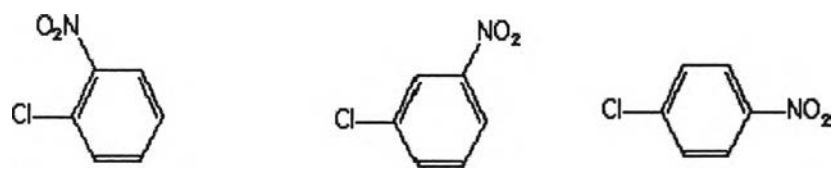
CHAPTER II
LITERATURE REVIEW

2.1 Chloronitrobenzenes

Chloronitrobenzenes or CNBs are important intermediate materials that are normally used in the azo and sulfur dye manufacture and extensively used in the synthesis of pesticides, fungicides, pharmaceuticals, preservatives, photochemicals and rubber chemicals. CNBs have three isomers, which are *o*-, *m*- and *p*-CNB. Chemical structure and chemical properties of each CNB isomer are shown in Figure 2.1 and Table 2.1, respectively.



o-chloronitrobenzene *m*-chloronitrobenzene *p*-chloronitrobenzene

Figure 2.1 Three isomers of CNBs (orgchem.colorado.edu).

Table 2.1 Chemical properties of each CNB isomer (David and Blangey, 1949)

Substances	Boiling point (°C)	Melting point (°C)
o-CNB	246	32.5
m-CNB	236	44.0
p-CNB	242	83.6

The types of isomer products depend on the operating path in the production process. There are two main pathways, which are typically used to produce the CNBs isomer as following (David, 1949):

2.1.1 Nitration of Chlorobenzene (CB)

In this process, a mixture of 52.2% sulfuric acid, 35.5% nitric acid, and 12% water is used to produce chloronitrobenzenes. Practically, CB is nitrated by acid mixture at 40–70°C. The nitration product is a mixture of 34% *o*-CNB, 65% *p*-CNB and 1% *m*-CNB or one-third of *o*-CNB and two-thirds of *p*-CNB. In the part of separation, the bulk of the para-compound crystallizes out on cooling and can be obtained simply by centrifuging. Careful fractionation through an efficient column yields the first fraction enriched in the para isomer and the last fraction enriched in the ortho isomer. The residual mixture cannot be separated into its constituents by fractional distillation alone because the boiling points lie too close together. However, in large scale operations, the noncrystallizing middle fractions, and the eutectic mixture from the centrifuging operation, are put back in the process so that the separation is finally complete (Robert, 1968). Additionally, a considerable proportion of waste sulfuric acid contaminated with organic compounds is produced. Complicated and expensive works are required to treat the wastewater before discharge to the public (Priegnitz, 1980a; Priegnitz, 1980b; Ralt *et al.*, 2003).

2.1.2 Chloronation of Nitrobenzene (NB)

In this reaction, sufficient chlorine is needed to produce a crude chlorination mixture containing unchlorinated nitrobenzene, *m*-CNB, isomeric mono (*o*- and *p*-) CNBs and di-CNBs. The *m*-CNB is the major and desired constituent (Albert, 1957). In the aspect of operating condition, it requires very careful operation and succeeds only if the reaction is carried out in the complete absence of moisture. Even traces of water can prevent or retard the chlorination excessively. Thus, it is essential that the apparatus and the starting materials must be dried thoroughly. Anhydrous ferric chloride is the most satisfactory chlorine carrier. The nitrobenzene is dried by heating for several hours in a round-bottomed flask at 80–100°C while a stream of dry air is drawn through it by means of a wide capillary tube (David and Blangey, 1949).

หอสมุดกลาง สำนักงานวิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

2.2 CNB Separation and Purification

The industry is very interested in obtaining in the high purity of CNB isomers. Distillation technique is extremely difficult to separate CNB isomers into their pure form because of their close boiling points. Thus, other techniques are investigated *e.g.* crystallization, fractionation, and adsorption. The qualities of each desired product depend on the techniques that are used.

2.2.1 Crystallization

The separation of chemical isomers by means of crystallization finds many applications in industry due to low energy consumption and high product purity. Nevertheless, crystallization cannot provide the complete separation of these components because only one component is separated into its pure form at the temperature above the eutectic temperature and then, a mixed crystal is formed. According to this phenomenon, the eutectic depressant is needed, usually used in an extractive crystallization, for shifting the mixture to the other side of the normal eutectic point and removed from the mixture. The big disadvantage of this system is often difficult to remove and results in an impure product (Robert, 1968).

Robert (1968) from Philips Petroleum Company employed the combination of crystallization and fractionation for segregating *o*- and *p*-CNB isomers. This invention was to offer a method for enhancing a yield of *o*- and *p*-CNB, which can be recovered in high purity from a CNB mixture without the use of the eutectic depressant. The procedure of this method was to cool the mixture to approximately the eutectic temperature, 14°C. *p*-CNB was then crystallized and removed. The mother liquor was fractionated to increase the concentration of *o*-CNB in the mixture and cooled to approximately 14°C again. For this time, *o*-CNB was crystallized and removed.

Monsanto Company improved a process for chemical isomers separation. The development was the presence of water in the crystallizer to improve the crystallization method. In other words, crystallization from solution was applied by using the differences in solubility at specific temperatures. From the old fashion of crystallization, the procedure is always conducted under anhydrous condition in

order to avoid the corrosion that can damage the equipments. However, the corrosion problem can be prevented for this invention by introducing small amounts of a caustic solution in the crystallizer during the process (Roberto, 1974).

Moreover, PPG industries launched the invention relating to the treatment of the CNB isomeric mixture to purify *m*-CNB product from the chlorination of NB process. The mixture of CNB isomers was presented in a partial miscible solvent at a temperature below the melting point of *m*-CNB causing the solidification of *m*-CNB. The other CNB isomers were soluble in the solvent. The solidified product was collected by filtration to provide a product enriched in *m*-CNB. It appeared from the evidence that the process was not a conventional crystallization or recrystallization process for the reason that the CNB isomers were not first dissolved in the solvent and then caused to crystallize from it (Priegnitz, 1980b; Priegnitz, 1980c).

2.2.2 Adsorption

Guo *et al.* (2004) used HZSM-5 zeolite as an adsorbent to separate the mixture of *p*- and *o*-CNB. The objectives of this work were to treat the wastewater containing CNBs with a degradable technique. HZSM-5 zeolite is frequently adopted as the adsorbent in aromatic compounds due to the similar dimension of its channel to the dynamic diameter of benzene molecule, 0.58 nm. The result revealed that the maximum adsorption amounts of *p*-CNB in the zeolite was higher than that of *o*-CNB at different adsorption temperature. Moreover, the diffusivity of *p*-CNB was higher than *o*-CNB about 100 times at 300°C.

It is well known that certain crystalline aluminosilicates—faujasite (FAU) zeolite—can be used to separate hydrocarbon species from mixtures. The separation of *o*-CNB from the feed CNB mixture was conducted by using type X and Y zeolites containing the exchanged cation. One or more cations were selected from the consisting of Groups IA, IIA and the transition metals. In the first adsorption stage, selectively adsorbent adsorbs substantially all of the *o*-CNB to the substantial exclusion of the others and recovering high-purity *o*-CNB. After that, the unadsorbed isomers were passed to a second adsorption stage where they were contacted with another selected adsorbent that selectively adsorbing substantially all para isomers

and recovering in high purity *p*-CNB as well as in the first stage. A desorption step may be used to desorb the adsorbed isomers in each stage (Priegnitz, 1980a; Priegnitz, 1980b).

Lerdsakulthong (2007) investigated the static adsorption behavior of *m*- and *p*-CNB on FAU zeolite with a variety of alkali and alkali earth ion exchange. The results revealed that Y zeolites preferentially adsorb *m*-CNB more than *p*-CNB due to the higher molecular dipole moment. The total adsorption capacities and selectivity increase for both X and Y zeolites with the decreasing in size of the cation due to the higher acid strength of the adsorbents. Moreover, the effect of desorbent was also studied. A series of benzene, toluene, *o*-xylene, nitrobenzene, and *o*-dichlorobenzene were used as desorbents. Nitrobenzene performed the most appropriate desorbent due to its balance between the adsorbent-adsorbates and adsorbent-desorbent interactions.

2.3 Crystallization

Crystallization is one of the oldest unit operations in the portfolio of industrial and/or laboratory separations. Almost all separation techniques involve formation of a second phase from a feed, and processing conditions must be selected that allow relatively easy segregation of the two or more resulting phases (Kroschwitz, 1993).

Crystallization is the process whereby a solvent-solute system's thermodynamic properties are modified so as to precipitate at least part of the solute in solid form. It is widely used in inorganic chemistry and high added value organic chemistry. The petrochemical industry resorts to crystallization in some special cases. The reason for this relative unpopularity is related to a number of downsides. Those are sometimes considerable energy costs, operations that are difficult to handle, high investments, and high maintenance costs (Wauquier, 2000). Crystallization can be carried out either in the presence of a solvent (called crystallization from solution) or in the absence of a solvent (called crystallization from melt) (Roberto, 1974). Only crystallization from melts will be discussed here.

The term 'melt' strictly refers to a liquid close to its freezing point, but in its general industrial application it tends to encompass multi-component liquid mixtures that solidify on cooling. Melt crystallization is the common term applied to the controlled cooling crystallization and separation of such systems with the objective of producing one or more of the components in relatively pure form.

Melt crystallization is often considered to be commercially attractive since it offers the potential for low-energy separation compared with distillation as latent heats of fusion are generally much lower than latent heats of vaporization. The best example in Table 2.2 is that of water where there is almost a 7:1 difference in the two heat quantities. A further advantage of melt crystallization over distillation is that it operates at much lower temperatures, and this can be very helpful when processing thermally unstable substances. Moreover, melt crystallization holds great promise in situation, in which it can be substituted for crystallization from solution without the need to recovery and maintain the purity of a solvent. Processing costs are reduced substantially because there is no contaminated solvent to handle. In the aspect of environmental conservation, melt crystallization may be more environmentally benign (Kroschwitz, 1993).

Table 2.2 Enthalpies of crystallization and distillation (Mullin, 2001)

Substance	**Crystallization**		**Distillation**	
	Melting point (°C)	**Heat of crystallization (kJ/kg)**	**Boiling point (°C)**	**Heat of vaporization (kJ/kg)**
o-Nitrotoluene	-4.1	120	222	344
m-Nitrotoluene	15.5	109	233	364
p-Nitrotoluene	51.9	113	238	366
Benzene	5.4	126	80	394
Water	0	334	100	2260

In practice, however, the benefits of low-energy separation for industrial melt crystallization can be outweighed by operational problems associated with the need to separate purified materials from impure residues. Operating costs can also escalate if refrigeration, rather than normal cooling water, is required. Technical limitations to the theoretical possibilities for melt crystallization have been discussed in some detail elsewhere (Mullin, 2001).

Not all melts are amenable to separation by crystallization. The phase equilibrium will generally decide the feasibility of the process and often give guidance to the choice of the basic procedure to be followed. Only a eutectic system (Figure 2.2a) will allow the crystallization of a pure component from a melt in one step, but a solid solution system (Figure 2.2b) requires a sequence of fractionation steps to yield high-purity products.

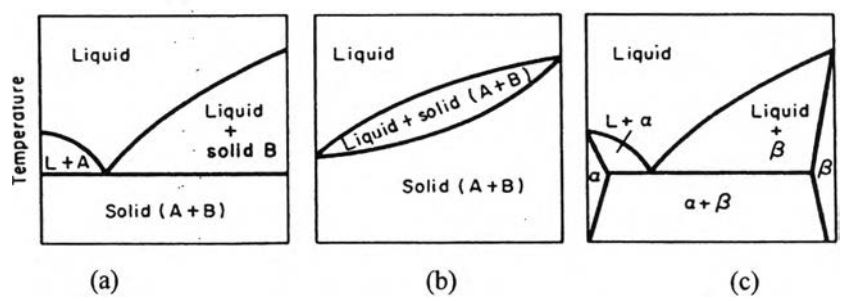


Figure 2.2 Binary solid-liquid phase diagrams encountered in melt crystallization: (a) simple eutectic; (b) simple solid solutions; (c) eutectic with limited solid solubility (α and β are solid solutions) (Mullin, 2001).

2.4 Crystal Characteristics

Key determinants of product quality that are frequently measured in the quality control section before launch the product to market are the morphology (including habit or shape and form), the size distribution (including mean and spread), and purity in order to ensure that the product specification achieves the quality standard or appropriates with the further application. In the sense of producer, purity is the most important than other in all separation processes.

2.4.1 Crystal Size Distributions

Particulate matter produced by crystallization has a distribution of sizes that varies in a definite way over a specific size range. A crystal size distribution (CSD) is most commonly expressed as a population (number) distribution relating the number of crystals at each size to the size or as a mass (weight) distribution expressing how mass is distributed over the size range. The two distributions are related and affect many aspects of crystal processing and properties, including appearance, solid-liquid separation, purity, reactions, dissolution, and other properties involving surface area (Kroschwitz, 1993). Population density (n) has dimensions number/ (volume) (length); it is a key quantity in the discussion of CSD, a function of the characteristic crystal dimension L, and it is defined so that it is independent of the magnitude of the system. When a total population density is used, the symbol is $\bar{n}$ and the units are number/ length. Population density is defined by letting ΔN be the number of crystals per unit system volume in a size range from L to L + ΔL, so that (Kroschwitz, 1993)

$$n = \lim_{\Delta L \to 0} it \frac{\Delta N}{\Delta L} \tag{2.1}$$

2.4.2 Purity

Although crystallization has been employed extensively as a separation process, purification techniques using crystallization have become increasingly important. Mechanisms by which impurities can be incorporated into crystalline products include adsorption of impurities on crystal surfaces, solvent entrapment in cracks, crevices and agglomerates, and inclusion of pockets of liquid. An impurity having a structure sufficiently similar to the material being crystallized can also be incorporated into the crystal lattice by substitution or entrapment. Among these mechanisms, inclusion formation has been extensively studied. It has also been suggested that the purity may be directly linked to size and habit of product crystals, but the interaction does not appear to be simple. It has been noted that the key to producing high purity crystals was to maintain the supersaturation, the departure from solution saturation usually caused by cooling of the mixture and/or by

evaporating solvent, at a low level so that large crystals were obtained (Rousseau, 1987; Kroschwitz, 1993).

Funakoshi *et al.* (2000) conducted an experiment for studying the purity of *m*-CNB crystal in batch crystallization. The results showed that the purity decrease of pure crystals was mainly caused by the inclusion of mother liquor into the crystal and by its adhesion on the crystal surfaces.

Local purity of *m*-CNB crystals was observed by Takiyama *et al.*, (2001). The crystal of *m*-CNB growing from its binary melts containing *p*-CNB was measured. From the experiment results of local purity, it was found that the faster the crystal face grows the more the purity of *m*-CNB decreases.

2.5 Phase Equilibrium: Phase Rule (Mullin, 2001)

The Phase Rule, developed by J. Willard Gibbs in 1876, related the number of the components, C, phases, P, and degrees of freedom, F, of a system by means of Equation (2.2). This type of diagram represents graphically, in two or three dimensions, the equilibria between the various phases of the system. The amount of information, which a simple solubility diagram can yield, is strictly limited. For a more complete picture of the behavior of a given system over a wide range of temperature, pressure and concentration, a phase diagram must be employed.

$$P + F = C + 2 \tag{2.2}$$

These three terms are defined as follows. The number of components of a system is the minimum number of chemical compounds required to express the composition of any phase. For example, in the system of water copper sulphate, five different chemical compounds can exist, $CuSO_4.5H_2O$, $CuSO_4.3H_2O$, $CuSO_4.H_2O$, $CuSO_4$ and H_2O; but for the purpose of applying the Phase Rule there are considered to be only two components, $CuSO_4$ and H_2O, because the composition of each phase can be expressed by Equation (2.3).

$$CuSO_4 + xH_2O \longleftrightarrow CuSO_4.xH_2O \tag{2.3}$$

A phase is a homogeneous part of the system. Thus, any heterogeneous system comprises two or more phases. Any mixture of gases or vapor is a one-phase system. Mixtures of two or more completely miscible liquids or solids are also one-phase systems, but mixtures of partially miscible liquids or a heterogeneous mixture of two solids are two-phase systems, and so on. The three variables that can be considered in a system are temperature, pressure and concentration. The number of these variables that may be changed in magnitude without changing the number of phases present is called the number of degrees of freedom. In the equilibrium system water-ice-water vapour, $C = 1$, $P = 3$, and from the Phase Rule, $F = 0$. Therefore, in this system there are no degrees of freedom: no alteration may be made in either temperature or pressure (concentration is obviously not a variable in a one-component system) without change in the number of phases. Such a system is called 'invariant'.

For the system water-water vapour $C = 1$, $P = 2$ and $F = 1$: thus, only one variable, pressure or temperature, may be altered independently without changing the number of phases. Such a system is called 'univariant'. The one-phase water vapour system has two degrees of freedom; thus, both temperature and pressure may be altered independently without changing the number of phases. Such a system is called 'bivariant'.

2.6 Solid-Liquid Phase Diagram (Mullin, 2001)

A typical example of a system, in which the components do not combine to form a chemical compound, is shown in Figure 2.3. Curves AB and BC represent the temperatures at which homogeneous liquid solutions of naphthalene in benzene beginning to freeze or to crystallize. The curves also represent, therefore, the temperatures above which mixtures of these two components are completely liquid. The name 'liquidus' is generally given to this type of curve. In aqueous systems of this type, one liquidus is the freezing point curve, the other the normal solubility curve. Line DBE represents the temperature at which solid mixtures of benzene and naphthalene begin to melt or the temperature below which mixtures of these two

components are completely solid. The name 'solidus' is generally given to line DE. The melting or freezing points of pure benzene and naphthalene are given by points A (5.5°C) and C (80.2°C), respectively. The small and large 'triangular' areas ABD and BCE represent mixtures of solid benzene and solid naphthalene, respectively, and benzene-naphthalene solution.

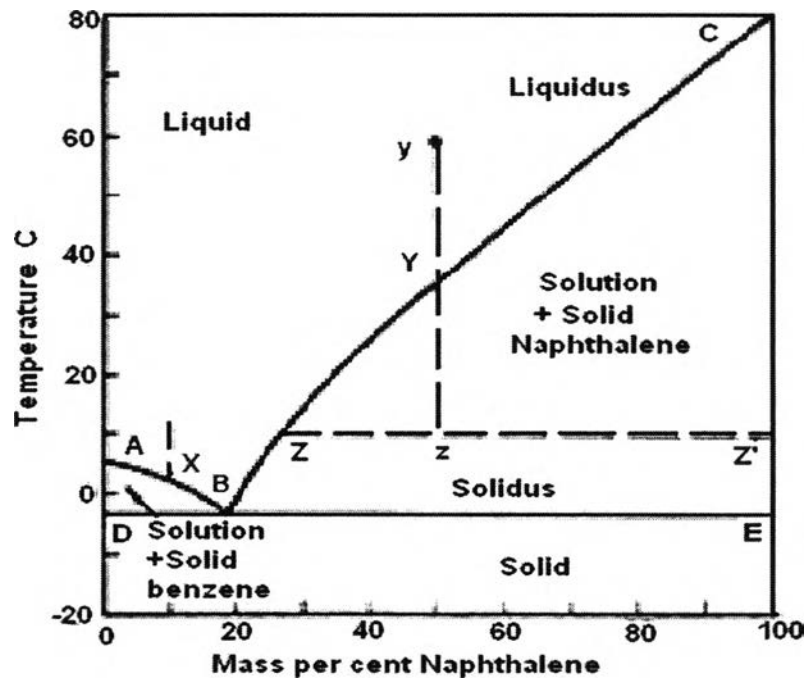


Figure 2.3 Phase diagram for the simple eutectic system naphthalene-benzene.

If a solution represented by point *x* is cooled, pure solid benzene is deposited when the temperature of the solution reaches point X on curve AB. As solid benzene separates out, the solution becomes more concentrated in naphthalene and the equilibrium temperature of the system falls, following curve AB. If a solution represented by point y is cooled, pure solid naphthalene is deposited when the temperature reaches point Y on the solubility curve; the solution becomes more concentrated in benzene and the equilibrium temperature follows curve CB. Point B, common to both curves, is the eutectic point (-3.5°C and 0.189 mass fraction of naphthalene), and this is the lowest freezing point in the whole system. At this point, a completely solidified mixture of benzene and naphthalene of fixed composition is

formed: it is important to note that the eutectic is a physical mixture, not a chemical compound. Below the eutectic temperature, all mixtures are solid.

If the solution y is cooled below the temperature represented by point Y on curve BC to some temperature represented by point z from Figure 2.3, the composition of the system as a whole remains unchanged. The physical state of the system has been altered, however; it now consists of a solution of benzene and naphthalene containing solid naphthalene. The composition of the solution, or mother liquor, is given by point z on the solubility curve, and the proportions of solid naphthalene and solution are given, by the so-called 'mixture rule', by the ratio of the lengths zZ to zZ',

$$\frac{\text{Mass of solid } C_{10}H_8}{\text{Mass of solution}} = \frac{zZ}{zZ'} \tag{2.4}$$

It should be understood that the term 'pure' when commonly used does not mean absolute 100% purity. In industrial crystallization practice, this is neither necessary nor indeed achievable, and for many bulk-produced chemicals a purity of greater than 95% is often accepted as justifying the designation 'pure'. In any case, a single crystallization step cannot produce 100% pure crystals for a variety of reasons, e.g., they can be contaminated with residual solvent or other impurities that have not been removed by washing, or have been incorporated into the crystal interstitially or as liquid inclusions, and so on. Furthermore, contamination commonly results from the existence of terminal solid solutions, which inevitably accompany both eutectic and chemical compound systems.

2.7 Adsorption

Most of chemical manufacturing operation requires the technique of separation processes to obtain and recovery a high quality product. In most circumstances, the efficiency of the separation process has a considerable effect on both the quality and the cost of the product. Liquid phase adsorption has long been used for the removal of contaminants present at low concentrations in process

streams (Kroschwitz, 1991). Liquid phase adsorption consists of two main pathways: adsorption and desorption. Adsorption of liquid adsorbate onto adsorbent is dictated by the characteristics of the adsorbate-adsorbent interaction. Desorption depends on the addition of a desorbent and its specific interactions with both adsorbent and adsorbate. Liquid phase adsorption mechanisms are highly complex. This is due to the interaction of solid adsorbents, liquid adsorbates, and liquid adsorbents during the separation process. By contrast, other convention separation process mechanisms are based primarily on the differences in the physical properties of the components. In the liquid phase adsorption matrix, a virtually infinite variability in liquid separation can be achieved as a result of the number of ways available for adsorbent and desorbent modification. Adsorbent variables include the framework structure, the counter exchanged ion, and water content. These variables are carefully modified to selectivity adsorb one particular component over others. To desorb the adsorbed component, a suitable solvent functioning as a desorbent first needs to be identified (Kulprathipanja *et al.*, 2002).

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 processes, it is convenient to define a separation factor:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B} \tag{2.5}$$

where X_A and Y_A are, respectively, the mole fractions 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 analogy 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 (Ruthven, 1984).

2.8 Zeolite

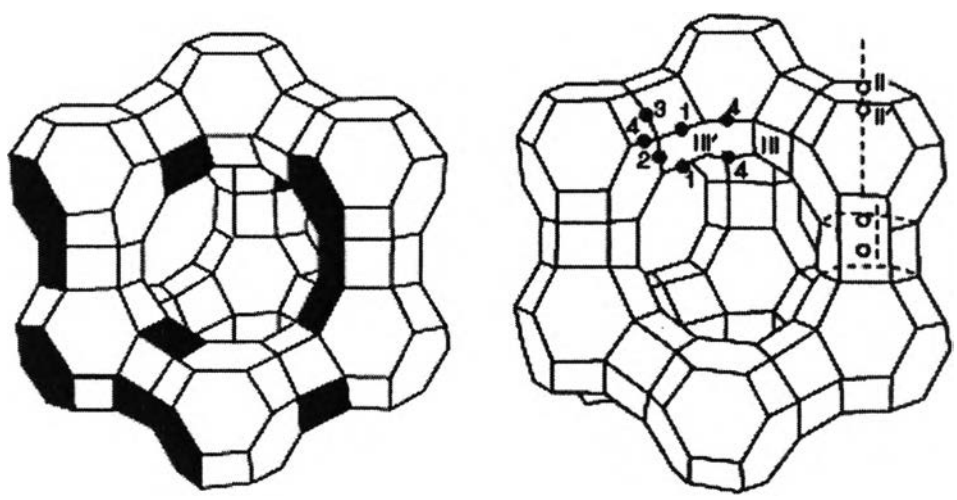
Zeolites represent an important group of adsorbents being used in most commercial liquid separation processes. This is due to the high selectivity and adsorption capacity of zeolite adsorbents. Zeolites are microporous crystalline aluminosilicates, consisted of TO_4 tetrahedra (T = Si, Al) with O atoms linking neighboring tetrahedra. The combination of Al and into the Si framework makes the framework negatively because the 4+ charge of Si is replaced by the 3+ charge of Al. Then, the framework needs cations, which are exchangeable ion, to combine within the structure to keep the overall framework neutral. Basically, the zeolite is composed of three components:

$$M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y\,].\,zH_2O$$

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. 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 shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline framework. The tetrahedral can be arranged in numerous ways, resulting in the possibility of some 800 crystalline structures, less than 200 of which have been found in natural deposits or synthesized in laboratories around the world (Thompson *et al.*, 1998). The void delimited by the aluminosilicate skeleton is organized into a network of cavities connected by pores of uniform size. The effective pore diameter, variable depending on the type of zeolite, is of the same order of magnitude (3 to 10 Å) as that of most organic molecules. This explains the name "molecular sieve" given to these adsorbents (Wauquier, 2000).

Types X, and Y remain the dominant zeolites and molecular sieves that are in commercial use for adsorption and ion exchange. These zeolites will be the main subject for discussion.

Unit cells of type X and type Y zeolites are shown in Figure 2.4. The cations are necessary to balance the electric charge of the aluminum atoms in $[AlO_4]^{-1}$, each having a net charge of -1. The water molecules can be removed with ease upon heating 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 interconnected by windows in each cage. The size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 to 8 Å. The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent due to the surface property in the cages) hence, the name molecular sieve. The windows of type X zeolite are referred to as 12-ring, which remain the largest windows in zeolites today (Yang, 2003).



(a) (b)

Figure 2.4 Line representations of zeolite structure: (a) 'unit cell' of types X and Y, or faujasite; (b) cation sites in types X and Y (16 I, 32 I', 32 II, 32 II', 48 III, and 32 III' sites per unit cell) (Yang, 2003).

The ratio of Si/Al in types X and Y are typically one to five. The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations. The cations can also be exchanged. The inner atoms in the windows are oxygen. The sizes of the windows then depend on the number of oxygen atoms in the ring (4, 5, 6, 8, 10, or 12). The aperture size, as well as the

cations. A description of the structures will be given for the zeolites, types X and Y, important in gas separation. As mentioned, these types have dominated the commercial use of zeolites for gas separation and purification as well as ion exchange.

The skeletal structure of types X and Y zeolites is the same as naturally occurring faujasite. The sodalite units are linked through 6-member prisms, as shown in the unit cell in Figure 2.4. Each unit cell contains 192 SiO_2 and AlO_2 tetrahedra. The number of aluminum ions per unit cell varies from 96 to 77 (Si/Al = 1 to 1.5) for Type X zeolite, and from 76 to 48 (Si/Al = 1.5 to 3) for type Y zeolite (Kroschwitz, 1991). Loewenstein's rule forbids the formation of Al-O-Al bridges (Loewenstein, 1954). Thus, the maximum number of Al corresponds to a Si/Al ratio of 1. The framework of faujasite has the largest central cavity pore volume of any known zeolite, amounting to about 50% void fraction in the dehydrated form. The free diameter of the central cavity is 13.7 Å (Eulenberger *et al.,* 1967). A unit cell, when fully hydrated, contains approximately 235 water molecules, primarily in the central cavity. The volume of the central cavity, however, accounts for only a small fraction (1/5–1/8) of the pore volume of the unit cell since there are portions of other central cavities from the neighboring unit cells, as well as window spaces that are also contained in the same unit cell. The aperture is formed by the 12-member oxygen rings with a free diameter of approximately 7.4 Å. The size of the unobstructed 12-ring is approximately 8.1 Å (Breck, 1974). Three major locations for the cations are indicated in Figure 2.4b. The locations are center of the 6-member or hexagonal prism (I) and opposite to I and located in the sodalite cage (I'), similar to I and I' but further from the central cavity (II and II'), and the 12-ring aperture (III and III'). The commercial 10X zeolite contains Ca^{+2} as the major cation, and Na^{+} is the major cation for 13X zeolite. The BET surface area measured with N_2 for zeolites falls in the range between 500 and 800 m^2/g (Yang, 2003).