membranes are dense membranes. From Fig. 3c, the cross-section of poly(BA-eda) shows a few marks due to sample preparation process, but no flaw was observed in this case.

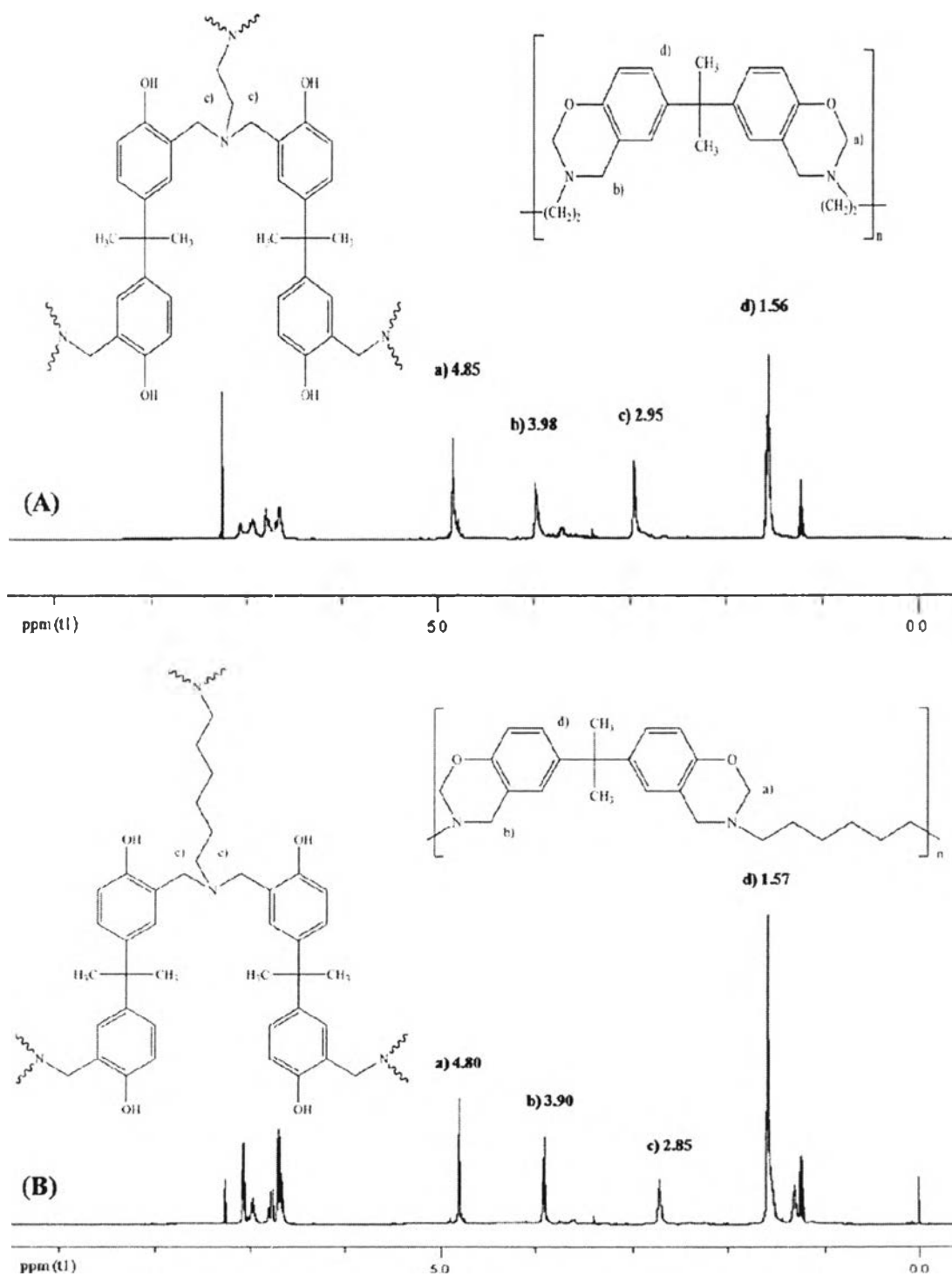


Figure 5.2 $^1\text{H-NMR}$ spectra of polybenzoxazine precursors: poly(BA-eda) (A) and poly(BA-hda) (B).

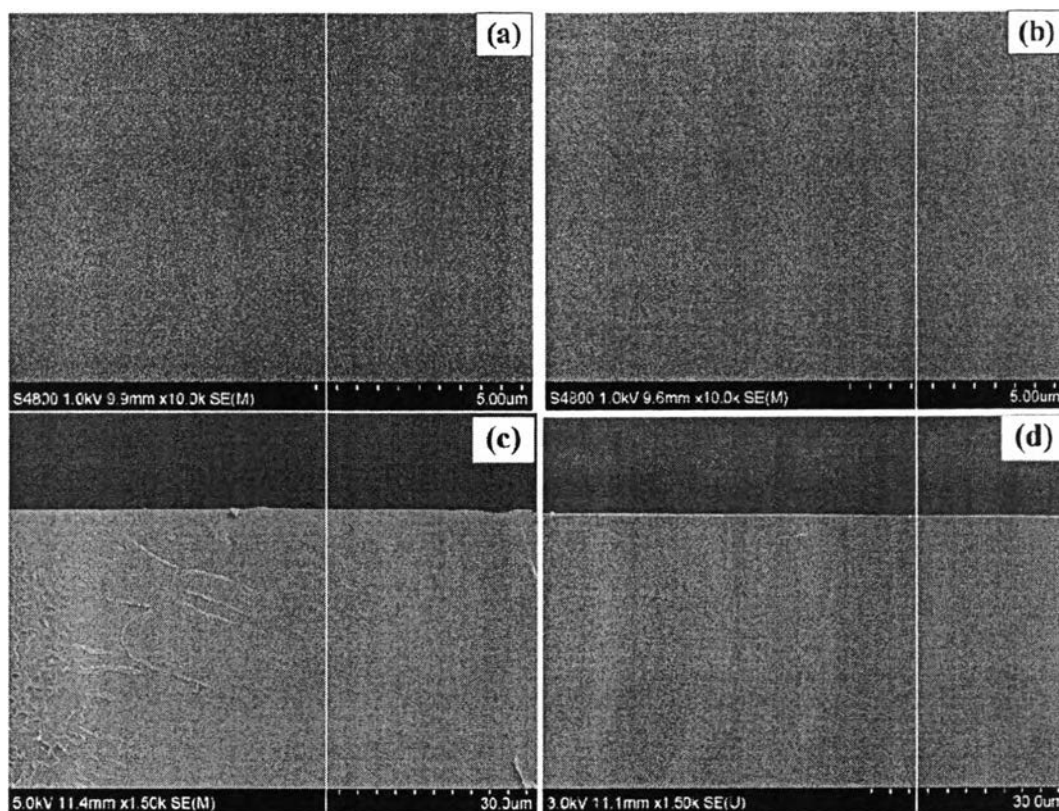


Figure 5.3 SEM micrographs of surface and cross-section of poly(BA-eda) (a)(c) and poly(BA-hda) (b)(d), respectively.

5.4.2 Pervaporation Analysis

5.4.2.1 Effect of feed temperature

In this study, the effect of the feed temperature, from 40° to 70 °C at 10 °C intervals, was studied using 200 µm of thickness of poly(BA-eda) and poly(BA-hda) membranes and 10:90 ethanol:water. The results show that at low temperatures of 40° and 50 °C of feed mixtures, poly(BA-eda) had high permeation flux but rather low separation factor, as presented in Figure 5.4 and Table 5.1, respectively.

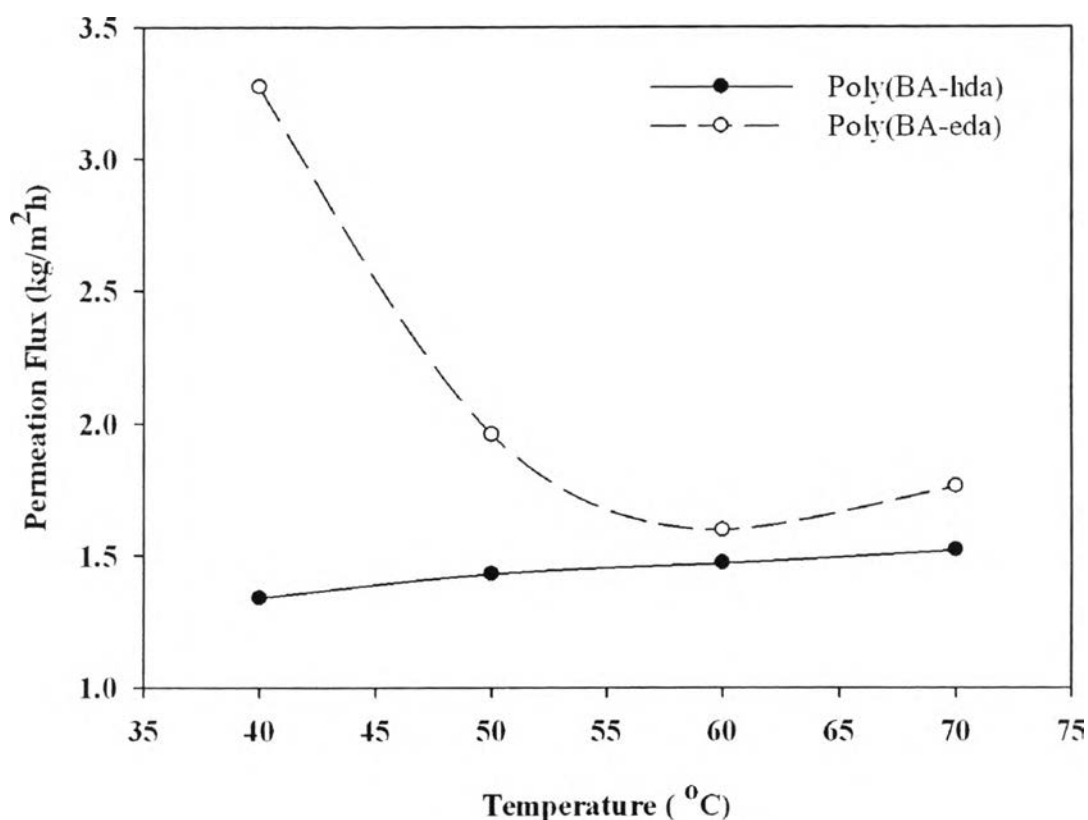


Figure 5.4 Total permeation fluxes of poly(BA-eda) and poly(BA-hda) membranes as a function of the feed temperature.

Table 5.1 Separation factors of ethanol-water using poly(BA-eda) and poly(BA-hda) membranes as a function of the feed temperature

Polybenzoxazine membrane	Separation factor (α)			
	40 °C	50 °C	60 °C	70 °C
poly(BA-eda)	1.25	20.55	>10,000	>10,000
poly(BA-hda)	>10,000	>10,000	>10,000	>10,000

Huang and Yeom [14] also investigated the effect of pervaporation temperature and suggested that the apparent activation energy was a function of permeate concentrations, due to the plasticizing effect of permeates and the

interaction between permeates and the polymer. The Arrhenius-type equation was used to explain the relationship between temperature and permeation flux similar to the explanation of Qunhui *et al.* [15]

$$J = J_0 \exp\left(\frac{-E_p}{RT}\right) \quad (5.3)$$

where J_0 is permeation rate constant, R is gas constant, T is temperature in terms of Kelvin, and E_p is the activation energy for permeation, which can be obtained from the slope of the curve plotted between $\ln J$ and $1/T$. The activation energy shows the amount of energy in excess of the average energy level required to permeate through the membrane.

From the principle of pervaporation, the permeate component undergoes a liquid-vapour phase change when it passes through a dense polymeric membrane, and finally only the vapour phase passes through the permeate side. Therefore, the separation performance and the activation energy are generally determined from the vapour phase of the permeated side. In the case of poly(BA-hda) membrane, we found that the average activation energy calculated from all testing temperatures was 3.74 kJ/mol. However, in the case of poly(BA-eda) membrane, the vapour phase appeared at only high testing temperatures (60° and 70 °C) while at low temperatures (40° and 50 °C) there was some liquid in the permeate side that cannot be used to calculate the activation energy. Therefore, the energy activation of both poly(BA-hda) and poly(BA-eda) membranes could be compared at only high testing temperature. The activation energy of poly(BA-hda) was 3.18 kJ/mol, while that of poly(BA-eda) membrane was 9.40 kJ/mol, meaning that at high temperature poly(BA-eda) membrane needed higher energy for water molecules to permeate through membrane more than poly(BA-hda) membrane. Thus, poly (BA-eda) membrane showed higher permeation flux than poly (BA-hda) membrane. Moreover, at high temperature, both membranes showed high permeation fluxes and high separation factors, consistent with the explanation of Quihui *et al.* [15] that at high temperature the interactions of the permeates, such as those between water–water, water–ethanol and ethanol–ethanol, became weaker, but the interaction between

permeates and membrane was restored, resulting in more water passing through the membrane. In addition, the solubility parameter, which is the ratio of molar attraction and molar volume constants, can also be used to support the affinity of membranes toward ethanol. The solubility of water, ethanol, poly(BA-hda), and poly(BA-eda) membranes is presented in Table 5.2. It can be seen that the solubility of both poly(BA-hda) and poly(BA-eda) membranes has better affinity toward ethanol than water, allowing more water to pass through.

Table 5.2 Solubilities of water, ethanol, poly(BA-hda), and poly(BA-eda)

Materials	Solubility (cal) ^{0.5} /(cm) ^{1.5}
water	18.63
ethanol	8.33
poly(BA-hda)	11.11
poly(BA-eda)	12.65

As discussed earlier, the temperature strongly affects the separating performance. At low temperature, however, the poly (BA-eda) membrane showed a high permeation flux and low separation factor because polymer molecules contain a shorter aliphatic chain length $[-(\text{CH}_2)_2-]$, leading to less ethanol absorption, thus causing both ethanol and water to pass through and finally condense into a liquid phase which is a mixture of ethanol and water. Moreover, Quihui *et al.* [15] suggested that at low temperature the interactions between permeate molecules became stronger and the interaction between permeates and membrane became weaker, making both water and ethanol pass through the membrane. However, poly (BA-hda) membrane, in which polymer molecules have a longer aliphatic chain length $[-(\text{CH}_2)_6-]$, could absorb more ethanol and allow only water molecules to pass through, resulting in low permeation flux with high separation factor.

5.4.2.2 Effect of feed concentration

The feed concentration studied was varied from 5 to 20% ethanol using poly(BA-eda) and poly(BA-hda) membranes with a thickness of 200 μm via pervaporation at 70 °C feed temperature, as shown in Figure 5.5. The mixture concentration slightly affected the permeation flux. The permeation flux increased with an increase in ethanol concentration. This is probably due to an increase in membrane-free volume when ethanol concentration increased, resulting in an increase in side-chain mobility. As a result, small-size water cluster can easily pass through the membrane-free volume. The results are in agreement with the work of Mohammadi [4], who studied pervaporation of dilute alcoholic mixtures using PDMS membrane. Huang *et al.* [16] also studied the effect of ethanol concentration on the separation of polyphosphazene with three different pendant groups and concluded that an increase of ethanol content enhanced ethanol sorption into the membrane, and, as a result, the membrane swelled more. These results were similar to those from our study in which both membranes showed high permeation flux when ethanol concentration was increased, especially in the case of poly(BA-hda) membrane containing a longer aliphatic chain length $[-(\text{CH}_2)_6-]$, the permeation flux increased with an increase in ethanol concentration due to higher ethanol absorption, resulting in a greater swelling ability that allowed more water molecules to pass through. However, poly(BA-eda) membrane containing a shorter aliphatic chain length $[-(\text{CH}_2)_2-]$ showed a slight increase in the permeation flux due to a lower ethanol absorption capacity. However, the separation factor of both membranes with all feed concentrations showed more than 10000. Thus, changing the feed concentration did not have a significant effect on the separation performance.

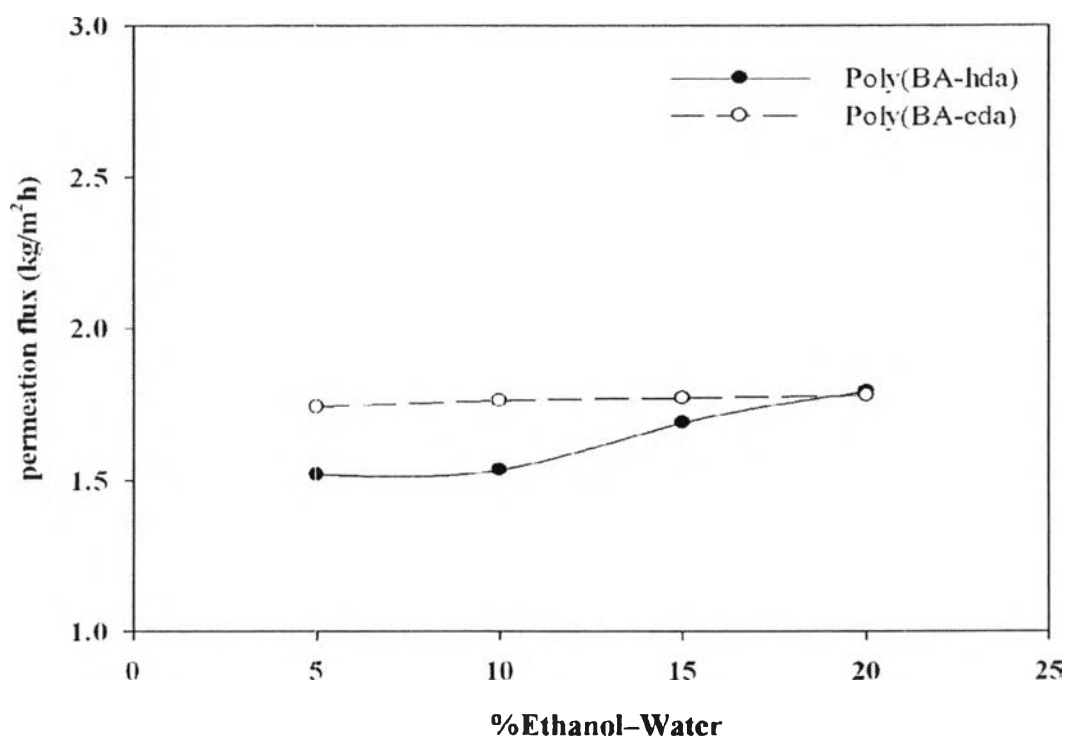


Figure 5.5 Total permeation fluxes of poly(BA-eda) and poly(BA-hda) membranes as a function of the feed concentration.

5.4.2.3 Effect of membrane thickness

Using the appropriate temperature of 70 °C, which provided the highest permeation flux and high separation factor, and 10:90 ethanol:water, the effect of membrane thickness (100, 200, and 300 μm) was investigated. When compared at the same thickness, the permeation flux was higher when poly(BA-eda) membrane was used, as shown in Figure 5.6 and Table 5.3. As discussed earlier, poly(BA-eda) membrane, containing a shorter aliphatic chain length $[-(\text{CH}_2)_2-]$, provided less ethanol sorption, allowing more water to pass through the membrane to the permeate side. Undoubtedly, the tendency of the permeation fluxes of both membranes decreased with an increase in the thickness of the membranes, consistent with Villaluenga *et al.* [17] Qunhui *et al.* [15] also studied the effect of various thicknesses of multi-layered membrane on the permeation flux and found that the

swelling profile in the membrane was a function of the thickness. In our study, at the lowest thickness (100 μm), poly (BA-hda) membrane presented a very large amount of the total permeation flux due to a high degree of membrane swelling. Meanwhile, some ethanol molecules were also adsorbed in the membrane, resulting in some ethanol molecules present in the permeate. Nevertheless, the permeation flux of the thinnest poly(BA-eda) membrane (100 μm) could not be obtained since this membrane was more rigid, causing the membrane to be brittle and more easily damaged after swelling.

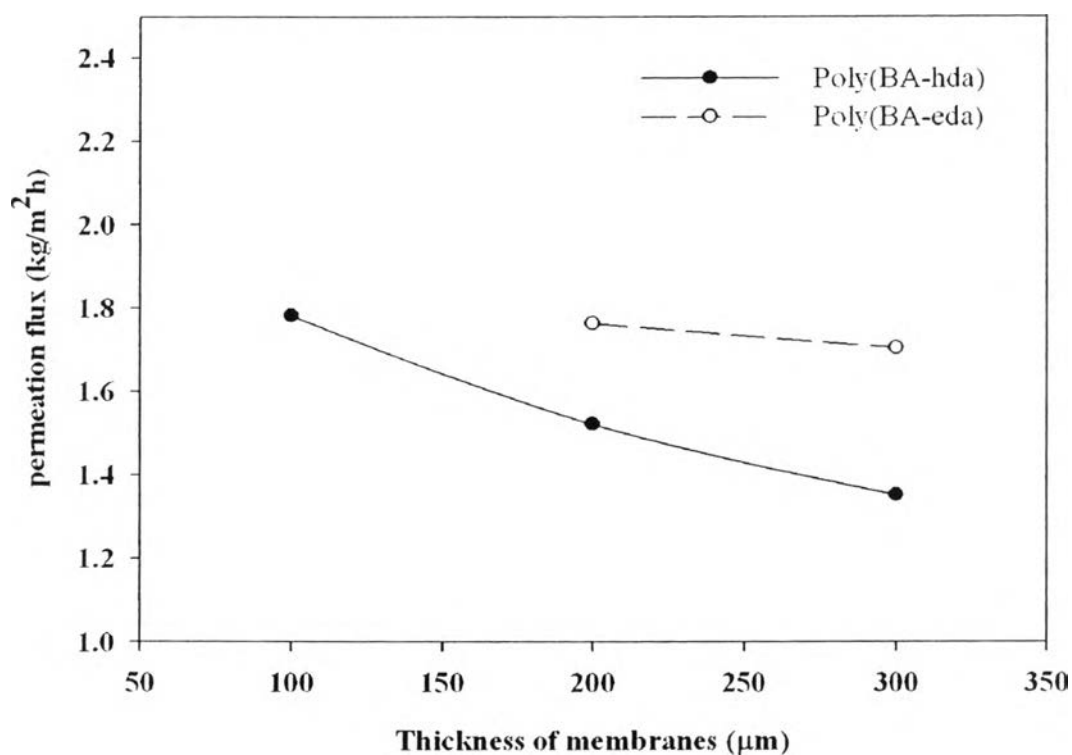


Figure 5.6 Total permeation fluxes of poly(BA-eda) and poly(BA-hda) membranes as a function of the membrane thickness.

Table 5.3 Separation factors of poly(BA-eda) and poly(BA-hda) membranes as a function of membrane thickness

Polybenzoxazine membrane	Separation factor (α)		
	100 μm	200 μm	300 μm
poly(BA-eda)	-	>10,000	>10,000
poly(BA-hda)	76.59	>10,000	>10,000

5.5 Conclusions

Polybenzoxazine membranes, including poly(BA-eda) and poly(BA-hda), were successfully prepared using quasi-solventless technique and employed to separate ethanol-water mixture in pervaporation process. The membrane thickness, the feed temperature and the feed concentration affected the separation performance. The permeation flux increased with an increase in the feed temperature and with a decrease in the membrane thickness. The suitable temperature of the feed solution and the thickness of the poly(BA-eda) and poly(BA-hda) membranes for 10:90 ethanol:water separation via the pervaporation process were 70 °C and 200 μm , respectively. Additionally, poly(BA-eda) membrane can be used for 20:80 ethanol:water separation.

5.6 Acknowledgements

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5.7 References

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