CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Pervaporation

Pervaporation processes are membrane based separations of one or more components of liquid mixtures diffusing through a selective membrane evaporate under low pressure on the downstream side, and are removed by a vacuum pump or chilled condenser. Thereby, a transfer of mass from a liquid phase to the vapor phase through a polymeric membrane is performed. Figure 2.1 shows the principle of pervaporation and the general flow scheme of such a membrane separation unit. The liquid feed mixture to be separated flows along one side of the membrane while the various feed components are permeating into and through the membrane at different rates. Therefore, the liquid retentate leaving the unit on the same side of the membrane as the feed enters is depleted in the components permeating preferentially. Consequently, the vapor permeate collected on the other side of the membrane is enriched in the preferentially permeating component (Schleiffelder *et al.*, 2001).

The driving force for the mass transport of each component through a nonporous polymeric membrane is the difference of the chemical potential between feed side and permeate side, depending on temperature, pressure, and the mole fraction of all components present in the mixture. In pervaporation, the difference of the chemical potential between the feed side and permeate side mainly is achieved by keeping the permeate pressure much lower than the feed pressure. The different permeation rates of the components are due to the differences in solubility and diffusivity in the membrane polymer:

$$P = S \cdot D \qquad (2.1)$$

where S is the solubility coefficient and D is the average diffusion coefficient. The solubility coefficient is determined by the condensibility of the penetrants, by the polymer-penetrant interactions and by the amount of free volume existing in the glassy polymer. The average diffusion coefficient is a measure of the mobility of the penetrants between the upstream and downstream conditions in the membrane. The diffusion coefficient depends on packing and motion of the polymer segments and on the size and shape of the penetrating molecules.

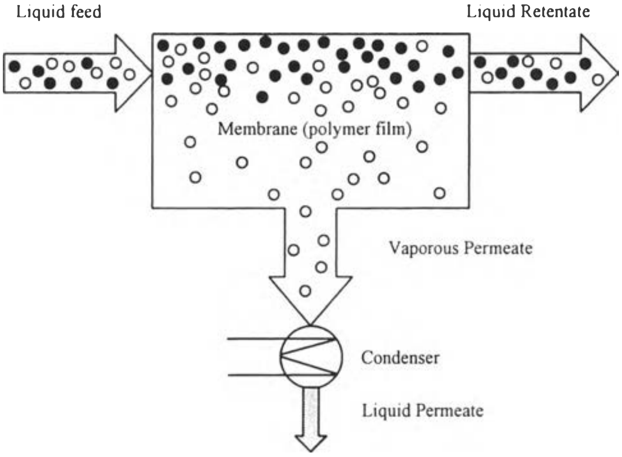

Figure 2.1 A schematic of pervaporation process (Schleiffelder *et al.*, 2001).

The mass transport through a polymeric membrane as shown in Figure 2.1 can be described with the solution diffusion model. Based on this model, the components are permeating through a polymeric membrane by a three steps process, the sorption of the component on the membrane surface (feed side), the diffusion of the component through the membrane and the desorption of the component on the permeate side of the membrane.

2.1.2 Selectivity

The primary requirement for an economic separation process is an adsorbent with sufficiently high selectivity, capacity and life. The selectivity may depend on a difference in either adsorption kinetics or adsorption equilibrium, but most of the adsorption processes in current use depend on equilibrium selectivity. In considering such the processes, it is convenient to define a separation factor:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B} \tag{2.2}$$

where X_A and Y_A are, respectively, the moles fraction of component A in adsorbed and fluid phases at equilibrium. The separation factor defined in this way is precisely analogous to the relative volatility, which measures the ease with which the components may be separated by distillation. The analogous is, however, purely formal and there is no quantitative relationship between the separation factor and relative volatility. For two given components, the relative volatility is fixed whereas the separation factor varies widely depending on the adsorbent. Since the separation factor generally varies with temperature and often also with composition, the choice of suitable conditions to maximize the separation factor is a major consideration in process design. For an ideal Langmuir system, the separation factor is independent of composition and equal to the ratio of the Henry's law constants of two relevant components. Preliminary selection of suitable adsorbents can therefore sometimes be made directly from available Henry's constants (Ruthven, 1984).

2.1.3 Zeolites

Zeolites are microporous crystalline aluminosilicates. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of regular dimensions into which guest molecules can penetrate. Since the micropore structure is determined by the crystal lattice, it is precisely uniform with no distribution of pore size. It is this feature that distinguishes the zeolites from the traditional microporous adsorbents.

In considering zeolite frameworks, it is convenient to regard the structures as built up from assemblages of secondary building units, which are themselves polyhedra made up of several SiO_4 and AlO_4 tetrahedra. The secondary building units and some of the commonly occurring polyhedra are shown schematically in Figure 2.2. In these diagrams, each vertex represents the location of the oxygen atoms or ions, which are very much larger than the tetrahedral Si or Al atoms. Each aluminum atom introduces one negative charge on the framework, which must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a very important role in determining the adsorptive properties. Changing the exchangeable cation by ion exchange provides a useful and widely exploited means of modifying the adsorptive properties (Ruthven, 1984).

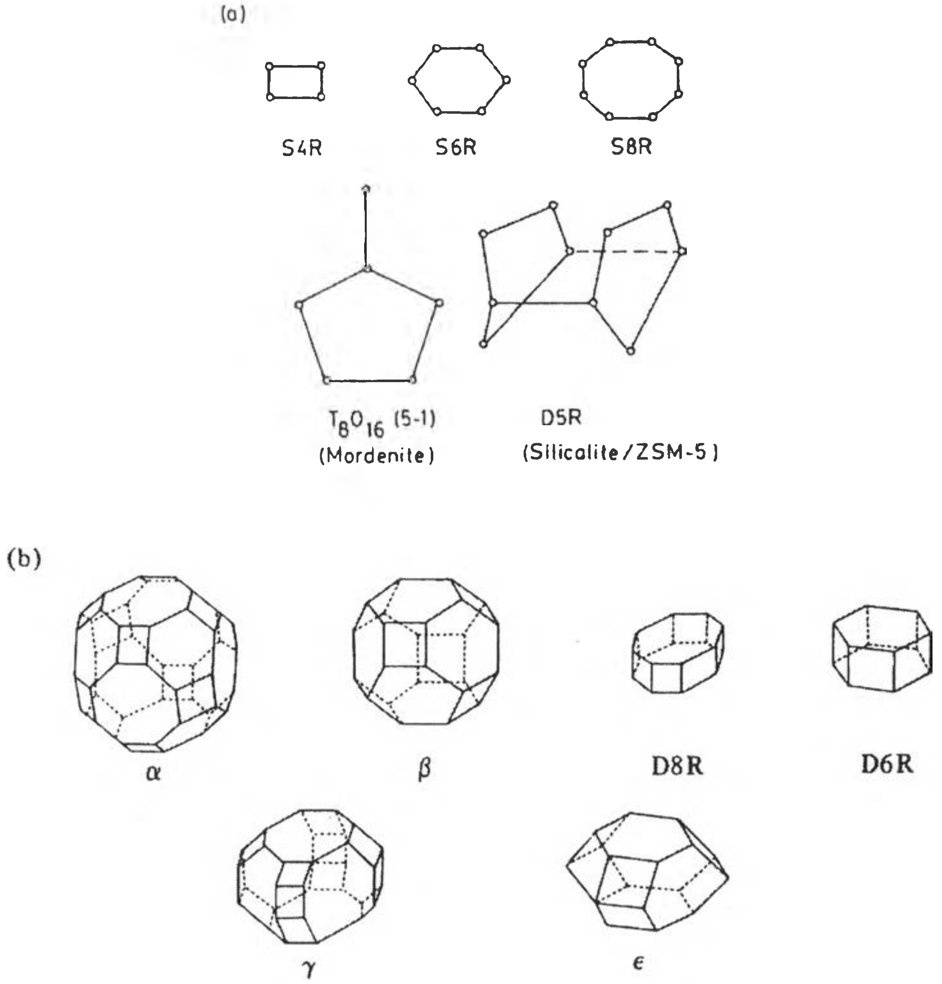

Figure 2.2 Secondary building units and commonly occurring polyhedral units in zeolite framework structures (Ruthven, 1984).

2.1.4 Zeolite Selection

Zeolite is selected such that xylene isomers can diffuse through at different rates. Examples of zeolites suitable for use including intermediate pore size zeolites. Intermediate pore size zeolites have pore size in the range of between about 5 and 7 angstroms. Examples of useful intermediate pore size zeolites include ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SUZ-4, SSZ-23, SSZ-25, cesium modified SSZ-25, SSZ-28, SSZ-32, SSZ-33, SSZ-36 and silicalite.

Preferred intermediate pore size zeolites include silicalite and ZSM-5 (Miller *et al.* 2002).

2.1.5 Polymer Selection

A polymer should permit passage of xylene isomers (or other mixtures to be separated) in the vapor state, such that *p*-xylene diffuses at a faster rate through the polymer. Preferably, the rate at which *p*-xylene passes through the polymer is at least 1.5 times faster than the rate at which other xylene isomers through the polymer. Flexible polymers are preferred over rigid polymers. Examples of suitable polymers include cellulose polymers, polyaramides, polyamides, polymides, polyamide/imides, polyamidehydrazides, polyhydrazides, polyimidazoles, polybezoxazoles, polyester/amide, polyester/imide, polycarbonate/amides, polysulfone/amides, polysulfone/imides, and the like, copolymers and blend thereof. Preferably, the polymers include at least one of either of cellulose polymers, polyamides, polyaramides, polyamide/imides or polyimides. Most preferably, the polymers include polyaramides (Miller *et al.*, 2002).

2.2 Literature Review

Several authors reported the separation of xylene isomers through zeolite membranes and polymeric membranes; however, the results are inconsistent.

McCandless *et al.* (1987) studied separation of C_8 aromatic isomers through commercial polymer films. The membranes were tested in conventional pervaporation apparatus. Twelve polymer films were tested. The results showed that the best separation for all three mixtures, *p*-/*o*-xylene, *p*-/*m*-xylene, and *p*-xylene/ethylbenzene, was given by the polyimide films, but the parylene films and cellulose acetate also exhibited some relatively high separation factors. Moreover, they found that temperature greater than 200°C was required to obtain a reasonable flux through the polyimide film and a pressure of about 300 psi was necessary to keep the feed stream liquid.

Keizer *et al.* (1998) studied two components permeation through thin zeolite MFI membranes supported by a flat porous α-Al_2O_3 substrate. The membranes were prepared by the MISC (muti in situ crystallization) method. It was shown that this type of zeolite showed poor separation factors for *p*-/*o*-xylene mixtures at low temperature. Increasing the temperature to approximately 130°C and using a very dilute xylene mixture in helium, very high separation factors up to 200 were achieved in vapor permeation experiments.

Wegner *et al.* (1999) studied pervaporation of pure xylene isomers and their binary mixtures through polycrystalline zeolite MFI membranes. The membranes were synthesized on α-alumina supports by the hydrothermal method. The results showed that all xylene isomers could permeate through the polycrystalline zeolite membranes. For all isomers, a successive decrease of pervaporation flux with pervaporation time and the brownish coloration of the membranes were observed in the temperature range of 26-75°C. The pervaporation flux of a pure xylene isomer at 26°C in the first 10 h pervaporation experiment decreased in the order: *m*-xylene>*p*-xylene>*o*-xylene. For long permeation times, the order was reversed, implying that the fouling affects the isomer molecules to a different degree. No separation was observed for binary *p*-/*o*-xylene and *p*-/*m*-xylene mixtures in the investigated temperature range (26-75°C).

Chen *et al.* (2000) prepared a polyvinyl alcohol (PVA) membrane filled β-cyclodextrin (β-CD). The membrane was prepared by casting an aqueous solution of PVA and β-CD oligomer and used for separation of *p*-/*m*-xylene mixtures by pervaporation. Compared with the PVA membrane, the solubilities of pure *p*-xylene and pure *m*-xylene in the PVA/β-CD membrane increased from 0.92, 0.78 to 10.4, 2.6 g (xylene)/100 g (dried membrane) at 25°C, respectively, and the solubility selectivity S_p/S_m increased from 1.18 to 4.0. Also, the diffusion coefficients of *p*-xylene and *m*-xylene decreased from 8.45×10^{-12} and 8.23×10^{-12} to 6.83×10^{-12} and 7.23×10^{-12} m^2/s at 25°C, respectively. The separation factor of the PVA/β-CD membrane for *p*-xylene was considerable enhanced from 1.35 to 2.96, and the permeation rate decreased from 190 to 95 g/m^2 h for a 10 wt% feed *p*-xylene concentration at 25°C. They found that the effect of β-CD on the solubilities of *p*-

xylene and *m*-xylene was more important on the diffusion coefficients of *p*-xylene and *m*-xylene for improvement in the pervaporation performance. Moreover, the effects of β-CD on the solubility, the diffusion coefficient, and pervaporation have been interpreted by the inclusion phenomenon in the cavity.

Matsufuji *et al.* (2000) prepared MFI-type zeolitic membranes by a vapor-phase transport (VPT) method on porous α-alumina flat disks. The pervaporation tests for xylene isomers were performed at 30°C. The results showed that *p*-xylene was the most permeate component in the unary system. However, *m*-xylene and *o*-xylene permeated faster than *p*-xylene in the binary and ternary systems. The separation factor of *p*-/*m*-xylene in the binary system at steady state was 0.43, showing *meta*-selectivity and the separation factors of $\alpha_{(p\text{-}/m\text{-xylene})}$, $\alpha_{(p\text{-}/o\text{-xylene})}$ and $\alpha_{(m\text{-}/o\text{-xylene})}$ in the ternary system at steady state were 0.16, 0.18 and 1.1, respectively. The adsorption of *m*-xylene in the pores of MFI membranes seems to inhibit the permeation of *p*-xylene.

Nair *et al.* (2001) focused on the separation of xylene isomers using silicalite (MFI) membranes, as well as several other hydrocarbons mixtures using faujasite membranes. In the case of silicalite membranes, the results showed that high (20-300) *p*-/o-xylene separation factors were obtained. They found that the selectivity depended on the membrane microstruction. The faujasite membranes had high selectivities (40-150) in the separation of binary mixtures containing one aromatic component, and modest selectivities (4-9) for the separation of unsaturated from saturated low molecular weight hydrocarbon.

Scheleiffelder *et al.* (2001) studied closslinkable copolyimides for the membrane-based separation of *p*-/*o*-xylene mixtures. Pervaporation experiments were carried out at 60°C using a feed mixture of 50:50 *p*-/*o*-xylene with different crosslinked and non-crosslinked 6FDA-based copolyimides. It was found that crosslinkable carboxylic acid containing copolyimides were stable towards *p*-/*o*-xylene mixture at 60°C. In addition, crosslinkable carboxylic acid containing copolyimides was stable towards *p*-/*o*-xylene at 60°C. The normalized flux through the different membranes strongly depended on the polymer backbone structure but it was also influenced by the crosslink agent. For *p*-/*o*-xylene mixtures, normalized fluxes were between 0.04 and 25 kg μm m^{-2} h^{-1} with separation factors between 1.15 and 1.47.

Xomeritakis *et al.* (2001) studied separation of xylene isomer vapors with oriented MFI membranes made by seeded growth using vapor permeation technique. The membranes were evaluated for separation of xylene isomers with single component, binary and ternary permeation experiments in the range of 22-300°C and feed partial pressure up to 1 kPa. The permeation results suggested a strong relationship between membrane microstructure and performance for *p*-xylene separation from *o*-xylene.

Miller *et al.* (2002) directly invented a mixed matrix composite (MMC) membrane capable of separating *p*-xylene from mixtures including *p*-xylene and *m*-xylene, and process for purifying *p*-xylene using the membrane. Mixed matrix membranes (MMM's) including SPO-silicalite and cellulose acetate (CA)-ZSM-5 were prepared. The membranes were tested under two test conditions, 45°C for pervaporation mode and 150°C for vapor phase mode. The results showed that, for SPO-silicalite and CA-ZSM-5 MMC membranes, the selectivities (*p-*/*m*-xylene) for the pervaporation mode were 6 and 4, respectively, and the selectivities for the vapor phase mode were 1.2 and 2, respectively.

Santiworawut (2003) investigated performance of MMM's for C_8 aromatics, olefins, and paraffins separation. Polyimide membrane and polyimide-based MMM's, 20 wt% silicalite/polyimide, 20 wt% NaY/polyimide, and 20 wt% activated carbon/polyimide were used. The extraction and pervaporation were carried out. The results showed that for n-olefin/n-paraffin separation, both polyimide and polyimide-based MMM's were selective for n-paraffin over n-olefin. For n-paraffin/C_8 aromatics separation, all membranes were selective for C_8 aromatics over n-praffins. It was also found that the results from the extraction and pervaporation were consistent. Moreover, the separation of C_8 aromatics from the extraction and pervaporation was low and negligible. In addition, the temperature hardly affected the separation.