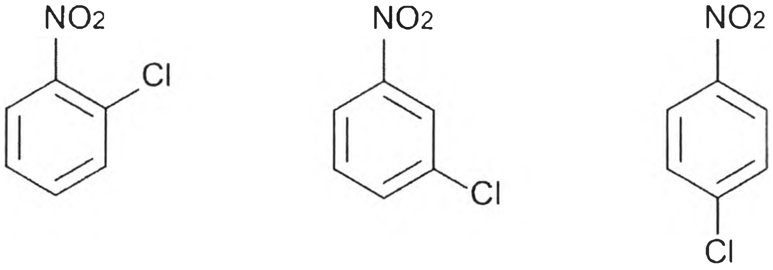
CHAPTER II
LITERATURE REVIEW

2.1 Chloronitrobenzenes

Chloronitrobenzenes (CNBs) are used as chemical intermediates in numerous industries including pesticides, fungicides, pharmaceuticals, preservatives, photochemicals and rubber. Commercially, CNBs are prepared by nitrification of chlorobenzene (CB) in the presence of mixed acid, which gives a mixture of about two-thirds *p*-CNBs, one-third *o*-CNBs and a small amount of *m*-CNB. Furthermore, both *o*- and *p*-CNB are being used more than *m*-CNB because of its industrial applications (Dunn, 1967; Demuth *et al.*, 2002; Priegnitz, 1980). 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 reported in Table 2.1.



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

Figure 2.1 Three isomers of Chloronitrobenzene (commons.wikimedia.org).

Table 2.1 Physical properties of Chloronitrobenzene isomers (Dunn, 1967; druglead.com; Myerson, 2002)

Substances	Boiling point (°C)	Freezing point (°C)	Density (g/mL)	ΔH_m (cal/mol)
o- CNB	246	32.5	1.305	4546
m-CNB	236	44.5	1.534	4629
p-CNB	242	83.5	1.520	4965

Generally, CNBs are produced by two main pathways, which are nitration of chlorobenzene (CB) and chlorination of nitrobenzene (NB) depending on the desired isomer products.

Nitration of CB, which is the main procedure of nitrochlorobenzene, uses a mixture of sulfuric acid, nitric acid, and water; however, this process consumes large amount of dilute spent sulfuric acid, which cannot be eliminated and affect the environment. On the other hand, nitration of CB with nitric acid alone is a safer procedure than using sulfuric acid; for instance, CB is nitrated with 95% nitric acid (HNO_3), the optimum conditions are as reaction temperature 65 °C, molar ratio HNO_3 : CB is 2.5, and residence time in the main and surge reactors 45 minutes. The yield of CNB was 97.5% and consisted of 68-70 % *p*-CNB, 29.5-31.5 % *o*-CNB, and 0.1-0.5 % *m*-CNB. Obviously, large amounts of acids to be recovered, long reaction time, and difficulties in temperature control of the process hinder industrial implementation (Veretennikov *et al.*, 2001).

For chlorination of NB, this process occurs at 35-45 °C in the presence of iron (III) chloride and the *m*-CNB is the major product. The reaction is carried out by using a series of reactors with a residence time of 5 hours. The operating condition aspect requires careful operation and succeeds only if the equipment and materials are used in the complete absence of water. Moreover, even traces of moisture can retard the chlorination excessively (Friedrich *et al.*, 1961). Final purification of *m*-CNB may be achieved chemically by caustic hydrolysis of the residual *o*- and *p*-CNB and washing them out as nitrophenols (David and Blangey, 1949; Booth, 1991).

2.2 Crystallization

Crystallization is a chemical solid-liquid separation technique, where solute in the solution transfer from liquid to pure solid crystalline phase (en.wikipedia.org). Crystallization can be carried either in the presence of a solvent, which is called crystallization from solution or in the absence of a solvent called crystallization from melt (Lee, 1974). Generally, the solids are separated from the crystallizer liquid, washed, and discharged to downstream equipment for additional treatment (Moyer and Rousseau, 1987).

Crystallization is one of the most important separation technologies, widely used in many industries, especially inorganic industry because of the purification of products during final stages of manufacturing. It is distinguished from other techniques that can often provide a better separation and a more energy efficient process (Ruemekort and Scholz, 2004). But when two compounds are similar in crystal structure and molecular, i.e. isomorphic compounds, the system may be forming a solid solution and then product purity cannot be achieved by one stage. In this case, multiple recrystallizations are needed to get the relatively pure component lead to operations that are difficult to handle and high maintenance cost (Nie *et al.*, 2006).

2.2.1 Solution Crystallization

Crystallization from solution accomplishes the separation of the components in a mixture by using the differences in solubility at specific temperature (Lee, 1974). A diluent solvent is added to the mixture; the solution is then directly or indirectly cooled and/or solvent is evaporated to effect crystallization. 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).

2.2.2 Melt Crystallization

Melt crystallization is a separation technique. It comprises the cooling crystallization of a material from a melt without using a solvent. It can be an alternative to distillation when the boiling points of the components in a melt are close together. Furthermore, melt crystallization has the potential of ultrapurification. For example, the feed contains 70–80% by weight of the desired material and the product has an assay of 99.99% by weight. To attain this purity, melt crystallization has to be repeated (Van't Land, 2005).

Melt crystallization is in essence very simple. If an impure molten material is cooled to its freezing point and further heat is removed, then some of the material will solidify. In most systems, this solid will be a pure component. Impurities will concentrate in the remaining melt, when is known as the residue. Purified product is recovered by separating the solid from the residue and remelting it (Wynn, 1992).

There are many potential advantages of melt crystallization. The volume of material being processed is considerably less, equipment costs and energy consumption are thus much lower. No solvent recovery is necessary. The impurities are recovered in molten form and can be recycled, incinerated, or treated in some other fashion without an intermediated solvent-removal step and the product is not contaminated with solvent (Wynn, 1992). The differences between melt and solution crystallization are shown in Table 2.2

Table 2.2 Differences between melt and solution crystallization (Schweitzer, 1997; Wynn, 1992)

Melt crystallization	Solution crystallization
Compact equipment	Larger equipment
No solvent emissions	Potential for solvent emissions
Reduced environmental hazard	Possible environmental hazard
Moderate growth rate	Higher growth rate
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).

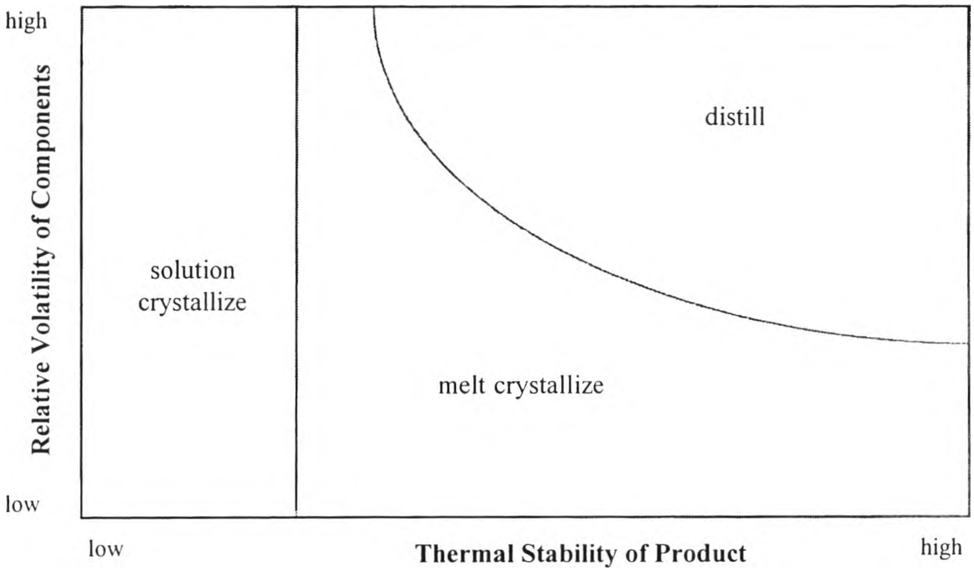


Figure 2.2 Application of melt crystallization in organic separations (Schweitzer, 1997).

2.3 Phase Equilibrium

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 rang of pressure, temperature, and concentration, a phase diagram has to be employed. This type of the diagram represents graphically, in two or three dimensions, the equilibia between the various phases of the system. The phase rule, developed by J. Willard Gibbs in 1876, relates the number of components, C, phase, P, and degrees of freedom, F, of a system by means of Equation (2.1) and these three terms are defined as follows (Mullin, 2011):

$$P + F = C + 2 \tag{2.1}$$

The number of components of a system is the minimum number of chemical compounds required to express the composition of any phase; for instance, 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 (2.2).

$$CuSO_4 + xH_2O \longleftrightarrow CuSO_4.xH_2O \qquad (2.2)$$

A phase is a homogeneous part of the system. Thus, any heterogeneous system comprises two or more phases. Any mixture of gases or vapour 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’ (Mullin, 2001).

2.3.1 Phase Diagram

The phase diagram is important with regard to the efficiency and applicability of melt crystallization. Melt crystallization can be applied when the phase diagram is of the eutectic type. For example, *p*-xylene and *m*-xylene form a eutectic mixture. It is more difficult to apply melt crystallization when the phase diagram is of the solid solution type. Solid solutions may be formed if the components are similar in size and shape on a molecular scale (Van't Land, 2005). 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. A binary eutectic system with limited solid solubility, which would prevent one-step crystallization from producing a pure component, is shown in Figure 2.3c (Mullin, 2001).

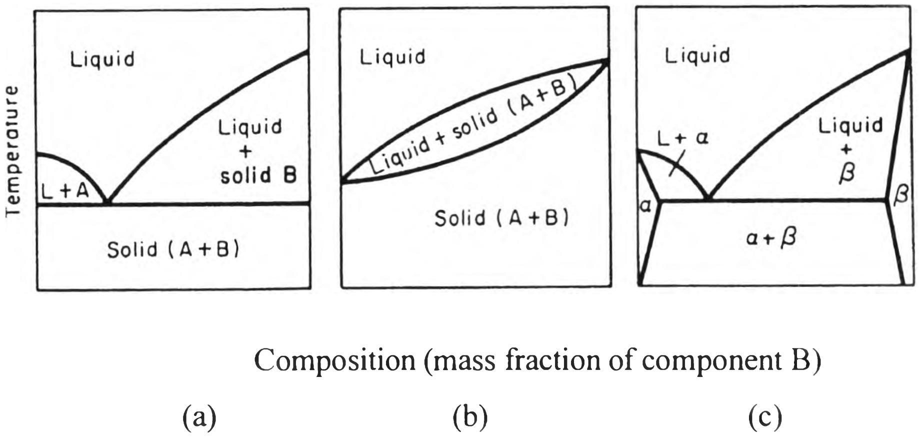


Figure 2.3 Some binary solid-liquid phase diagrams encountered in melt crystallization: (a) simple eutectic; (b) simple solid solutions; (c) eutectic with limited solid solubility (α and β are solid solutions) (Mullin, 2001).

2.3.2 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 2.3. 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).

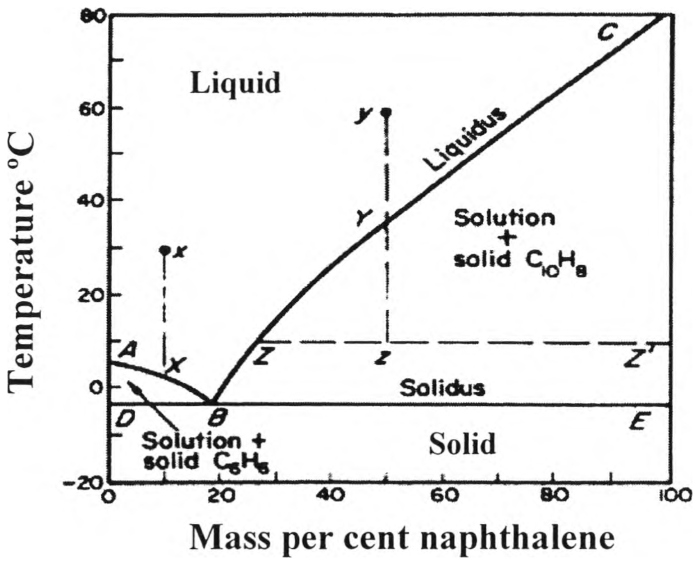


Figure 2.4 Phase diagram for the simple eutectic system naphthalene-benzene (Mullin, 2001).

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 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, 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'*.

$$\frac{\text{Mass of solid } C_{10}H_8}{\text{Mass of solution}} = \frac{zZ}{zZ'} \qquad (2.3)$$

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).

2.4 Supersaturation

A saturated solution is in thermodynamic equilibrium with the solid phase, at a specified temperature. It is often easy, however, e.g. by cooling a hot concentrated solution slowly without agitation, to prepare solutions containing more dissolved solid than that represented by equilibrium saturation. Such solutions are said to be supersaturated (Mullin, 2001).

The relationship between supersaturation and spontaneous crystallization led to a diagrammatic representation of the metastable zone on a solubility-supersolubility diagram as shown in Figure 2.5. The lower continuous solubility curve can be located with precision. The upper broken supersolubility curve, which represents temperatures and concentrations, at which uncontrolled spontaneous crystallization occurs, is not as well defined as that of the solubility curve. Its position in the diagram is considerably affected by, amongst other things, the rate, at which supersaturation is generated, the intensity of agitation, the presence of trace impurities and the thermal history of the solution. The diagram is divided into three zone (Mullin, 2001):

1. The stable (unsaturated) zone, where crystallization is impossible.
2. The metastable (supersaturated) zone, between the solubility and supersolubility curve, where spontaneous crystallization is impossible. However, if a crystal seed were placed in such a metastable solution, growth would occur on it.
3. The unstable or labile (supersaturated) zone, where spontaneous crystallization is possible, but not inevitable.

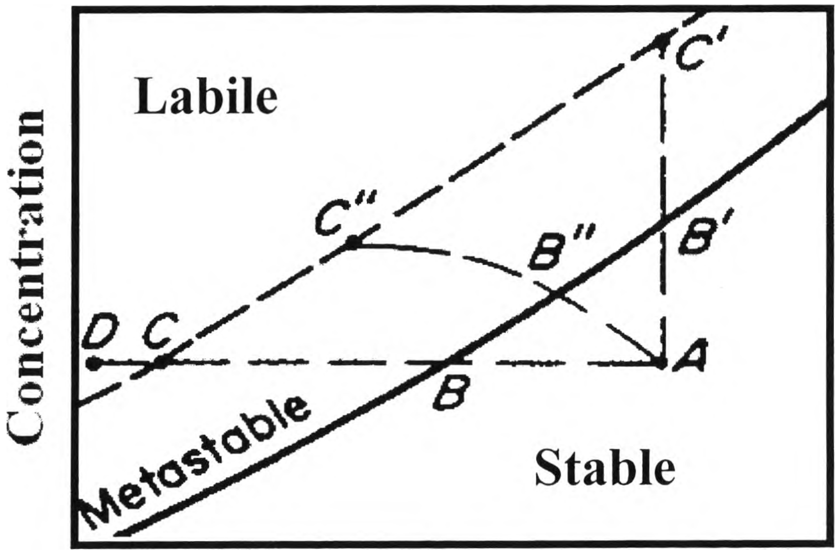


Figure 2.5 Solubility-supersolubility diagram (Mullin, 2001).

If a solution represented by point *A* in Figure 2.5 is cooled without loss of solvent (line *ABC*), spontaneous crystallization cannot occur until conditions represented by point *C* are reached. At this point, crystallization may be spontaneous or it may be induced by seeding, agitation or mechanical shock. Further cooling to some point *D* may be necessary before crystallization can be induced (Mullin, 2001).

Supersaturation can also be achieved by removing some of the solvent from the solution by evaporation. Line AB'C' represents such an operation carried out at constant temperature. Penetration beyond the supersolubility curve into the labile zone rarely happens, as the surface, from which evaporation takes place is usually supersaturated to a greater degree than the bulk of the solution. Crystals, which appear on this surface, eventually fall into the solution and seed it, often before conditions represented by pointed C' are reached in the bulk of the solution. In practice, a combination of cooling and evaporation is employed, and such an operation an operation is represented by the line AB"C" in Figure 2.5 (Mullin, 2001).

2.5 Product Quality

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 term of quality and economy of the separation process crystallization, crystal size distribution, CSD, and purity are strongly important (Rousseau, 1993).

2.5.1 Purity

It is difficult to predict the purity of crystals because this property depends on a variety of thermodynamical, kinetic, mechanical, and fluid dynamic parameters. In the case of crystallization from the melt, it is known that the level of impurity is mostly governed by the impure melt adhering to the crystals, but this can also be true of crystals obtained from solution. As a rule, the interior of crystals grown at a very low growth rate is very pure, which is the advantage of the unit operation crystallization. According to the thermodynamic equilibrium, very few impurities are incorporated as units that do not desorb and diffuse back into the bulk of the solution fast enough or melt when crystal growth rates reach economically reasonable values (Mersmann, 2001).

A well-formed crystal itself is nearly pure, but it retains mother liquor when removed from the final magma (the two-phase mixture of mother liquor and crystals), and if the crop contain crystalline aggregates, considerable amounts of mother liquor may be occluded within the solid mass. When retained mother liquor of low purity is dried on the product, contamination results, the extent of which depends on the amount and degree of impurity of the mother liquor retained by the crystals.

In practice, much of the retained mother liquor is separated from the crystals by washing with fresh solvent. The effectiveness of these purification steps depends on the size and uniformity of the crystals (McCabe *et al.*, 2005).

2.5.2 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 basic quantity in the theory of CDS is the population density. To understand the meaning of this variable, assume that a distribution function of the cumulative number of crystals in the magma, in number per unit volume of mother liquor, is known as a function of L, the crystal size. The population density n is defined by Equation (2.4).

$$n \equiv \frac{d(N/V)}{dL} = \frac{1}{V}\frac{dN}{dL} \tag{2.4}$$

where V is the volume of mother liquor in the magma and N is the number of crystals of size L and smaller in magma (McCabe *et al.*, 2005).

2.6 Adsorption

Adsorption is a mass transfer process, in which a substance is transferred from a liquid phase to the surface of a solid adsorbent and becomes bound by physical and or chemical interactions (Rashdi *et al.*, 2011). Most chemical manufacturing operation requires the technique of separation processes to obtain and recover 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 exchange 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 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).

2.7 Zeolite

Zeolite is crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium, and calcium. Chemically, they are represented by the empirical formula:

$$\mathrm{M}_{2/n}\mathrm{O} : \mathrm{Al}_2\mathrm{O}_3 : y\mathrm{SiO}_2 : w\mathrm{H}_2\mathrm{O} \tag{2.6}$$

where y is 2 or greater, n is the cation valence, and w represents the water contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions. The framework structure contains channels or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange. The water may be removed reversibly, generally by the application of heat, which leaves intact a crystalline host structure permeated by micropores which may amount to 50% of the crystals by volume (Keller *et al.*, 1987).

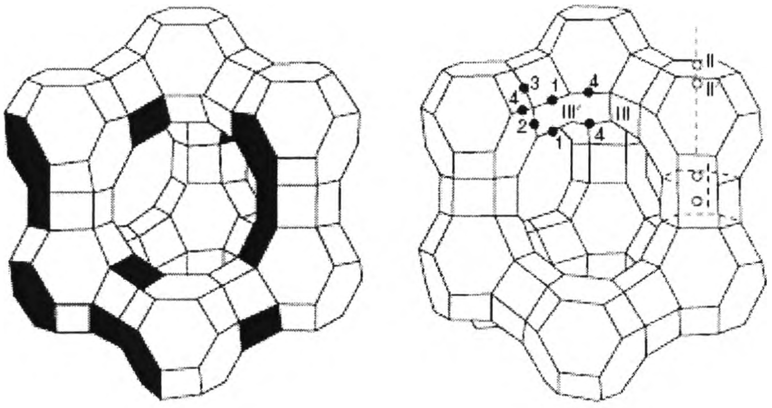
The structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure, represented by

$$M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y].\ wH_2O \qquad (2.7)$$

where n is the valence of cation M, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and y/x usually has values of 1-5. Recently, however, high-silica zeolites have been prepared, in which y/x is 10-100 or even higher (Keller *et al.*, 1987).

2.7.1 Zeolites Type X and Y

Unit cells of type X and type Y zeolites are shown in Figure 2.6. 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).



(a) (b)

Figure 2.6 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. 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 2.6. 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., 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 2.6b. 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).

2.8 Chloronitrobenzene Separation Process

Chloronitrobenzene isomers are used as chemical intermediates in various process; thus, it is essential to obtain each isomer with a purity as high as possible. Nevertheless, it is extremely difficult to get high purities of each isomer by distillation due to their close boiling points. Other appropriate separations are considered *e.g.* crystallization, adsorption and fractionation. The qualities of each desired product depend on the techniques that are used.

Dunn *et al.* (1967) from Philips Petroleum Company provided a method, a combination of crystallization and fraction to separate CNB isomers in order to obtain high purity of *o*-CNB and *p*-CNB. The presence of a binary eutectic mixture at 33.5 wt% *p*-CNB and 66.5 wt% *o*-CNB can obtain maximum recovery of *p*-CNB from a mixture comprising on 66 wt% *p*-CNB, 32 wt% *o*-CNB, 1 wt% *m*-CNB, and 1wt% *di*-CNB cooled to the eutectic temperature approximately 14°C and *p*-CNB was crystallized in there. After removal of the para crystals, the mother liquor was fractioned to increase the concentration of *o*-CNB and cooled to the eutectic temperature 14°C again to get the ortho crystals. By operating in this process, the need of a eutectic depressant was eliminated due to the change of mixture component to the other side of eutectic point.

Guo *et al.* (2005) studied selective adsorption of *p*-CNB from an aqueous mixture containing *p*-CNB and *o*-CNB by the used of HZSM-5 zeolite as an adsorbent. The objectives of this work were to treat the wastewater containing CNBs with a degradable technique. The result revealed that maximum adsorption amounts of *p*-CNB were higher than those of *o*-CNB in HZSM-5 zeolite. The adsorption capacity of HZSM-5 zeolite was approximately 4 mol/unit cell to get maximum concentration of *p*-CNB. The purity of 97.6% *p*-CNB and 95.2% *o*-CNB was achieved from the appropriate adsorption.

Guo *et al.* (2009) investigated selective adsorption and separation of *p*-CNB and *o*-CNB by the used of silicate-1 zeolite as an adsorbent. The result showed that *p*-CNB was preferentially absorbed in the zeolite intersections with acid sites. The key factors in controlling adsorption rate constants of CNBs in the silicalite-1 zeolite are the adsorption temperature and adsorption amounts. Adsorption rate constants and equilibrium adsorption amounts of *o*-CNB are lower than those of *p*-CNB in silicalite-1 zeolite. Under the optimal adsorption condition, the purity of 94.9% *p*-CNB and 96.1% *o*-CNB can be recovered.

Funakoshi *et al.* (2001) examined the changes of agglomeration phenomena and agglomerate purity with the size and number of seed crystals for mixtures of *m*-CNB and *o*-CNB in batch crystallization. The result showed that the size of *m*-CNB particles was controlled by agglomeration. When the number of seed crystals was larger and its size was smaller, the amount of purity decreased with the larger agglomerates. Moreover, agglomerate purity decreased with the increase in the number of element crystals constituting agglomerates and the amount of mother liquor entrained during agglomeration became larger when the elementary crystals agglomerated more densely.

Takiyama *et al.* (2002) observed local purities of *m*-CNB crystals. 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 higher the purity of *m*-CNB decreases. Furthermore, each crystal face has different activation energy and pre-exponential factor, while the difference in the linear growth rates is due to the difference in the growth mechanism.

Lerdsakulthong (2007) investigated adsorptive separation of *m*- and *p*-CNB on FAU zeolites at static equilibrium condition. This experiment varied a series of X and Y zeolites, the type of alkaline ion exchanged cations, and desorbents. For single component adsorption, the Y zeolite preferentially adsorbed *m*-CNB more than *p*-CNB due to higher molecular dipole moment. The adsorption capacities *m*-CNB and *p*-CNB on the series of X and Y zeolites increase with the decrease in the size of the cation due to the increase in the adsorbent acid strength. For the binary component adsorption, the adsorption capacities were nearly constant. The *m*-/*p*-CNB selectivities of NaY were the highest for both low and high equilibrium condition. Nitrobenzene seems to be the most appropriate desorbent due to its balance between the adsorbent-adsorbates and adsorbent-desorbent interactions

Yensukjit (2008) studied the adsorption of *m*- and *p*-CNB on the FAU zeolites with alkaline earth exchanged cations under static conditions and also investigated the effect of FAU on precipitate composition in the crystallization. For single component adsorption, the adsorption capacities of *m*- and *p*-CNB on the both X and Y zeolite with increasing in the cation size because some adsorption site are blocked by a large cation and the Y zeolite had a higher adsorbtion capacity than the X zeolite, while CaY gave the highest adsorption capacities because the adsorption capacities of CNBs on both types of zeolite depended on the acid-base interaction. For binary component adsorption, the adsorption capacities depended on both the cation size and the acid strength, but they could adsorb lower than BaX, BaY, SrY and CaY. CaY gave the highest *m*-/*p*-CNB selectivity. In the crystallization, NaX, NaY, CaX, and CaY were used and the results showed that the zeolites could shift the precipitate composition to be rich in *p*-CNB with the purity as high as 85-94 wt% and NaY gave the highest purity of *p*-CNB in the precipitates. However, the effects of the adsorption and the composition gradient were proved to have no influence during the experiment. The purity of *p*-CNB in the precipitates depended on the position and shape of them, and type of zeolites.

Pattanapaiboonkul (2009) revealed the effect of feed compositions on the *m*- and *p*-CNB crystallization. Below the eutectic composition, the feed composition gave the *p*-CNB enriched-precipitates, 95.04 wt%. At the eutectic composition, amorphous precipitates with the CNB composition closed to the feed compositions were obtained. Above the eutectic composition, a crystal formed and their compositions were rich in *m*-CNB, 92.73 wt%. When the effect of adding a zeolite (NaX, CaX, BaX, NaY, and CaY) on the *m*- and *p*-CNB crystallization was investigated, the result showed that the presence of the zeolites did not affect the feed composition but had a great influence on the precipitate composition. At the eutectic composition, the amorphous precipitates become crystal precipitates with the composition being rich in *p*-CNB. The precipitate composition from the feed above the eutectic composition was shifted from being rich in *m*- to *p*-CNB, but the precipitate composition below the eutectic composition remained rich in *p*-CNB. The cation, type of the zeolite, and position of the precipitates had a significant effect on the precipitate composition in the feed below the eutectic composition more than those in the feed at and above the eutectic composition. The precipitates near the zeolites had higher purity of *p*-CNB than the precipitates far from zeolites. Temperature variation in the solution during the experiment had no effect. Although effects of types of adsorbents on the crystallization were investigated, the precipitate composition was still shifted from *m*- to *p*-CNB.

Yairit (2010) studied the influence of feed compositions on precipitate composition and crystallization temperature. At the eutectic composition, the precipitates compose of 62.95 wt% *m*-CNB and 37.05 wt% at *p*-CNB. Below the eutectic composition, the precipitates were enriched with 91.08 wt% *p*-CNB, while above the eutectic composition, the precipitates were rich in *m*-CNB, 89.85 wt%. The effects of number of a zeolite showed that the feed solution with 5 grains of the zeolites resulted in the precipitates with high *p*-CNB compositions than that from the solution with 10 grains of the zeolites. The precipitates near the zeolites had *p*-CNB purity higher than those far from the zeolites. For the precipitates in the feed above the eutectic composition, the zeolites can shift the precipitate composition from being rich in *m*-CNB to *p*-CNB. Furthermore, the presence of seeds can induce the crystallization of the precipitates following the phase diagram at the feed composition and the purity of the precipitates decrease with the increase in the number of the seeds. Seeds and zeolites also had a great influence on the crystallization temperature. Nucleation could be induced by using zeolites at a lower temperature than that required for the crystallization without any zeolite.