



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Bisphenol-A (BA,  $C_{15}H_{16}O_2$ ) was purchased from Aldrich, Germany. Formaldehyde ( $CH_2O$ , analytical grade) was purchased from Merck, Germany. Hexamethylene diamine (hda,  $C_6H_{16}N_2$ ) was purchased from Fluka, Switzerland. Cardanol was purchased from Satya Cashew Chemicals Pvt.Ltd., India. 1,4- Dioxane ( $C_4H_8O_2$ ) was purchased from Labscan, Ireland. All chemicals were used without further purification to synthesize cardanol-modified polybenzoxazine membrane. And NaA zeolite with a pore size of  $0.2 \mu m$  were supported by senior in my group (Kunnakorn *et al.*, 2011)

### 3.2 Equipments

#### 3.2.1 Proton Nuclear Magnetic Resonance Spectroscopy ( $^1H$ -NMR)

$^1H$ -NMR spectra was recorded on a Varian Mercury 300 (300 MHz) instrument. To identified chemical composition in the range of 1-5ppm. The prepared polybenzoxazine precursors were dissolved in deuterated chloroform ( $CDCl_3$ ) for 24 hours prior to investigate.

#### 3.2.2 Attenuated Total Reflectance Infrared Spectrometer (ATR-IR)

An Attenuated Total Reflectance Infrared Spectrometer (ATR-IR); Nicolet Nexus 670 by using ZnSe  $45^\circ$ , was used to identify the structural characteristics of polybenzoxazine membrane, cardanol-modified polybenzoxazine membrane and zeolite-filled cardanol-modified polybenzoxazine membrane in absorption mode with 64 scans and a resolution of  $4 cm^{-1}$  and wave numbers range of  $4000-650 cm^{-1}$ .

#### 3.2.3 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC); Perkin-Elmer DSC 7, was used to study the polymerization process and the glass transition temperature ( $T_g$ ) of polybenzoxazine membrane, cardanol-modified polybenzoxazine membrane and

zeolite-filled cardanol-modified polybenzoxazine membrane. The samples were heated from 30 °C to 280 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere with a flow rate of 10 ml/min.

#### 3.2.4 Thermogravimetric Analyzer (TGA)

The thermal properties of polybenzoxazine membrane, cardanol-modified polybenzoxazine membrane and zeolite-filled cardanol-modified polybenzoxazine membrane were investigated by using Thermo gravimetric Analyzer(TGA); Perkin Elmer, The sample was loaded on the aluminum pan and heated from 30 °C to 900 °C at a heating rate of 20 °C/min under N<sub>2</sub> flow of 50 mL/min.

#### 3.2.5 Scanning Electron Microscope (SEM)

The morphology of polybenzoxazine membrane, cardanol-modified polybenzoxazine membrane and zeolite-filled cardanol-modified polybenzoxazine membrane were investigated by using a scanning electron microscope, Hitachi S-4800, with an accelerating voltage of 2 kV. Samples were coated with Platinum under vacuum before observation.

#### 3.2.6 Universal Testing Machine (Lloyd)

The mechanical properties of polybenzoxazine membrane, cardanol-modified polybenzoxazine membrane and zeolite-filled cardanol-modified polybenzoxazine membrane were investigated by using Lloyd/LRX Universal Testing Machine at a crosshead speed of 50 mm/min. The results of each sample were determined from an average of at least 5 tests

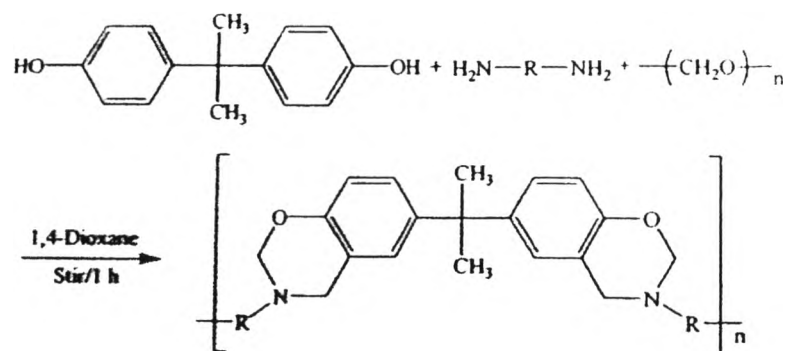
#### 3.2.7 Gas Chromatography (GC)

The compositions of the feed solutions and permeates were measured by gas chromatography on an Agilent GC-6890. A HP-PLOT-Q (30 m × 0.25 mm I.D.) column was used. Sample of 0.5 μL were injected under the following condition: the carrier gas was helium and set at 55 kPa for TCD were maintained. The isothermal oven temperature was set at 200 °C, while the injector and detector temperatures were set at 200 °C and 250 °C, respectively.

### 3.3 Methodology

#### 3.3.1 Synthesis of Polybenzoxazine Precursors

The polybenzoxazine precursor was synthesized by using bisphenol-A (BPA,  $C_{15}H_{16}O_2$ ), formaldehyde ( $CH_2O$ ), and 1,6-hexanediamine (hda,  $C_6H_{16}N_2$ ), as reactants with a molar ratio of 1:4:1, respectively. Firstly, bisphenol-A (3.42 g) was dissolved in 1,4 dioxane (5 g) in glass bottle and stirred until the clear solution was obtained. Then formaldehyde solution (4.87 g) was added into the bisphenol-A solution and stirred continuously for approximately 20 min. The reaction was cooled and temperature was kept under  $10^\circ C$  by using an ice bath. After that aliphatic diamine was added dropwise into the mixture while continuously stirring for approximately 1 hour until transparent yellow viscous liquid was obtained. Fig 3.1 shows about the synthesis process of benzoxazine precursor.



**Figure 3.1** The synthesis of polybenzoxazine precursor.

#### 3.3.2 Preparation of Cardanol-modified Polybenzoxazine Membrane

Cardanol was added into the mixture at  $80^\circ C$  and stirred continuously for 1 hour. The amounts of cardanol were varied. After that, the mixtures were left to cool down and then cast on a glass plate which was wrapped with aluminum foil with a thickness of approximately  $300\ \mu m$  by using Elcometer 3580 casting knife film applicator from elcometer/inspection equipment. The membranes were dried at room temperature in air for one day yielding transparent

red-wine membranes. The membranes were then placed in an air-circulating oven at 80°C for 24 hours to remove excess solvent. Cardanol contents in polybenzoxazine were varied from 1, 3, 5, 7, and 10 wt%.

### 3.3.3 Preparation of Zeolite-filled Cardanol-modified Polybenzoxazine Membrane

Various contents of NaA zeolite were dispersed in 1,4-Dioxane and stirred for 3 hours and sonicated for 10 minutes in order to improve the dispersion of NaA zeolite particles in the solution. Then, NaA zeolite particles were primed by adding approximately 5wt% of total amount of cardanol-modified polybenzoxazine, to increase the compatibility between NaA zeolite and polymer and also to minimize the aggregation of NaA zeolite particles. After that, the mixture was stirred and sonicated to enhance the homogeneity. Then, the remaining cardanol-modified polybenzoxazine was added, the mixture was further stirred continuously for 6 hours before cast on a glass plate which was wrapped with aluminum foil with a thickness of approximately 300 µm by using Elcometer 3580 casting knife film applicator from elcometer/inspection equipment. Finally, the membranes were dried at room temperature in air for one day yielding yellowish membranes. The membranes were then placed in an air-circulating oven at 80°C for 24 hours to remove excess solvent. NaA zeolite contents in cardanol-modified polybenzoxazine were varied from 1, 5, and 10 wt%

### 3.3.4 Characteristics of Prepared Membranes

The structural characteristics of benzoxazine precursor were measured by using Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR). The thermal stability of membranes was investigated by using Thermogravimetric analysis (TGA). The polymerization process and the glass transition temperature (T<sub>g</sub>) were measured by using Differential scanning calorimetry (DSC). The chemical structure and sorption behaviors of membrane were investigated by using Attenuated Total Reflectance Infrared Spectrometer (ATR-IR). The membrane morphology was investigated using a scanning electron microscope (SEM). The mechanical properties of membrane were investigated by using Lloyd/LRX Universal Testing Machine. The quantities of ethanol and water were determined by using a gas chromatograph

(GC) and the permeation flux and separation factor were investigated by using prevaporation apparatus.

### 3.3.5 Swelling and Sorption Behavios Study

The cardanol-modified polybenzoxazine membranes and zeolite-filled cardanol-modified polybenzoxazine membranes (approximately 200  $\mu\text{m}$  thick and 25 mm  $\times$  25 mm in size) were placed in the mixture: ethanol, water, and various mixtures of ethanol and water (20, 40, 60, 80 % by volume of ethanol), for 8 h at room temperature to ensure the attainment of swelling equilibrium. At the specific time, the membranes were removed from the mixture and blotted with a tissue to remove excess liquid before weighed and replace in the mixtures. The procedure was repeated until a constant weight for each sample was obtained and sorption behaviors of membrane were investigated by using Attenuated Total Reflectance Infrared Spectrometer (ATR-IR). The degree of swelling,  $D_s$ , was defined by the following equation.

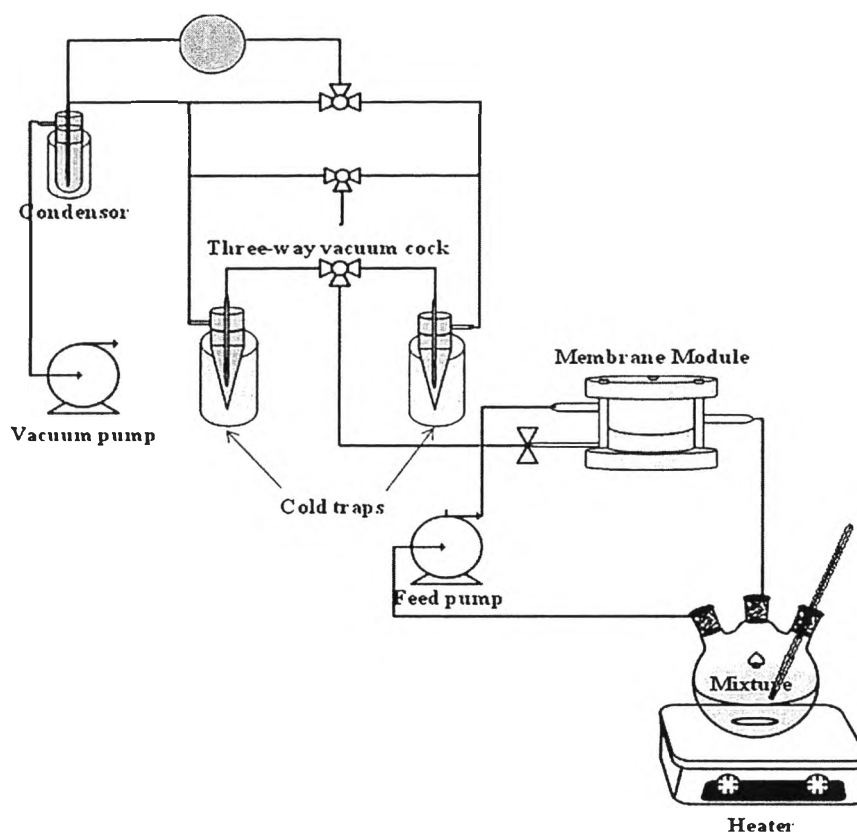
$$D_s = ((W_t - W_0)/W_0) \times 100\% \quad (3.1)$$

Where  $W_t$  = The weight of the swollen membrane (g)  
 $W_0$  = The initial weight of the membrane (g)

The results obtained from each condition were the average of 3 tested membrane samples.

### 3.3.6 Pervaporation System

A schematic diagram of the system used to carry out the ethanol-water mixture separation experiments was shown in Fig 3.2. The membrane is placed in a stainless steel module. The feed temperature is maintained at 70°C in the cell. The flow rate of 900 ml/min was used to circulate the mixture from the feed reservoir to a permeation cell. The ethanol contents in feed solution were varied from 10 wt%, 20, 40, 50, 60, 80, and 90 wt%. This condition was similar to the work done by Hsueh *et al.*, carried out the experiment using different of the ethanol/water rations. Moreover, The effects of NaA zeolite contents on the permeation flux and seperation factor were investigated.



**Figure 3.2** Experimental set up for pervaporation apparatus.

A Teflon gasket was also applied on the membrane to avoid leaking. The capacity of the upper cell compartment was approximately 100 ml while the area of the membrane in contact with the liquid was  $22.1 \text{ cm}^2$ . A water bath on a hot plate was used to control the feed solution temperature. The mixture was stirred continuously during the experiments. Vacuum was applied to the permeate side of the membrane, and the permeate vapor was condensed and collected in a cold trap immersed in liquid nitrogen.

The performances of the membranes were determined by measuring %ethanol in the permeate side to calculate the permeation flux of water ( $\text{g/cm}^2\text{h}$ ) and the separation factor of the ethanol/water mixture. The quantities of ethanol and water were determined by using gas chromatography (GC). Samples of  $0.5 \mu\text{L}$  were injected under the following conditions; the carrier gas is helium and the pressure

was set at 55 kPa for TCD. The isothermal oven temperature was set at 200 °C while the injector and detector temperature were set at 200 °C, respectively.

### 3.3.6.1 Pervaporation Analysis

The permeation flux of water (g/cm<sup>2</sup>h) and the separation factor of the ethanol/water mixture were determined by using the quantities of ethanol and water obtained from GC, as follows;

3.3.6.1.1 Permeation flux of water (J, kg/m<sup>2</sup>h); The J can be calculate from equation 3.1

$$J = M/At \quad (3.2)$$

Where

- M = Permeate weight (kg)
- A = Effective membrane surface area (m<sup>2</sup>)
- t = Pervaporation time (h)

3.3.6.1.2 Seperation factor ( $\alpha_{\text{water/ethanol}}$ ); The  $\alpha_{\text{water/ethanol}}$  was calculated from equation 3.2

$$\alpha_{\text{water/ethanol}} = (Y_{\text{water}}/Y_{\text{ethanol}})/(X_{\text{water}}/X_{\text{ethanol}}) \quad (3.3)$$

Where

- $Y_{\text{water}}$  = the weight fraction of water in the permeate side
- $Y_{\text{ethanol}}$  = the weight fraction of ethanol in the permeate side
- $X_{\text{water}}$  = the weight fraction of water in the feed
- $X_{\text{ethanol}}$  = the weight fraction of ethanol in the feed