Simulation based ionic liquid screening for benzene–cyclohexane extractive separation

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HIGHLIGHTS

- $[C_4mim][AlCl_4]$ is selected as proper solvent to separate benzene and cyclohexane.
- COSMO-RS is applied to screen solvent from combinations of 12 cations and 22 anions.
- Interaction between ionic liquids and benzene is investigated by DFT calculation.
- Continuous extraction processes are simulated using $[C_4mim][AlCl_4]$ and sulfolane as solvent.

ARTICLE INFO

ABSTRACT

In order to screen ionic liquids (IL) as suitable solvents for the separation of benzene and cyclohexane, the extraction efficiency of ILs (12 cations and 22 anions) was estimated based on COSMO-RS predictions of infinite dilution activity coefficients of benzene and cyclohexane in different ILs..$[C_4mim][AlCl_4]$ was found to be the most promising solvent. To provide deep insight on how the IL structure influences the extraction efficiency, molecular interactions between IL ions and benzene were determined from DFT calculations. Moreover, liquid–liquid equilibrium data of the ternary system benzene–cyclohexane–$[C_4mim][AlCl_4]$ were experimentally determined and used to fit parameters of the NRTL activity coefficient model. Based on the NRTL model the continuous extraction process was simulated and compared with a reference process using sulfolane as solvent. For the extraction process using $[C_4mim][AlCl_4]$, high cyclohexane product purity (99.65 wt%) and high benzene recovery efficiency (98.03%) can be reached with at much lower energy consumption and higher product yield compared to conventional extraction solvents. In conclusion, the ionic liquid $[C_4mim][AlCl_4]$ is a promising solvent for the extractive separation of benzene and cyclohexane.

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1. Introduction

As an important industrial chemical, cyclohexane can be produced by catalytic hydrogenation of benzene. Due to the limitation of the reaction equilibrium, non-converted benzene is entrained into the cyclohexane product and must be removed. Since benzene and cyclohexane have very close boiling points and can even form an azeotrope, it is difficult to separate this mixture. In industry, the separation is commonly achieved by liquid–liquid extraction using organic compounds, such as sulfolane, as the solvent. In current processes, the organic solvent is normally withdrawn from the top of the regenerator as vapor stream and returned to the bottom of the extractor as liquid stream. The vaporization of solvent results in high regeneration cost (Schneider, 2004). In addition, the volatility of organic solvents can lead to serious environmental problems.

Ionic liquids (ILs) are innovative solvents entirely composed of ions. Their negligible vapor pressure makes the regeneration much easier, namely by evaporation or pervaporation of the other mixture components (Seddon, 1997; Huddleston et al., 1998). Due to much lower energy consumption and investment costs, extraction processes with ILs as solvents are economically feasible (Meindersma and de Haan, 2008). Moreover, the large number of possible cation and anion combinations makes it possible to tailor a highly efficient ionic liquid solvent for a specific separation task (Huddleston et al., 2001). Over the past decade, ILs have been

widely studied as solvents for aromatic/aliphatic liquid–liquid separations (Arce et al., 2007a, 2007b, 2008a, 2008b, 2009, 2010; Ferreira et al., 2012; Meindersma and De Haan, 2012; Zhang et al., 2007). According to Meindersma et al. (2010), more than 120 ILs have been identified as possible candidates aromatic/aliphatic separation since the first application reported by John et al. (1982). It was found that ILs composed of anions with delocalized electron (e.g., $[RSO_4]^-$ and $[AlCl_4]^-$) show much better extraction efficiency than other ILs. In several experimental studies, the separation of benzene and cyclohexane was chosen as a benchmark case (Wang et al., 2008a, 2008b; González et al., 2010a, 2010b; Zhou et al., 2012a, 2012b).

Due to the huge number of cations and anions, it is necessary to apply reliable theoretical methods to guide the screening of ILs for separation processes. So far, various predictive methods have been developed for modeling the thermodynamic properties of IL-containing systems, e.g., the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) (Paduszyński and Domańska, 2012; Domańska et al., 2012) and the Conductor-like Screening Model for Real Solvents (COSMO-RS) model (Klamt and Eckert, 2000). As a quantum chemistry based predictive method, the COSMO-RS model has been proven to be a powerful tool for fast IL solvent screening, including the separation of aliphatic and aromatic hydrocarbon mixtures (Anantharaj and Banerjee, 2010, 2011a; Banerjee and Khanna, 2006; Burghoff et al., 2008; Gutiérrez et al., 2010, 2012). Importantly, the available COSMO database covers a large number of common cations and anions, which makes it very efficient for screening of ILs as solvents (Klamt and Eckert, 2000; Diedenhofen et al., 2003).

In order to explain why a selected IL has a pronounced extraction efficiency, it is necessary to determine the specific molecular interactions between the solute molecules and IL ion pairs (Rezabal and Schäfer, 2013). Quantum chemical calculations are the best approach for studying the cation–anion interactions, and interactions between ILs and solute molecules (Dong et al., 2006, 2012; Dong and Zhang, 2012; Nockemann et al., 2006; Cabaço et al., 2011; Lü et al., 2012). On the basis of the well-founded Hohenberg–Kohn theorem, density functional theory (DFT) provides a sound method for obtaining information of energetics, structures, and properties of atoms and molecules at high enough accuracy and at much lower computational costs than traditional *ab initio* wave function techniques (Geerlings et al., 2003).

Due to their higher molecular weight, most of the reported ILs cannot provide a high mass-based extraction efficiency, which may obstruct their applications (Meindersma et al., 2010). Therefore, a potential IL identified with the help of COSMO-RS might not be qualified for industrial application. Hence, the extraction performance of ILs as solvents needs to be further evaluated through extraction process simulations. For simulating a continuous extraction process, ternary liquid–liquid equilibrium (LLE) data need to be determined and correlated with a thermodynamic activity coefficient model, such as the NRTL model (Renon and Prausnitz, 1968).

The objective of this work is to screen ILs as potential solvents to extract benzene from mixtures with cyclohexane based on simulations on different scales, i.e., COSMO-RS predictions, DFT calculations, and process simulations. First of all, infinite dilution extraction efficiencies of ILs composed of 12 cations and 22 anions were calculated by using the COSMO-RS model. The interaction energy and the natural bond orbital (NBO) were analyzed by quantum chemical calculations to investigate the suitability of selected ILs from the molecule point of view. For further confirming the extraction performance of the selected IL and exploring its potential for industrial application, process simulations were carried out using Aspen Plus 12.1. Since the molar content of the

unreacted benzene in mixtures with cyclohexane in practice is lower that 20%, special attention was paid to the removal of the reactant at low-concentrations of benzene (Zhou et al., 2012b).

2. Ionic liquid screening

2.1. COSMO-RS model

COSMO-RS is a quantum chemistry based statistical thermodynamics model for the prediction of thermodynamic properties of fluids (Klamt and Eckert, 2000). There are generally two steps in the COSMO-RS prediction procedure, namely (1) the quantum chemical COSMO computation for the molecular species involved, and (2) the COSMO-RS statistical thermodynamic treatment. A standard COSMO-RS prediction only requires the screening charge density (SCD) information of the interested compounds. The SCD distribution of a compound is normally obtained from quantum chemical calculation using the DFT approximation. The SCD needs to be calculated only once and afterwards it can be stored in a COSMO file. Nowadays, the available COSMO database already contains COSMO files of a huge number of common solvents and IL cations and anions. This makes the COSMO approach very fast and efficient when predicting thermodynamic properties, e.g., activity coefficients, of various systems (Klamt and Eckert, 2000, 2004).

In this work, infinite dilution activity coefficients of benzene and cyclohexane in ionic liquids, composed of 12 common cations and 22 common anions, were calculated by using the COSMOthermX software package (COSMOlogic GmbH & Co. KG, Version C3.0, Release 13.01) based on the COSMO-RS method. Among the 12 cations, four main types of cations with different side chain length were selected to evaluate the impact of cation classes and side chain lengths on solvent extraction efficiency. For the 22 anions, F-containing and Cl-containing anions, sulfate- and phosphate-anions with different alkyl substituents were chosen to investigate the influence of delocalized electron of anions on the extraction efficiency. The detailed information about the considered 12 cations and 22 anions is provided in Tables S1 and S2, respectively.

Among the studied cations and anions, $[AlCl_4]^-$ is not in the current COSMO database. Therefore, the COSMO file of $[AlCl_4]^-$ was determined from quantum chemical calculation at the BP-TZVP level by Gaussian 03W (Frisch et al., 2004). COSMO files of other ions, benzene, and cyclohexane were taken directly from the latest COSMO database (version: BP_TZVP_C21_0111). An IL can be treated as either a single compound or a mixture of ions. In this work, cations and anions are treated as individual species with equal molar fractions (Diedenhofen and Klamt, 2010).

2.2. Extraction efficiency at infinite dilution

The activity coefficient of a solute i in a solvent S is calculated from the difference between the chemical potentials of the solute in the solvent μ_S^i and in the pure solute μ_i^i

$$\gamma_S^i = \exp\left(\frac{\mu_S^i - \mu_i^i}{RT}\right) \tag{1}$$

The solute distribution coefficient at infinite dilution β_i^∞, which indicates the extraction capacity of the solvent, can be expressed in terms of the infinite dilution activity coefficient of the solute in the solvent

$$\beta_i^\infty = \left(\frac{1}{\gamma_i^\infty}\right)^{ILphase} \tag{2}$$

where the subscript i represents benzene or cyclohexane. The extraction selectivity is defined as the ratio of the composition of