

CHAPTER I

INTRODUCTION

Chloronitrobenzenes (CNBs) are important intermediates in the preparation of dyes, pharmaceuticals, and pesticides. There is a particularly high demand for *o*-CNB about 35%. *p*-CNB, too, has a number of industrial uses. Since there are only very limited industrial applications for *m*-CNB, its production is generally undesired (Demuth *et al.*, 2003). CNBs are produced commercially by chlorinating nitrobenzene and nitrating chlorobenzene. The components of each isomer product depend on the process that is chosen in the production. To obtain a specific purity of each isomer, a separation process is needed (Priegnitz, 1980).

Adsorption is one of the suitable techniques that are used to separate CNBs into a pure form (Roberto, 1974). It consists of two main pathways: adsorption and desorption, where FAU zeolites are frequently used as an adsorbent in the chemical industry due to their high selectivity and adsorption capacity. It can decrease energy consumption and provide a high-purity product (McCabe *et al.*, 2005). Moreover, an appropriate adsorbent is an important factor in the adsorptive separation. The other attractive technique for separating CNB isomers is crystallization, which can be carried out either in the presence of solvent (solution crystallization) or the absence of solvent (melt crystallization) (Roberto, 1974).

Crystallization is considered to be commercially attractive since it offers potentially low-energy separation compared with distillation because latent heats of fusion are generally much lower than latent heats of vaporization (Mullin, 2001). 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 CNBs, a combination of separation processes has been developed such as the combination of crystallization and fractionation for CNB separation (McCabe *et al.*, 2005).

Lersakulthong (2007) examined adsorptive separation of *m*- and *p*-CNB on FAU zeolites using static equilibrium condition. The FAU zeolite adsorbed *m*-CNB more than *p*-CNB. The adsorption capacity increased with the decrease in the size of the cation. Yensukjit (2008) studied the adsorption of *m*- and *p*-CNB on the FAU

zeolites with alkaline earth exchanged cations under static conditions. The adsorption capacity of *m*- and *p*-CNB on both X and Y zeolites with increasing in the cation size and the Y zeolite was a higher than the X zeolite. Pattanapaiboonkul (2009) 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. Yairit (2010) studied the effects of number of a zeolite and showed that the feed solution with 5 grains of the zeolite had high *p*-CNB composition than that from 10 grains of the zeolite. Neaungjumnong (2011) investigated 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 adsorbents influenced the crystal composition but did not affect the feed solution composition. The crystals near the adsorbents had higher *p*-CNB purity than those far from the adsorbents. Thiensuwan (2012) studied the effects of feed compositions on the *m*- and *p*-CNB crystallization. The phase diagram of *m*- and *p*-CNB with and without KY zeolite was constructed. 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 objective of this work was to study the crystallization of CNB to obtain an insight on how the presence of a zeolite or other adsorbents affected the phase diagram of the *m*- and *p*-CNB mixture. Emphasis was on the eutectic composition, where it was expected that the present of the adsorbent may significantly affect the crystallization.