

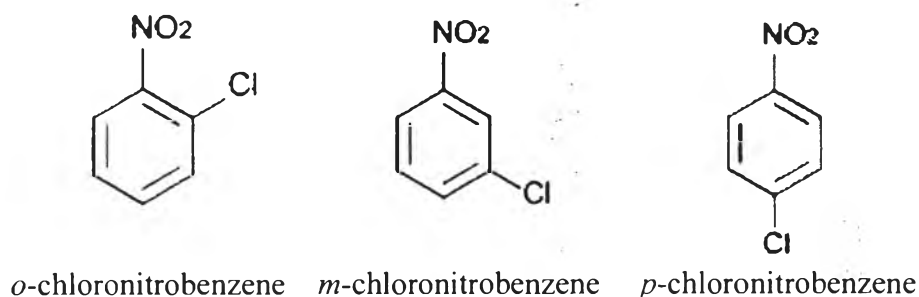


## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Chloronitrobenzenes

Chloronitrobenzenes (CNBs) are important organic intermediates, which are extensively used in the production of dyes, pesticides, pharmaceuticals and rubber chemicals. Generally, CNBs are prepared by nitration of chlorobenzene (CB) in the presence of nitric and sulfuric acid, which gives a mixture consisting of approximately 60–65% of *p*-CNB, 34–39% of *o*-CNB and a small amount of *m*-CNB (<1%) (Sikdar and Garry, 1998). Isomers of CNBs 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.



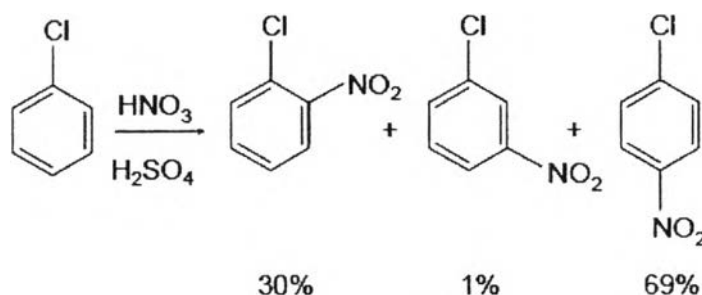
**Figure 2.1** Chloronitrobenzene isomers (commons.wikimedia.org).

**Table 2.1** Physical properties of chloronitrobenzene isomers (Adkins, 1996)

	Boiling point (°C)	Melting point (°C)	Density (g/mL)	Flash point (°C)
<i>o</i> -CNB	246	32.5	1.368	123
<i>m</i> -CNB	236	44	1.534	103
<i>p</i> -CNB	242	83	1.520	110

CNBs are produced by two main processes, nitration of chlorobenzene (CB) and chlorination of nitrobenzene (NB); depending on the desired amount of each isomer.

Nitration of CB with sulfuric acid-nitric acid mixtures is the main procedure for CNB production. The drawback of this procedure is a large amount of dilute spent sulfuric acid as waste. The present-day procedures of recovery of spent sulfuric acid do not eliminate its environmental impact. The growing importance of environmentally safe processes requires a search for new nitration procedures without using sulfuric acid. One of such procedures can be nitration of CB with nitric acid alone, which can be recovered on the industrial scale by environmentally safer procedures, compared to sulfuric acid. As seen from published data, the major attention was focused on the use of 67-68% nitric acid for nitration. For example, it was proposed to carry out nitration of CB with a 20-30-fold molar excess of nitric acid in a tubular reactor or cascade of reactors at 90°C or by adding CB to an excess of boiling nitric acid with simultaneous removal of the reaction water. Apparently, long reaction time, large amounts of acids to be recovered, and difficulties in temperature control of the process hinder the industry (Veretennikov *et al.*, 2001). Nitration of CB is shown in Figure 2.2.



**Figure 2.2** Nitration of chlorobenzene (depts.washington.edu).

For chlorination of NB, sufficient chlorine is needed to produce a crude chlorination mixture containing unchlorinated NB, *m*-CNB, isomeric mono (*o*- and *p*-) CNBs and di-CNBs. The *m*-chloronitrobenzene is the major and desired constituent (Bloom and Graham, 1957). In an 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. Anhydrous ferric chloride is the most satisfactory chlorine carrier. NB 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).

## 2.2 Crystallization

Crystallization is a process where solid particles are formed from homogeneous phase. This process can occur in the freezing of water to form ice, in the formation of snow particles from a vapor, the formation of solid particles from a liquid melt, or the formation of solid crystals from a liquid solution. Crystallization from a solution is the most important one commercially. In the crystallization, the solution is concentrated and usually cooled until the solute concentration becomes greater than its solubility at that temperature. Then the solute comes out of the solution, forming crystals of approximately pure solute (Geankoplis, 2003).

Crystallization 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).

### 2.2.1 Solution Crystallization

Crystallization is an important separation technology, and is widely used in the chemical and many other industries for the purification of products during their final stages of manufacturing. But when two compounds are similar in molecular and crystal structure, i.e. isomorphous compounds, the system may be forming a solid solution and then pure product cannot be obtained via a single crystallization stage. In these cases, multiple recrystallizations are needed to get the relatively pure component (Nie *et al.*, 2006). 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 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 one of the separation techniques applied in the separation of organics (such as close boiling hydrocarbons), isomers, heat sensible materials and so on. Furthermore, melt crystallization has the potential of ultrapurification. For example, the feed contains 70–80 wt% of the desired material and the product has an assay of 99.99 wt%. To attain this purity, melt crystallization has to be repeated (Van't Land, 2005). The use of melt crystallization for separation of organic mixtures has increased rapidly in the chemical industry over the past few years. In melt crystallization, the impurities are recovered in the molten form and can be cycled, incinerated, or treated in some other fashion without an intermediate solvent removal step (Kim and Mersmann, 1997).

Melt crystallization is a clean technology for the separation of organics without using a solvent. The product is not contaminated with solvent, so solvent recovery is not necessary. The differences between melt and solution crystallization are shown in Table 2.2. One major advantage of melt crystallization as a separation technology becomes obvious when comparing the energy required for the phase change for melt crystallization (solid/liquid) to distillation (liquid/vapor). Another advantage is reflected in investment and running costs (Myerson, 2001). The main problems of these methods are low product purity, low heat transfer efficiency and high energy consumption, associated with scale up problems (Kim and Mersmann, 1997).

**Table 2.2** Differences between melt and solution crystallization (Schweitzer, 1997)

<b>Melt crystallization</b>	<b>Solution crystallization</b>
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

On comparing distillation and melt crystallization, it can be stated that the heat of evaporation (in Joules per kilogram) for a given compound is greater than the heat of fusion. A factor of three is not uncommon. Furthermore, the process temperatures at distillation are generally much higher than those at melt crystallization. For melt crystallization, low-level energy usually suffices. However, some melt crystallizations take place at subzero temperatures (e.g., the separation of *p*-xylene from a mixture of ethylbenzene, *p*-xylene, *o*-xylene, and *m*-xylene occurs industrially at -40/-65°C). It is interesting to note that pure *p*-xylene melts at +13°C. A further aspect is that the melt crystallization process must often be repeated several times. Because of all these aspects, it cannot be stated that the variable costs of melt crystallization are always lower than the variable costs of distillation (Van't Land, 2005).

## 2.3 Phase Equilibrium

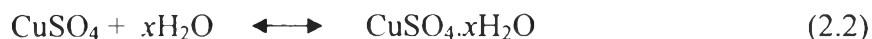
### 2.3.1 Phase Rule

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 (2.1). 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 (Mullin, 2001).

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

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,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CuSO}_4$  and  $\text{H}_2\text{O}$ ; but for the purpose of applying the Phase Rule there are considered to be only two components,  $\text{CuSO}_4$  and  $\text{H}_2\text{O}$ , because the composition of each phase can be expressed by Equation (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'.

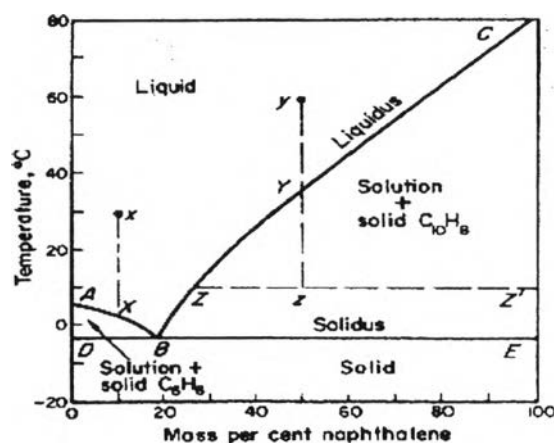
For the system water-water vapour  $C = 1$ ,  $P = 2$  and  $F = 1$ : thus, only one variable, pressure or temperature, may be altered independently without changing the number of phases. Such a system is called 'univariant'. The one-phase

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).

### 2.3.2 Solid-Liquid Phase Diagram

Solid-liquid phase diagrams represent the relationship between temperature and composition. If a phase diagram is known, a good impression of the separability of the components of a mixture by a crystallization process can be obtained. The discussion will be restricted to phase diagrams obtained at atmospheric pressure. Furthermore, binary mixtures will be considered only as the diagrams become more complex when there are more than two components (Van't Land, 2005).

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 2.3** 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 mix-

tures 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 ( $5.5^{\circ}\text{C}$ ) and C ( $80.2^{\circ}\text{C}$ ), 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 ( $-3.5^{\circ}\text{C}$  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.

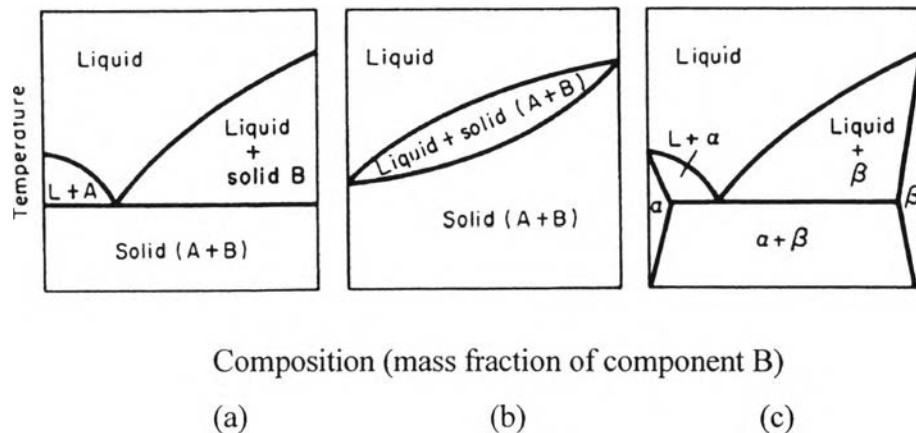
If the solution  $y$  is cooled below the temperature represented by point  $Y$  on curve  $BC$  to some temperature represented by point  $z$ , the composition of the system, as a whole, remains unchanged. The physical state of the system has been altered; however, it now consists of a solution of benzene 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  $zZ'$ .

$$\frac{\text{Mass of solid C}_{10}\text{H}_8}{\text{Mass of solution}} = \frac{zZ}{zZ'} \quad (2.3)$$



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).

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. Eutectic systems may be formed if the components are different in size and shape on a molecular scale. 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 2.4a) will allow the crystallization of a pure component from a melt in one step, but a solid solution system (Figure 2.4b) requires a sequence of fractionation steps to yield high-purity products (Mullin, 2001).



**Figure 2.4** Some binary solid-liquid phase diagrams encountered in melt crystallization: (a) simple eutectic; (b) simple solid solutions; (c) eutectic with limited solid solubility ( $\alpha$  and  $\beta$  are solid solutions) (Mullin, 2001).

## 2.4 Precipitation

Precipitation very often refers to nothing more than crystallization, although sometimes it also implies an irreversible process, e.g. many precipitates are virtually insoluble substances produced by a chemical reaction, whereas the products of most conventional crystallization processes can usually be redissolved if the original conditions of temperature and solution concentration are restored. Another distinguishing feature of precipitation processes is that they are generally initiated at high supersaturation, resulting in fast nucleation and the consequent creation of large numbers of very small primary crystal.

Although precipitation, like all crystallization processes, consists of three basic steps (supersaturation, nucleation, and growth) two subsequent secondary steps usually have a profound effect on the final crystalline product. The first is agglomeration, which generally occurs soon after nucleation, and the second is ageing, a term used to cover all irreversible changes that take place in a precipitate after its formation (Mullin, 2001).

### 2.4.1 Agglomeration

Small particles in liquid suspension have a tendency to cluster together. Such terms as ‘agglomeration’, ‘aggregation’, ‘coagulation’ and ‘flocculation’ have all been applied in this area. If the supersaturation sticks the agglomerating crystals strongly together by crystal growth between the mother particles, the process is called agglomeration (Mullin, 2001).

To obtain agglomerates, three successive steps have to occur:

1. The collision of two particles
2. A sufficient time interval during which two particles stay together enough to stick with the help of the flow
3. The attachment of two particles caused by agglomeration

The key parameters of this process are

- The nature of the solvent (viscosity)
- The size and the habit of the crystals
- The population density of the crystals, which has a very important direct influence on the collision frequency

Interparticle collision may result in permanent attachment if the particles are small enough for van der Waals forces to exceed the gravitation forces, a condition that generally obtain for sizes  $<1 \mu\text{m}$ . Of course, not all interparticle collisions result in permanent contact and in lyophobic systems charge stabilization greatly decreases the rate of agglomeration.

Two types of agglomeration for colloidal particles in suspension:

1. Perikinetic (static fluid, particles in Brownian motion)
2. Orthokinetic (agitated dispersions)

Both modes can occur in precipitation processes, but in a stirred precipitator orthokinetic agglomeration clearly predominates. The relationship between agglomerate size  $D$  and time  $t$  may be expressed by

$$D^3(t) = A_1 + B_1 t \quad (\text{perikinetic}) \quad (2.4)$$

and

$$\log D(t) = A_2 + B_2 t \quad (\text{orthokinetic}) \quad (2.5)$$

where  $A$  and  $B$  are particle-fluid system constants (Mullin, 2001).

## 2.5 Product Quality

The product quality of inorganic or organic crystalline solids produced in the chemical and pharmaceutical industries is influenced by controlling the crystallization step as a very important chemical engineering process (Kuhberger and Mersmann, 1997). 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 Purity

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 contains 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

In commercial crystallization not only are the yield and purity of the crystals important but also the sizes and shapes of the crystals. It is often desirable that crystals be uniform in size. Size uniformity is desirable to minimize caking in the package, for ease of pouring, for ease in washing and filtering (Geankoplis, 2003).

The size and shape of particles in a particulate product are important for several reasons. The efficiency of any process for production of a particulate material relies on the size, shape, and size distribution. A very small mean size product

is difficult to centrifuge, wash, and package. Many products must be dissolved for subsequent use and a broad size range leads to variation in time necessary for dissolution among product crystals. Shape can also be important in applications such as pharmaceuticals wherein different crystal faces have different dissolution rates, leading to variation in bioavailability for crystals of different shapes. Therefore, any comprehensive discussion of crystallization must include the genesis of size and size distribution, as well as its possible measurement and control (Myerson, 2001).

The basic quantity in the theory of crystal size distribution (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 (2.6)

$$n \equiv \frac{d(N/V)}{dL} = \frac{1}{V} \frac{dN}{dL} \quad (2.6)$$

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

Most chemical manufacturing operation requires separation processes to obtain and recover a high quality product. In most circumstances, efficiency of a separation process has a considerable effect on both quality and cost of a product. Liquid phase adsorption has long been used for the removal of contaminants present at low concentrations in process streams. Adsorption from the liquid phase is used to recover reaction products that are not easily separated by distillation or crystallization. Some of the same types of solids are used for both vapor-phase and liquid-phase adsorption, though often adsorbents with larger pores are preferred for use with liquids. Most adsorbents are highly porous materials, and adsorption takes place primarily on the wall of the pores or at specific sites inside the particle. Because the pores are generally very small, the external surface area is orders of

magnitude greater than the external area and is often 500 to 1,000 m<sup>2</sup>/g. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. Regeneration of adsorbent can then be carried out to obtain the adsorbate in concentrated or nearly pure form (McCabe *et al.*, 2005).

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. 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 conventional 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 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 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:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B} \quad (2.7)$$

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

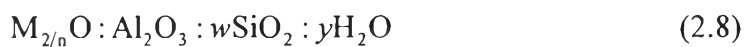
components may be separated by distillation. The analogy is, however, purely formal and there is no quantitative relationship between the separation factor and relative volatility. For two given components, the relative volatility is fixed whereas the separation factor varies widely depending on the adsorbent (Ruthven, 1984).

## 2.7 Zeolite

Zeolites are described as a three-dimensional network of fundamental structural units consisting of silicon-centered  $\text{SiO}_4$  and aluminum-centered  $\text{AlO}_4$  tetrahedral interconnected by a mutual sharing of apical oxygen atoms. The space between the tetrahedra is occupied by water molecules and subsequent dehydration of partial dehydration results in a crystal structure interlaced with channels of molecular dimension.

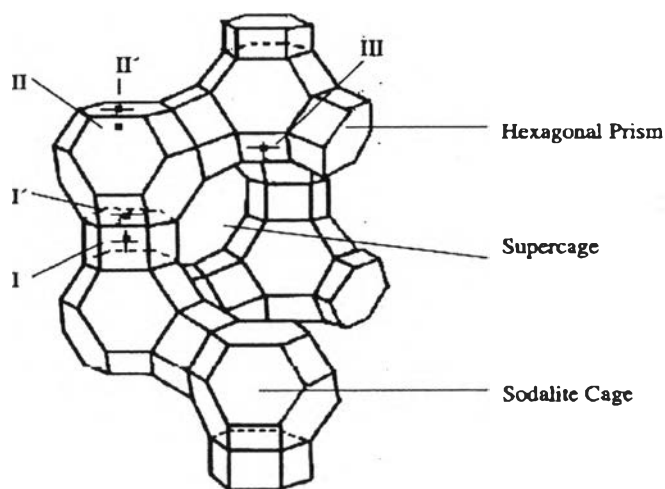
Thus, the crystalline aluminosilicates are often referred to as molecular sieves and separations performed with molecular sieves are generally thought to take place by a physical "sieving" of smaller from larger molecules appearing in the feedmixture. In the separation of aromatic hydrocarbon isomers, however, the separation of the isomers apparently occurs because of differences in electrochemical attraction of the different isomers and the adsorbent rather than on pure physical size differences in the isomer molecules (Priegnitz, 1980).

In a hydrated form, the preferred crystalline aluminosilicates generally encompass those zeolites represented by the Formula (2.6) below:



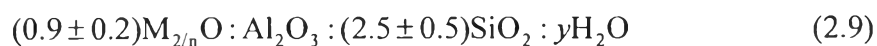
where  $M$  is a cation, which balances the electrovalence of the tetrahedra and is generally referred to as an exchangeable cationic site,  $n$  represents the valence of the cation,  $w$  represents the moles of  $\text{SiO}_2$ , and  $y$  represents the moles of water. The cations may be any one of a number of cations which will hereinafter be described in detail (Priegnitz, 1980).

Faujasite zeolites have several cations sites within their structure of sodalite cage units, tetrahedrally connected through sodalite hexagonal faces. Hexagonal and subsequent geometrical designations refer to the interconnecting framework of metal atom tetrahedra,  $MO_4$  (see Figure 2.5). The sodalite cage has an approximately 0.66 nm internal diameter with six-ring windows of approximately 0.26 nm. The sodalite interconnection creates a three dimensional structure with twelve-ring windows of approximately 0.74 nm in diameter about a “supercage” of approximately 1.18 nm diameter. The sodalite interconnections are hexagonal prisms whose six-rings are those of the adjacent sodalite cages. Cation sites I and I' are at the center of the hexagonal prism or on the hexagonal prism axis, offset toward the sodalite cages, respectively. Likewise II, II' are axial sites slightly offset from or nearly at the center of the sodalite six-rings, opening into the supercage, respectively. Site III is on the supercage side of a sodalite four-ring (Doetschman *et al.*, 2006).



**Figure 2.5** Faujasite X cage and the cation exchange sites I-III (Doetschman *et al.*, 2006).

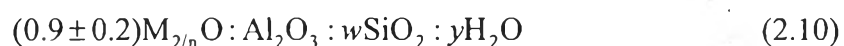
The type X structured zeolite in the hydrated or partially hydrated form can be represented in terms of mole oxides as shown in Formula (2.7) below:





where  $M$  represents at least one cation having a valence of not more than 3,  $n$  represents the valence of  $M$ , and  $y$  is a value up to about 9 depending upon the identity of  $M$  and the degree of hydration of the crystal. The cation  $M$  may be one or more of a number of cations such as the hydrogen cation, the alkali metal cation, or the alkaline earth cations or other selected cations, and is generally referred to as an exchangeable cationic site (Priegnitz,1980).

The type Y structured zeolite in the hydrated or partially hydrated form can be similarly represented in terms of mole oxides as in Formula (2.8) below:



where  $M$  is at least one cation having a valence of not more than 3,  $n$  represents the valence of  $M$ ,  $w$  is a value greater than about 3 up to 8, and  $y$  is a value up to about 9 depending upon the identity of  $M$  and the degree of hydration of the crystal (Priegnitz,1980).

The term "type X zeolite" and "type Y zeolite" as employed herein shall refer not only to type X structured and type Y structured zeolites containing sodium cations as the cation  $M$  indicated in the formulas above but also shall refer to those containing other additional cations such as cations included in Groups IA, IIA and the transition metals of the Periodic Table of Elements. Typically both the type X and type Y structured zeolites as initially prepared and as used as a base material for the special adsorbent described herein are predominantly in the sodium form. The term "exchanged cationic site" generally refers to the site in the zeolite occupied by the cation  $M$ . This cation, usually sodium, can be replaced or exchanged with other specific cations, such as those mentioned above, depending on the type of the zeolite to modify characteristics of the zeolite (Priegnitz,1980).

The type X or type Y zeolites containing a cation selected from the group consisting of Groups IA, IIA and the transition metals of the Periodic Table of Elements are suitable for separation in a two stage system of the isomers of chloronitrobenzene from a feed mixture comprising all three isomers. Particularly preferred adsorbents for both stages are those comprising type X or type Y zeolites containing

potassium cobalt or calcium at the exchangeable cationic sites. The adsorbents used in each stage may or may not have the same composition and if the composition is the same, the physically same adsorbent may or may not be utilized in both stages, however, it is preferred that the adsorbents used in each stage be physically distinct (Priegnitz, 1980).

Cationic or base exchange methods are generally known to those familiar with the field of crystalline alumino silicate production. They are generally performed by contacting the zeolite with an aqueous solution of the soluble salts of the cation or cations desired to be placed upon the zeolite. The desired degree of exchange takes place and the sieves are removed from the aqueous solution, washed and dried to a desired water content. It is contemplated that cation exchange operations may take place using individual solutions of desired cations to be placed on the zeolite or using an exchange solution containing a mixture of cations, where two or more desired cations are placed on the zeolite (Priegnitz, 1980).

## 2.8 Chloronitrobenzene Separation Process

Chloronitrobenzene isomers are used as chemical intermediates so it is necessary to obtain each isomer with a purity as high as possible. However, it is very difficult to achieve that by distillation due to their close boiling points. Other appropriate separations are considered *e.g.* crystallization, adsorption and fractionation.

Dunn (1986) from Philips Petroleum Company applied crystallization to separate CNB isomers in order to obtain high purity of *p*-CNB and *o*-CNB by a combination of crystallization and fractionation. The mixture consisting of 66.0 wt% *p*-CNB, 32 wt% *o*-CNB, 1 wt% *m*-CNB and 1 wt% di-nitrochlorobenzene was fed to the system. The composition of para isomer of feed was on the right side of eutectic point so para crystals were obtained when this mixture was cooled to the temperature approximately 14°C. The mother liquor was separated from the para crystals and fractionated to increase the concentration of *o*-CNB. This mixture was on the other side of the eutectic point. When it was cooled to the temperature approximately 14°C again, the ortho crystals were obtained. The eutectic depressant was eliminated due to the change of mixture component to the other side of eutectic point.

Guo *et al.* (2009) studied separation and selective adsorption of *o*-CNB and *p*-CNB by Silicalite-1 zeolite. The result showed that maximum adsorption amount of *p*-CNB was higher than those of *o*-CNB in the Silicalite-1 zeolite. Adsorption rate constant of *p*-CNB was higher than those of *o*-CNB due to two important factors, the adsorption temperature and the adsorption amounts. The purity of 94.9% *p*-CNB and 96.1% *o*-CNB was achieved from the appropriate adsorption conditions.

Funakoshi *et al.* (2001) examined the changes of agglomeration phenomena and purity of agglomerates 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 crystal was larger and its size was smaller, the agglomeration occurred. Moreover, the influences of agglomeration to the purity were considered. While the number of seed crystals and the number of element crystals were larger, the purity decreased from agglomeration.

Lerdsakulthong (2007) studied adsorptive separation of *m*- and *p*-CNB in the presence of FAU zeolites at static equilibrium conditions. This experiment varied type of zeolites, type of alkaline ion exchanged cations, and desorbents. For single component adsorption, *m*- and *p*-CNB could pass through the zeolite pore so adsorption mechanism was not controlled by the molecular diffusion. According to the molecular dipole moment, the Y zeolite preferentially adsorbed *m*-CNB more than *p*-CNB. The adsorption capacities increased with decreasing the size of cation due to the increase in the adsorbent acid strength. For 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 conditions. When desorbents were considered, nitrobenzene was the most suitable adsorbent.

Yensukjit (2008) investigated the adsorption of *m*- and *p*-CNB on the FAU zeolites with alkaline earth exchanged cations. For single component adsorption, the adsorption capacities of *m*- and *p*-CNB increased with the decrease in the cation size and the increase in the acid strength. *m*-CNB was selectively adsorbed more than *p*-CNB, and the Y zeolite could adsorb more than the X zeolite 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. Moreover, effects of adsorption and composition gradient during the experiment were observed, and the purity of *p*-CNB in the precipitates depended on the position and shape of them, and type of zeolites.

Pattanapaiboonkul (2009) studied 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*-CNB to rich in *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 more 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.