CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Theory of Gas Transport in Membranes

The mechanism of gas separation by non-porous membranes is basically different from that of microporous membranes in which gasses are separated by differences in their molecular weights as they traverse pores by Knudsen diffusion. In non-porous membranes, the gas molecules actually dissolve and diffuse in the dense membrane matrix. Therefore, the mechanism of permeation is usually considered to consist of three steps: (1) absorption or adsorption upon the upstream boundary, (2) activated diffusion through the membrane, and (3) dissolution or evaporation from the downstream boundary. This 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 difference that leads to diffusion in the direction of decreasing activity (Kesting and Fritzsche, 1993).

Typical gradients for a binary mixture (A and B) are shown in Figure 2.1. Henry's law assumed to apply for each gas, and equilibrium is assumed at the interface.
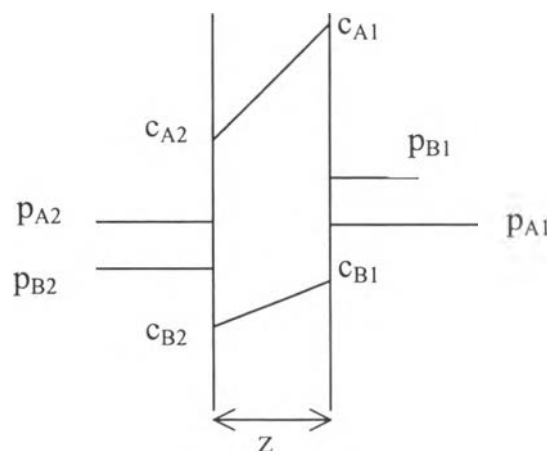

Figure 2.1 Gradients in a dense polymer membrane

where

C_{A2}, C_{A1} = Concentration of A at upstream and downstream boundary, respectively

C_{B2}, C_{B1} = Concentration of B at upstream and downstream boundary, respectively

p_{A2}, p_{A1} = Partial pressure of A at upstream and downstream boundary, respectively

p_{B2}, p_{B1} = Partial pressure of B at upstream and downstream boundary, respectively

Z = Membrane thickness

The gas-film resistances are neglected for this case, so the partial pressures at the gas-polymer interface are the same as those in the bulk. The flux for gas A, J_A, is

$$J_A = -D_A \left[\frac{dC_A}{dz} \right] = D_A \left[\frac{C_{A1} - C_{A2}}{z} \right] \qquad (2.1)$$

where D_A =   Diffusion coefficient

The concentrations are related to the partial pressures by the solubility coefficient S, which has units such as mol/cm^3-atm (S is the reciprocal of the Henry's law coefficient).

$$C_A = p_A S_A \qquad\qquad C_B = p_B S_B \qquad (2.2)$$

Using Eq.(2.2) to replace to the concentration gradient with a pressure gradient gives

$$J_A = \frac{D_A S_A (p_{A1} - p_{A2})}{z} \qquad (2.3)$$

The product $D_A S_A$ is the flux per unit pressure gradient, which is called the permeability coefficient q_A and is often expressed in Barrers, where 1 Barrer = 10^{-10} cm^3(STP)-cm/cm^2-sec-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, which is called the permeability, P_A : (McCabe *et al.*, 1993)

$$J_A = \frac{q_A(p_{A1} - p_{a2})}{z} = P_A(p_{A1} - p_{A2}) \qquad (2.4)$$

P_A is a measure of the membrane's ability to permeate gas. The ability of a membrane to separate two gases, for example A and B, is the ratio of their permeabilities, α_{AB}, called the membrane selectivity.

$$\alpha_{AB} = \frac{P_A}{P_B} \qquad (2.5)$$

Since the permeability depends on both D_A reflecting the mobility of the individual molecules in the membrane material, and the other S_A reflecting the number of molecules dissolved in the membrane material. Thus Eq.(2.5) can also be rewritten as :

$$\alpha_{AB} = \frac{D_A}{D_B}\frac{S_A}{S_B} \qquad (2.6)$$

The ratio of D_A/D_B is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio of S_A/S_B is the ratio of the Henry's law sorption coefficients of two gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of two gases. The balance between the sorption selectivity and the mobility selectivity determines whether a membrane material is selective for large or small molecules in a gas mixture. Membranes with both high permeability and selectivity are desirable. A higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units. The higher selectivity, the higher purity product gas (Orthmer, 1981).

A facilitated or reactive membrane is explained by the principle of facilitated transport mechanism for gas transport. The membrane used to perform the separation contains a carrier, which preferentially reacts with one of the components to be transported across the membrane. The carrier agent reacts with the permeating component on the feed side of the membrane and then diffuses across the membrane to release the permeant on the product side of the membrane. The carrier agent is

then reformed and diffuses back to the feed side of the membrane. Thus, the carrier agent acts as a selective shuttle to transport one component from the feed to the product side of the membrane (Grant, 1991).

The example of facilitated transport mechanism is shown in Figure 2.2. Carbon dioxide dissolves into the membrane at the feed side boundary and reacts with carbonate ions in the presence of water. The flux of solute CO_2 from the high to the low-pressure side of the membrane is enhanced by the additional flux of reaction products. At the low-pressure side of the film, the reaction is reversed and CO_2 is released from the membrane. The carrier species diffuses back to the high-pressure side of the membrane. To maintain zero current flow, the flow of bicarbonate must be twice the absolute value of the flux of carbonate (Chen et al., 2001)

| A = CO_2 | C = Carbonate |
| W = Water | B = Bicarbonate |
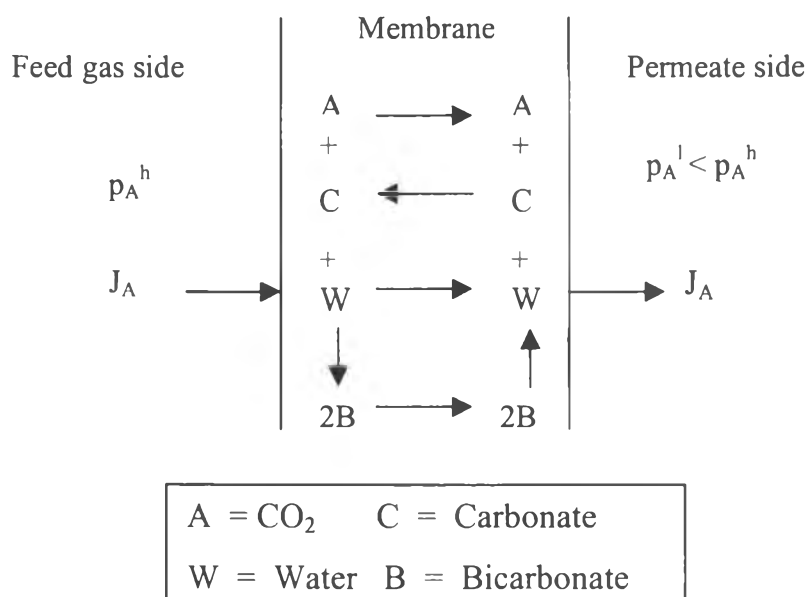
Where $p_A{}^h$, $p_A{}^l$ = Partial pressure of A at feed gas side and permeate side, respectively

J_A = Flux of A

Figure 2.2 Diffusion and reaction of CO_2 across a membrane

2.2 Literature Review

2.2.1 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 are asymmetric membranes composed of one material and composite membrane composed of a variety of materials. Both types are made from many polymers. The polymeric membranes are increasingly used in the study of various of gas separations such as silicone membrane for O_2/N_2 separation, cellulose acetate membrane for CO_2 removal from natural gas and silicone-coated polysulfone membranes for hydrogen recovery from waste streams (Baker *et al.*, 1991).

Pellegrino and Kang (1995) measured CO_2 and CH_4 gas permeation through polyperfluorosulfonate ionomer (PSFI) that was sovalted with water, methanol, ethanol, and 1-propanol. The increased permeabilities of CO_2 when the membrane was swelled by the solvent in the sequence of ethanol>methanol>water implied the effect of polar solvents. The higher permeability of CH_4 compared to the value measured from the dry PSFI film was observed. They suggested that the solvents penetrated into polymer phase and increased the permeability, which was resulted from the increase in diffusivity.

Yamasaki *et al.* (1997) prepared asymmetric membranes from polysulfone/N,N-dimethyl acetamide solutions by the phase inversion technique. The oxygen permeance was inversely proportional to the immersion time. This was resulted from the increased skin layer thickness as increasing immersion time. Beuscher and Goodings (1999) commercialized a flat sheet and a hollow fiber composite membrane for volatile organic compounds after their investigation in the permeation properties of silicone rubber coated composite membranes. The other four polymeric materials made from poly(phenylene oxide), polysulfone, ethylcellulose and cellulose acetate were studied by Sridhar and Khan (1999) for the separation of propylene from propane. Their results of high permeabilities and reasonably good selectivities made ethylcellulose to be the most promising for

commercial applications. Polyimides based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was another very promising material for membrane-base separation of olefin/paraffin mixtures. Bickel and Koros (2000) obtained the ideal ethylene/ethane separation factor ranged between 3.3 and 4.4 and the ideal propylene/propane separation factor ranged between 10 and 16 at a feed pressure of 3.8 atm and 308 K.

2.2.2 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 a porous support prepared by casting and curing an emulsified mixture of them on a porous polysulfone support (Kulprathipanja and Kulkarni, 1986). The permeation rates of SO_2, H_2S, NH_3, CO_2, H_2, N_2 and C_2H_6 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-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_2/N_2 separation. The results showed that the selectivity for O_2 over N_2 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_2 from H_2. It had been

known that a plain cellulose acetate membrtane had a greater permeability for H_2 whereas a silicalite had a greater adsorption affinity for CO_2. The mixed matrix membrane comprising cellulose acetate having silicalite as the solid participate adsorbent showed a reverse selectivity for CO_2 over H_2 compared to a pure cellulose acetate membrane (Kulprathipanja et al., 1992).

Suer et al. (1994) studied the permeabilities of O_2, N_2, CO_2 and H_2 and the selectivities of CO_2/O_2, H_2/N_2 and CO_2/N_2 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 a zeolite percentage in the matrix increases. The permeability increase was more pronounced for H_2 and CO_2. Selectivities of CO_2/O_2, H_2/N_2 and CO_2/N_2 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_2/CH_4, CO_2/Ar and H_2/CH_4 separations on polyethersulfone(PES)/42 wt% of 4A-zeolite mixed matrix membrane in comparison to pure PES membrane. They found that the permeabilities of most gases (Ar, O_2, CO_2 and H_2) were significantly improved and others (N_2 and CH_4) 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 loading by Tantekin et al. (2000). The permeabilities of O_2, N_2 and CO_2 on the silicalite-polydimethysiloxane (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_2/O_2, O_2/N_2 and CO_2/N_2 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 a mixture of silicone rubber and Ag-zeolite on 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 the ethylene/ethane selectivity, and 3) silicone rubber was not suitable polymer to form Ag-zeolite MMM.

However, the mixed matrix membrane with emulsified liquid PEG have limited stability resulted form the possible PEG leakage. Vijitjunya (2001) selected NaX-zeolite to stabilize PEG by the absorption of PEG into its pores. The effect of the absorbed PEG on olefin separation was examined. In addition, some diol isomers such as 1,4-butanediol, 1,2-butanediol and 2,3-butanediol have been studied in place of PEG. It was postulated that hydroxyl group position on the carbon chain of diols could play a significant role in olefin selectivity enhancement.

In the same year, Rattanawong (2000) developed a solid-polymer mixed matrix membrane for an olefin/paraffin separation. NaX-zeolite, AgX-zeolite and silicalite were incorporated into cellulose acetate (CA) polymer and used as adsorbent. It was found that CA membrane was selective for ethylene over ethane and propylene over propane. For MMMs, 20wt% silicalite/CA MMM was selective for propylene over propane. However, NaX-zeolite/CA and AgX-zeolite/CA MMMs were reverse selective for olefin over paraffin.

2.2.3 Facilitated Transport Membranes

Many polymeric membranes have been developed for CO_2 separation. However, among these membranes, the separation factors of CO_2 over N_2 or CH_4 are rather low. To increase CO_2/N_2 selectivity, the use of facilitated transport membranes has been proposed. In facilitated transport membranes, the transport of CO_2 is augmented by reversible reactions between CO_2 and certain carriers in the membrane, but N_2 and CH_4 do not react with the carriers and can only permeate via the solution-diffusion mechanism. As expected, selectivities are significantly higher than those, which CO_2 doesn't react with the carriers. This technique has been

known and widely studied for many years. Moreover, the extensive mathematical models have also been developed (Park *et al.*, 2000).

Matsuyama *et al.* (1994, 1996, 1997 and 1999) studied a new type of cation-exchange membrane that was prepared by grafting acrylic acid (AA) onto a microporous polyethylene (PE) membrane by use of plasma-glasma-grafted polymerization technique in 1994. The facilitated transport of CO_2 through the plasma-grafted membrane containing etylenediamine was studied. The obtained membrane showed remarkably high CO_2 permeability and selectivity of CO_2 over N_2. The newly prepared membrane was stable. Continuously, in 1996 ion exchange membranes were prepares by grafting AA and methacrylic acid to the substrates by the use of the plasma-graft polymerization technique. Experiments on the facilitated of CO_2 through the grafted membrane were carried out by using various diamines, diethylenetriamine and triethylenetetramine as the carrier. Among all membranes tested, the AA grafted membrane-containing ethylenediamine as the carrier showed the highest selectivity of CO_2 over N_2. The use of polytetrafluoroethylene (PTFE) and homogeneous poly[1-(trimethylsilyl)-1-propane] (PTMSP) substrates were effective for increasing the permeation rate of CO_2. A series of experiments on the facilitated transport of CO_2 through supported liquid membranes impregnated with aqueous solutions of various amines as carriers was performed, and the effects of the reaction rate and the chemical equilibrium of the reaction between CO_2 and amine on the permeability of CO_2 were investigated in 1997. The feed gas was a mixture of CO_2 and CH_4. High CO_2 permeabilities were obtained with the monoprotonated ethylenediamine membrane due to its moderate chemical equilibrium constant K_{eq} which is favorable for both fast absorption of CO_2 at the feed side of the membrane and fast stripping at the sweep side. Low CO_2 permeabilities were obtained with the 2-amino-2-methyl-1-propanol membranes due to their low reactivity. The CO_2 permeability through the monoethanolamine membrane, which is too large a K_{eq} value at low temperature, increased with increasing temperature due to the decrease in K_{eq} and also due to the increase in the reaction rate. In addition in 1999, polyethyleneimine (PEI)/poly(vinyl alcohol) (PVA) blend membranes were prepared. The polymeric carrier PEI was retained in the blend membranes by the entanglement with PVA chains. The CO_2 permeance decreased with an increase in

CO_2 partial pressure in feed gas, whereas the N_2 permeance was nearly constant. This result clearly showed that only CO_2 was transported by the facilitated transport mechanism. The CO_2 and N_2 permeabilities increased monotonically with the PEI weight percent in the blend membrane, whereas the selectivity of CO_2 over N_2 showed a maximum. The prepared membrane was stable.

Park *et al.* (2000) focused on the characteristics of facilitated transport of CO_2 through hydrophilic polymeric membranes with an immobilized aqueous potassium carbonate (K_2CO_3) solution. The rate of permeation for CO_2 increased with increasing K_2CO_3 concentration, decreasing membrane thickness, and decreasing CO_2 partial pressure. The permeation rate for CO_2 was predicted by a theoretical model based on mass transfer accompanied by a reversible chemical reaction, such as hydration reaction of CO_2, reaction of CO_2 with OH^-, or dissociation of HCO_3^-. The permeation rate for CO_2 increased by adding K_2SO_4, PEG, or DBC to the aqueous K_2CO_3 solution. By assuming that these additives enhanced the hydration reaction of CO_2, these forward-reaction rate constants were higher than those without additives about 15-36 times.

Chen *et al.* (2000) focused on immobilized glycerol-based liquid membranes in hollow fibers. For selective separation of CO_2 from a mixed gas (CO_2 and N_2) feed having low concentrations of CO_2. The immobilized liquid membranes (ILMs) investigated consist of sodium carbonate (Na_2CO_3)-glycerol solution. The hollow fiber-based ILMs were studied at selected CO_2 partial pressure differences, relative humidity (RHs), as well as carrier concentrations. The sweep gas was always dry helium and it flowed on the shell side. Generally, lower permeances and greater CO_2/N_2 selectivity values were observed at lower feed stream RHs and also lower CO_2 partial pressure differential. Prolonged runs lasting for 300 h showed that the hollow fiber-based ILM permeation performances were stable.

Chen *et al.* (2001) continued to develop glycerol-based ILMs for the selective separation of CO_2 from a mixed gas (CO_2,N_2) feed. The items of specific interest are replacement of the carrier sodium carbonate (Na_2CO_3) by glycine-Na in glycerol, ILM thickness reduction performance of environmentally benign carriers, e.g., glycine-Na vis-a-vis toxic and volatile carriers, e.g., ethylenediamine. As the glycine-Na concentration was increased, N_2 permeability decreased while the CO_2

permeability increased drastically at lower glycinate concentrations and level off at higher glycinate concentrations. The effect of feed relative humidity, lower feed stream RH yielded lower species permeances but greater CO_2/N_2 selectivities. The ILM stability was also tested with a 25-day-long experiment.