

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Background

Membrane separation has gained attractive in chemical technology and is being used increasingly in a broad range of applications. The key property that is exploited in every application is the ability of a membrane to control the permeation of a chemical species in contact with it. The membrane may be thin layers of rigid materials such as porous glass or sintering metals but more often they are flexible films of synthetic polymers prepared to have a high permeability for certain types of molecules (McCabe *et al.*, 1993).

Gas separation via membranes is one of the most exciting and significant new unit processes to have appeared in many years. Gas permeability through all membranes is a function of membrane properties, the nature of the permeant species, and the interaction between membrane and permeating species (Kesting and Fritzsche, 1993).

Structurally, membranes can be categorized as being either a porous or non-porous dense membrane. Functionally, membranes may be either passive or reactive depending upon the membranes' ability to alter the chemical nature of the permeating species. Membrane can also be categorized as being either neutral or charged according to their ionic nature (Lloyd, 1985).

An isotropic microporous membrane, the first type of structural membrane, is similar in its structure and function to a conventional filter. However, the pore diameter of the membrane is less than the conventional filter. The pore diameters are in the range of 0.01-10  $\mu\text{m}$ . The mechanisms of gas permeation through porous membranes are classified into 3 types. If the membrane pores are very small or smaller than 0.5-2 nm, the diffusion of

gases through the pores is governed by micropore diffusion. If the pores are smaller than 0.1  $\mu\text{m}$ , the diffusion of gases through the pores is governed by Knudsen diffusion, and the transport rate of different gases is inversely proportional to the square root of the molecular weight. If the pores are larger than 0.1-10  $\mu\text{m}$ , gases permeate through the membrane by convective flow and no separation occurring (Koros and Jones, 1994).

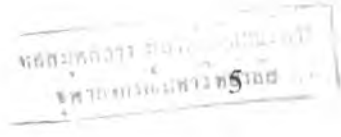
For a nonporous dense membrane, the second type of structural membrane, the separation of various components of gas mixture is directly related to their relative transport rates within the membrane, which is determined by their diffusivity and solubility in the membrane material. The mechanism of permeation consists of 3 steps: 1) absorption or adsorption upon the upstream boundary, 2) activated diffusion through the membrane, and 3) dissolution or evaporation from the downstream boundary. The solution diffusion mechanism is driven by a difference in thermodynamic activity existing at the upstream and downstream faces of a membrane. The activity difference causes a concentration gradient that leads to diffusion in the direction of decreasing activity (Rousseau, 1987).

## 2.2 Theory

The gas permeability on a polymer membrane can be described by a mean permeability coefficient,  $P$ , that is defined by the isothermal relation (Stern *et al.*, 1987):

$$P = \frac{J_s \times \delta}{p_h - p_l} \quad (2.1)$$

where  $J_s$  = the steady state rate of gas permeation through unit membrane area,



$\delta$  = the membrane thickness,

$p_h$  = high pressure streams of the component, and

$p_l$  = low pressure streams of the component.

Based on the Fick's Law and Henry's Law, the permeability coefficient,  $P_A$  of penetrant A is the product of a kinetic parameter,  $D_A$  (the average diffusion coefficient), and a thermodynamic parameter,  $S_A$  (the solubility coefficient) (Singh and Koros, 1996):

$$P_A = D_A S_A \quad (2.2)$$

The permeability coefficient  $P_A$  is often expressed in Barrers, where 1 Barrers =  $10^{-10}$  cm<sup>3</sup> (STP)-cm/cm<sup>2</sup>-s-cmHg.

Since the actual membrane thickness is not always known or specified for commercial membranes, it is customary to use the flux per unit pressure difference and thickness, which will be called "permeability",  $P_A/\delta$ .

The selectivity of a polymer membrane for a penetrant A relative to another penetrant C is characterized by an "ideal separation factor",  $\alpha_{(A/C)}$  which is defined by the relationship

$$\alpha_{(A/C)} = \frac{P(A)}{P(C)} \quad (2.3)$$

Using Eq. 2.3,  $\alpha_{(A/C)}$  can be written as the product of the diffusivity selectivity and solubility selectivity of the gas (Zimmerman *et al.*, 1997):

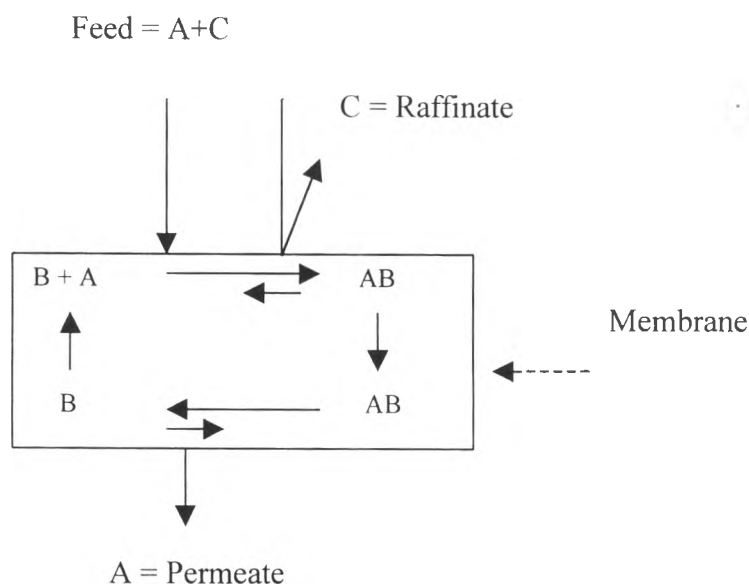
$$\alpha = \frac{D_A S_A}{D_C S_C} \quad (2.4)$$

where  $D_A/D_C$  is the ratio of the diffusivity selectivity, reflecting the different sizes of two molecules. The ratio  $S_A/S_C$  is the ratio of Henry's law sorption

Facilitated or reactive membrane is explained by the principle of facilitated transport mechanism for gas transport. Active transport is achieved with a carrier species. The carrier must react with the permeate molecules to form a reversible complex. The carrier shuttles the permeant between the membrane boundaries. Permeant will be transported in the direction of higher to lower permeant concentrations. When contacted with a feed mixture containing only one component that the carrier can react with, only the transport of that one component will be “facilitated” across the membrane. The facilitated transport can be describe as:

A feed mixture of “A” and “C” are contacted with a membrane containing carrier “B” such as  $Ag^+$  or  $Cu^+$ . A reversible complex “AB” is formed between “A” and “B” (Eq. 2.5). By contrast, “C” does not react with “B” (Eq. 2.6).





**Figure 2.1** Mechanism for facilitated transport of component A by carrier B.

The facilitated transport of “A” across the membrane is shown in Figure 2.1. At the top of the membrane surface “A” reacts with “B” to form “AB”. “AB” diffuses across the membrane where it dissociates back to “A” and “B”. “A” is released from the membrane and “B” diffuses back to the top surface, when “B” can react with “A” to repeat the process (Hughes *et al.*, 1986).

### 2.3 Literature Review

The process industries produce a wide variety of chemicals and components, which present the manufacturer with a need for separation, concentration and purification of a range of materials. The last 30 years have seen the introduction of the membrane separation to replace techniques of distillation, adsorption, extraction and crystallization due to the high energy consumption and capital investment of these technologies (Scott and Hughes, 1996). Recently, the mixed matrix membrane and facilitated or reactive

membrane have been developed by modifying morphology of polymeric membrane to enhance the permeability of gases and selectivity for the separation.

### 2.3.1 Polymeric Membranes

In the early 1960s, the Loeb-Sourirajan process was developed for making defect-free, high flux, ultrathin skinned reverse osmosis membranes by cellulose acetate. It was continually developed for gas and hydrocarbon separation. It is divided into 2 types which were asymmetric membranes –composed of one material and composite membrane- composed of a variety of materials. Both types are made from a lot of polymers. The polymeric membranes are increasingly used to study the effect of a variety of gas separations such as silicone membrane for O<sub>2</sub>/N<sub>2</sub> separation, cellulose acetate membrane for CO<sub>2</sub> removal from natural gas and silicone-coated polysulfone membranes for hydrogen recovery from waste streams (Baker *et al.*, 1991).

To develop the application of membrane for gas separation, more permeation data on hydrocarbon through polymeric membrane were studied. In particular, the olefin/paraffin separation is of great significance because olefins play an important role as starting materials in chemical synthesis.

Ito and Hwang (1989) studied on cellulose acetate membrane that was tested by measuring the permeabilities of propane and propylene and calculated selectivity for separation. They found that the cellulose acetate membrane was selective for propylene over propane. The permeability of propane was lower than  $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) * cm / cm}^2 \text{ * s * cmHg}$  and the selectivity of propylene to propane was about 2.5.

Sridhar and Khan (1999) developed the propylene/propane separation. They investigated the performance of ethylcellulose (EC),

polyphenylene oxide (PPO), cellulose acetate and polysulfone membrane. For cellulose acetate membrane, the permeabilities of propane and propylene were about  $5.8$  and  $15.2 \times 10^{-10}$  cc\*cm/cm<sup>2</sup>\*s\*cmHg, respectively and the selectivity of propylene to propane was about 2.6.

Additionally, Staudt and Koros (2000) investigated polyimides based on 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) membranes to measure the permeabilities of the pure gases; ethylene, ethane, propylene and propane and the mixed gases with 50:50 of olefin/paraffin. The ideal selectivity of ethylene to ethane was between 3.3 and 4.4 and propylene to propane was between 10 and 16. In the mixed gas permeation experiments, up to 20% lower selectivity was found for the ethylene/ethane separation and up to 50% reduced selectivity for the propylene/propane separation compared to the ideal selectivity.

### 2.3.2 Mixed Matrix Membranes

The mixed matrix membrane had been developed in the late 1980's at UOP. The desirable characteristics of mixed matrix membrane that must be possessed by the membranes include a high selectivity of one or more gases from other gases as well as a relatively high flux (Kulprathipanja *et al.*, 1988a, 1988b and 1988c).

The first type of mixed matrix membrane was silicone rubber with poly(ethylene glycol) (PEG) on porous support prepared by casting and curing an emulsified mixture of them on porous polysulfone support (Kulprathipanja and Kulkarni, 1986). The permeation rates of SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> were evaluated through a dense silicone rubber membrane and silicone rubber-PEG mixed matrix membrane. The results showed that the gas permeance was a function of critical temperature while the gas selectivities were observed to be similar for each of the dense silicone rubber membranes. For the mixed matrix membrane, the gas permeance

slightly decreased while the selectivities of polar/non-polar gas were significantly improved due to the enhancement in solubility of polar gas in PEG. Observed gas permeance dependent on type of backing for the silicone rubber-PEG mixed matrix membrane indicated that PEG not only had the capacity of altering the permeability of silicone rubber but also acted on the polymeric support material by softening it and causing its pores to shrink (Serivalsatit, 1999).

The other type of mixed matrix membrane was silicalite/cellulose acetate. This membrane was studied on O<sub>2</sub>/N<sub>2</sub> separation. The results showed that the selectivity for O<sub>2</sub> over N<sub>2</sub> increased to between 3 and 4 in comparison to the selectivity through pure cellulose acetate membrane about 2.99 (Kulprathipanja *et al.*, 1988b). Additionally, it was developed to separate CO<sub>2</sub> from H<sub>2</sub>. It had been known that a plain cellulose acetate membrane had a greater permeability for H<sub>2</sub> whereas a silicalite had a greater adsorptive affinity for CO<sub>2</sub>. The mixed matrix membrane comprising cellulose acetate having silicalite as the solid participate adsorbent showed a reversed selectivity for CO<sub>2</sub> over H<sub>2</sub> compared to a pure cellulose acetate membrane (Kulprathipanja *et al.*, 1992).

Suer *et al.* (1994) studied on the permeabilities of O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> and the selectivities of CO<sub>2</sub>/O<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> on the zeolites/polyethersulfone mixed matrix membranes. Zeolites 3A, 4A, 5A and 13X were incorporated in the membrane at various quantities. The results of 4A and 13X indicated that permeabilities of gases at first decreased slightly followed by a substantial increase, as the zeolite percentage in the matrix increases. The permeability increase was more pronounced for H<sub>2</sub> and CO<sub>2</sub>. Selectivities of CO<sub>2</sub>/O<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> were substantially increased for the case of 50 wt% zeolite loading in comparison to zeolite-free membrane.

Battal *et al.* (1995) investigated on the permeabilities and selectivities of CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/Ar and H<sub>2</sub>/CH<sub>4</sub> separations on polyethersulfone





(PES)/42wt% of 4A-zeolite mixed matrix membrane in comparison to pure PES membrane. They found that the permeabilities of most gases (Ar, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>) significantly improved and others (N<sub>2</sub> and CH<sub>4</sub>) did not change on the PES/4A-zeolite mixed matrix membrane. The selectivities for these gas separations increased in the mixed matrix membrane due to the shape-selective properties of zeolites, the interactive potentials and adsorptive capacities of zeolites and the induced microstructure of membranes

After that, the effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membrane was investigated at two different zeolite loadings by Tantekin *et al.* (2000). The permeabilities of O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> on the silicalite-polydimethylsiloxane (PDMS) mixed matrix membranes were determined to enhance with increasing particle size. The variation occurring in the permeability values with changing of the particle size was much more pronounced at the higher zeolite loading. However, the ideal selectivity values of CO<sub>2</sub>/O<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> on mixed matrix membranes were less affected by the changing the particle size.

For olefin/paraffin separation, Sukapintha (2000) developed liquid-polymer mixed matrix membrane. The permeability and selectivity of ethylene/ethane separation were studied on mixture of silicone rubber and Ag-zeolite on a with/without polyethylene glycol (PEG) treated porous polysulfone support mixed matrix membrane. Results could be concluded as: 1) Ag-zeolite did not enhance the ethylene/ethane selectivity, 2) PEG enhanced ethylene/ethane selectivity, and 3) silicone rubber was not a suitable polymer to form Ag-zeolite MMM.

Zimmerman *et al.* (1997) developed mixed matrix composite (MMC) membrane, incorporating molecular serving materials within polymeric substrates, may provide economical, high performance gas separation membranes because zeolites, CMS and rigid rod polymer were difficult and expensive to process even though they offered attractive transport

properties if defects at the molecular sieve/polymer interface could be eliminated. MMC membrane could replace the thin, higher performance polymeric layer with tightly packed (more than 50%) molecular sieving media, such as zeolite or carbon molecular sieve, in a moderated performance polymeric scaffold. In addition, careful matching of the intrinsic permeability and selectivity predictions were presented for such optimized membranes of zeolite 4A and CMS in Ultem and Udel matrices using two idealized expressions to predict MMC theory. The former was developed to describe for cases where the molecular sieve phase was assumed to be continuous and discontinuous penetrant pathways. The later was developed to describe conduction in non-homogeneous binary metallic mixtures.

### 2.3.3 Facilitated Transport or Reactive Membrane

The principles of facilitated transport were used to develop highly permeability and selectivity of membrane. Facilitated transport membrane process has been known for many years and widely researched. Silver ion was used as the carrier for olefins in the membrane. LeBlance *et al.* (1980) introduced the ion-exchange type carrier membranes for olefin gas separations. They used poly(tetrafluoroethylene)-graft-sulfonated styrene ion-exchange membrane containing silver ions. The membrane gave high olefin gas selectivity over paraffin. In 1988, Ho *et al.* (1988) studied the separation of C<sub>2</sub>-C<sub>5</sub> olefin from paraffin and linear  $\alpha$ -olefins from internal and branched olefins of the same carbon number via reversible complexation with the novel solution of cuprous hexafluoroacetylacetonate (diketonate) in a weakly complexing solvent. The results showed the increasing interaction at the double bond of the solvent was increased olefin Cu (I) complex.

Olefin/paraffin separation by fabricated transport membranes like the supported liquid membranes of AgNO<sub>3</sub> solution showed the selectivity factor in the separation of ethylene and ethane increased with increasing

carrier concentration (Teramoto *et al.*, 1986) and ethylene transport was inversely proportional to the membrane wall thickness (Tsou *et al.*, 1994).

However, facilitated transport membranes have not been applied to industrial applications because there are a lack of membrane and carrier stability. A solution to this problem is the development of the reactive polymer membranes that do not require solvent for carrier to react with the olefin penetrant. Sungpet *et al.* (1997) reported the ethylene/ethane separation using Nafion-poly (pyrrole) composite membrane in the absence of solvent. Blends of ionically conductive and electrically conductive polymers were found to have the appropriate electronic environment to allow reaction of silver(I) ion and ethylene. The results for the ethylene/ethane separation were obtained with composite membranes of silver(I)-form Nafion and 2 wt% poly (pyrrole). Ethylene/ethane separation factors with the silver(I)-form Nafion-poly(pyrrole) composite membranes increased from 8 to 15 as temperature decreased. Ethylene permeabilities ratio increased from 0.2 to 1 Barrer over the temperature range of 30°C to 70°C. The permeability ratio of mixed gas of ethylene/ethane about 2 was observed with non-reactive proton-form Nafion-poly(pyrrole) composite membranes.

Hsiue and Yang (1996) developed PE-g-AA- $Ag^+$ , SR-g-AA- $Ag^+$  and PTMSP-g-AA- $Ag^+$  membrane for olefin and paraffin separation. In 1997, the silicone rubber-graft-poly (acrylic acid)- $Ag^+$  (SR-g-AA- $Ag^+$ ) membranes were prepared for C<sub>4</sub> olefin/paraffin separation. Experimental results indicated that the separation factors increased and the permeability coefficient decreased with an increase in AA% grafted (Yang and Hsiue, 1997).

Swollen complex membrane of linear low density polyethylene-graft-poly(acrylic acid)- $Ag^+$  (LLDPE-g-AA- $Ag^+$ ) were studied and compared with SR-g-AA- $Ag^+$  and PTMSP-g-AA- $Ag^+$ . The glycerol in these membranes functions as a plasticizer for polymer chains and more

importantly as an activator for AA- $Ag^+$  complexes. The PTMSP-g-AA- $Ag^+$  complex membrane was found to reach high gas permeability and high olefin/paraffin selectivity (Yang and Hsiue, 1998).

Ethylcellulose (EC) membranes were modified by Bai *et al.* (2000) for the recovery of propylene from a gas mixture, having the same composition as the absorber tail gas (ATG) of a fluid catalytic cracking unit of HPCL refinery. The mixture contains C<sub>1</sub>-C<sub>5</sub> hydrocarbons and non-hydrocarbons such as CO, CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub>. Various metals such as silver, ruthenium, palladium and iridium were incorporated into EC membranes to modify the membrane permeation properties for selectively increasing the propylene flux by facilitating its transport. Ethylcellulose membranes appeared to have good potential for the commercial recovery of propylene from a hydrocarbon rich off-gas mixture containing the olefin as a major constituent. A reasonably high selectivity of 5.1 accompanied by high transport rates was obtained for propylene with respect to propane in the multicomponent mixture. Amongst the metal-incorporated membranes, the best results were obtained with a silver (5wt%)-EC membrane which yielded a permeate stream of around 65 mol% propylene.