CHAPTER III
EXPERIMENTAL

3.1 Materials

Analytical grade 1,4-dioxane and ethanol (99.9% purity) were purchased from Labscan, Ireland. Bisphenol-A (BPA, 97% purity), tetraethylenepentamine (tepa, 85% purity), and diethylenetriamine (deta, 99% purity) were purchased from Aldrich, Germany. Formaldehyde (AR grade, 37wt%. in water) was purchased from Merck, Germany. Tubular porous α-alumina support, having an 11 mm O.D., a 9 mm I.D was purchased from National Metal and Materials Technology Center (MTEC), Thailand.

3.2 Characterizations

Differential scanning calorimeter (DSC, PerkinElmerDSC7) was used to study the polymerization process of the PBZ membrane. The samples were heated from 30° to 280 °C using a heating rate of 10 °C/min under a N_2 atmosphere with a flow rate of 10 mL/min. The membrane morphology was investigated using a scanning electron microscope (SEM, JEOL model JSM-5410LV) with an accelerating voltage of 1.5 kV. Samples were coated with platinum under vacuum before observation. Gas chromatography (GC/TCD, Agilent Technologies model 6890N, G 1540N) equipped with a HP-PLOT-Q (30 m x 0.25 mm I.D.) column was used to determine the ethanol quantity in both feed and permeate. Sample of 0.5 μL was injected under the following conditions: helium carrier gas set at 55 kPa for TCD detector, oven temperature isothermally set at 200°C, 200° and 250 °C injector and detector temperatures, respectively (Pakkethati, Boonmalert et al. 2011).

3.3 Methodology

3.3.1 Synthesis of the PBZ Precursors

The PBZ precursors were prepared by mixing BPA, formaldehyde,

and tepa/deta at a mole ratio of 1:4:1, respectively [3]. Firstly, BPA (6.84 g, 30 mmol) was dissolved in 1,4-dioxane (15 mL) in a 50 mL glass bottle and stirred until a clear solution was obtained. A formaldehyde solution (9.73 g, 324 mmol) was then added to the BPA solution. The temperature was kept at 10 °C by using an ice bath. Multifunctionalamine was then added dropwise into the mixture while continuously stirring for approximately 10 min until a transparent yellow viscous liquid was obtained.

3.3.2 Preparation of the PBZ Membranes

-       A tubular porous α-alumina support was cut into 6.5 cm length, cleaned by washing twice with deionized water for 15 min to remove dirt from the surface, and calcined in a furnace at 400 °C for 3 h to burn off any impurities from its surface (Kunnakorn, Rirksomboon et al. 2011). The PBZ solution to be coated on the alumina tube was prepared by using various concentrations of 5– 40 %(w/w) PBZ prepared from 3.3.1. The top and bottom parts of the support tube were Teflon sealed before immersing into the PBZ-solution, followed by curing the tube in an oven at the curing temperature of each PBZ type to obtain PBZ-membrane on outer surface of the support tube.

3.3.3 Swelling Study

The cured PBZ-membrane films were measured the initial weight (m_0, about 0.1 g) before immersing in the following solvents: ethanol, water, and 50:50 ethanol:water, at 70 °C (the same as pervaporation analysis condition). The PBZ-membranes were periodically taken out, wiped dry, and weighed to obtain the mass of membrane after swelling (W_t). The degree of swelling (G_s) of the membrane is defined as (Pakkethati, Boonmalert et al. 2011).

$$G_s = \frac{(W_t - W_0)}{W_0} \times 100\% \qquad (3.1)$$

where W_0 = the initial weight of the membrane

                W_t = the weight of the swollen membrane

3.3.4 Pervaporation Study

A schematic of the pervaporation experiment is shown in Schematic 3.1 (Namboodiri, V. V. and L. M. Vane 2007). The tube was placed in a stainless steel module. A flow rate of 900 mL/min was used to circulate the mixture from the feed reservoir containing a 50:50 ethanol:water mixture to a permeation cell. The pervaporation temperature was fixed at 70 °C. The performance of the membrane on the alumina tube was determined by measuring % ethanol in the permeate side and calculating the permeate water flux (kg/m^2h) and the separation factor. The quantities of ethanol and water were determined using a GC. The permeation flux (J, eq.3.2) and the separation factor (eq. 3.3) were determined as follows:

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

where
M = permeate weight (kg),

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

t = pervaporation time (h)

$$\alpha_{water-ethanol} = (Y_{water} / Y_{ethanol}) / (X_{water} / X_{ethanol}) \qquad (3.3)$$

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

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

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

$X_{ethanol}$ = the mole fraction of ethanol in the feed.
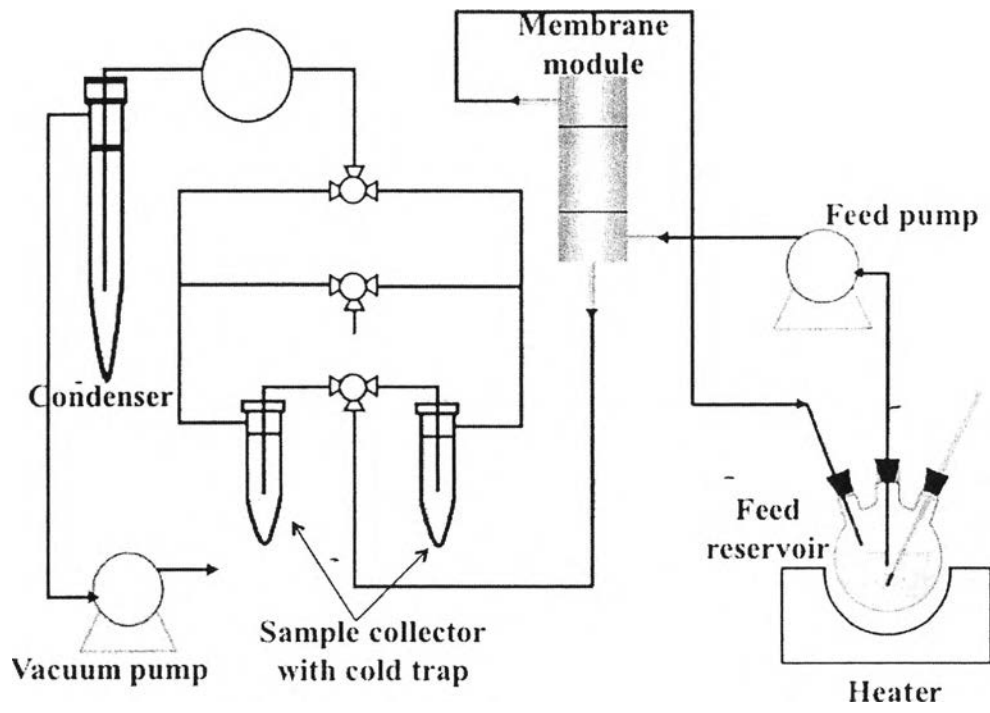
Schematic 3.1 Pervaporation apparatus.