



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Adsorption

In adsorption processes, one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and separation is accomplished. In commercial processes, the adsorbent is usually in the form of small particles on fixed bed. The fluid that is a solution of several different chemical species is pass through the bed (Geankoplis, 1993). A species present in the fluid phase is said to be adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid. Adsorption takes place because of the interaction between the species present on the fluid phase and solid surface. The following is a list of qualitative criteria for deciding whether adsorption might be such an alternative (Yang, 1997).

1. Relative volatility between the key components to be separated is in the order of 1.2 to 1.5 or less. An example for this case is the separation of isomers, where the separation factor for adsorption is practically infinity by using zeolites.

2. Bulk of the feed is a relatively low-value, more volatile component, and the product of interest is on a relatively low concentration. In such situation, large reflux ratios can be required in distillation and can result in high energy requirements.

3. Two groups of component to be separated have overlapping boiling ranges. Several distillation columns are required for such the separation, even though various relative volatilities may be large. This separation may be efficiently achieved by adsorption if the two groups contain chemically or geometrically dissimilar molecules – that is, with a high separation factor.

4. A low temperature and a high pressure are required for liquefaction.

5. Factors favorable for adsorption separation exist. The major cast for pressure swing adsorption is in the compressor costs. If the mixture is available at an elevated pressure, the costs for separation are substantially reduced. The gas throughput and product purities are also important considerations. The costs for

adsorption separation are generally lower than distillation for small to medium throughputs, and when high-purity products are not required.

2.2 Selectivity

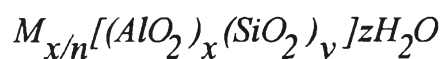
In selective adsorption processes, an adsorbent is an important element. Many parameters are evaluated for the determination of the effectiveness of adsorbent such as selectivity, capacity and lifetime. The selectivity may vary with differences in either adsorption kinetics or adsorption equilibrium. The separation factor is defined as

$$\alpha_{AB} = \frac{(X_A/X_B)}{(Y_A/Y_B)} \quad (2.1)$$

where X_A and Y_A are equilibrium mole fraction of component A in adsorbed and fluid phases, respectively. 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. However, the analogy is purely formal, and there is no quantitative relationship between the separation factor and relative volatility. For two given components, the relative volatility is fixed while the separation factor varies widely depending on the adsorbent. Because the separation factor generally depends on temperature and often also with composition, the separation factor is a major consideration in the process design. For an ideal Langmuir system, the separation factor is independent on composition and equal to the ratio of the Henry's law constants of the two relevant compositions. Therefore, preliminary selection of suitable adsorbent can, sometimes, be made directly from available Henry's constants (Ruthven, 1984).

2.3 Zeolites

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium, and calcium, represented by the stoichiometry:



where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M , and z is the number of water molecules in each unit cell. Unit cells are shown in Figure 2.1. The cations are necessary to balance the electrical charge of the aluminum atoms, each having a net charge of -1 . The water molecules can be removed with ease upon heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are usually interconnected by six windows on each cage. The cages can be occluded by large amounts of guest molecules in place of water. The size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 \AA^2 to 10 \AA^2 . The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent because of the surface property on the cages) – hence the name molecular sieve (Yang, 1997).

The primary structural units of zeolites are the tetrahedra of silicon and aluminum, SiO_4 and AlO_4 . These units are assembled into secondary polyhedral building units such as cubes, hexagonal prisms, octahedra, and truncated octahedra. The silicon and aluminum atoms, located at the corners of the polyhedra, are joined by a shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline framework. The ratio Si/Al is commonly one to five. The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations and the cations can also be exchanged. The inner atoms in the windows are oxygen. The size of the windows depend, then, on the number of oxygen atoms on the ring – four, five, six, eight, ten, or twelve. The aperture size, as well as the adsorptive properties, can be further modified by the number and type of exchanged cations. A description of the

structures will be given only for the zeolites important in gas separation, Type A and Types X and Y.

The skeletal structure of Types X and Y zeolites are the same as that of the naturally occurring faujasite. The sodalite (also called β -cages) units are linked through six member prisms as shown in the unit cell in Figure 2.1. Each unit cell contains 192 (Si, Al) O_4 tetrahedra. The number of aluminum ions per unit cell varies from 96 to 77 for Type X zeolite, and from 76 to 48 for Type Y zeolite. The difference between the X and Y sieves lies in the Si/Al ratio, which is within the range 1-1.5 for X and 1.5-3.0 for Y. There is a corresponding difference in the number of exchangeable univalent cations, which varies from about 10-12 per cage for X to as low as 6 for high silica Y. This framework has the largest central cavity volume of any known zeolite, amounting to about 50% void fraction in the dehydrated form. A unit cell, when fully hydrated, contains approximately 235 water molecules, most in the central cavity. The aperture is formed by the twelve-member oxygen rings with a free diameter of approximately 7.4 Å. Three major locations for the cations are indicated in Figure 2.2. The locations are: center of the six-member prism (I) and opposite to I in the sodalite cage (I'); similar to I and I' but further from the central cavity (II and II'); and at twelve-member aperture (III and III'). The distribution of the cations between the various sites depends both on the nature and number of the cations and is affected by the presence of traces of moisture. The adsorptive properties of X and Y sieves may therefore be greatly modified by ion exchange and improvement selectivity can sometimes be obtained by using mixed cationic forms.

Whereas large aromatic molecules such as xylene molecules (diameter~7 Å) enter only supercages, small molecules such as water can be adsorbed in both supercages and sodalite cages. The adsorption sites of both water and xylene molecules are mainly located near the cations, which neutralize the negative charges of the framework (Pichon, 1999).

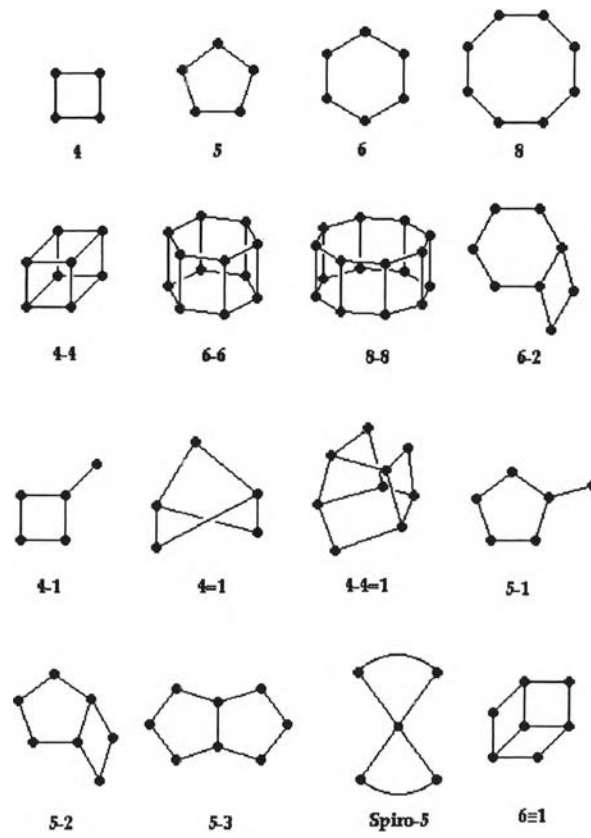


Figure 2.1 Secondary building units (SBU's) in zeolites. The corner of the polyhedra represent tetrahedral atoms.

(<http://www.ch.ic.ac.uk/vchemlib/course/zeolite/structure.html>).

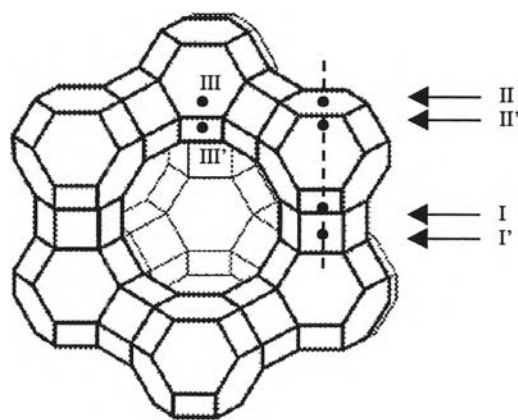


Figure 2.2 Faujasite structure. Cation positions are indicated by roman numerals.

(<http://www.kjemi.uio.no/~pouln/cspositions.htm>)

2.4 Related Work

There is no fundamental thermodynamic difference between liquid and vapor adsorption since the composition of an adsorbed phase in equilibrium with a liquid must be precisely the same as that in equilibrium with the corresponding saturated vapor. However, a qualitative difference arises because vapor phase adsorption studies are generally carried out at relatively low loading whereas, in the liquid phase adsorption, the total adsorbed-phase concentration is always at or near the saturation limit. There is also a difference in kinetics. Mass transfer in liquid phase is slower but same order of magnitude in adsorption capacity and selectivity. When feed concentration is changed, the adsorption capacity does not change much over the entire composition range. Moreover, the separation factor does not change with composition (Hulme *et al.*, 1991).

The works performed on Y zeolites with monovalent cations revealed that both LiY and NaY were selective for *m*-xylene, while KY, RbY, and CsY were selective for *p*-xylene. Divalent cations exchanged zeolites, BaY and BaX, were also selective for *p*-xylene (Lachet *et al.*, 1998).

Adsorption of C₈ aromatics in the presence of toluene on KY and KBaX zeolites was studied by Ngamkitidachakul (2000) with C₈ aromatics concentration in the range of 1.25 - 20 wt%. It was found that KY zeolite adsorbed more *p*-xylene and toluene than KBaX zeolite did. For KBaX zeolite, the result showed that, at high xylene/toluene mole ratios, *o*-xylene was the least adsorbed species whereas *p*-xylene was the most adsorbed one. At low xylene/toluene mole ratios, the most adsorbed species was *o*-xylene. For KY zeolite, at high xylene/toluene mole ratios, the adsorption of C₈ aromatics showed the same trend as with KBaX zeolite but, at low xylene/toluene mole ratios, a trend of C₈ aromatics adsorption cannot be observed. Adsorption of C₈ aromatics decreased as temperature increased because the adsorption process is exothermic. But at the full capacity of both zeolites, temperature has very little effect on selectivity of *p*-xylene relative to the other C₈ aromatics. The author applied the following model to predict the distribution coefficient.

$$K = \frac{q}{c} = k + AC^m \quad (2.2)$$

where q is solute concentration based on particle volume (g/cm^3) and c is solute concentration in bulk phase (g/cm^3). m was set equal to 1 for a linear expression of the above equation. k is the apparent Henry's law constant, the slope of the equilibrium line at infinite dilution. A and k were determined by fitting the equation to the experimental data. The model fit well with the experimental data at high temperature but there were some deviations at the low temperature.

In 2001, Varayanond investigated the effect of temperature on the liquid phase adsorption. The adsorption capacity of the zeolites was the same at different temperatures. At low temperature, the adsorption efficiency was high for all species but the rate of adsorption was low. Furthermore, the selectivity increased as the operating temperature decreased. Thus, the liquid phase adsorption process must be operated at a temperature that balances between the selectivity and transfer rate. Moreover, he also found that *p*-xylene selectivity and adsorption capacity decreased as the water content in the zeolite increased. The selectivity of *p*-xylene over *m*-xylene was the highest followed by *o*-xylene and ethylbenzene. In addition, the selectivity from the pulse test was higher than that from the single component experiment. In order to determine separation factor (α_{AB}), the following model was used.

$$\frac{\alpha_{12}}{k_1/k_2} = \frac{1 + 2A_{21} \left(\frac{k_2 Y_2}{k_1 Y_1} \right) + A_{12} \left(\frac{k_2 Y_2}{k_1 Y_1} \right)^2}{\left(\frac{k_2 Y_2}{k_1 Y_1} \right)^2 + 2A_{12} \left(\frac{k_2 Y_2}{k_1 Y_1} \right) + A_{21}} \quad (2.3)$$

The complicated statistical model was simplified by setting cross coefficients to unity ($A_{12}=A_{21}=1$), the expression reduced to a constant separation factor.

$$\alpha_{12} = \frac{k_1}{k_2} = \frac{(X_1/X_2)}{(Y_1/Y_2)} \quad (2.4)$$

when k_1 and k_2 were obtained by experimental data. This simplified model fit well at the low concentration range.

Furlan (1992) found that by using Ba^{2+} and K^+ exchanged X zeolites, the optimum water content on X zeolites with a value around 3.25 wt% selectively adsorbed *p*-xylenes over *o*-xylenes. But the water content in the adsorbent had a small influence on the separation between *p*-xylene and ethylbenzene. The preferential adsorption of *p*-xylene was mainly attributed to the physical interaction forces between *p*-xylene and the surface. These forces were enhanced through variation of water content in the adsorbent.

Generally, acid sites of zeolites are of the Brønsted or Lewis type. The first one consists of basic OH groups and the second one consists of the framework oxygen atoms. The charges on these oxygen determine their strength, i.e. the number of potential basic sites is equal to that of oxygen atom in the framework. However, there are several parameters identified to affect the basicity. They are the electronegativity of the framework atoms, the bonds angles and bond lengths, the structure ionicity, the crystallographic sitting of the oxygen, the location of Al (pairs, Al gradients). The average negative charge of structural oxygen increased with the Al content of the framework and with decreasing electronegativity of the exchangeable cations. The basicity can be experimentally measured using, for instance, pyrrole as a probe molecule (Barthomeuf *et al.*, 1991) or using the Electronegativity Equalization Method (EEM). Similar results can be obtained from calculations of averaged charges on framework oxygens with Sanderson's model of electronegativity (Heidler *et al.*, 1996). The Sanderson's intermediate electronegativity of zeolite, S_{int} , is expressed by

$$S_{int} = (S_M^p S_{Si}^q S_{Al}^r S_O^t)^{1/(p+q+r+t)} \quad (2.5)$$

where S_M , S_{Si} , S_{Al} , and S_O represent the Sanderson's electronegativity of the counter cation, silicon, aluminum, and oxygen, respectively, and p , q , r and t represent the number of the corresponding element in a unit cell (Choi *et al.*, 1996). S_{int} of di-valence series cations exchanged X and Y zeolites can be calculated as shown in Table 2.1.

Table 2.1 Calculated S_{int} of di-valence series cations exchanged X and Y zeolites

	Sanderson's intermediate electronegativity		
	2.0X	2.5X	Y
Be	2.8373	2.8579	2.9268
Mg	2.7690	2.7956	2.8856
Ca	2.6992	2.7319	2.8430
Sr	2.6434	2.6808	2.8087
Ba	2.6227	2.6619	2.7958

In 2001, Varanyanon studied the acid-base interaction between C_8 aromatic and faujasite zeolite by changing the water content in zeolite (LOI). He found that *p*-xylene selectivity decreased at higher LOI. In previous work, acid-base interaction between the C_8 aromatics and X and Y zeolites exchanged with mono-valence series cation was investigated by Suntornpun (2002). The results showed that solely acid-base interaction can not be used to explain the adsorption mechanism for the whole range of the studied cations. Effects of cation size and zeolite type must be taken into account. The heat of adsorption was also studied. The trend of ΔH of each component on KY was consistent with the selectivity. *p*-xylene, the most adsorbed species had the highest ΔH followed by ethylbenzene, *o*-xylene and *m*-xylene.