

CHAPTER I

INTRODUCTION

One of several challenging problems in the petrochemical and chemical fields is a separation of azeotropic and close-boiling mixtures (Earle *et al.*, 2006). The mixtures cannot be easily separated by a simple distillation because the vapor phase has the same composition as the liquid phase. Most of them are binary homogeneous mixtures classified as two main systems; (1) aqueous systems (i.e. one component in the mixtures is water e.g. water + ethanol mixture) and (2) non-aqueous systems such as alcohol + aliphatic hydrocarbons system (e.g. ethanol + hexane mixture), aromatic + aliphatic hydrocarbons system (e.g. benzene + hexane mixture), aromatic + cyclic hydrocarbons system (e.g. toluene + methylcyclohexane (MCH) mixture), and aromatic + aromatic system (e.g. ethylbenzene (EB) + p-xylene (PX) mixture) (Lek-utaiwan *et al.*, 2008, Martínez Reina *et al.*, 2012, Pereiro *et al.*, 2012, Kulajanpeng, 2014).

Several alternative technologies for separation processes have been developed to solve this problem, for instance, adsorption, extraction, membranes and advanced distillations (e.g. azeotropic distillation, extractive distillation and pressure swing distillation) (Pereiro *et al.*, 2012). Extractive distillation (ED) is the most efficient separation process considering on its energy consumption, solvent usage and total economic cost (Julka *et al.*, 2009). As consequence of ED technique involving with adding a heavy chemical (entrainer) to extract one of the components in the azeotropic mixtures (i.e. target solute), the separation of the azeotrope can be done by breaking the azeotrope and increasing the relative volatilities of the mixture (Pereiro *et al.*, 2012). However, various liquid solvents, solid salts and hyperbranched polymers (Hypol) previously used as conventional entrainers may cause some environmental impacts such as volatile organic compounds (VOC) emitted to the atmosphere (Lei *et al.*, 2003). A number environmental issues and economic aspects are more convinced gradually to figure out how to select the suitable entrainer (Momoh, 1991, Kerton *et al.*, 2013).

Ionic liquids (ILs) are proposed as the eco-friendly innovative compounds, which are initially synthesized from a simple anion, cation and alkyl chain (on

cation) until have been well-known as “green solvents” or “designer solvents” (Rogers *et al.*, 2002, Zhao *et al.*, 2005). Owing to the flexibility of ILs in design, group contribution (GC) methods are determined to tailor their molecular structure and predict their critical properties (Valderrama *et al.*, 2009). In addition, the other properties of ILs such as thermal stability, non-volatility and non-flammability as well as a good performance of azeotropic separation are expressed that ILs are suitable to be the most potential replacement used entrainers in the extractive distillation (Kulajanpeng, 2014).

Nevertheless, the design and selection of the suitable ILs as entrainers has been the significant topic of discussion so far. To screen of ILs as entrainers and design of the best IL-base separation process, a systematic methodology established is not only the best tools to demonstrate but also helps a reduction of extensive experimental works and a minimization of the energy requirement and solvent usages (Roughton *et al.*, 2012).

According to the previous systematic methodology of Kulajanpeng (2014), only aqueous system was successfully demonstrated using Hildebrand solubility parameter along with the miscibility of ILs with the target solute as a key parameter in the screening criteria. The best IL-based separation process provides ED column and IL recovery column, consists of flash evaporation and stripper, were designed and simulated by ProII program (Kulajanpeng, 2014).

In this work, the objectives of the research are to prove whether this proposed methodology of Kulajanpeng (2014) is still viable in non-aqueous systems or not and further develop it for generic systems through the demonstration of five case studies; water + ethanol, ethanol + hexane, benzene + hexane, toluene + MCH, and EB + PX mixtures. The improved systematic methodology are composed of three main stages; selection (i.e. mixture selection, separation process selection and IL pre-selection), verification (i.e. verification of mixture and IL), and comparison (i.e. VLE, simulation and economic comparison). The part of screening criteria, Hildebrand solubility parameter along with capacity and selectivity of ILs with the target solute are more effectively used as a key parameter instead of the miscibility of ILs. Furthermore, the investigation of the mixture behavior, confirmed target solute and separation capability of ILs are considered in verification stage of this improved

methodology. The best IL-based separation process including ED column and flash evaporation as IL recovery is finally selected through the comparison results from separation capability of ILs, the terms of energy requirement and solvent usages from simulation process and the economic evaluation in order to get a supported decision-making in an investment compared to conventional solvents. In conclusion, the four best ILs were successfully identified, i.e. [MMIM][DMP] from ethanol + water, [EMIM][BTI] from ethanol + hexane mixture, [EMIM][EtSO₄] from benzene + hexane mixture, and [HMIM][TCB] from toluene + (MCH) mixture. Unfortunately, the proposed screening criteria cannot effectively demonstrate with the isomer mixture, i.e. EB + PX mixture in this case, due to the similarity of these isomers causing no differences of two feasible target solutes in calculated Hildebrand solubility parameter, selectivity and capacity. Beyond that, best ILs in this contribution was obtained from available IL data from literature database at the moment. If possible in the future work, the IL database is suggested to be updated and re-run to seek for the best ILs in the other particular azeotropic systems since IL data have been reporting continuously.