# CHAPTER I
# INTRODUCTION

Chloronitrobenzene (CNB) isomers consist of *m*-, *o*- and *p*-CNB. They 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. The CNB isomers are also used as raw materials in the syntheses of polyamides and have been recently investigated as a cathode material for magnesium reserved batteries (Ribeiro da Silva *et al.,* 2008). 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. The nitration of chlorobenzene produce products distribution of the ortho, meta, and para isomers, which is different from that obtained by the chlorination of nitrobenzene (Cook, 1980).

The industry is very interested in obtaining pure para and ortho isomers of CNB. These isomers have particular utility as chemical intermediates in various processes and have been very difficult to obtain because their separation by distillation is extremely difficult due to the close proximity of their boiling points (Dunn, 1967). In the case of chemical isomers having similar boiling points and solubilities, separation by crystallization can be advantageously employed (De Lano *et al.,* 1966). However, its drawback is that it does not provide a possible means for complete separation because of the presence of the eutectic point. To obtain higher purity of CNB, a combination of separation processes has been developed to the combination of crystallization and fractionation (Dunn, 1967).

High-purity chemicals can be obtained by further crystallization or distillation if these chemicals have different physicochemical properties. Separation becomes very difficult if the recovered mixture consists of isomers compounds. Thus, it is highly desirable to directly recover these high-purity chemicals by selective adsorption (Guo *et al.,* 2009). The process can recover a high quality product and reduce the energy costs. The efficiency of adsorptive separation depends on an adsorbent and desorbent. Adsorptive separation with a suitable adsorbent and

desorbent can separate the isomers by selectively adsorbing/desorbing desired products and excluding others.

Lerdsakulthong (2007) investigated adsorptive separation of *m*- and *p*-CNB on FAU zeolites using static equilibrium condition. The Y zeolite adsorbed *m*-CNB more than *p*-CNB. The adsorption capacities increased with the decrease in the size of the cation due to the increase in the adsorbent acid strength. 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. 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. Pattanapaiboonkul (2009) and Yairit (2010) studied the influence of feed compositions on precipitate composition and crystallization temperature. The crystallization of *m*- and *p*-CNB at the eutectic composition provided precipitates with the CNB composition. Above the eutectic composition, the crystals were rich in *m*-CNB. Below the eutectic composition, the crystals were rich in *p*-CNB. The effects of number of a zeolite showed that the feed solution with 5 grains of the zeolites has high *p*-CNB compositions than that from 10 grains of the zeolites. In the feed above the eutectic composition, the zeolites can shift the precipitate composition from being rich in *m*-CNB to *p*-CNB. Neaungjumnong (2011) investigated the effects of adsorbents (NaX, CaX, BaX, NaY, CaY, KY, $Al_2O_3$, $SiO_2$, activated carbon and glass bead) on equilibrium binary component adsorption of *m*-CNB and *p*-CNB. The adsorbents did not affect the feed solution composition but had influenced the crystal composition. 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.

The objective of this work was to study the crystallization of CNB to obtain an insight on how the presence of a zeolite on other adsorbents affects the phase diagram of the *m*- and *p*-CNB mixture.