Liquid–liquid extraction of toluene from *n*-heptane using binary mixtures of *N*-butylpyridinium tetrafluoroborate and *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids

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ABSTRACT

Liquid–liquid extraction of toluene from heptane using binary mixtures of the ionic liquids *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide ([bpy][Tf$_2$N]) and *N*-butylpyridinium tetrafluoroborate ([bpy][BF$_4$]) have been investigated at 313.2 K and atmospheric pressure. On the basis of the experimental liquid–liquid equilibrium data for the pseudoternary system *n*-heptane + toluene + mixed ionic liquids, the values of the distribution ratio and selectivity were calculated and compared to those for the pure ionic liquids, for sulfolane, and those predicted by an ideal mixing rule. The results showed that the use of binary mixture of {[bpy][BF$_4$] + [bpy][Tf$_2$N]} at a mole solvent composition of 0.7 for [bpy][BF$_4$] improves both the distribution ratio of toluene and the selectivity with respect to those of sulfolane. Thus, this mixed ionic liquid could be considered an environmentally benign alternative solvent for the aromatic extraction process.

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1. Introduction

The removal of aromatic hydrocarbons of some petroleum streams and the important use of these compounds as raw materials have resulted in a continuous attempt to improve current industrial processes for the separation of aromatic compounds from aliphatics [1,2]. This separation is challenging due to their boiling points in a very close range and azeotrope formation [3]. Liquid–liquid extraction with organic solvents such as sulfolane is the most widely used technology for the isolation of aromatic fractions from aromatic/aliphatic mixtures. However, according to Weissermel and Arpe [4,5] no feasible processes are available from an economical point of view for the extraction of aromatic and aliphatic hydrocarbons in the range below 20 wt.% aromatics in the feed mixture. Most of ethylene crackers feeds contain 10–25 wt.% aromatic compounds that should be removed to improve the efficiency of the process [5].

Over the last years, ionic liquids (ILs) have been suggested as an alternative to conventional organic solvents for the extraction of aromatics due to their nonvolatile nature. This interesting property would lead to a lesser complex and greener process because of the easier regeneration of the solvent by simple operations such as flash distillation [6]. Among the ILs thus far investigated with

this proposal [7–40] only a few have shown both a higher extractive capacity of aromatics and selectivity than those of sulfolane, taken this organic solvent as a benchmark [5]. Nevertheless, the combination of both extractive properties is indeed a requisite for a solvent to be appropriate for use. Several attempts have been made to optimize the properties of ILs for a given application, including the search of new and unusual ILs in addition to the mixing of 'green' co-solvents such as water, ethanol, or compressed CO$_2$. However, as far as we know, there are only a work that uses mixtures of ionic liquids as solvents [41], although Fletcher et al. [42] suggested that mixing two different ILs may confer to the mixture improved and unexpected properties. Using mixed conventional organic solvents for the extraction of aromatics is commonly practiced to balance between selectivity and extractive capacity of different solvents [43].

In previous works [32–39], we have tested some ILs for the separation of toluene from *n*-heptane at 313.2 K and atmospheric pressure. Among all of them, *N*-butylpyridinium tetrafluoroborate ([bpy][BF$_4$]) IL showed higher selectivity but lower extractive capacity than sulfolane [32], and the opposite occurred for *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide ([bpy][Tf$_2$N]) IL [35]. Mixing these two ILs could be achieved an intermediate situation in which values of selectivity and extractive capacity were higher than sulfolane. Moreover, the relatively higher viscosity observed in ILs with BF$_4$ anions could be offset by the lower viscosity of the Tf$_2$N-based ILs. The use of [bpy][Tf$_2$N] could also improve the chemical stability of the mixed solvent with respect to

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the pure [bpy][BF$_4$] IL, which is a less stable and a more hydrophilic IL.

Bearing these aspects in mind, firstly we have explored the influence of {[bpy][BF$_4$] + [bpy][Tf$_2$N]} mixtures at different compositions on selectivity and extractive capacity for the separation of toluene from n-heptane/toluene mixtures containing 10.5% molar of toluene at 313.2 K and atmospheric pressure. Based on these results, liquid–liquid equilibrium (LLE) were determined for the system n-heptane + toluene + {[bpy][BF$_4$] + [bpy][Tf$_2$N]} at 313.2 K and atmospheric pressure, with a constant [bpy][BF$_4$] mole fraction in the mixed IL solvent of 0.7. The selectivity and the extractive capacity were calculated from the LLE data. The quality of the experimental LLE data was tested using the Othmer–Tobias correlation. In addition, the phase diagram was plotted and the LLE data were correlated by the nonrandom two-liquid (NRTL) model.

2. Experimental

2.1. Chemicals

N-heptane and toluene over molecular sieves were supplied by Sigma–Aldrich with mass fraction purity greater than 0.995 and 0.997, respectively. Their water mass fractions were less than 0.00005. The ILs N-butylpyridinium bis(trifluoromethylsulfonyl)imide ([bpy][Tf$_2$N]) and N-butylpyridinium tetrafluoroborate ([bpy][BF$_4$]) were provided by Iolitec GmbH with quoted mass fraction purities greater than 0.99, and halides and water mass fractions less than 0.0001. Water content and purity of the reagents were given by the manufacturers. All chemicals were used as received without further purification. To prevent water hydration, they were kept in their original tightly closed bottles in a desiccator. When any chemicals were used, they were always manipulated inside a glove box under a dry nitrogen atmosphere.

2.2. Experimental procedure and analysis

The LLE experiments were performed in 8 mL vials with screw caps providing hermetic sealing. Mixtures of known masses of toluene/n-heptane feed were transferred to tared vials. After the vials were reweighed the pure or mixed IL was gravimetrically added to the feed. The vials were then placed in a shaking incubator at 313.2 K with a shaking speed of 800 rpm for 5 h and then settled overnight. This was carried out according to the procedure previously reported [36]. The estimated error in the mole fraction in the prepared feed mixture was less than 0.001.

Samples from the n-heptane-rich phase were analyzed by ^{1}H NMR. The spectra showed no detectable signals arising from the ILs, so the IL mole fractions in the n-heptane-rich phases appear to be negligible. Thus, gas chromatographic analyses of each layer plus an overall mass balance on hydrocarbons in the mixture were done to determine the phase compositions. Because of the nonvolatile nature of the IL, a precolumn is needed in the gas chromatograph to collect the pure or mixed ILs present in the lower layer in order not to disrupt the analysis. A detailed description of the equipments and the analysis conditions can be found elsewhere [36].

An area normalization method with response factors was carried out to determine the hydrocarbon molar ratio in each layer. The gas chromatography response factors for the hydrocarbons were calculated by using standard mixture samples of pure n-heptane and toluene. The compositions of these standard samples were obtained through weighing with an electronic balance having a precision of ±0.0001 g. Toluene in the mixture was chosen as the standard, and its response factor was set to 1.0. The response factor for n-heptane was then calculated using the renormalization
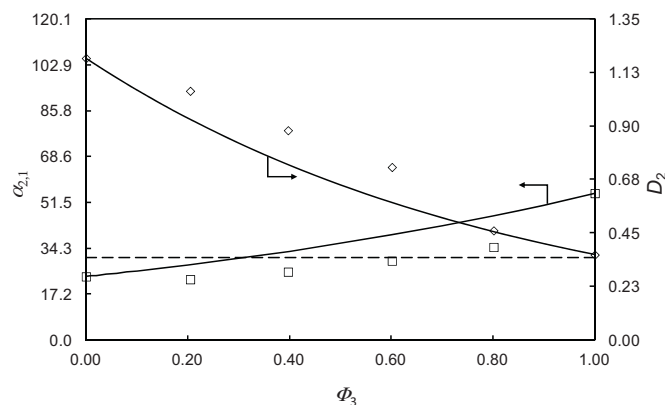

Fig. 1. Separation factors (□) and distribution ratios of toluene (◇) versus [bpy][BF$_4$] mole fraction in the mixed IL solvent (Φ_3) for the pseudoternary system n-heptane (1) + toluene (2) + {[bpy][BF$_4$] (3) + [bpy][Tf$_2$N] (4)} at T = 313.2 K and atmospheric pressure (10.5% molar of toluene in feed and solvent-to-feed ratio of 0.9). The dashed line represents the separation factor and distribution ratio of sulfolane at the same conditions [10]. The solid lines represent the separation factors and distribution ratios for the mixed IL solvents following the ideal behavior defined by Eq. (4).

method before every run of samples to ensure measurement accuracy. Samples were taken in triplicate and each of them injected six times in the GC. The average compositions are the ones reported here. The estimated uncertainties in the compositions, calculated as the standard deviation of the measurements, were less than 0.002.

3. Results and discussion

3.1. Screening LLE experiments with mixed {[bpy][BF$_4$] + [bpy][Tf$_2$N]} ILs

The LLE data for the pseudoternary system n-heptane (1) + toluene (2) + {[bpy][BF$_4$] (3) + [bpy][Tf$_2$N] (4)} at 313.2 K, atmospheric pressure, and several [bpy][BF$_4$] mole fractions in the mixed IL solvent (Φ_3) are shown in Table 1.

The influence of mixed {[bpy][BF$_4$] + [bpy][Tf$_2$N]} ILs on selectivity and extractive capacity was evaluated by the distribution ratios of n-heptane and toluene (D_1 and D_2), and the separation factor ($\alpha_{2,1}$). The values of D_1, D_2, and $\alpha_{2,1}$ are also shown in Table 1, and they were calculated from the experimental LLE data as follows:

$$D_1 = \frac{x_1^{II}}{x_1^{I}} \tag{1}$$

$$D_2 = \frac{x_2^{II}}{x_2^{I}} \tag{2}$$

$$\alpha_{2,1} = \frac{x_2^{II} x_1^{I}}{x_2^{I} x_1^{II}} \tag{3}$$

where x is the mole fraction, superscripts I and II refer to the n-heptane-rich and IL-rich phases, respectively, and subscripts 1 and 2 to n-heptane and toluene, respectively.

As can be seen in Table 1, no IL was detected in the n-heptane-rich phase. This behavior is the same as previously reported for the pure ILs [32,35]. Thus, no extra operation will be needed to purify the raffinate phase for recovering the solvent if a binary mixture of these ILs is used for industrial aromatic extraction purposes.

The values of distribution ratio of toluene (D_2) and the separation factor ($\alpha_{2,1}$) are plotted in Fig. 1 versus the [bpy][BF$_4$] mole fraction in the mixed IL solvent (Φ_3). These results were compared with those of sulfolane [10] and also with those predicted from