

CHAPTER I

INTRODUCTION

Separation of azeotropic or close boiling mixtures is a challenging task in various chemical processes. An azeotrope can be either homogeneous, containing completely miscible mixtures—a single phase, or heterogeneous, composed of two liquid phases. Approximately 90% of all azeotropic mixtures are homogeneous (Lide, 2001). Separation of these mixtures cannot be done by simple distillation. There are several potential processes used for separating azeotropes: extractive distillation, azeotropic distillation, pressure swing distillation, liquid–liquid extraction, adsorption, and membranes (Pereiro *et al.*, 2012). The most common and efficient separation process in the azeotropic systems is the extractive distillation. This technique involves adding a new heavy chemical compound, namely an entrainer, to remove one of the components in the azeotrope, thus altering the relative volatility of the mixture (Pereiro *et al.*, 2012). Volatile organic solvents are commonly used as conventional entrainers in extractive distillation; however, there are a lot of disadvantages as they produce volatile organic compound (VOC) emissions and require high energy consumption (Li *et al.*, 2009).

With an increasing concern about environmental issues, in addition to the new principles of green chemistry, ionic liquids (ILs) as “green solvents” or “designer solvents” have recently become attractive replacement options for many conventional organic solvents used in extractive distillation due to their many unique structures and properties including non-volatility, non-flammability, thermal stability, high dissolvability—as well as good performance in altering the relative volatility of the azeotropic mixtures (Li *et al.*, 2009, Pereiro *et al.*, 2012). As “designer solvents”, the chemical and physical properties of an ionic liquid can be tuned or tailored for use in a multitude of specific applications by an optimal design or selection of the cation, anion, and cation alkyl chain length (Pereiro *et al.*, 2012, Roughton *et al.*, 2012). Hence, ILs can be fine-tuned with specific properties to perform as an excellent entrainer in the extractive distillation processes and help reduce the energy consumption and environmental impact as compared to the

conventional organic solvents (Seiler *et al.*, 2004, Pereiro *et al.*, 2012, Roughton *et al.*, 2012).

The main problem with designing or selecting an ionic liquid as an entrainer is the tremendous number of variations of cation and anion combinations (Holbrey and Seddon, 1999). It is too time-consuming and too cost-intensive to conduct experiments (Jork *et al.*, 2005). Predictive thermodynamic property models and methodology/tools for screening optimal ionic liquid entrainers clearly show a reduction in experimental work and optimizing of the energy consumption for azeotropic separation.

The purposes of this research are to improve the methodology for the screening of ILs as entrainer and for the design of ILs-based separation processes in various homogeneous binary azeotropic mixtures, and to improve design flexibility for other azeotrope series. Starting from first screening ILs based on their stability, toxicity, and environmental impacts. Then, ILs are further screened based on their miscibility with the target solute component and their Hildebrand solubility parameters. For the final evaluation, an extractive distillation column and IL recovery column are designed and simulated to determine the optimal process for IL-based separation of homogeneous azeotropic systems. The design flexibility for azeotropic separation process with the same IL entrainer and product purity and other design parameters, such as reflux ratio, number of stages, feed stage location, and IL flow rate, were investigated with respect to the change in size of the alcohol (carbon numbers of the alkyl part of the alcohol).