

## Chapter 1

### Introduction

Fossil fuel takes millions of years to make and it is not renewable. The quantity of fossil fuel such as crude oil keeps decreasing which its price continuously increases. Therefore, alternative fuel is of interest in order to reduce the use of fossil fuel. In Thailand, gasohol, a mixture of 90% gasoline and 10% ethanol, is expected to be mostly used as alternative to gasoline in the future. Gasohol has higher octane (antiknock) property than gasoline and burns more slowly, coolly and completely, resulting in reduced emission of some pollutants (Encyclopedia, 2007). As well, Thailand has a potential to produce ethanol out of domestic crops such as molasses, tapioca, maize, sugar cane, etc. However, ethanol used as fuel requires 99.5 %wt which can not be produced from fractional distillation since ethanol forms a constant-boiling mixture (azeotrope) with water at the composition of 95.6 %wt ethanol and 4.4 %wt water with the boiling point of 78.15 °C. To obtain 99.5 %wt pure ethanol, a highly effective separation process is required. Pervaporation is one of the interesting separation process because it is recognized as a process for separating azeotropic mixtures and close-boiling point compounds. It is generally less energy consuming than distillation.

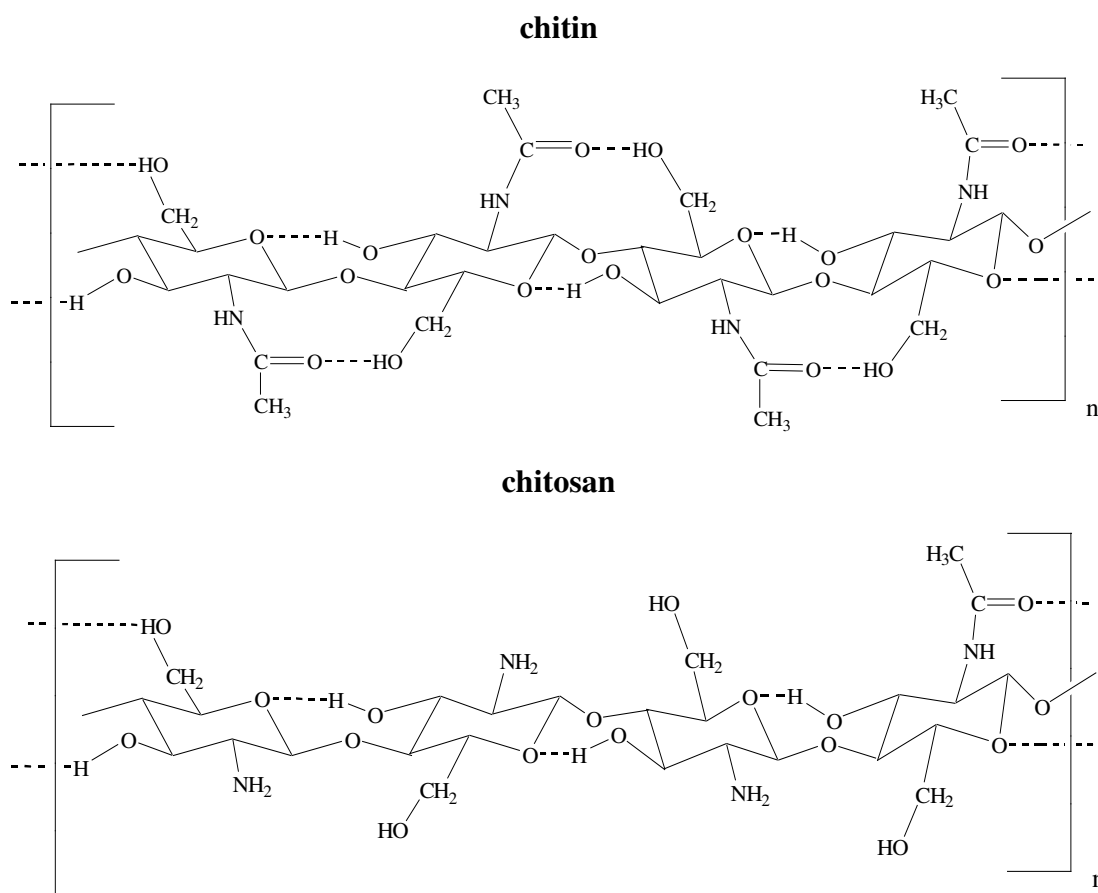
Thailand has emerged as one of the world's leading suppliers of frozen seafood products. Therefore, each year more than 100,000 mega tons of the dregs are generated from seafood industries. The dregs from seafoods, such as crabs, shrimps, and squids, can be transfigured to the raw materials for producing chitin and chitosan which are the value-added products in this industry. Besides, chitosan can be well formed to be a membrane and it prefers water to pass through rather than organic substances. Therefore, chitosan membranes can be used for dehydration of water-alcohol mixtures.

In this study, pervaporation performance of prepared chitosan membranes for separation water from aqueous ethanol mixtures was investigated.

### 1.1 Chitin – Chitosan

Chitin occurs widely in cell walls of many lower organism such as fungi and bacteria. It is also found in cuticles of insects and exoskeletons of crustaceans, i.e. lobster, crab and shrimp. As far as the cuticle is concerned, chitin is accompanied, besides proteins, by an important inorganic fraction, mostly constituted by calcium carbonate and phosphate (Allan et al., 1978). Chitosan can be found in fungi. Arcidiacono and Kaplan (1992) reported that chitosan isolated directly from the fungal cell wall has a higher degree of deacetylation than that from commercial chemical conversion of crustacean chitin.

Chitin is a crystalline polysaccharide as demonstrated by X-ray diffraction, infrared spectrophotometry, isotope exchange, thermal analysis, hydrolysis and chromatography data (Muzzarelli, 1973). It has the same backbone as cellulose, but the 2-hydroxyl groups have been replaced by acetamide groups, resulting in mainly  $\beta$ -(1 $\rightarrow$ 4)-2-acetamido-2-deoxy-D-glucopyranose structural units. Chitosan is the *N*-deacetylated derivative of chitin, as the deacetylation extent may vary and it is rarely found in nature. It should be kept in mind that chitin and chitosan do not have a fixed stoichiometry: in practice chitin is poly-*N*-acetyl glucosamine deacetylated a very little while chitosan is the same, deacytelated as far as possible, but not enough to be called polyglucosamine. Structural examples of chitin and chitosan are shown in Figure 1.1 (Rathke and Hudson, 1994).



**Figure 1.1** Structural examples of chitin and chitosan.

### 1.1.1 Physicochemical Characteristics of Chitosan

Chitin and chitosan are heteropolymers. Neither random nor block orientation is meant to be implied for chitin and chitosan. Properties of chitin and chitosan such as degree of *N*-deacetylation, molecular weight, solubility and crystallinity properties are discussed in brief.

### **Degree of *N*-acetylation**

Degree of *N*-acetylation can be defined as the ratio of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units. This ratio has a striking effect on solubility and solution properties of chitin and chitosan. Chitosan is chitin which is *N*-deacetylated to such an extent that it becomes soluble in dilute aqueous acetic and formic acids. In chitin, the acetylated units prevail (degree of acetylation typically 0.90). Chitosan is the fully or partially *N*-deacetylated derivative of chitin with a typical degree of acetylation of less than 0.35. To determine this ratio, attempts have been made with many analytical tools, which include IR spectroscopy, pyrolysis gas chromatography and UV spectroscopy (Kumar, 2000).

### **Molecular weight**

Average molecular weight of chitosan can be simply obtained by viscometric measurement and calculated using Mark-Houwink equation as follow:

$$[\eta] = KM^a = 1.81 \times 10^{-3} M^{0.93} \quad (1-1)$$

The constants *K* and *a* have been widely determined using viscometry in combination with either light-scattering or chromatographic methods. Their most complete results of *K* and *a* were presented by Wang et al. (1991), as shown in Table 1.1. Generally, converting chitin into chitosan lowers the molecular weight, changes the degree of deacetylation and alters the charge distribution, which in turn influences the agglomeration.

**Table 1.1** Comparison of Mark-Houwink constants

Solvent	Temp. (°C)	DD (%)	K (l/g)	a	Method <sup>§</sup>	Range of $\overline{M}_v$ ( $\times 10^4$ )
0.2M CH <sub>3</sub> COOH/ 0.1M NaCl/4 urea	-	-	$8.93 \times 10^{-2}$	0.71	SD	-
0.167M CH <sub>3</sub> COOH/ 0.47M NaCl	25	90- 100	111.5	0.147	SD	1.5-0.16
0.1M CH <sub>3</sub> COOH/ 0.2M NaCl	25	~80	$1.81 \times 10^{-3}$	0.93	EA	63-0.480
2% CH <sub>3</sub> COOH/ 0.1M CH <sub>3</sub> COONa	25	82-88	$1.38 \times 10^2$	0.85	SD	1.5-0.61
0.2M CH <sub>3</sub> COOH/ 0.1M CH <sub>3</sub> COONa	30	78-99	-	-	LALLS	8.5-4.9
0.2M CH <sub>3</sub> COOH/ 0.1M CH <sub>3</sub> COONa	30	69 84 91 100	$0.104 \times 10^{-3}$ $1.424 \times 10^{-3}$ $6.589 \times 10^{-3}$ $16.80 \times 10^{-3}$	1.12 0.96 0.88 0.81	LS	25.1-1.94   1.94

§ SD = sedimentation and diffusion

LS = light scattering

AE = analysis for end group

LALLS = low angle laser light scattering

## **Solubility**

Chitin is a highly crystalline and intractable material, and only a limited number of solvents are known as applicable reaction solvents. Chitin and chitosan degrade before melting, this is typical for polysaccharides with extensive hydrogen bonding. Thus, it is necessary to dissolve chitin and chitosan in an appropriate solvent system to impart functionality (Kumar, 2000). Chitosan is the form of free amine groups insoluble in water, sulfuric acid, bases and organic solvents while soluble in dilute  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOH}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ .

## **Crystallinity**

In the solid state, chitosan is a semicrystalline polymer. Single crystals of chitosan were obtained using fully deacetylated chitin of low molecular weight. The electron diffraction diagram can be indexed in an orthorhombic unit cell ( $\text{P}2_12_12_1$ ) with  $a = 0.807$  nm,  $b = 0.844$  nm,  $c = 1.034$  nm; the unit cell contains two antiparallel chitosan chains, which can be differentiated by infrared and solid-state NMR spectroscopy together with x-ray diffraction (Rinaudo, 2006).

### **1.1.2 Application of chitin-chitosan**

Due to its natural abundance and specific biological properties, chitin and chitosan are attractive materials for multiple applications including the following:

#### **Cosmetics**

Chitin is a particularly effective hydrating agent. There are two benefits: firstly, it supplies water, and secondly it avoids dehydration. In addition, the great benefit of chitin and its derivatives is the lasting quality of their hydrating effect. Chitosan forms a protective tensor film on the skin's surface that can fix other active principles for the skin. So, other hydrating agents, solar filters, organic acids or other

active principles can be combined with the derivatives of chitin. Chitin and chitosan allow active principles to be placed in close contact with the skin by means of a medium that is not only a film-forming tensor but also hydrating. This is a new double benefit that makes chitosan of great interest in cosmetics. Therefore, chitin and chitosan are used in skin creams, shampoos, lacquers, varnishes, etc.

### **Medicine**

Chitosan is an excellent medium for carrying and slowly releasing of medicinal active principles in plants, animals and human. Since it is undigested by stomach and it is a good means of retarding the release of encapsulated products that must reach the intestine without undergoing any transformation.

### **Water Treatment**

Chitin and chitosan have two properties that are of interest for water treatment: firstly, they are important chelation agents and secondly, they are heavy metal traps. In drinking water treatment, they are used to remove organic compounds and heavy metals, and in sewage treatment, they are used for precipitating certain anionic wastes and capturing pollutants such as polychlorobenzene (France-chitine, 2006).

### **Agriculture**

Chitosan has plant protecting and antifungal properties. It can trigger defensive mechanisms in plants against infections and parasite attacks, in very low concentrations in the order of a few milligrams per cubic metre of water. It can be used in solution, in powder form or as coatings of seeds. Apart from its specifically antifungal action, it strengthens the root system, thickens the stem and stimulates the plant's synthesis of protective agents.

## **Paper Manufacture**

Chitosan is used in the manufacture of paper (France-chitine, 2006) because chitosan molecules resemble cellulose. It replaces amine groups for example guar gum and polysynthetic polysaccharides. The paper produced from chitosan has a smooth surface and is more resistant to moisture. The examples of papers produced from chitosan are toilet paper, wrapping paper and cardboard.

### **1.2 Ethanol**

Ethanol or ethyl alcohol is a flammable, colorless and a monohydric primary alcohol. It melts at  $-117.3\text{ }^{\circ}\text{C}$  and boils at  $78.5\text{ }^{\circ}\text{C}$ . It is miscible with water. It reacts with active metals to form the metal ethoxide and hydrogen. It reacts with carboxylic acids to form esters and water.

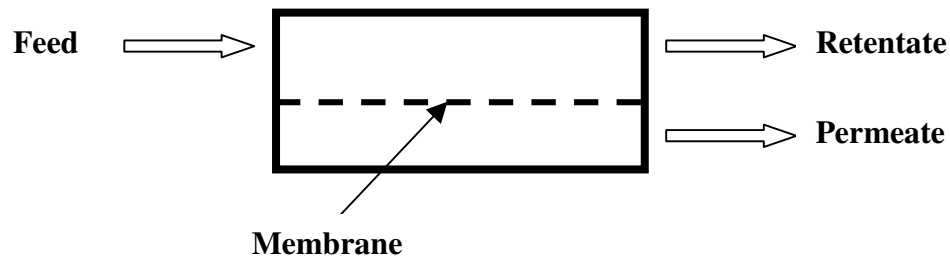
Absolute or anhydrous alcohol generally refers to purified ethanol, containing no more than one percent water. Ethanol forms a minimum-boiling azeotrope with water at a composition of 4.4 %wt water with a boiling point of  $78.15\text{ }^{\circ}\text{C}$  at atmospheric pressure. It is not possible to obtain absolute ethanol from water-ethanol mixture by fractional distillation. The best that can be obtained is the constant boiling azeotrope which is 95.6 %wt ethanol. Several approaches are used to produce absolute ethanol. One is distillation of ethanol-water azeotrope after adding a small quantity of benzene. Benzene, ethanol, and water form a ternary azeotrope with a boiling point of  $64.9\text{ }^{\circ}\text{C}$ . Since this azeotrope is more volatile than the ethanol-water azeotrope, it can be fractionally distilled out of the ethanol-water mixture, extracting essentially all of the water in the process. The bottoms from such a distillation is anhydrous ethanol, with several parts per million residual benzene. Benzene is toxic to humans, and cyclohexane has largely supplanted benzene in its role as the entrainer in this process (Wikipedia, 2007). Currently, the most popular approach of purification 95.6 %wt purity is desiccation using adsorbents such as starch, zeolites, or molecular sieves, which adsorb water preferentially. The



concentration of ethanol is above 95.6 %wt and can be further distilled. The sieve is heated to remove water and reused. Alternatively, pervaporation is an energy efficient combination between membrane permeation and evaporation. It is considered as an attractive alternative to other separation methods for the separation of constant-boiling azeotropes (Mahesh, 2006).

### **1.3 Membrane process**

The principle of membrane process is shown in Figure 1.2. Feed, a mixture of two or more components is separated by means of one or more species move through membrane faster than another or other species. The movement of any species across the membrane is caused by one or more driving forces. These driving forces arise from a gradient of chemical potential or electrical potential. A gradient in chemical potential may be due to a concentration gradient or pressure gradient or both (Winston, 1992). Driving force of each membrane process is shown in Table 1.2. Feed mixture that does not pass through the membrane is called retentate, and that passes through the membrane is called permeate. Although the feed, retentate and permeate are usually liquid or gas, the membrane may be nonporous polymeric film, porous polymer, ceramic, or liquid. The membrane must not dissolve and disintegrate. The important factor that indicates the ability of separation is the flow rate of substance that pass through membrane or permeate flux. Unit of flux is volume or weight or mole of permeate per time. In addition, the ability of separation is also considered from separation factor or rejection coefficient (Seader, 1998). Many of the industrially important membrane separation operations are listed in Table 1.3.



**Figure 1.2** Principle of membrane process.

#### **1.4 Pervaporation, PV**

In pervaporation process is the separation of two or more components pass through the membrane at different diffusion rates. Concentration and vapor pressure gradients are used to allow one component preferentially permeates across the membrane. Component that passes through membrane will be vapor. Vapor sample can be trapped in the permeate side (Figure 1.2) by decreasing temperature of substance, then it will condense and becomes liquid at room temperature. Two types of membranes are used in pervaporation: hydrophilic membranes removing water from organic solutions, and hydrophobic membranes recovering organics substances from solutions. Applications of pervaporation are dehydration of alcohol solution, removal of organics from water, continuous water removal from condensation reactions such as esterifications, separation heat sensitive products, etc.

**Table 1.2** Important membrane separation processes (Robert, 1971)

<b>Process</b>	<b>Driving force (s)</b>	<b>Species transported</b>	<b>Principal result</b>
Gas, vapor, liquid permeation	Diffusion and solution	All	Enrichment
Dialysis	Concentration	Solute	Solute leaves concentrated solution
Ultrafiltration	Pressure	Solvent	Solvent leaves concentrated solution
Reverse osmosis	Pressure	Solvent	Solvent leaves concentrated solution
Electrodialysis	Electromotive force	Ionic solution	Solute removed

**Table 1.3** Examples of Applications and Alternative Separation Processes

(<http://www.pacificro.com/membrsep.htm>)

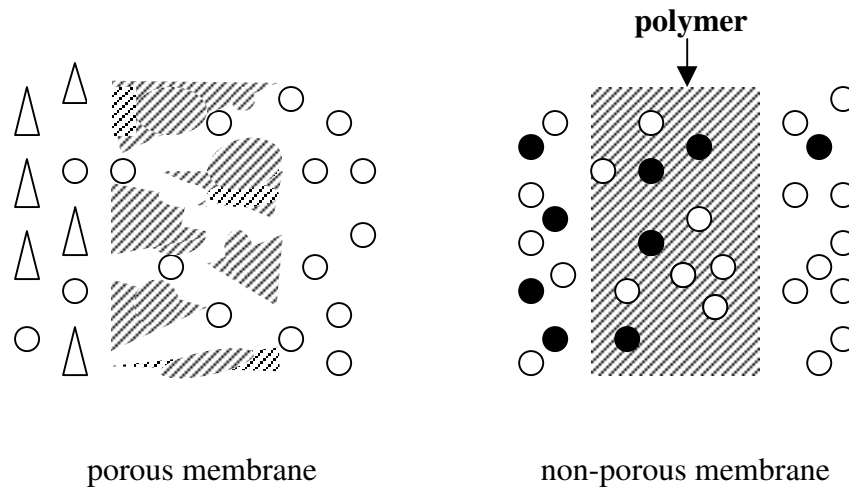
<b>Process</b>	<b>Applications</b>	<b>Alternative Processes</b>
Microfiltration	Separation of bacteria and cells from solutions	Sedimentation, Centrifugation
Ultrafiltration	Separation of proteins and virus, concentration of oil-in-water emulsions	Centrifugation
Nanofiltration	Separation of dye and sugar, water softening	Distillation, Evaporation
Reverse Osmosis	Desalination of sea and brackish water, process of water purification	Distillation, Evaporation, Dialysis
Dialysis	Purification of blood (artificial kidney)	Reverse osmosis
Electrodialysis	Separation of electrolytes from nonelectrolytes	Crystallization, Precipitation
Pervaporation	Dehydration of ethanol and organic solvents	Distillation
Gas Permeation	Hydrogen recovery from process gas streams, dehydration and separation of air	Absorption, Adsorption, Condensation
Membrane Distillation	Water purification and desalination	Distillation

### 1.5 Advantages of membrane process

1. Able to separate following shape or size of molecules.
2. Separation can be carried out under ambient conditions.
3. Energy consumption is generally low because separation takes place without changing phase. For example, desalinization of seawater using reverse osmosis or electrodialysis process requires less energy than distillation.
4. It doesn't have surplus because the products of membrane process can be used both permeate and retentate.
5. Scale-up can easily be accomplished because of its modular structure.
6. Process can be either batch or continuous process.

### 1.6 Synthetic membranes

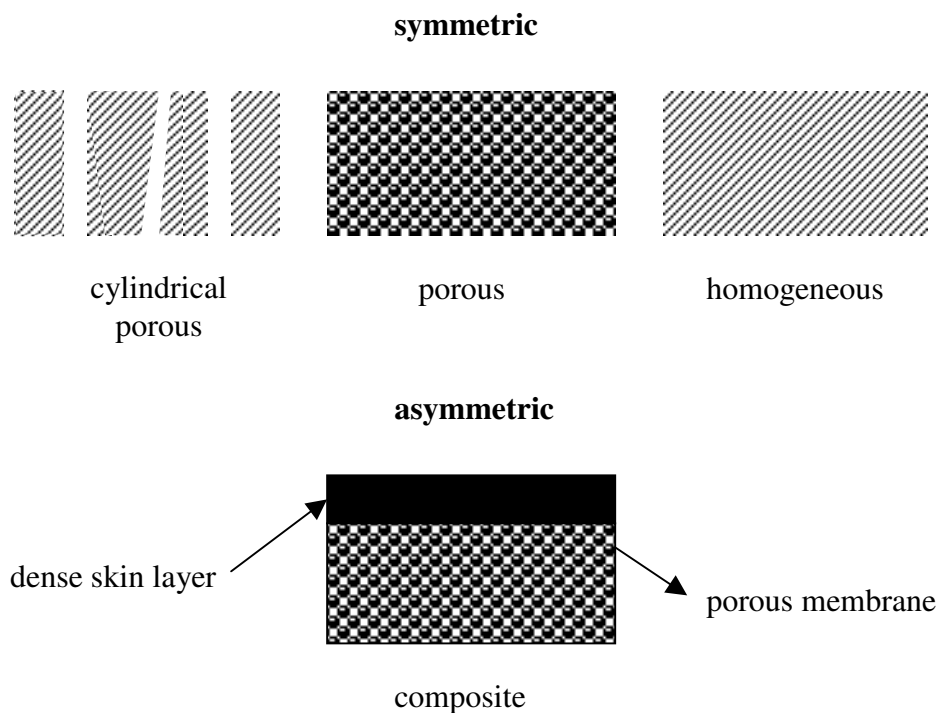
A membrane can be considered as a permselective barrier between two phases. Mass transport of a component across the membrane occurs due to the presence of a driving force. The type of separation is mainly determined by the membrane morphology. Roughly, two types of membrane structures can be distinguished: porous membrane and non-porous membrane. A schematic drawing is depicted in Figure 1.3. In porous membranes fixed pores are present. In order to avoid confusion the definition of pore sizes as adopted by the IUPAC (1985) will be used: macropores,  $>50$  nm; mesopores,  $2 < \text{pore size} < 50$  nm; and micropores,  $< 2$  nm. This means that microfiltration, ultrafiltration and nanofiltration membranes are porous membranes. Microfiltration membranes contain macropores (pore range  $\approx 0.05$ - $5$   $\mu\text{m}$ ), ultrafiltration membranes contain mesopores (pore range  $\approx 2$ - $50$  nm), and nanofiltration and reverse osmosis membranes contain micropores (pore range  $< 2$  nm). The latter membranes are in fact intermediate between porous ultrafiltration membranes and non-porous gas separation and pervaporation membranes. The term 'non-porous' is rather ambiguous because in the latter pores are present on a molecular level to allow transport. The existence of these dynamic 'molecular pores' can be adequately described in terms of free volume (Howell et al., 1993).



**Figure 1.3** Schematic drawing of porous and non-porous membranes.

The membrane morphology given schematically in Figure 1.3 is a simplification and only serves to illustrate the basic principles in structure, transport and application more readily. The morphology can be classified further into symmetric and asymmetric structure, as shown schematically in Figure 1.4. The thickness of symmetric membrane (porous or non-porous) ranges roughly from 10 to 200  $\mu\text{m}$ . The mass transfer resistance is determined by the total membrane thickness. A decrease in membrane thickness results in an increased permeation rate. Asymmetric membrane consists of dense top layer with a thickness of 0.1-0.5  $\mu\text{m}$  supported by a porous sublayer with a thickness of about 50-150  $\mu\text{m}$ . This membrane combines the high selectivity of a dense membrane with the high permeation rate of a very thin membrane. The resistance to mass transfer is determined to a large extent by the thin top layer.

Another type of asymmetric membrane is of a composite type. In composite membrane, the top layer and sublayer originate from different polymeric materials; each layer can be optimized independently. Generally the support layer is already an asymmetric membrane on which a thin dense layer is deposited. Several methods have been developed to achieve this such as dip-coating, interfacial polymerisation, in-situ polymerization and plasma polymerization (Howell et al., 1993).



**Figure 1.4** Schematic drawing of symmetric and asymmetric membrane cross-section.

### 1.7 Review of Literatures

Devi et al. (2006a) studied poly(vinyl alcohol)-chitosan blend membranes crosslinked with glutaraldehyde and used for dehydration of 1,4-dioxane. Membranes were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) to assess, respectively, the intermolecular interactions, thermal stability and crystallinity. Equilibrium sorption studies were carried out in pure liquids and binary mixtures of different compositions of water-1,4-dioxane to assess the polymer-liquid interactions. The crosslinked membranes showed a good potential in breaking the azeotrope of 82 %wt aqueous 1,4-dioxane giving a selectivity of 117 with a reasonable water flux of 370 g/m<sup>2</sup> h. The effect of operating parameters such as feed composition, membrane thickness and permeate pressure was evaluated. With increasing feed water compositions, the membrane performance exhibited a reduction in selectivity with an improvement in flux due to increased swelling. However, with increasing

membrane thickness, selectivity has improved, but flux decreased. Higher permeate pressure caused a reduction in both flux and selectivity.

Ariyaskul et al. (2006) investigated homogeneous membranes by casting the solution of blended chitosan and poly(vinyl alcohol) (PVA) on a glass plate. The percent weight of chitosan in the membrane was varied from 0 to 100 %wt. The membrane thickness was in the range of 15–30  $\mu\text{m}$ . The membranes were heated at 150 °C for an hour. After that the membranes were crosslinked using glutaraldehyde and sulfuric acid in acetone aqueous solution. The membranes were tested at 30–60 °C for dehydration performance of 50–95 %wt isopropanol aqueous solutions. The swelling degree in water and the total flux increased with increasing chitosan content in membranes. The permeate flux decreased when isopropanol in the feed increased for all membranes. However, water content in permeate and isopropanol concentration in the feed formed complex relationship for different chitosan content membranes. The membrane containing chitosan 75 %wt performed the best. For the feed solution containing 90 %wt isopropanol at 60 °C, the permeate flux was 644  $\text{g}/\text{m}^2 \text{ h}$  with water content of nearly 100 %wt in the permeate. At 55 %wt isopropanol in the feed at 60 °C, the permeate flux was 3812  $\text{g}/\text{m}^2 \text{ h}$ . In the range of 55–95 %wt of isopropanol in the feed, the water content in permeate was more than 99.5 %wt. This membrane showed very excellent performance with good mechanical strength. It is promising to develop this membrane for industrial uses.

Devi et al. (2005) reported that 84% degree of deacetylation of chitosan membranes crosslinked with toluene-2,4-diisocyanate and tested for dehydration of isopropanol by pervaporation method. The membrane appears to have a good potential for breaking the aqueous azeotrope of 87.5 %wt isopropanol with a high selectivity of 472 and a substantial water flux of 390  $\text{g}/\text{m}^2 \text{ h}$  10  $\mu\text{m}$ . The influence of operating parameters such as feed composition, membrane thickness and permeate pressure on membrane performance like flux and selectivity was investigated. With an increase in feed water concentration, the membrane performance was found to be affected substantially due to an increase in the extent of swelling of the polymer, thereby resulting in an increase of flux, but at the expense of selectivity. Increasing membrane thickness decreased the flux, but improved the

separation selectivity. On the other hand, higher permeate pressure could result in a reduction of both flux and selectivity.

Dhanuja et al. (2005) investigated polyion complex membranes made by blending 84% deacetylated chitosan and poly (acrylic acid) and tested for the separation of isopropanol–water mixtures. The membranes were characterized by FT-IR to verify the formation of the polyion complex, XRD to observe the effects of blending on crystallinity, DSC to investigate the thermal stability, and tensile testing to assess their mechanical stability. Amongst the blends tested, the crosslinked membranes having 60 %wt of chitosan were found to have good potential for breaking the aqueous azeotrope of 87.5 %wt of isopropanol yielding a high selectivity of 1736 at a reasonable flux of  $140 \text{ g}/\mu\text{m}^2 \text{ h}$   $10 \mu\text{m}$ . Membrane selectivities were found to improve with decreasing permeate pressure but remained relatively constant for variable membrane thickness. Increasing membrane thickness decreased the flux and higher permeate pressure caused a fall in membrane performance.

Dubey et al. (2005) studied bacterial cellulose membranes impregnated with chitosan (CTSN-BCM) used for separation of ethanol-water by pervaporation (PV) process. The PV potential of CTSN–BCM was compared with that of parent polymers and also with the blends of CTSN with poly(vinyl alcohol) (PVA). When evaluated against pervaporation of 95:5 w/w EtOH/H<sub>2</sub>O azeotrope at  $24 \pm 1 \text{ }^\circ\text{C}$ ; CTSN–PVA (1:1) blend showed comparatively higher selectivity (22.0) but a poorer flux ( $1700 \text{ g } \mu\text{m}/\text{m}^2 \text{ h}$ ). The temperature dependence of selectivity and flux through CTSN–BCM was also investigated. Substantially high pervaporation separation index (PSI) of the order of  $35000 \text{ g } \mu\text{m}/\text{m}^2 \text{ h}$  and low energy of activation of 10 kJ/mol is indicative of the potential of CTSN–BCM in the pervaporation separation of EtOH/H<sub>2</sub>O azeotrope.

Kanti et al. (2004) investigated polyion complex membranes made by blending 84% deacetylated chitosan and sodium alginate biopolymers followed by



crosslinking with glutaraldehyde and used for the separation of ethanol–water mixtures by pervaporation process. The membranes were characterized by FTIR to verify the formation of the polyion complex, XRD to observe the effects of blending on crystallinity, DSC and TGA to investigate the thermal stability, and tensile testing to assess their mechanical stability. The effect of experimental parameters such as feed composition, membrane thickness and permeate pressure on separation performance of the crosslinked membranes was determined. The crosslinked blend membranes were found to have good potential for breaking the azeotrope of 0.135 mol fraction of water and a high selectivity of 436 was observed at a reasonable flux of 220 g  $\mu\text{m}/\text{m}^2\text{h}$ . With increasing feed water concentration, the membrane performance was found to be affected substantially by increase in the extent of swelling of the polymer, which resulted in a rise in flux but a reduction in selectivity. Increasing membrane thickness decreased the flux and higher permeate pressure caused a reduction in both flux and selectivity.

Won et al. (2003) studied the crosslinked chitosan membranes for separation of binary DMC (dimethyl carbonate)/water, DMC/methanol and methanol/water mixtures and ternary DMC/methanol/water mixtures in a temperature range of 25–55 °C. The experimental results showed that the membrane could be used effectively to break the DMC/methanol azeotrope and to remove a small amount of water from DMC. It was also shown that coupling effect was important in pervaporation separation of multi-component mixtures due to interactions among the permeating species.

Jiraratananon et al. (2002) studied chitosan-hydroxyethylcellulose membrane by using cellulose acetate as a porous support. The membranes were tested for dehydration performance of ethanol–water mixtures of ethanol concentrations 70–95 %wt in the laminar flow region, at temperatures of 50–70 °C and at permeate pressures of 3–30 mm of Hg. The effects of operating conditions also revealed that pervaporation of low water content feed carried out at high feed flow rate and at low temperature and permeate pressure was an advantage.

Huang et al. (2001) investigated chitosan composite membranes used for separation of methanol/MTBE (methyl *tert*-butyl ether) mixtures by pervaporation experiments. When anionic surfactants were added into the cationic chitosan solution, the solution viscosity was drastically decreased due to the collapsed chain conformation. Pervaporation characteristics of surfactant modified chitosan membranes were substantially improved due to the decreased membrane thickness and possible enhanced affinity to methanol.

Huang et al. (2000) studied composite chitin membranes supported by porous polyetherimide substrate and tested for pervaporation separation of ethanol/toluene and methanol/toluene mixtures. Chitin was obtained by modifying chitosan to its original form of chitin by the *N*-acetylation reaction. It was found that the incorporation of additional acetyl groups into chitosan structure decreased total flux and increased separation factor from 401 g/m<sup>2</sup> h;  $\alpha=34$  (pure chitosan) to 282 g/m<sup>2</sup> h;  $\alpha=126$  (70% DA chitosan) for 10 %wt EtOH feed mixture and from 681 g/m<sup>2</sup> h;  $\alpha=159$  (pure chitosan) to 484 g/m<sup>2</sup> h;  $\alpha=607$  (70% DA chitosan) for 10 %wt MeOH feed mixture. It was concluded that chitin composite membranes could be a good candidate for this pervaporation system.

Kim et al. (2000) investigated pervaporation characteristics using the polyion complex composite (PIC) membranes for the separation of MTBE/methanol mixtures. The polyion complex reaction took place by the ionic crosslinking reaction between the carboxylate groups ( $-\text{COO}^-$ ) of sodium alginate and the protonated amine groups ( $-\text{NH}_3^+$ ) of chitosan. The polyion complexation depended upon the content of counter ions. Especially, PIC membrane prepared from 2.0 %wt sodium alginate solution and 2.0 %wt chitosan solution appeared to be permeated only methanol from the feed, with the flux of over 240 g/m<sup>2</sup> h. As the operating temperature increased from 40 to 55 °C, the permeation rate of methanol increased, but that of MTBE decreased. These results were due to the physicochemical and structural properties of polyion complex membranes.

Chanachai et al. (2000) investigated chitosan/hydroxyethylcellulose (CS/HEC) blended membranes crosslinked with a urea–formaldehyde–sulfuric acid

mixture. The chemically crosslinking structure of blended membrane was analyzed by IR spectroscopy. The CS/HEC-3/1 and CS/HEC-9/1 blended membranes are appropriate for the dehydration of ethanol–water and isopropanol–water mixtures, respectively. These membranes have high selectivity and promising flux, especially at high alcohol concentration (e.g.,  $J = 112 \text{ g/m}^2 \text{ h}$ , separation factor  $\alpha_{w/e} = 10,491$  for 90 %wt ethanol solution and  $J = 175 \text{ g/m}^2 \text{ h}$ ,  $\alpha_{w/i} = 26091$  for 90 %wt isopropanol solution). Flux increased while the separation factor decreased with increasing water content in the feed.

Ge et al. (2000) studied the impact of fabrication conditions on the chitosan (CS) membrane structure by using pervaporation (PV) process. Chitosan homogenous membranes were fabricated by casting a chitosan/acetic acid solution, then heating it at various temperatures and for different periods of post-heating time, followed by chemically cross-linking with  $\text{H}_2\text{SO}_4$ . The PV separation tests using the resulting membranes demonstrate that the chitosan membranes are capable of separating water–ethanol mixtures. The optimized conditions for chemical cross-linking of membranes were found to be 0.5 M of  $\text{H}_2\text{SO}_4$  and 10 min reaction time at ambient temperature. It was observed in orthogonal tests that the effect of membrane preparation temperature on the separation factor was significant. Further studies showed that the separation factor was the highest when the heating temperature was 343 K. The results from differential scanning calorimetric (DSC) and X–ray diffraction analyses suggested that the chitosan membranes contain two major different types of crystals, and the crystal degree of the chitosan membranes changed with membrane preparation temperature, i.e. the fractions of two types of crystal changed as temperature changed.

Huang et al. (1999) studied chitosan-polysulfone composite membranes tested for pervaporation dehydration of aqueous isopropanol mixtures. The polysulfone substrate was immersed into hydrophilic binding polymer solutions such as polyvinyl alcohol, polyacrylic acid, and hydroxyethylcellulose before the casting of chitosan layer to increase the affinity between the thin chitosan layer and porous polysulfone layer which resulted in increased geometrical stability of the

chitosan/polysulfone composite membranes. The chitosan layer was crosslinked with glutaraldehyde and  $\text{H}_2\text{SO}_4$  in acetone solution to control the permselectivity.

Moon et al. (1999) studied novel two-ply dense composite membrane which using successive castings of sodium alginate and chitosan solutions for pervaporation dehydration of isopropanol and ethanol. The pervaporation performance of the two-ply membranes with sodium alginate layer facing the feed side and crosslinked or insolubilized in sulfuric acid solution was compared with that of the pure sodium alginate and the chitosan membranes in terms of flux and separation factors. It was shown that although flux of the two-ply membrane was lower than that of the pure sodium alginate and chitosan membranes, separation factor at various alcohol concentrations was in between values of the two pure membranes. For the dehydration of 90 %wt isopropanol–water mixtures the performance of the two-ply membrane which was moderately crosslinked in formaldehyde was found to match the high performance of the pure sodium alginate membrane. This two-ply membrane had fluxes of  $70 \text{ g/m}^2 \text{ h}$  at 95 %wt EtOH,  $554 \text{ g/m}^2 \text{ h}$  at 90 %wt PrOH and separation factors of 1110 at 95 %wt EtOH, 2010 at 90 %wt PrOH and its mechanical properties were better than that of the pure sodium alginate membrane.

Nam and Lee (1999a) investigated the efficiency of pervaporation separation of methanol/methyl-*t*-butyl ether (MTBE) mixture through chitosan composite membranes modified with sulfuric acid and four surfactants. Effects of feed concentration, temperature, crosslinking degree and type of surfactants were studied. The chitosan composite membranes modified with sulfuric acid showed pervaporation performance of over 70 %wt methanol in permeate and flux of  $100 \text{ g/m}^2 \text{ h}$  measured at 25 °C. At 50 °C, separation factor decreased while flux increased exceeding  $300 \text{ g/m}^2 \text{ h}$ . For the membrane complexed with surfactants, permeate showed 98.3 %wt methanol concentration and  $470 \text{ g/m}^2 \text{ h}$  of permeate flux at 25 °C. With increasing operating temperature, permeate flux remarkably increased to  $1170 \text{ g/m}^2 \text{ h}$  and permeate showed 97.8 %wt methanol concentration.

Nam and Lee (1999b) investigated an ionically surface crosslinked chitosan composite membranes used for pervaporation of ethylene glycol–water

mixtures. Chitosan membranes exhibited an optimum dehydration performance from ethylene glycol (EG)–water mixtures at 80 min crosslinking time. At 80 °C and 80 %wt EG feed concentration, permeation flux of 1130 g/m<sup>2</sup> h and water concentration of permeate greater than 99.5 %wt were achieved. Effects of operational conditions including EG feed concentration, operating temperature, and annealing temperature on the pervaporation performance of chitosan composite membranes were investigated. At EG concentrations from 70 to 95 %wt, water concentration was higher than EG concentration in the permeate and permeation flux decreased with increasing EG feed concentration. Annealing of chitosan composite membranes reduced permeation flux and separation performance. At high EG concentration in the feed mixture, the membranes were more sensitive to operating temperature and had higher activation energy of permeation. Water selective chitosan membranes can be applied to evaporation–pervaporation hybrid system for dehydration in the recycle of anti-freezing agent and EG production process.

Shieh and Huang (1998) studied chitosan-*N*-methylol nylon 6 membranes used for separation of ethanol–water mixtures. Their pervaporation performance was investigated in terms of acid (H<sub>2</sub>SO<sub>4</sub>) post-treatment, feed concentration, blend ratio and temperature. When feed solution having low water content, an increase in chitosan content caused a decrease in permeability and an increase in separation factor. When feed solution having high water content, the permeability increased with an increase in chitosan content, while the separation factor showed a maximum value around 60 %wt chitosan.

### **1.8 Research objectives**

1. To build a permeation cell and design the experimental setup for testing the pervaporation process.
2. To prepare effective chitosan membranes used for separation of ethanol-water mixture by pervaporation process.
3. To characterize the obtained chitosan membranes.
4. To investigate the separation performance of the prepared chitosan membrane using the home made permeation cell.