Systematic screening methodology and energy efficient design of ionic liquid-based separation processes

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ABSTRACT

A systematic methodology for the screening of ionic liquids (ILs) as entrainers and for the design of ILs-based separation processes in various homogeneous binary azeotropic mixtures has been developed. The methodology focuses on the homogeneous binary aqueous azeotropic systems (for example, water + alcohols). Additionally, a Hildebrand solubility parameter group contribution model for ILs, and ILs miscibility database have been developed to screen the miscibility of the ILs with the target solute component and these parameters are considered as the main criteria for the screening of ILs. ILs were further screened based on a combination of criteria such as stability, toxicity, and their environmental impacts. All best ILs were used as entrainers, and an extractive distillation column (EDC) and ionic liquid recovery column were designed and simulated with a process simulator to determine the overall energy consumption of the ILs-based separation processes. Among all candidates, the best IL was selected based on the minimum energy requirement obtained from the simulation. Finally, the modification of the separation process to obtain design flexibility for other azeotropic series with respect to the change in size of the target solute was investigated using the same separation process and IL entrainer to obtain the same product purity. The proposed methodology has been evaluated through a case study of binary alcoholic aqueous azeotropic separation: water + ethanol and water + isopropanol.

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1. Introduction

Azeotropic or close boiling mixtures are widely observed in the chemical, petrochemical and/or biochemical industries, especially, a homogeneous azeotropic mixture, containing completely miscible mixtures in a single phase (Lide, 2005). Since the concentrations of vapour and liquid are the same at the azeotropic point, these mixtures cannot be efficiently separated by using a simple distillation. The separation of these mixtures still remains a challenging task in chemical engineering field. Several enhanced distillation-based separation techniques are used for azeotropic separation, namely, extractive distillation (ED), azeotropic distillation, and pressure swing distillation (Li et al., 2007). ED exhibits the most common and energy efficient separation processes comparing to others (Pereiro et al., 2012; Quijada-Maldonado et al., 2014). By

introducing an external chemical compound called an entrainer: a miscible, high boiling, and relatively non-volatile solvent, one of the components in the azeotrope can be removed, thus the relative volatility of the mixture is altered, allowing the mixtures to be separated.

With respect to an increasing concern of the environmental issues, in addition to the new green chemical principles, ILs have been proposed as solvents used in ED that do not cause environmental problems like traditional solvents that have a VOC problem (for example, benzene and other aromatic solvents) (Boschetti et al., 2007). Therefore, a clean separation process which reduces pollutant emissions at the source is being proposed, with less waste (Lei et al., 2014; Pereiro et al., 2012; Seiler et al., 2004). The global interest in ILs is due to their unique excellent properties, i.e., non-volatility, non-flammability, thermal and chemical stability, and high dissolvability, including a wide range of solubilities and miscibilities (Freemantle, 2010; Li et al., 2009; Pereiro et al., 2012). ILs are also recognized as "designer solvents" since the physical, chemical and biological properties of ILs can be "tuned" or "tailored" for specific

applications through the design/selection of cation, anion, and alkyl chain length of the cation (Gutiérrez Hernández, 2013; Karunanithi and Mehrkesh, 2013; McLeese et al., 2010; Pereiro et al., 2012; Roughton et al., 2012). It seems highly probable that this feature will also allow the toxicity of ILs (Biczak et al., 2014) and their environmental impact to be reduced (Ventura et al., 2013). Hence, the ED processes with fine-tuned ILs as entrainer have been chosen and considered as the method to reduce energy consumption, material demands, and environmental impact. Consequently, ILs can be also recycled with high purity in the recovery processes (Gutiérrez Hernández, 2013; Mai et al., 2014; Pereiro et al., 2012; Roughton et al., 2012; Seiler et al., 2004). However, the designing or selecting of IL as an entrainer by trial-and-error method is time-consuming and cost-intensive to conduct experiments due to the tremendous number of variations of cation, anion, and alkyl chain length combinations (Holbrey and Seddon, 1999; Plechkova and Seddon, 2008). This presents a great challenge to determine optimal IL as entrainer for azeotropic separation with a smaller subset of suitable candidates from the large number of the feasible ILs.

Several efforts have been reported on the development of methodology/tool for design of ILs used in ED processes. Gutiérrez et al. (2012) presented thermodynamic and phase stability analyses concept to select the ILs as entrainer using a quantum chemical based "conductor-like screening model for real solvents" (COSMO-RS) to predict the activity coefficients and selectivity at infinite dilution of solutes in ILs by COSMOtherm software. However, the COSMO-RS only provided qualitative results (Diedenhofen and Klamt, 2010; Gutiérrez et al., 2012; Jork et al., 2005; Verma and Banerjee, 2010). A continuing work from the same research group, Meindersma et al. (2012), presented a conceptual process designs and pilot plant experiments of the ethanol + water separation for both the conventional solvent and selected IL as entrainer. Later, Roughton et al. (2012) reported the development of methodology/tool for the simultaneous design of ionic liquid used as entrainers and azeotropic separation processes using a computer-aided molecular design (CAMD) method, and group contribution (GC) models. A Hildebrand solubility parameter GC model for ILs was employed to screen the designed IL with the nearest value to a specific azeotropic concentration. Nevertheless, a small range of solubility parameter group contributions may not have covered sufficient number of the potential ILs studied in this work. Their proposed methodology was applied for acetone + methanol and ethanol + water azeotropic separation processes, whereas, the overall process designs was based on the proposed IL-based azeotropic separation process by Seiler et al. (2004). The results significantly showed a reduction in experimental work and optimizing of the energy consumption as well as less solvent usage for azeotropic separation.

Although, various predictive property models and methodologies/tools for IL selection have been reported in literature in recent years, the integrated and systematic methodology for screening, and design efficient separation process, as well as the design flexibility study is still limited in the ILs-based separation. This has led to the aim of this paper to improve/develop the systematic methodology for the screening of ILs as potential solvents and for the design of ILs-based separation processes to provide an energy efficient separation process that is clean from an environmental point of view and efficient from separation efficiency and energy consumption points of view in various homogeneous binary azeotropic mixtures, and to improve the design flexibility for other azeotrope series in order to obtain the conceptual process design.

2. Screening methodology and tools

The previous methodology proposed by Kulajanpeng et al. (2014) and Roughton et al. (2012) was adopted and applied in this work to develop a new systematic methodology for the screening of ILs as entrainers and for the design of ILs-based separation processes in various homogeneous binary azeotropic mixtures. The overall methodology including the descriptions is shown in Fig. 1. Several experimental data, predictive property models, as well as tools were required. The supporting database and the predictive models have been developed for this work, namely, an ILs miscibility database, and an extended Hildebrand solubility parameter GC model for ILs. A knowledge base and an extended Hildebrand solubility parameter GC model were used to create and screen all potential feasible candidates (Steps-1&2). ICAS-utility toolbox and PRO/II were used to design and simulate the separation processes (Steps-3&4). The Non Random Two Liquids (NRTL) model was employed in this work to predict the vapour−liquid equilibrium (VLE) of the ternary systems containing the ILs. The ease of NRTL parameters can be utilized in several simulation packages, such as ICAS-utility toolbox, and PRO/II which was applied in this work.

2.1. IL selection methodology

The proposed methodology of this work consists of four main steps: generation of ILs miscibility database (step-1); ILs screening (step-2); design and simulation of separation process based on minimum energy requirement (step-3); modification of the separation process to obtain design flexibility for other azeotropic series (step-4). A list of the needed methods, models and tools in the approach is outlined in Table 1.

2.1.1. Step-1: generation of ILs miscibility database
The purpose of this step is to create the ILs miscibility database. The ILs miscibility database was considered through the plot between the solubility (x_i) of ILs in the target components against the Hildebrand solubility parameter (δ_i) of ILs. The extended Hildebrand solubility parameter GC model was employed to predict the Hildebrand solubility parameter of the ILs, the details of which are given in Section 3.2.1.

The solubility (x_i) of ILs in the target component for poorly miscible liquids can be estimated to the infinite−dilution activity coefficient (Batista et al., 2011) by

$$x_i = \frac{1}{\gamma_i^\infty} \tag{1}$$

where γ_i^∞ is the infinite−dilution activity coefficient of the component *i*. The γ_i^∞ can be taken from the literature and/or calculated from predictive thermodynamic models, i.e., UNIQUAC, UNIFAC, or NRTL models. Due to availability of the experimental data in recent years, the γ_i^∞ and/or x_i used in this work were collected from (Klähn et al., 2010; Pereiro et al., 2012). It should be noted that the solubility of ILs in the target components is the mole fraction of IL in the target solute component. To ensure total miscibility of IL in the target solute component, the solubility should be equal to unity to avoid any phase splitting.

2.1.2. Step-2: screening of ILs
This step is aimed to find a set of feasible IL candidates as entrainer for the aqueous azeotropic systems. A feasible set of no more than 5 ILs are selected based on their miscibility, stability, toxicity and environmental impact. Then, all of these best candidates will be used as entrainer in the ED processes in the next step.