

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. These isomers have particular utility as chemical intermediaries in various processes. CNBs are produced commercially by chlorination of nitrobenzene and nitration of chlorobenzene.

The chlorination of nitrobenzene produces an isomeric mixture containing the meta isomer as the major CNB constituent. This process occurs at 35-45 °C in the presence of iron (III) chloride, and *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).

The nitration of chlorobenzene produces product distribution of the ortho, meta and para isomers differ from that obtained by the chlorination of nitrobenzene (Cook, 1980). The main procedure of CNB uses a mixture of sulfuric acid, nitric acid, and water. 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. One of such procedures can be nitration of chlorobenzene with nitric acid alone. It was found that for nitration with 95 % HNO₃ the optimum conditions are as follows: molar ratio HNO₃/CB 2.5, reaction temperature 65 °C and residence time in the main and surge reactors 45 minute.

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 (Veretennikov *et al.*, 2001).

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

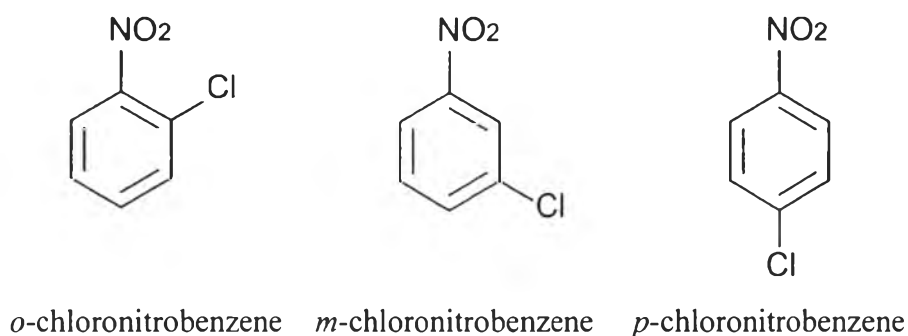


Figure 2.1 Three isomers of CNB (commons.wikimedia.org).

Table 2.1 Physical properties of chloronitrobenzene isomers (Dunn, 1967; drug-lead.com; Myerson, 2002)

Substances	Boiling point (°C)	Freezing point (°C)	Density (g/mL)	ΔH_m (cal/mol)
<i>o</i> -CNB	246	32.5	1.305	4,546
<i>m</i> -CNB	236	44.5	1.534	4,629
<i>p</i> -CNB	242	83.5	1.520	4,965

2.2 Crystallization

Crystallization is a chemical solid-liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. Crystallization is often used in chemicals synthesis because it can separate close-boiling mixtures and reduce damage to heat-sensitive materials and since it can obtain a pure compound in a single stage, crystallization is widely used as a purification step. Compared with distillation, crystallization also has many other advantages, such as low energy requirement and low-temperature operation

(Rogger, 1973). 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 (cheresources.com).

2.2.1 Solution Crystallization

In solution crystallization, the crystals are separated away from a solvent, often water. In the case of inorganic solids particularly, the operating temperature is far below their melting points (pacontrol.com).

Solution cooling crystallization is a widely used industrial separation technology, but there still exists many problems in its operation optimization due to the complicated process mechanism. In order to increase the mean size of crystal products and improve crystal size distribution (CSD), lots of operation policies such as optimized cooling profile and controlled supersaturation degree of system have been put forward. Among them, the method of loading seeds is of high effectiveness and is broadly applied in industrial production. Being different from the case of unseeded crystallization, the seeded crystallization process usually has lower nucleation rate and better CSD of products. This is because most solute molecules in solution are precipitated on the seed surfaces, when seeds are loaded (Huang *et al.*, 2010).

2.2.2 Melt Crystallization

Melt crystallization is a clean technology for the separation of organics without using a solvent. There are two different types of melt crystallization method; one of these applies a cold surface, on which a crystal layer is produced from the stable melt, and the other employs a simple stirred vessel, in which a crystal suspension is produced by cooling the entire melt. For recovery of the crystals formed, the former uses a temperature gradient technique or a mechanical device, and the latter uses subsidiary equipment such as filters and centrifuges. In melt crystallization as well as industrial crystallization by cooling, the liquid phase

is cooled in an indirect heat exchanger with metallic surfaces, through which heat is extracted from the solution. The main problems of these methods are low product purity, low heat transfer efficiency and high energy consumption (Kim and Mersmann, 1997).

In melt crystallization, two or more substances of comparable melting points are separated by some degree of cooling. The degree of completeness of such separations depends on the phase equilibrium relations. When the crystals must be refined to remove occluded substances, the recovered material may leave the process in molten form. Subsequently, it may be solidified as flakes or sprayed granules (pacontrol.com).

Melt crystallization is the most common technique to obtain a highly pure product from mixtures exhibiting such a behavior. However, melt crystallization is often not applicable for high melting compounds such as diastereomeric salts or heat sensitive materials such as amino acids. In addition, complete separation cannot be achieved if eutectic points are present. Therefore, using an appropriate crystallization solvent to reduce the viscosity, decrease the operating temperature, and overcome any eutectic limitation is an attractive alternative (Lin *et al.*, 2008).

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).

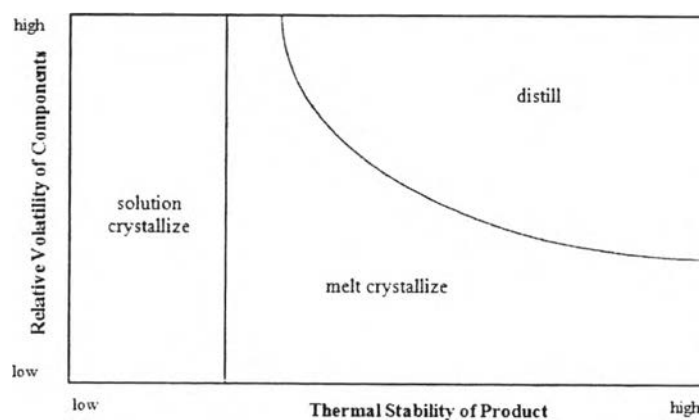


Figure 2.2 Application of melt crystallization in organic separations (Schweitzer, 1997).

2.3 Phase Equilibrium

The physical properties of chemistry were generally used with two or more phases. It can coexist in thermodynamic equilibrium with each other, with the nature of the transitions between phases, and with the effects of temperature and pressure upon equilibrium. Many superficial aspects of the subject are largely qualitative. For example, the empirical classification of types of phase diagrams but the basic problems always are susceptible to quantitative thermodynamic treatment, and in many cases, statistical thermodynamic methods can be applied to simple molecular models (answers.com).

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, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, CuSO_4 and H_2O , but for the purpose of applying the Phase Rule, there are considered to be only two components, CuSO_4 and H_2O , because the composition of each phase can be expressed by Equation (2.2).



A phase is a homogeneous part of 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 of 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 of 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

A phase diagram is a common way to represent the various phases of a substance and the conditions, under which each phase exists. A phase diagram is a plot of pressure (P or $\ln P$) vs. temperature (T). Lines on the diagram represent conditions (T, P), under which a phase change is at equilibrium. That is, at a point on a line, it is possible for two (or three) phases to coexist at equilibrium. In other regions of the plot, only one phase exists at equilibrium. 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).

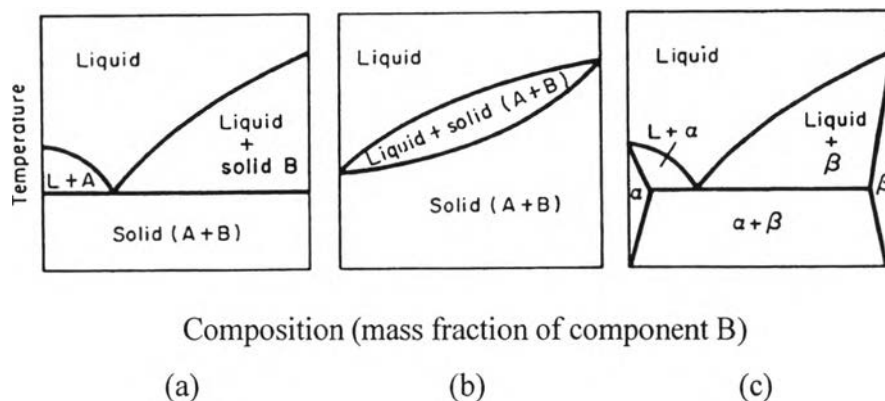


Figure 2.3 Some binary solid-liquid phase diagrams encountered in melt crystallization: (a) simple eutectic; (b) simple solid solutions; (c) eutectic with limited solid solubility (α and β are solid solutions) (Mullin, 2001).

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).

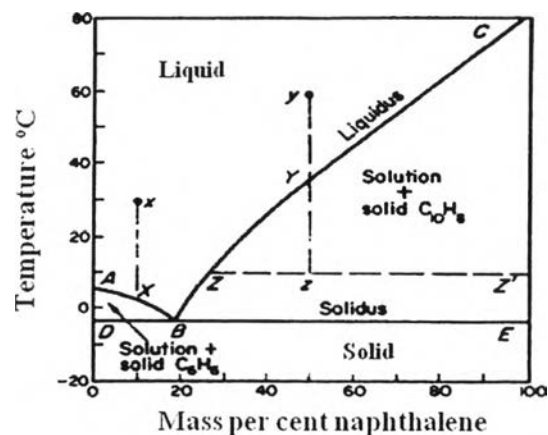


Figure 2.4 Phase diagram for the simple eutectic system naphthalene-benzene (Mullin, 2001).

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'*.

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

In industrial crystallization practice, many bulk-produced chemicals with 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 one that is in equilibrium with the solid phase and will remain unchanged indefinitely at a particular temperature and composition of other constituents. Greater than normal concentrations also can be maintained in what is called a supersaturated condition which is metastable. Metastability is sensitive to mechanical disturbances such as agitation, ultrasonics and friction, and the introduction of solid particles. Under those conditions, solids will separate out until normal saturation is obtained. When great care is taken, the metastable state is reproducible. A thermodynamic interpretation of metastability can be made in terms of the Gibbs energy of mixtures (pacontrol.com). 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.

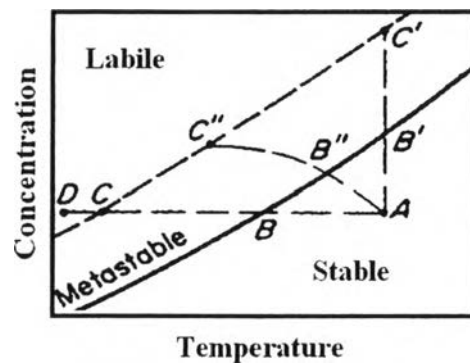


Figure 2.5 Solubility-supersolubility diagram (Mullin, 2001).

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 5 (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 (Kühberger and Mersmann, 1997). Requirements for crystal products are usually high purity, a specific crystal size distribution and a desired crystal shape (Samad *et al.*, 2010).

2.5.1 Purity

The purity of crystals depends on a variety of thermodynamical, kinetic, mechanical, fluid dynamic parameters, on the equilibrium distribution of impurities, the quantity and concentration of the impurity (König and Schreiner, 2001). For the melt crystallization, pure crystals will only be obtained if they are grown very slowly at near equilibrium conditions. Higher growth rates generally result in concentrated mother liquor being included into crystal mass.

Product particles from suspension type crystallizers are often agglomerated, and purity of such products is, in general, lower than that expected from the phase equilibrium. It is said that the purity of product particles becomes lower when crystals are agglomerated. Therefore, the decreasing of the product purity by agglomeration is a serious problem to the chemical and pharmaceutical industry. The mechanism of purity decrease by agglomeration is not clearly understood. The purity decrease of single crystals mainly occurs by inclusion of mother liquor into the crystals and by its adhesion on the crystal surfaces (Funakoshi *et al.*, 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 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

When crystallization processes involve a large number of crystals of varying sizes, a crystal size distribution (CSD) is needed to fully characterize the system. The study of CSDs is fundamental to understanding the dynamics, structure, and properties of condensed matter. Solid-liquid interactions give rise to nucleation, growth, and dissolution of crystals, processes that are described by the kinetics of deposition and dissociation at the solid-liquid interface (Giridhar and McCoy, 2002).

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).

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

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 process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process.

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 Zeolite

Zeolites are a large group of natural and synthetic hydrated aluminum silicates. It is commonly used as commercial adsorbents. They are characterized by complex three-dimensional structures that can accommodate a wide variety of cations, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and others (chemistryexplained.com). They are represented by the empirical formula:



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. 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



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).

Zeolites are produced in large amounts for various fields of industrial application. Large quantities of Y zeolites are used in cracking and hydrocracking

catalysts; A and X zeolites are used as ion exchangers in laundry detergents and for sorption and separation processes (Lechert *et al.*, 1996).

Faujasite is synthesized, as are other zeolites, from alumina sources such as sodium aluminate and silica sources such as sodium silicate. Other aluminosilicates such as kaolin are used as well. The ingredients are dissolved in a basic environment such as sodium hydroxide aqueous solution and crystallized at 70 to 300 °C (usually at 100 °C). After crystallization, the faujasite is in its sodium form and must be ion exchanged with ammonium to improve stability. The ammonium ion is removed later by calcination, which renders the zeolite in its acid form. Depending on the silica-to-alumina ratio of their framework, synthetic faujasite zeolites are divided into X and Y zeolites. In X zeolites, that ratio is between 2 and 3, while, in Y zeolites, it is 3 or higher. The negative charges of the framework are balanced by the positive charges of cations in non-framework positions. Such zeolites have ion-exchange, catalytic, and adsorptive properties. The stability of the zeolite increases with the silica-to-alumina ratio of the framework. It is also affected by the type and amount of cations located in non-framework positions. For catalytic cracking, the Y zeolite is often used in a rare earth-hydrogen exchanged form.

By using thermal, hydrothermal or chemical methods, some of the alumina can be removed from the Y zeolite framework, resulting in high-silica Y zeolites. Such zeolites are used in cracking and hydrocracking catalysts. Complete dealumination results in faujasite-silica (commons.wikimedia.org).

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 X zeolite are referred to as 12-ring, which remains the largest windows in zeolites today (Yang, 2003).

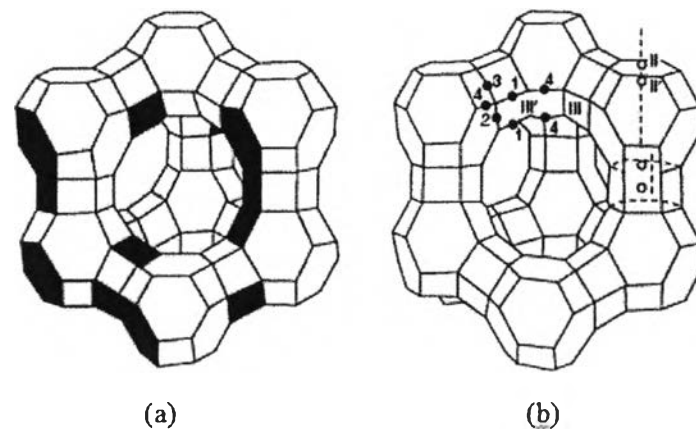


Figure 2.6 Line representations of zeolite structure: (a) ‘unit cell’ of types X and Y, or faujasite ; (b) cation sites in types X and Y (16 I, 32 I’, 32 II, 32 II’, 48 III, and 32 III’ sites per unit cell) (Yang, 2003).

The ratio of Si/Al in 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 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., $\text{Si/Al} = 1$ to 1.5) for X zeolite, and from 76 to 48 ($\text{Si/Al} = 1.5$ to 3) for 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 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).

Y Zeolite is the active component in catalysts for the processing of gas-oil by fluid catalytic cracking. However, the catalytic performance of this zeolite depends on the framework Si/Al molar ratio, and the increase of the silicon content improves its thermal and hydrothermal stability. Unstable Y zeolite (USY) is commonly prepared by postsynthesis treatments (Chatelain *et al.*, 1996). When used as a catalyst, the zeolite can be employed without modification or the catalytic properties can be altered by incorporation of, for example, metal clusters such as Pt. To achieve a deeper understanding of the catalytic process, locating the metal clusters in the zeolite is imperative. The primary need is to establish if the clusters are intrazeolitic, i.e. located inside the zeolite cavities and channels, or situated on the external surfaces of the zeolite. The system with platinum incorporated in Y or X zeolite has previously been investigated by transmission electron microscopy. Due to the instability of zeolites in the electron beam the crystals disintegrate rapidly leaving an amorphous residue. Recording images of crystals with intact, not beam-damaged, frameworks is very difficult and most of the previous reports are based on results from micrographs of zeolite crystals where the framework is damaged or completely amorphous. This poses a problem since the localization of the platinum clusters may be altered due to migration of the metal during the destruction of the framework. (Jan-Olov *et al.*, 1996).

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 is not complete separation *o*-CNB and *p*-CNB into their pure form. Because at 14 °C, the mixture is containing 33.5 wt% *p*-CNB and 66.5 wt% *o*-CNB. From a mixture of these isomers, only one component is readily separated in pure form by crystallization, depending on the composition of mixture. For the maximum recovery of *p*-CNB from a mixture comprising on 66 wt% *p*-CNB, 32 wt% *o*-CNB, 1 wt% *m*-CNB, and 1 wt% *di*-CNB at 14 °C and *p*-CNB was crystallized. 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 used 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) studied investigate The effects of adsorbents (NaX, CaX, BaX, NaY, CaY, KY, Al₂O₃, SiO₂, 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 provides 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 had influence on 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.