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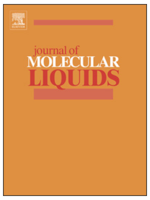

Ionic liquids for the separation of benzene and cyclohexane – COSMO-RS screening and experimental validation

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ABSTRACT

The separation of benzene and cyclohexane from their mixture is difficult to perform via conventional distillation because of their close boiling points. In this work, liquid-liquid extraction using ionic liquids (ILs) is suggested for this purpose and 16 cations and 13 anions were selected to form 208 possible ILs screened with the Conductor-like Screening Model for Real Solvents (COSMO-RS) module. The screening result was experimentally validated by liquid–liquid extraction using four of the top ranked ILs, namely 1-ethyl-3-methylimidazolium acetate ([C_2mim][Ac]), 1-ethyl-3-methylimidazolium dicyanamide ([C_2mim][$N(CN)_2$]), 1-ethyl-3-methylimidazolium thiocyanate ([C_2mim][SCN]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2mim][Tf_2N]). The ternary liquid–liquid equilibria for these ILs with benzene and cyclohexane were investigated at 25 °C and 1 atm with feed concentration of benzene ranging from 10 to 60 wt%. Good agreement was achieved between the tie-lines obtained from the COSMO-RS model and those obtained experimentally. The performance of ILs used in this study was compared with organic solvents, other ILs, and deep eutectic solvents reported in literature. The results of selectivity and distribution ratio confirmed that COSMO-RS was a reliable method for solvent screening and demonstrated the suitability of the selected ILs as extracting solvents. In all ternary systems, no IL was detected in the cyclohexane layer and the concentration of cyclohexane in the IL layer was very low. This observation indicated that there was minimum cross-contamination between the phases and therefore less energy will be required for the solvent recovery.

1. Introduction

Benzene and cyclohexane are two of the most valuable products that are widely processed in the petrochemical industry. At present, nearly all cyclohexane is produced by the catalytic hydrogenation of benzene [1]. In this process, the cyclohexane with high purity can only be produced via complex process control that involves a complex heat integration and economic study [2, 3]. Therefore, this method usually produces a mixture of benzene and cyclohexane. The unreacted benzene in the reactor's effluent must be removed to produce pure cyclohexane. However, the separation of benzene and cyclohexane by conventional distillation is quite difficult and challenging because they have close boiling points (80.1 °C for benzene and 80.7 °C for cyclohexane).

The conventional techniques employed for the separation of benzene and cyclohexane from their mixture include azeotropic distillation and extractive distillation [4]. In azeotropic distillation, a strongly polar entrainer is introduced to form an azeotropic mixture with cyclohexane, which alters the vapor–liquid equilibrium (VLE) curve for this mixture. Meanwhile, the extractive distillation method uses the entrainer to reduce the volatility of benzene. Despite their potential at an industrial scale, both processes suffer from several disadvantages such as process complexity, high capital and operating costs, and high energy consumption [5, 6]. Moreover, these processes are carried out by adding a third compound as the entrainer; the removal of the third compound from the distillate introduces higher process complexity and cost to the adopted method. In addition, azeotropic distillation and extractive distillation are only suitable for high (>90%) and medium (65–90%) concentration of benzene, respectively. Liquid–liquid extraction (LLE) is widely used in the industry because of the mild operating conditions and simplicity. Although LLE is suitable for separating low concentrations of benzene (20–65%), there is still no industrial process available for concentrations <20 wt%. While the pervaporation process was reviewed as a potential technique, it was limited by the challenges encountered during economic evaluation [5]. Several reports have demonstrated the excellent performance of industrial organic solvents such as ethylene glycol, tetra-ethylene glycol, sulfolane, and *N*-methylpyrrolidone as extractants [7–9]. However, their application is associated with several challenges because these solvents are usually volatile, toxic and flammable.

Interestingly, ionic liquids (ILs) have become a progressively popular class of solvent in the last decades as their potential in many industrial

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applications has become more diverse. Compared to other solvents, ILs are exceptionally non-flammable, non-volatile, environmentally benign, and thermally stable over a wide range of temperature. ILs have also been recognized for their remarkable ability to break the azeotropic properties in many mixtures such as ethanol-water, alcohol-alkane, aromatic-aliphatic, ketone-alkane, etc. [10]. The reports of new data for ternary phase equilibria between several ILs, benzene, and cyclohexane proved the feasibility of using ILs as an extracting solvent [11–14].

The necessity of developing a screening process is based on the idea that many other ILs having high extracting performances might remain undiscovered. This is because of the availability of a large number of available cations and anions, which makes the selection of potential ILs through experimental work a time-consuming and expensive process. In order to develop an effective selection procedure, the potential ILs should undergo a preliminary screening. Therefore, the use of reliable predicting tools is crucial. In this regard, a computational program known as the conductor-like screening model (COSMO-RS) has attracted significant attention and gained influence in research activity because of its ability to describe the thermodynamic properties and behavior of ILs. By combining the statistical thermodynamics and quantum chemical calculations, COSMO-RS can determine and predict the thermodynamic properties of mixtures without requiring any experimental data.

For the separation of benzene and cyclohexane by liquid-liquid extraction, COSMO-RS screening was previously performed by Lyu et al. using 12 cations and 22 anions, which found 1-butyl-3-methylimidazolium tetrachloroaluminate, $[C_4mim][AlCl_4]$ as the best IL [15]. In their study, the new $[AlCl_4]^-$ anion was introduced using quantum chemical calculations and included into the anion list. Gonfaa et al. used COSMO-RS to perform a preliminary screening of various ILs and utilized nitrile functionalized ILs to separate benzene and cyclohexane by the extractive distillation process [16]. Recently, deep eutectic solvent (DES), which is often regarded as an analogue of ILs was utilized as a solvent for this process. Some DESs have been screened using COSMO-RS for the separation of benzene and cyclohexane, [17] and other aromatic-aliphatic mixtures [18].

In this work, we disregarded the pre-determined ions or functional groups, and adopted a basic approach by choosing only the common cations and anions. This will provide a baseline for an advanced selection of ILs as the screened ILs would be potentially available in the market, and less complex or easy to synthesize. Furthermore, the nature of the selected ILs in this study can be developed further to enhance their extractive performance such as by modifying the structure [19], developing a binary IL mixture [20], or using co-solvents [21].

2. Computational methods

The computational calculations were carried out using the COSMOtherm software with BP-TZVP C30_1401 parameterization. The data prediction was obtained through density functional theory (DFT) calculations, utilizing the Becke-Perdew (BP) functional with the resolution of identity (RI) approximation and the Triple-ζ Zeta Valence Potential (TZVP) basis set. For the selection of cation, four types of cyclic cations were chosen: imidazolium, pyridinium, piperidinium, and pyrrolidinium. As shown in Table 1, each of these cations was expanded into four kinds of methyl-alkyl groups to study the effect of cation alkyl length. Meanwhile, for the selection of anion, thirteen common and less complicated anions were shortlisted, as shown in Table 2.

2.1. Prediction theory

For predictions involving ILs, the electroneutral approach was adopted where the IL is assumed to undergo complete dissociation into its respective cation and anion. Therefore, as shown in Eq. 1, the sigma profile of the IL (P_{IL}) was the linear addition of the sigma profiles of both cation (P_{cation}) and anion (P_{anion}), such that the profile of the IL behaved as the profile of a single molecule.

$$P_{IL}(\sigma) = P_{anion}(\delta) + P_{cation}(\delta) \tag{1}$$

2.2. Calculation methodology

The activity coefficient at infinite dilution (γ) was obtained from the *Chemical Potential* menu in the COSMO-RS software, where the mole fractions of benzene and cyclohexane were set to zero. The methods and calculations required to obtain activity coefficient at infinite dilution has been described in detail by Klamt [22]. At infinite dilution, the capacity (C^∞) and selectivity (S^∞) of the IL are given by Eqs. 2 and 3, respectively.

$$C^\infty = \frac{1}{\gamma_1^\infty} \tag{2}$$

$$S^\infty = \frac{\gamma_2^\infty}{\gamma_1^\infty} \tag{3}$$

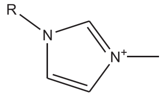
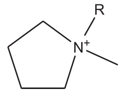
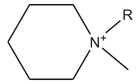
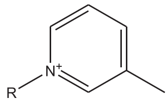
where $\gamma_1^\infty$and γ_2^∞ are the activity coefficients at infinite dilution for benzene and cyclohexane, respectively. The performance index at infinite dilution (PI^∞) of each IL was calculated as a product of capacity and selectivity at infinite dilution using Eq. 4:

$$PI^\infty = C^\infty \times S^\infty \tag{4}$$

2.3. Chemicals and materials

The details of the chemicals used in this work are summarized in Table 3 where all of them were used as received without further purification. For the determination of the ternary composition in the extract and raffinate phase at equilibrium, Nuclear Magnetic Resonance (NMR) spectroscopy was performed using either deuterated chloroform (≥99.8%, stabilized with silver) or deuterated methanol (99.8%).

Table 1
List of cation in the COSMO-RS screening.

No	Cation name	Abbreviation	Chemical structure
1	1-alkyl-3-methylimidazolium	$[C_nmim]^+$	 R = 2, 4, 6, 8
2	1-alkyl-1-methylpyrrolidinium	$[C_nmpyrro]^+$	 R = 2, 4, 6, 8
3	1-alkyl-1-methylpiperidinium	$[C_nmpip]^+$	 R = 2, 4, 6, 8
4	1-alkyl-3-methyl-pyridinium	$[C_nmpyr]^+$	 R = 2, 4, 6, 8