

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

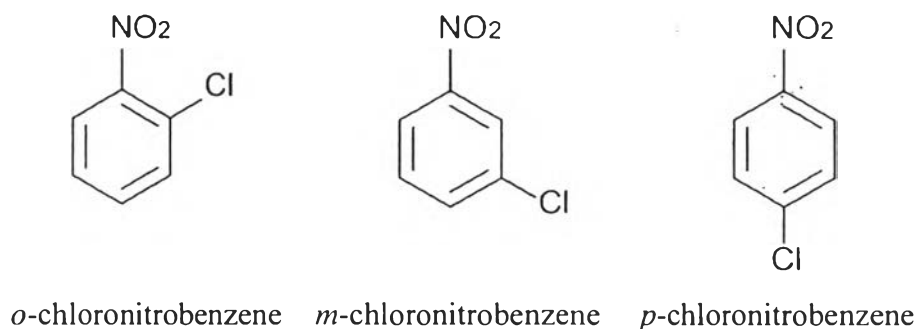
#### 2.1 Chloronitrobenzenes

Chloronitrobenzene (CNB) isomers are widely used as basic chemical intermediates in the manufacture of azo and sulphur dyes, rubbers, photograph film, antioxidants, gasoline additives, corrosion inhibitors, agricultural chemicals, pharmaceuticals, and industrial agents (Silva *et al.*, 2008). The industry is very interested in obtaining in pure form the para and ortho isomers of CNB. CNBs are produced commercially by chlorination of nitrobenzene (NB) and nitration of chlorobenzene (CB).

For nitration, CB is nitrated at 40-70 °C with a mixed acid consisting of 52.5 wt% sulfuric acid, 35.5 wt% nitric acid, and 12 wt% water. The product is a mixture of isomers containing about 34 wt% *o*-CNB, 65 wt% *p*-CNB, and 1 wt% *m*-CNB. 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 (Adkins, 1996; Demuth *et al.*, 2002).

For chlorination, this process produces an isomeric mixture containing *m*-CNB as the major product. NB dried by heating for several hours in a round-bottomed flask reacts with sufficient chlorine at 40-45 °C to produce a crude chlorination mixture containing unchlorinated NB, *m*-CNB, *o*-CNB, *p*-CNB, and dichloronitrobenzene (Bloom *et al.*, 1957). The reaction is carried out in complete absence of moisture; thus, the apparatus and starting materials must be dried (David and Blangey, 1949).

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.



**Figure 2.1** Three isomers of CNB (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)	$\Delta H_m$ (cal/mol)
<i>o</i> -CNB	246	32.5	1.305	4546
<i>m</i> -CNB	236	44.5	1.534	4629
<i>p</i> -CNB	242	83.5	1.520	4965

## 2.2 Crystallization

Crystallization is the process for the formation of solid crystals from a uniform solution. More than 80% of the substances used in pharmaceuticals, fine chemicals, agrochemicals, food and cosmetics are isolated or formulated in their solid form. Crystallization is in general the last chemical purification step in the production of ingredients. Since the properties of a solid material (polymorphism) can dramatically affect the process or the product's compliance and effect (dissolution rate for example), monitoring and controlling the isolation of solids for the various applications through crystallization is of paramount interest. Crystallization is also a chemical solid-liquid separation technique, in which mass

transfer of a solute from the liquid solution to a pure solid crystalline phase occurs (novasep.com). Crystals are grown in many shapes, which are dependent upon downstream processing or final product requirements. Crystal shapes can include cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic, and trigonal. In order for crystallization to take place, a solution must be "supersaturated". Supersaturation refers to a state, in which the liquid (solvent) contains more dissolved solids (solute) than can ordinarily be accommodated at that temperature (reciprocalnet.org).

### 2.2.1 Solution Crystallization

Crystallization from solution is a widely applied unit operation in both the pharmaceutical and bulk chemical industries for solid-liquid separations. Its extensive use is based on the fact that this single operation is both a separation and a purification process, whereby a solid crystalline product can be isolated with high purity and with relatively low capital and operating costs. The production of a solid-phase material provides a unique opportunity to control both the size and number of crystals produced. Typically for a pharmaceutical crystallization, the size and shape of the crystals are very important parameters. Product quality and efficacy are often contingent on adequate control of particle size and shape in the crystallizer. The size of material produced in a crystallizer can have a detrimental impact on downstream unit operations such as the filtration rate, drying, and formulation operations (Barrett, 2005).

### 2.2.2 Melt Crystallization

The melt crystallization, a clean technology with low energy consumption for the separation of organics (e.g. close boiling hydrocarbons, isomers, heat sensible materials) without using solvent, has found its wide applications in chemical, pharmaceutical, food and material industries (Kim and Mersmann, 1997). The principle of melt crystallization is to cool a melt in a controlled way to crystallize its fraction (Shan, 2012).

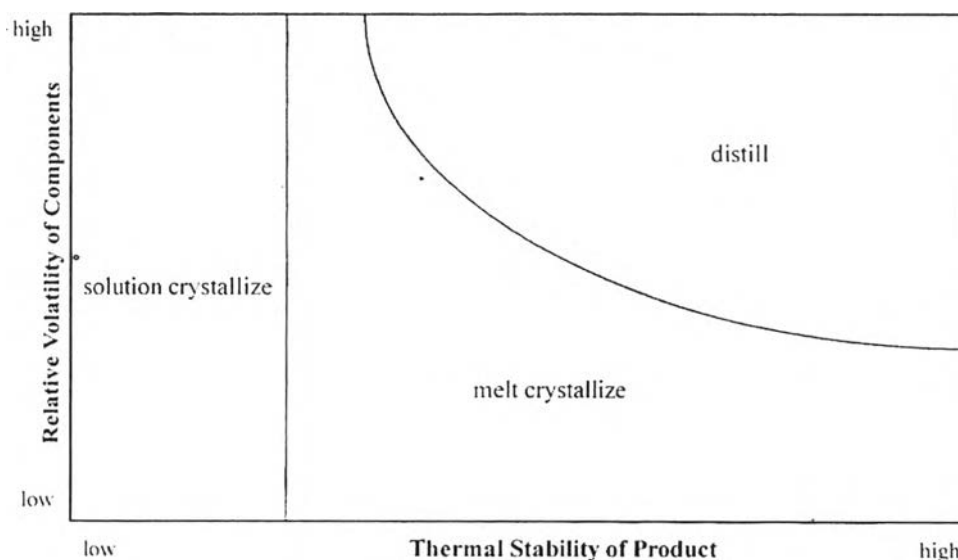
The differences between melt and solution crystallization are shown in Table 2.2. One major advantage of melt crystallization as a separation technology

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, 2002). 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). The advantages of melt crystallization are in the relatively low energy demand of the freezing process and in the high selectivity of crystallization. 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).

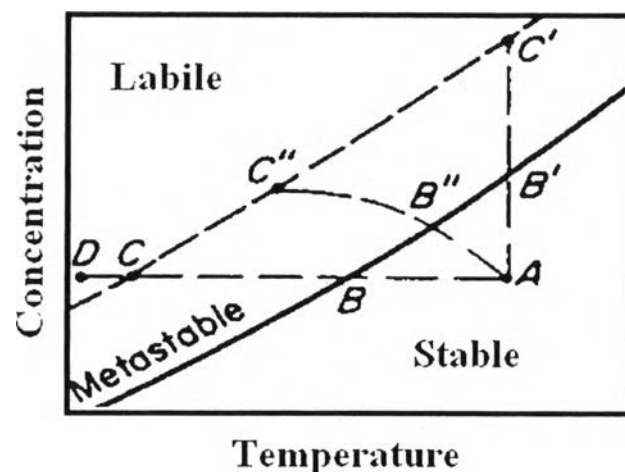
### 2.3 Saturation and Supersaturation

A solution that is in equilibrium with the solid phase is said to be saturated with respect to that solid. However, it is relatively easy to prepare a solution containing more dissolved solid than that represented by saturation condition, and such a solution is said to be supersaturated. Uncontaminated solutions in clean containers, cooled slowly without disturbance in a dust free atmosphere, can readily be made to show appreciable degrees of supersaturation. The state of supersaturation is a necessary feature of all crystallisation operations. ‘Labile’ (unstable) and ‘metastable’ supersaturation; refer to supersaturated solutions, in which spontaneous deposition of the solid phase, in the absence of solid nuclei, will and will not occur, respectively (Mullin, 2001).

The relationship between supersaturation and spontaneous crystallization leads to a diagrammatic representation of the metastable zone on a solubility-supersolubility diagram, as shown in Figure 2.3. 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 is 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 2.3** Solubility-Supersolubility Diagram (Mullin, 2001).

If a solution represented by point *A* in Figure 2.3 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. 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

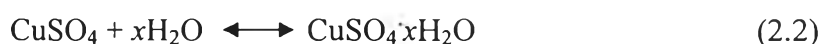
temperature. Penetration beyond the supersolubility curve into the labile zone rarely happens, as the surface, from which evaporation takes place is usually supersaturated to a greater degree than the bulk of the solution. Crystals, which appear on this surface, eventually fall into the solution and 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 "ABC" in Figure 2.3 (Mullin, 2001).

## 2.4 Phase Equilibrium

The amount of information that 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 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, 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; for instance, 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.

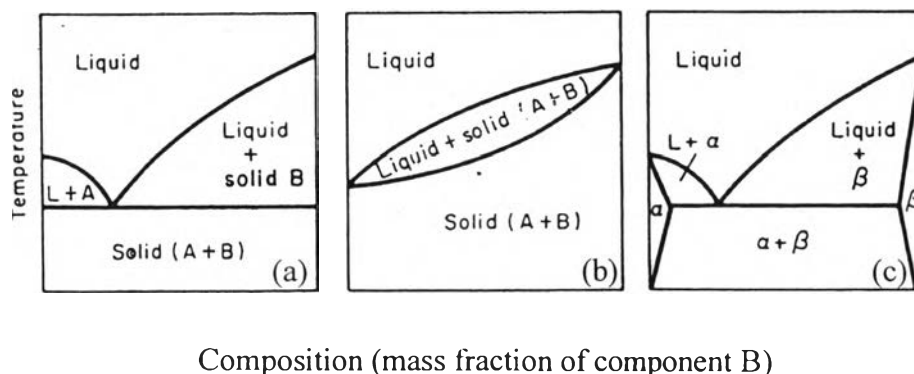
The three variables that can be considered in a system are temperature, pressure, and concentration. The number of these variables that may be changed in magnitude without changing the number of phases present is called the number of degrees of freedom. In the equilibrium system water-ice-water vapour,  $C = 1$ ,  $P = 3$ , 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 water-water vapour system,  $C = 1$ ,  $P = 2$ , 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).

#### 2.4.1 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 2.4a) 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. A binary eutectic system with limited solid solubility, which would prevent one-step crystallization from producing a pure component, is shown in Figure 2.4c (Mullin, 2001).

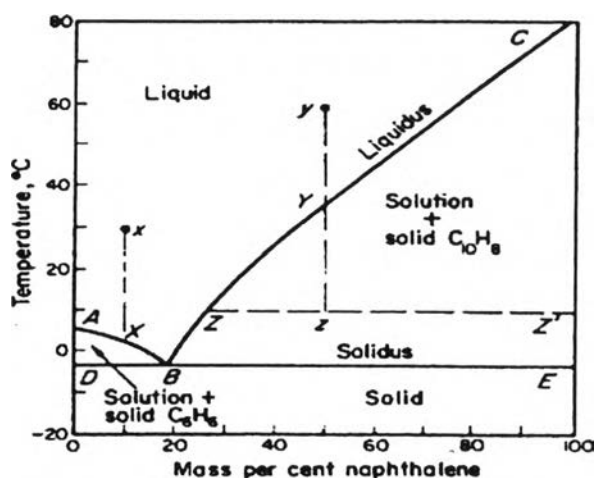




**Figure 2.4** Some binary solid-liquid phase diagrams encountered in melt crystallization: (a) simple eutectic; (b) simple solid solutions; (c) eutectic with limited solid solubility ( $\alpha$  and  $\beta$  are solid solutions) (Mullin, 2001).

#### 2.4.2 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 2.5. 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 2.5** 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  $A$  ( $5.5^{\circ}\text{C}$ ) 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  $zZ'$ .

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

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).

## 2.5 Product Quality

Product quality aspects of a crystalline material such as dissolution rate, stability, taste and colour generally can be related to solid form, crystal size distribution and purity. The crystal product quality is in turn determined by the subsequent processes taking place during crystallization: supersaturation generation, nucleation, crystal growth, secondary nucleation, and agglomeration (aidic.it).

### 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

The crystal size distribution (CSD) may, in fact, be referred to the number of crystals, the volume or the mass of crystals with reference to a specific size range, or the cumulative values of number, volume or mass of crystals up to a fixed crystal size. The first approach refers to a density distribution, whereas the second one to a cumulative size distribution. However, it is also useful to represent the CSD by means of a lumped parameter as an average size, the coefficient of variation, or other statistical parameters, which may be adopted for the evaluation of a given commercial product (Angelo, 2012).

The basic quantity in the theory of CSD 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, known as a function of  $L$ , the crystal size. The population density  $n$  is defined by Equation (2.4).

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

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).

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

Physisorption or physical adsorption is a type of adsorption, in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces, which cause physisorption.

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid)

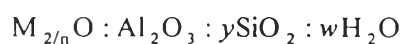
#### Common adsorbents

- Activated carbon - a char-like material with high surface area.
- Silica gel - hard, granular, porous material made by precipitation from sodium silicate solutions treated with an acid.
- Activated alumina - aluminum oxide activated at high temperature and used primarily for moisture adsorption.

Aluminosilicates (molecular sieves) - porous synthetic zeolites used primarily in separation processes (cpe.njit.edu).

## 2.7 X and Y Zeolites

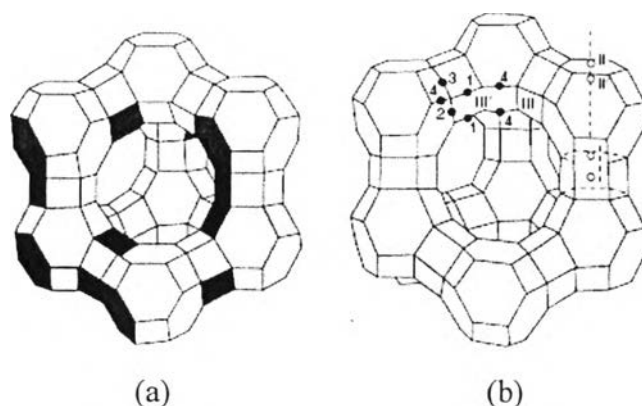
Zeolites indicate an important group of adsorbents being used in most commercial liquid separation processes. This is due to the high selectivity and adsorption capacity of zeolite adsorbents. Zeolites are crystalline aluminosilicates of group IA and group IIA elements, such as sodium, potassium, magnesium and calcium (Breck, 1974). Chemically, they are represented by the empirical formula:



where  $y$  is 2 – 200,  $n$  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 three-dimensional, four-connected framework of  $AlO_4$  and  $SiO_4$  tetrahedra linked to each other by the sharing of oxygen ions. Each  $AlO_4$  tetrahedron in the framework bears a net negative charge, which is balanced by an extra-framework cation. The framework structure contains intracrystalline 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 the micropores and voids, which may amount to 50% of the crystals by volume. The intracrystalline channels or voids can be one-, two- or three-dimensional. The preferred type has two or three dimensions to facilitate intracrystalline diffusion in adsorption and catalytic applications (Flanigen, 2001).

Unit cells of type X and type Y zeolites are shown in Figure 2.7. 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 2.6** 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 2.7. Each unit cell contains 192 SiO<sub>2</sub> and AlO<sub>2</sub> 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 2.7b. 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<sup>+2</sup> as the major cation, and Na<sup>+</sup> is the major cation for 13X zeolite. The BET surface area measured with N<sub>2</sub> for zeolites falls in the range between 500 and 800 m<sup>2</sup>/g (Yang, 2003).

## 2.8 Chloronitrobenzene Separation Process

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 crystallization technique cannot completely separate *o*-CNB and *p*-CNB into their pure form. From a mixture of these isomers, only one component is readily separated in pure form by crystallization, depending on the composition of mixture. 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 use 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 wt% *p*-CNB and 95.2 wt% *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 use of silicalite-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 wt% *p*-CNB and 96.1 wt% *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 increased 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 both X and Y zeolites with increasing in the cation size and the Y zeolite had a higher adsorption 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 became 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 composed 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.

Neaungjumnong (2011) investigated the effects of adsorbents (NaX, CaX, BaX, NaY, CaY, KY, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, activated carbon and glass bead) on equilibrium binary component adsorption of *m*-CNB and *p*-CNB. The crystallization of *m*- and *p*-CNB at the eutectic composition provided precipitates with the CNB composition at temperature 23.0 °C. Above the eutectic composition, the crystals was rich in *m*-CNB, 84.77 wt%, by cooling to 23.3 °C; At below the eutectic composition, the crystals was rich in *p*-CNB, 90.40 wt% by cooling to 23 °C. The adsorbents did not affect the feed solution composition but influenced the crystal composition. In the feed at the eutectic composition, the amorphous solids became crystal forms with the composition being rich in *p*-CNB. The crystal composition from the feed above the eutectic composition was shifted from being rich in *m*-CNB to rich in *p*-CNB. The crystallization of the feed solution with 10 grains of adsorbents had slightly higher *p*-CNB purity than that from the solution with 5 grains. The crystals near the adsorbents had higher *p*-CNB purity than those far from the adsorbents. The *m*-/*p*-CNB ratio of the crystals was independent on the type of the adsorbent but depend on the size of adsorbent.

Thiensuwan (2012) studied the effects of feed compositions on the *m*- and *p*-CNB crystallization on the phase diagram of *m*- and *p*-CNB with and without the KY zeolite was constructed. The phase diagram of *m*- and *p*-CNB without the zeolite showed that, below the eutectic composition, crystals were rich in *p*-CNB, while above the eutectic composition, the crystals were rich in *m*-CNB. At the eutectic composition, an amorphous solid composition close to the feed composition was obtained. Effects of the KY zeolite on the CNB feed solution compositions were investigated. The feed compositions before and after adding the zeolite were almost the same. It may be concluded that the KY zeolite did not significantly affect the feed composition. The phase diagram of *m*- and *p*-CNB with the zeolite looks like that without the zeolite but the crystallization temperature at the eutectic composition was shifted from 23 °C to 20 °C. The result after adding the zeolite in the feed with the eutectic composition showed the change from the amorphous solid formation to the crystal formation with the crystal composition rich in *p*-CNB. The feed at 65.0

wt% *m*-CNB with the zeolite, its crystallization resulted in the crystal rich in *p*-CNB instead of rich in *m*-CNB as in the case without the zeolite.

Jukkaew (2013) studied the effect of zeolites and amorphous materials on the phase diagram of chloronitrobenzenes. The crystallization with the addition of KY zeolite resulted in the crystal formation, not the amorphous solid as in the case, where this is no zeolite. The eutectic composition is 65.5 wt% *m*-CNB, which was about 3 wt% *m*-CNB higher in the *m*-CNB composition than the amorphous solid composition, 62.9 wt% *m*-CNB, from the system without the zeolite. In addition, the new eutectic temperature was about 4 °C lower, 18.5 °C compared to 22.9 °C. NaX zeolite was then chosen for the study as the zeolite has high *m*-CNB selectivity than the KY and BaX zeolites. It can be seen that the presence of the NaX zeolite resulted in about the same affects as the KY and BaX zeolites despite its high *m*-CNB selectivity. Activated carbon and silica gel were selected because of their low *m*-CNB selectivity. It can be seen that the eutectic temperature is 16.5 °C, which was lower than the one without the activated carbon. The activated carbon had about the same effect on the eutectic temperature as the zeolites. The eutectic temperature was about 5.0 °C lower than that without the silica gel. The same behavior can also be observed when the KY zeolite was changed to other zeolites, BaX and NaX zeolites, or amorphous material, activated carbon and silica gel. For *m*-CNB selectivity or event type of solid material in the CNB mixture, the presence of a solid material had more and less the same behavior. It may be explained that the added materials may act as impurity in the form of seeding and change the boundary between the stable zone and metastable zone.