CHAPTER II
LITERATURE SURVEY

2.1 Background

Membranes have gained an important place in chemical technology and are 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)

For a nonporous dense membrane, the separation of various components of gas mixture is directly related to their relative transport rate 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).

For an isotropic microporous membrane, the membrane has 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 of the microporous membrane are in the range of 0.01-10 μm. The mechanisms of gas permeation through porous membranes are divided in 3 types. If the pores are larger than 0.1-10 μm, gases permeate through the membrane by

convective flow and no separation occurs. If the pores are smaller than 0.1 μm, the diffusion of gases through the pores is govern by Knudsen diffusion, and the transport rate of different gases is inversely proportional to the square root of the molecular weight. If the membrane pores are very small or smaller than 0.5-2 nm, the diffusion of gases through the pores is govern by micropore diffusion (Koros and Jones, 1994).

In membrane separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other component (Grant, 1991).

2.2 Theory

Facilitated transport is the active transport of permeant molecules across a membrane. 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:

$$A + B \Leftrightarrow AB \tag{2.1}$$

$$C + B \not\Leftrightarrow BC \tag{2.2}$$

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. 2.1). By contrast, "C" does not react with "B" (Eq. 2.2).

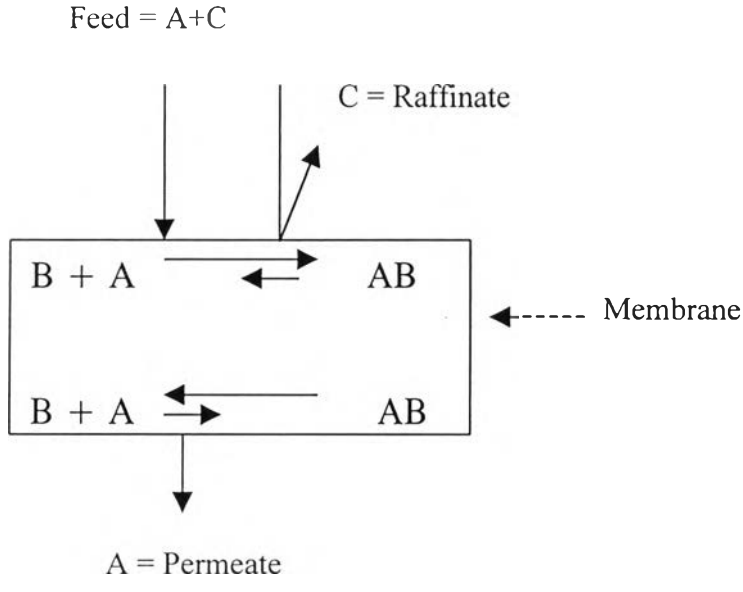

Figure 2.1 Mechanism for facilitated transport of component A by carrier B

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).

Olefin/paraffin mixtures could be separated by the facilitated transport method by incorporating silver ion as the carrier in a membrane. The gas permeability on a polymer membrane can be described by a mean permeability coefficient, P, that is defined by a the isothermal relation (Stern *et al.*, 1987):

$$P = \frac{J_S \times \delta}{p_h - p_l} \tag{2.3}$$

where J_s is the steady state rate of gas permeation through unit membrane area. δ is the membrane thickness. p_h and p_l are high and low pressure streams of the component, respectively.

Base 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):

$$P_A = D_A S_A \tag{2.4}$$

The permeability coefficient P_A is often expressed in Barrers, where 1 Barrers = 10^{-10} cm^3 (STP)-cm/cm^2-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, which will be called "permeability", P_A/δ.

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

$$\alpha_{(A/C)} = \frac{P(A)}{P(C)} \tag{2.5}$$

Using Eq. 2.4, $\alpha_{(A/C)}$ can be written as the product of the diffusivity selectivity and solubility selectivity of the gas (Zimmerman *et al.*, 1997):

$$\alpha = \frac{D_A S_A}{D_C S_C} \tag{2.6}$$

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

coefficients of the two gases and can be viewed as the solubility selectivity (Grant, 1991).

2.3 Literature Review

2.3.1 Gas Transport

Petrochemical mixtures are currently separated by physical and chemical adsorption processes, extractive distillation and cryogenic distillation (Orthmer, 1981). The high energy consumption and capital investment of these technologies provide the incentive for continuous efforts to develop more economic separation processes (Eldridge, 1993). Application of membrane technology as an alternative gas separation process has been investigated. The separation of gas from a two component gas by a porous membrane was studied both theoretically and experimentally. The theory based on the free molecular flow could not be applied to all the combinations of the gases experimentally studied. Experiment showed that the permeability coefficient of each component in the mixture was very close to that of each single component, but those of the mixture approached one another rapidly as the pressure increased (Kawai *et al.,* 1997).

CO_2 separation from a mixture of CO_2/C_2H_6 through membranes containing immobilized solutions of diethanolamine(DEA) and poly(ethylene glycol)(PEG) was studied by Saha and Chakma (1995). The reactive membranes with DEA showed higher permeation rates for CO_2 compared to the non-reactive PEG membranes. The CO_2 permeability increased with increasing concentration of the alkanolamine. It can be concluded that DEA increased CO_2 transport rate across the membrane.

2.3.2 Facilitated Transport

Facilitated transport membrane process has been known for many years and widely researched. 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_2-C_5 olefin from paraffin and linears α-olefins from internal and branched olefins of the same carbon number via reversible complexation with the novel solution of cuprous hexafluoroacetyacetonate (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.

The fluxes of styrene and ethylbenzene through perflurosulfonate ionomer membranes exchanged with sodium and silver ions were also reported (Koval *et al.,* 1989). The results showed the fluxes enhanced when Na^+ was replaced with Ag^+ due to the reversible formation of complexes with silver ion. Since styrene forms a more stable complex, its flux is enhanced significantly more than that of ethylbenzene.

In 1993, BP has developed a new membrane system for refinery and chemical plant olefin purification and recovery. Pilot plant experiments on propylene/propane and ethylene purge gas showed membrane stability and product purity of 98.5% or greater using refinery grade propylene feed (Davis *et al.,*1993). π-complexation has been previously considered for olefin/paraffin separation and purification by employing liquid solutions containing silver (Ag^+) or cuprous (Cu^+) ions (Eldridge, 1993).

Olefin/paraffin separation by fabricated transport membranes like the supported liquid membranes of $AgNO_3$ 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).

Teramoto *et al.* (1989) also proposed a new type of liquid membrane, namely flowing liquid membrane, which was much more stable than immobilized liquid membrane. These membranes showed higher permeability and stability when compared with the usual immobilized liquid membrane.

Perfluorosulfonated ionomer (PSI) membranes were used to investigate the separation of olefin/paraffin mixtures by means of silver-based facilitated transport of olefin. Oxygen-containing hydrocarbons present in the petrochemical mixture increased the flux of olefin and paraffin. However, the increased fluxes results in lower separation factors for pentene/pentane mixtures (Zyl and Linkov, 1997).

In facilitated transport of butene and propylene through synthesis of new poly(vinyl alcohol)(PVA) containing silver nitrate membrane showed high olefin flux and olefin/paraffin selectivity. Butene fluxes increased with increasing water content in the membrane until it was saturated with water and butene fluxes increased linearly with silver nitrate content in the PVA membrane (Ho and Dalrymple, 1994). Bai *et al.* (1998) studied the separation of propylene and propane by using poly (2,6-dimethyl-1,4-phenylene-oxide)(PPO). This membrane showed high ideal selectivity with respect to propylene. The PPO was incorporated with Silver (Ag (I)), Palladium (Pd (II)), Ruthenium (Ru (III)) and Iridium (Ir (III)). The flux and selectivities were improved when Ru(III) and Pd(II) were added. However, the significant improvements in the propylene permeabilities have been realized mainly due to the selective transport of propylene molecules mediated by the incorporation of selected metal ions. Yamaguchi *et al.* (1996) studied $AgBF_4$/Nafion blend membrane and Nafion 117 ion-exchange membrane with/without humidity in the feed. The $AgBF_4$/Nafion blend membrane with

low humidity showed a high facilitation effect for C_4 separation when compared to Nafion 117 ion-exchange membrane which required high humidity. Nafion 117 containing silver ions produced a higher separation factor and flux than obtained with silver form Nafion 117 membrane when the membrane was treated by heat.

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.

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_4 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).

2.3.3 Mixed Matrix Membrane

The mixed matrix membrane had been developed in the late 1980's. The desirable characteristics of mixed matrix membrane which 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. Many of the membranes which have been utilized for this separation process possess either a high selectivity or a high flux (Kulprathipanja *et al.,* 1988). Cellulose acetate (C.A.) is one of the membrane materials applied to separate of CO_2 from H_2. It has been known that a plain cellulose acetate membrane has a greater permeability for H_2 whereas a silicalite has a greater adsorptive affinity for CO_2. The mixed matrix membrane comprising cellulose acetate having silicalite as the solid participate adsorbent showed a reversed selectivity for CO_2 over H_2 compared to a pure cellulose acetate membrane (Kulprathipanja *et al.,* 1992).

Battal *et al.* (1995) studied the mixed matrix membrane of an amorphous glassy polymer (polyethersulfone) and hydrophilic zeolite (4A). Membrane containing zeolite filler 4A showed a better separation performance than membranes without zeolite due to the enhancement in permeabilities and selectivities. The increases of selectivities 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

Another type of membrane is a mixed matrix membrane of silicone rubber and poly(ehtylene glycol) (PEG) on porous support prepared by casting and curing an emulsified mixture of poly (ethylene glycol) and silicone rubber on 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 rubber-PEG mixed matrix membrane indicates that PEG not only has the capacity of altering the permeability of silicone rubber but also acts on the polymeric support material by softening it and causing its pores to shrink (Serivalsatit, 1999).

In this work, new types of mixed matrix membrane with Ag^{+} as a carrier were studied.