



CHAPTER II

LITERATURE REVIEW

2.1 Chloronitrobenzenes

Chloronitrobenzenes or CNBs are important starting materials for the manufacture of azo and sulfur dyes, and they are also used in the synthesis of fungicides, pesticides, pharmaceuticals, photochemicals, preservatives, and rubber chemicals (Demuth *et al.*, 2002). There are three isomers of CNBs, which are *o*-, *m*-, and *p*-CNB as shown in Figure 2.1, and the physical properties of the isomers are summarized in Table 2.1.



Figure 2.1 Isomers of CNBs (<http://orgchem.colorado.edu>).

Table 2.1 Physical properties of chloronitrobenzene isomers (Adkins, 1996; Sergey and Christoph, 2003)

Substances	Boiling point (°C)	Melting point (°C)	Density (g/mL)
<i>o</i> -CNB	246	32.5	1.368
<i>m</i> -CNB	236	44	1.534
<i>p</i> -CNB	242	83	1.520

Industrially, CNBs are prepared via two main processes, which are nitration of chlorobenzene (CB) and chlorination of nitrobenzene (NB) depending on the desired isomer products.

2.1.1 Production

For continuous or batch of nitration of CB, CB is nitrated with a mixed acid consisting of 52.5 wt% sulfuric acid, 35.5 wt% nitric acid, and 12 wt% water at 40-70°C. The product is a mixture of isomers containing about 34 wt% *o*-CNB, 65 wt% *p*-CNB, and 1 wt% *m*-CNB. The isomers can be separated by a combination of fractional crystallization and distillation. Moreover, a significant amount of waste sulfuric acid contaminated with organic compounds is produced during the reaction so complicated and expensive work-up is required (Booth, 1991; Adkins, 1996; Demuth *et al.*, 2002).

For chlorination of NB, this process occurs at 35-45°C in the presence of iron (III) chloride and produces an isomeric mixture containing 86 wt% *m*-CNB 10 wt% *o*-CNB and 4 wt% *p*-CNB. The reaction is carried out by using a series of reactors with a residence time of 5 h. The apparatus and starting materials must be dried. A combination of distillation and crystallization is utilized to purify the isomer products. Final purification of *m*-CNB may be achieved chemically by caustic hydrolysis of the residual *o*-CNB and *p*-CNB and washing them out as nitrophenols (David and Blangey, 1949; Booth, 1991).

2.1.2 Applicaion

CNBs are used almost exclusively as chemical intermediates in many industries. *o*-CNB is an important intermediate in the synthesis of colourants. Reduction with iron produces *o*-chloroaniline and electrolytic reduction followed by rearrangement of the resulting hydrazo derivative leads to 3,3'-di-chlorobenzidine, both of which are important diazo components. Moreover, treatment of *o*-CNB with aqueous sodium hydroxide, methanol- and ethanol-sodium hydroxide at 130°C produces many nitro compounds which are used as precursors of the derived amines and many other products (Booth, 1991).

Most *m*-CNB is reduced to *m*-chloroaniline, which is an important dye intermediate. Chlorination of crude *m*-CNB gives pentachloronitrobenzene, the use of which as a fungicide has led to several series of nitro-containing agrochemicals (Booth, 1991).

p-CNB can be converted to common chemical intermediates such as *p*-chloroaniline, *p*-nitrophenol, *p*-nitroaniline, and *p*-anisidine. Condensation of *p*-CNB with 2,4-dichlorophenol gives 2,4-dichloro-4'-nitrodiphenyl ether, which is used as a herbicide. In addition, *p*-CNB can also be reacted with aniline to give *p*-nitrodiphenylamine, which uses as important antioxidants for rubber (Budavari, 1989; Booth, 1991; Lewis, 1993).

2.2 CNB separation process

It is difficult to separate the isomers products of CNBs by using distillation alone because their boiling points lie too close together as shown in Table 2.1 (Dunn, 1968). Other separation processes such as crystallization, fractionation, and adsorption are focused by the chemical industry to obtain pure form of CNBs; however, the qualities of each desired product depend on the used processes. The examples of CNB separation process employed by many companies are shown below.

2.2.1 Crystallization

Dunn O. from Phillips Petroleum Company provided a method, a combination of crystallization and fractionation, for the CNB isomers separation to obtain high purity *o*-CNB and *p*-CNB. For this process, a mixture of CNB isomers, in which the para to ortho isomer ratio was greater than 33.5 to 66.5, was cooled to the eutectic temperature approximately 14°C, and *p*-CNB was crystallized in there. After removing the para crystals, the mother liquor was fractionated to increase the concentration of *o*-CNB in the mixture, and cooled to the eutectic temperature again causing *o*-CNB to crystallize. By operating this process, the need of eutectic depressant to shift the concentration of the mixture to the other side of the normal eutectic point was eliminated (Dunn, 1968).

Monsanto Company improved a process for separating *p*-CNB from a mixture of CNB isomers by crystallization in the presence of water. There are many outstanding improvements afforded by this process such as producing greater product recovery per batch, conveniently accomplished cooling without causing

caking, easier mobilizing of thick slurry, and minimizing manufacturing costs. Because the introduction of water can cause a corrosive effect on the equipment, adding a small amount of a caustic solution in the crystallizer during the process to minimize corrosion was required (Lee, 1974).

Moreover, PPG Industries applied crystallization in the purification process to provide a higher content of *m*-CNB. A mixture of CNB isomers produced from chlorination of NB was solidified in a partially miscible solvent at a temperature below the melting point of *m*-CNB causing *m*-CNB to solidify. After the solidification, the meta enriched CNB solid particles were collected and separated from the solvent by filtration. The amount of used solvent was typically in excess of that amount required just to dissolve the amount of ortho, para, and meta isomers miscible with solvent at the temperature of operation (Cook, 1980).

2.2.2 Adsorption

It is well known that certain crystalline aluminosilicates can be used to separate hydrocarbon species from a mixture; therefore, UOP Inc. employed the solid-bed adsorptive separation process by using a type X and type Y zeolite, which selectively adsorb *o*-CNB as an adsorbent for separating *o*-CNB from a CNB feed mixture. One or more exchangeable cations were selected from group IA, IIA, and the transition metals of Periodic Table of Elements. In the process, the adsorbent adsorbed substantially all of *o*-CNB and then unadsorbed CNBs were removed. After that, a desorbent material having a boiling point substantially different from that of the feed mixture was passed into the adsorbent and high purity *o*-CNB was recovered (Priegnitz, 1980).

Guo *et al.* investigated the use of HZSM-5 as an adsorbent in the adsorption process of *p*-CNB from a wastewater containing *p*-CNB and *o*-CNB. The objective was to treat the wastewater before discharging to public because of high toxicity and stability of CNBs. The results showed that HZSM-5 zeolite was an effective adsorbent to selectively adsorb *p*-CNB due to the similar dimensions of its channels to the dynamic diameter of benzene molecule (0.58 nm) and the maximum adsorption amounts of *p*-CNB in the zeolite were higher than that of *o*-CNB at different adsorption temperature. Moreover, the diffusivity of *p*-CNB at 27°C is

approximately 100 times higher compared to that of *o*-CNB. The remarkable difference in the adsorption amounts and in the diffusivities between *p*-CNB and *o*-CNB in HZSM-5 zeolite resulted in effective separation this mixture (Guo *et al.*, 2005).

Lerdsakulthong investigated the static adsorption behavior of *m*- and *p*-CNB on FAU zeolites with a variety of alkali and alkali earth ion exchanged cations. The result revealed that Y zeolites preferentially adsorbed *m*-CNB more than *p*-CNB due to the higher molecular dipole moment. The total adsorption capacities and selectivity increased for both X and Y zeolites with the decrease in the 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 seems to be the most appropriate desorbent due to its balance between the adsorbent-adsorbates and adsorbent-desorbent interactions (Lerdsakulthong, 2007).

Yensukjit studied the single and binary component adsorption behaviors of *m*- and *p*-CNB on FAU zeolites with a variety of alkaline earth exchanged cations under static conditions, and also investigated the effect of FAU zeolites on precipitate composition in the crystallization. In the single component adsorption, the results showed that the adsorption capacities of *m*- and *p*-CNB on zeolites with both type of exchanged cations increased with the acid strength of the zeolites, and *m*-CNB was selectively adsorbed by zeolites more than *p*-CNB due to a higher dipole moment or higher basicity. The Y zeolites had a higher adsorption capacity than the X zeolites while CaY gave the highest adsorption capacities. In the binary component adsorption, the total adsorption capacities of both CNBs also increased with the acid strength of the zeolites except MgX and MgY because of the effect of cation size and the competitive adsorption. Most of the zeolites preferably adsorbed *m*-CNB more than *p*-CNB due to a higher dipole moment or higher basicity except SrX while CaY gave the highest *m*-/*p*-CNB selectivity. However, the selectivity did not increase much with the increase in the acid strength of the zeolites. The adsorption capacities of CNBs on both type X and Y zeolites partly depended on the acid-base interaction in both types of adsorptions. In the crystallization, NaX, NaY, CaX, and CaY were used and the results showed that the addition of the

zeolites could shift the precipitate composition to be rich in *p*-CNB with the composition as high as 85-94 wt% and NaY gave the highest composition of *p*-CNB in the precipitates. Moreover, no effect of adsorption and composition gradient during the experiment was observed, and the composition of *p*-CNB in the precipitates depended on the position and shape of them, and type of zeolites (Yensukjit, 2008).

2.3 Crystallization

Crystallization is one of the most powerful purification methods available in process engineering. Apart from the fact that its final product has an attractive appearance, this process frequently proves to be cheapest and sometimes the easiest way in which a pure substance can be produced from an impure solution. Conventional distillation techniques cannot separate efficiently close-boiling liquids or those that form azeotropes, yet crystallization may often lead to their complete separation. Moreover, the choice of crystallization over distillation as the preferred separation technique may hinge on one or more of the following considerations:

- Crystallization is very helpful for the heat sensitive and high boiling point solute that can be decomposed at temperatures required to conduct distillation.
- If the product is desired in a particulate form, crystallization is required. For example, if a solute is purified via distillation then it must be solidified subsequently by flaking or prilling, crystallization may be more convenient scheme to employ in such cases.
- Comparative economics favor crystallization. Crystallization offers the potential for low-energy separation as latent heats of fusion are generally much lower than latent heats of vaporization as shown in Table 2.2.

These are evidence that the petroleum industry is now turning its attention to crystallization techniques to deal with difficult separations (Rousseau, 1987; Mullin, 2001).

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

Substances	Crystallization		Distillation	
	Melting point (°C)	Enthalpy of crystallization (kJkg ⁻¹)	Boiling point (°C)	Enthalpy of vaporization (kJkg ⁻¹)
<i>o</i> -Nitrotoluene	-4.1	120	222	344
<i>m</i> -Nitrotoluene	15.5	109	233	364
<i>p</i> -Nitrotoluene	51.9	113	238	366
Benzene	5.4	126	80	394
Water	0	334	100	2260

In the inorganic chemical industry, crystallization is employed heavily as a separation process particularly where salts are recovered from aqueous media. And in production of organic chemicals, crystallization is also used to recover product, to refine intermediate chemicals and to remove undesired salts; however, only one component of a mixture is readily separated in a pure form by crystallization, depending on the composition of mixture (Dunn, 1968; Rousseau, 1987).

Crystallization can be carried out either in the presence of a solvent—solution crystallization—or in the absence of a solvent—melt crystallization.

2.3.1 Solution crystallization

Crystallization from solution accomplishes the separation of components in a mixture by using the differences in solubility at the specific temperatures. A diluent solvent is added to the mixture; the solution is then directly or indirectly cooled and/or solvent is evaporated. The solid phase is normally formed and maintained somewhat below its pure-component freezing-point temperature (Rousseau, 1987).

There are many potential advantages of solution crystallization. The processing temperature can be lowered by adding a solvent and that is sometimes necessary to avoid product decomposition. The other benefit of solvent addition is

the reduction in viscosity of the liquid phase, leading to both improved crystallization kinetics and easier solid-liquid separation (Schweitzer, 1997).

2.3.2 Melt crystallization

The basic technique of melt crystallization is in essence very simple. It uses the differences in crystallization points. If an impure molten material is cooled to its pure-component freezing-point temperature and more heat is removed, then some of material will solidify. In most systems, this solid will be a pure component and impurities will concentrate in the remaining melt—residue. Purified product is recovered by separating the solid from the residue and remelting it.

The use of melt crystallization for the large-scale purification of organics has boomed over the past many years. In the USA alone, total onstream capacity is at least one billion pounds per year. The technique is now routinely used to purify naphthalene, *p*-xylene, disubstituted benzenes, acrylic acid, bisphenol A, and many other chemicals. Two factors are responsible for this growth: escalating requirements for purity and increasing environmental concerns.

Melt crystallization can easily reach the ppm purity levels associated with crystalline materials and it does so without the use of organic solvents.

Compared with solution crystallization, melt crystallization has other advantages:

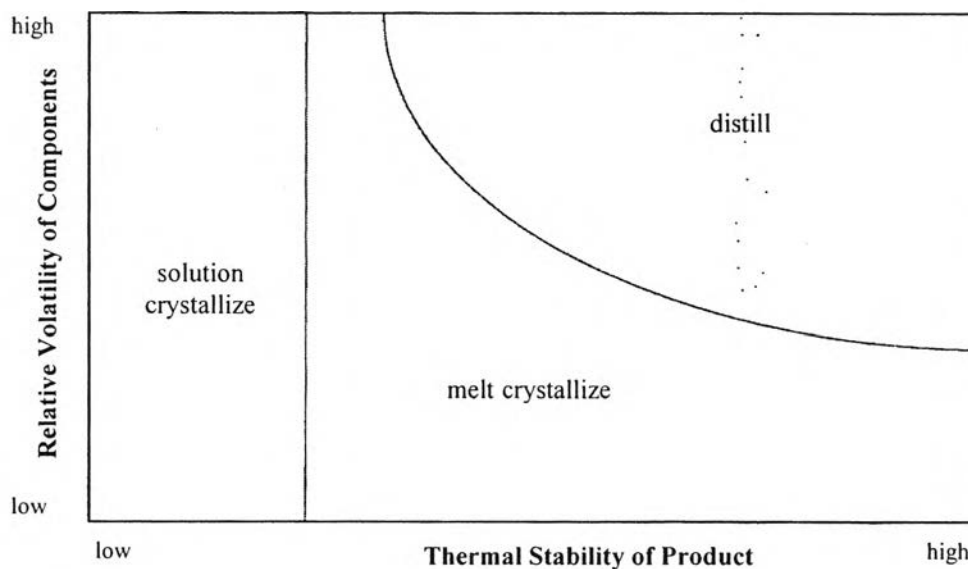
- The volume of material being processed is considerably less and equipment costs and energy consumption are much lower.
- No solvent recovery is necessary. The impurities are recovered in molten form and can be recycled, or treated in some other fashion, without an intermediate solvent-removal step.
- The product is not contaminated with solvent.

Table 2.3 summarizes the key differences between melt and solution.

Table 2.3 Differences between melt and solution crystallization (Schweitzer, 1997)

Melt crystallization	Solution crystallization
Compact equipment	Larger equipment
No solvent emissions	Potential for solvent emissions
No solvent recovery	Solvent recovery required
Higher operating temperatures	Lower operating temperatures
Higher viscosity fluid	Lower viscosity fluid
Good selectivity	Better selectivity
Crystallization only by cooling	Evaporative crystallization possible

A simple way of presenting where melt crystallization can be used to advantage in organic separation is shown in Figure 2.2. For a mixture of high relative volatility and whose components are thermally stable, distillation is normally the preferred separation technique. If relative volatility is low, then distillation becomes more difficult and melt crystallization is likely to be more attractive. If thermal stability is very low, then solution crystallization may be the only practicable separation method (Schweitzer, 1997).

**Figure 2.2** Application of melt crystallization in organic separations (Schweitzer, 1997).

To understand the fundamental of melt separation, one must first look at the phase equilibrium that drives the separation. 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 2.3a) will allow the crystallization of a pure component from a melt in one step, but a solid solution system (Figure 2.3b) requires a sequence of fractionation steps to yield high-purity products (Mullin, 2001).

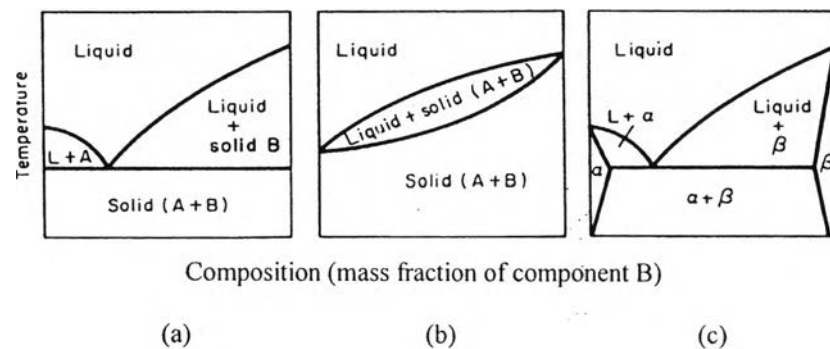


Figure 2.3 Some binary solid-liquid phase diagrams encountered in melt crystallization: (a) simple eutectic; (b) simple solid solutions; (c) eutectic with limited solid solubility (α and β are solid solutions) (Mullin, 2001).

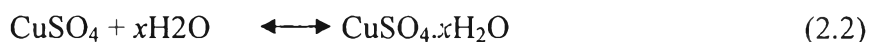
2.4 Phase equilibrium

2.4.1 Phase rule

The amount of information which the simple solubility diagram can yield is strictly limited. For a more complete picture of behavior of a given system over a wide range of temperature, pressure, and concentration, a phase diagram must be employed. The Phase Rule developed by J. Willard Gibbs (1876) relates the number of components, C , phases, P , and degrees of freedom, F , of a system by means of the Equation (2.1) and these three terms are defined as follows (Mullin, 2001).

$$P + F = C + 2 \quad (2.1)$$

The number of *components* of a system is the minimum number of chemical compounds required to express the composition of any phase. In the system water–copper sulphate, for instance, five different chemical compounds can exist, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, 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 (2.2).



A *phase* is a homogeneous part of a system; thus, any heterogeneous system comprises two or more phases. Any mixture of gases or vapors is a one-phase system. Mixtures of two or more completely miscible liquids or solid are also one-phase system, but mixture of two 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 vapor $C = 1$, $P = 3$, 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 a change in the number of phases. Such a system is called ‘invariant’.

For the system water–water vapor $C = 1$, $P = 2$, 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 ‘unvariant’. The one-phase water vapor 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’.

It may be said that the physical nature of a system can be expressed in terms of phases, and that the number of phases can be changed by altering one or more of

three variables: temperature, pressure or concentration. The chemical nature of a system can be expressed in terms of components, and the number of components is fixed for any given system.

However, in most crystallization processes, the main interest lies in the liquid and solid phases of a system. A knowledge of the behavior of the vapor phase is only required when considering sublimation processes. Because pressure has little effect on the equilibrium between liquids and solids, the phase changes can be represented on the temperature–concentration diagram; the pressure, usually atmospheric, is ignored (Mullin, 2001).

2.4.2 Solid-liquid phase diagram

A typical example of a system in which the components do not combine to form a chemical compound is shown in Figure 2.4. Curves *AB* and *BC* represent the temperatures at which homogeneous liquid solutions of naphthalene in benzene begin to freeze or crystallize. The curves also represent the temperature above which mixtures of these two components are completely liquid (Mullin, 2001).

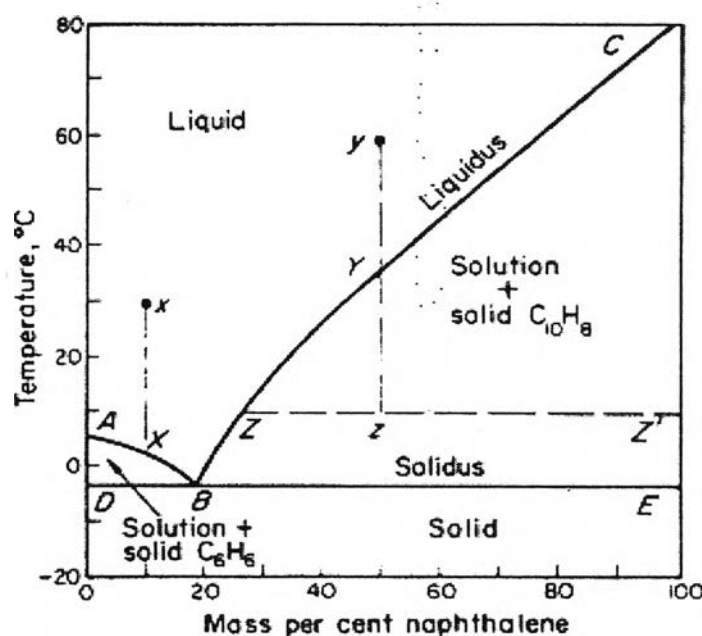


Figure 2.4 Phase diagram for the simple eutectic system naphthalene-benzene (Mullin, 2001).

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 this type of line. The melting or freezing points of pure benzene and naphthalene are given by point *A* (5.5°C) and *C* (80.2°C), respectively. The upper area enclosed by liquidus, *ABC*, represents the homogeneous liquid phase, i.e. a solution of naphthalene in benzene; that enclosed by the solidus, *DBE*, indicates solid mixtures of benzene and naphthalene. The small and large 'triangular' areas *ABD* and *BCE* represent mixtures of solid benzene and solid naphthalene, respectively, and benzene–naphthalene solution.

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 falls follow 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 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*, 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* and *zZ'*.

$$\frac{\text{Mass of solid C}_{10}\text{H}_8}{\text{Mass of solution}} = \frac{zZ}{zZ} \quad (2.4)$$

In industrial crystallization practice, many bulk-produced chemicals a purity of > 95% are 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 (Mullin, 2001).

2.5 Crystal characteristics

Key properties of product that are frequently required and well-defined by market demands before launching the product are a certain crystal size distribution (CSD), a certain crystal habit and purity in order to ensure that the product achieves the quality standard or appropriates with the further application. In terms of quality and economy of the separation process crystallization, crystal size distribution, CSD, and purity are strongly important (Rousseau, 1993).

2.5.1 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 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 (Rousseau, 1993).

The crystal population density, n , 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. The crystal population density (number of crystal per unit size per unit volume of system) is defined by Equation (2.5):

$$n = \lim_{\Delta L \rightarrow 0} \frac{\Delta N}{\Delta L} = \frac{dN}{dL} \quad (2.5)$$

where ΔN is the number of crystals in the size range ΔL per unit volume. The value on n depends on the value of L at which the interval dL is taken. When a total population density is used, the symbol is \bar{n} and the units are number/ length (Schweitzer, 1997).

2.5.2 Purity

In crystallization, purity has become increasingly important due to the presence of impurities in the system can have a profound effect CSD and crystal habit. Some impurities can suppress growth entirely; some may enhance growth, while others may modify the crystal habit. The mechanism by which an impurity affects crystal growth rate is considered to involve adsorption of the impurity onto the crystal surface. Once located on the surface, the impurity forms a barrier to solute transfer from the solution to the crystal. Additionally, the solvent selection can also impact on the crystal habit and growth rate. This can be due to the effect on mass transfer along with the structure of the interface between the crystal and solvent (Rousseau, 1987; Schweitzer, 1997).

2.6 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; therefore, an adsorption process eventually becomes the attractive option. In adsorption, molecules distribute themselves between two phases, one of which is a solid or adsorbent forming a distinct adsorbed phase while the other may be a liquid or a gas.

Liquid phase adsorption consists of two main pathways: adsorption and desorption. Adsorption of liquid adsorbate onto an adsorbent is dictated by the characteristics of the adsorbate-adsorbent interaction and desorption depends on the addition of a desorbent and its specific interactions with both the adsorbent and the adsorbate. Liquid phase adsorption mechanisms are highly complex due to the interaction of solid adsorbents, liquid adsorbates, and liquid adsorbents during the separation process. By contrast, other conventional separation process mechanisms are based primarily on the differences in the physical properties of the components, for instance, volatility in distillation, and solubility in absorption. Separation by adsorption depends on one component being more readily adsorbed than another. Virtually, 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 exchange ion, and water content. These variables are carefully modified to selectively 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).

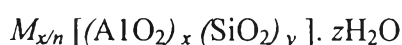
The primary requirement for an economic separation process is an adsorbent with sufficiently high selectivity, capacity, and life. The selectivity may depend on a difference in either adsorption kinetics or adsorption equilibrium but most of the adsorption processes in current use depend on equilibrium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

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B} \quad (2.6)$$

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).

2.7 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 crystalline aluminosilicates of alkali or alkali earth elements, such as sodium, potassium, and calcium, and are represented by the chemical composition:



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 A, 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.

Type X and Y zeolites

Structure of type X and type Y zeolites are shown in Figure 2.5. The cations are necessary to balance the electric charge of the aluminum atoms in AlO_2 ,

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).

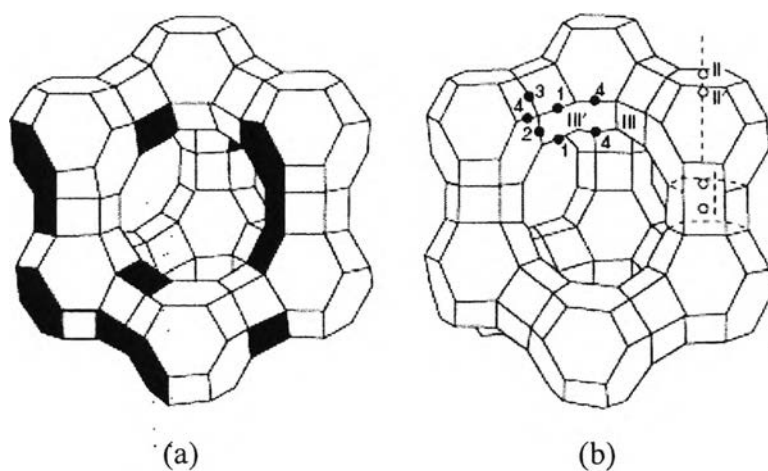


Figure 2.5 Line representations of zeolite structure: (a) 'unit cell' of types X and Y, or faujasite ; (b) cation sites in types X and Y (16 I, 32 I', 32 II, 32 II', 48 III, and 32 III' sites per unit cell) (Yang, 2003).

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 adsorption properties, can be modified further by the number and type of exchanged 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 (Yang, 2003).

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 2.5. Each unit cell contains 192 SiO_2 and AlO_2 tetrahedra. The number of aluminum ions per unit cell varies from 96 to 77 (i.e., $\text{Si}/\text{Al} = 1$ to 1.5) for Type X zeolite, and from 76 to 48 ($\text{Si}/\text{Al} = 1.5$ 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).