Group Contribution Approach in Simulation of DEC Separation Technique

Asghar Lashanizadegan[1] - Shahabedin Ayatollahi[2]

1- Yasuj University, Yasuj, Iran
2- Shiraz University, Shiraz, Iran
alashani@hotmail.com

ABSTRACT

Based on chemical equilibria in acid-base reactions and on precipitation of the resulting compounds in dissociation extractive crystallization (DEC) process, a separation model has been developed. The model utilizes the modified UNIFAC group contribution method. The validity of the model has been assessed by the experimental results achieved in the separation of *o*- and *p*-chlorobenzoic acids. The results have been compared with those obtained from the experiments at various concentrations and temperatures on predicted ternary diagrams.

Keywords: Simulation; UNIFAC; Chlorobenzoic acids; Dissociation extractive crystallization

Introduction

DEC process have been employed over the last decade for the separation of various industrial important mixtures of closely related isomeric and non-isomeric acids and bases [1-5]. All of the references reported the efficacy of the process in the separation of binary systems [6]. In this work, the specific objective of the theoretical study was to develop a predictive thermodynamic model based on a modified UNIFAC group contribution method that can be used to determine the concentrations of all species as well as the effectiveness of the process. In order to evaluate the validity of the model, separation of *o*-chlorobenzoic (*o*-CBA) and *p*-chlorobenzoic (*p*-CBA) has been experimentally investigated and the results are compared with the predicted ones.

From the screening procedure, methanol was found to be a suitable solvent for the separation of *o*-CBA and *p*-CBA, using piperazine as the reagent in the DEC technique [7]. Here, first the chemistry of acid-base reactions in methanol is considered. Secondly, a thermodynamic model is presented to predict the concentration of all species at the equilibrium state. Finally, the theoretical results are compared with those obtained from experiments. The details of separation experiments is reported in the previous paper [3].

Physicochemical aspects

Methanol is an amphiprotic solvent in which acid-base equilibria are similar to those in water. The autoprotolysis constant which expresses the ability of methanol to dissociate into the lyonium ion ($CH_3OH_2^+$) and lyate ion (CH_3O^-) is about 10^{-16}. The dissociation constants of *o*-/*p*-CBAs in methanol are 5.02×10^{-9} and 1.48×10^{-9}, respectively. When *o*-CBA and *p*-CBA are dissolved in methanol, because they are stronger acids than methanol, the following reactions are established:

$$\text{(1)}$$