

Synergistic liquid-liquid extraction of toluene from heptane with mixtures of [bmim]BF₄ and [omim]BF₄ ionic liquids

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Extraction of toluene from heptane using binary mixtures of the ionic liquids 1-butyl-4-methylimidazolium tetrafluoroborate [bmim]BF₄ and 1-methyl-3-octylimidazolium tetrafluoroborate [omim]BF₄ have been investigated at 313 K and atmospheric pressure. On the basis of the experimental liquid-liquid equilibrium data, the values of distribution ratio and selectivity for the binary mixtures of the ionic liquids were calculated and compared to those of the pure ionic liquids and sulfolane. None of these two pure ionic liquids showed simultaneously values of distribution ratio and selectivity greater than those of sulfolane. However, our results show that the use of binary mixtures of ([bmim]BF₄ + [omim]BF₄) has a synergistic effect on toluene extraction. Both the distribution ratio and selectivity are improved with respect to those predicted by an ideal mixing. As a result, it was found that a mixed ionic liquid solvent with a composition of 80 molar % [bmim]BF₄ presents values of selectivity and distribution ratio nearly equal to those of sulfolane.

1. Introduction

Liquid-liquid extraction with polar solvents is the most widely used method for the isolation of aromatic fractions from aromatic/aliphatic mixtures. However, according to Weissermel and Arpe (2003) 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.

Ionic liquids (ILs) are organic salts which have melting point around ambient temperature and consist of large organic cations based on imidazolium, pyridinium, quaternary ammonium or phosphonium ions and others, and anions such as chloride, bromide, hexafluorophosphate, tetrafluoroborate, alkylsulfates, alkylsulfonates, triflate, bis (triflyl)imide, etc. Compared to conventional organic solvents, the application of ILs for extraction processes is promising because of their non-volatile nature (Huddleston et al, 1998). This facilitates solvent recovery using techniques as simple as flash distillation or stripping. In this way, extraction of aromatics from aromatic/aliphatic mixtures with ILs has already been explored in some papers by measurements of (liquid + liquid) equilibrium (LLE) for a variety of (IL + hydrocarbon) systems (Meindersma et al., 2005).

A good number of ILs are found that display considerably greater distribution ratios or selectivities than those of sulfolane which is the most popular solvent in aromatic extraction. However, in the large list of ILs so far investigated, there are few ones that possess simultaneously high distribution ratio and selectivity for aromatic extraction. But it is the combination of high distribution ratio and selectivity what makes a solvent appropriate to use. Several attempts have been made to optimize the properties of ILs for a given application, including the search for new and unusual ILs in addition to the mixing of 'green' co-solvents such as water, ethanol or compressed CO₂. However, as far as we know, no paper reported the use of binary IL mixtures to extract aromatic hydrocarbons, although it has been shown that mixing two different ILs may confer on the mixture improved and unexpected properties (Fletcher et al., 2003). Using mixed conventional organic solvents for the extraction of aromatics is commonly practised to balance between selectivity and distribution ratio of different solvents (Lababidi et al., 2006).

Consequently, the aim of this work is to explore the influence of binary IL mixture composition on the selectivity and distribution ratio for the extraction of toluene from heptane. Binary mixtures formed from the ILs 1-butyl-4-methylimidazolium tetrafluoroborate [bmim]BF₄ and 1-methyl-3-octylimidazolium tetrafluoroborate [omim]BF₄ were the subject of our study. This IL selection was made on the basis of their popularity in the literature, the fact that these ILs are mutually miscible in all proportions and the prospect of studying mixtures composed of ILs that compared to sulfolane have a greater selectivity but a less distribution ratio such as [bmim]BF₄, and a less selectivity but a greater distribution ratio such as [omim]BF₄.

2. Experimental

2.1 Chemicals

Heptane (≥ 99.5 wt. %) and toluene (≥ 99.7 wt. %) over molecular sieve were purchased from Sigma-Aldrich and used as received, without further purification. Sulfolane (≥ 99.5 wt. %) was provided by Fluka and also used as received. The ILs 1-butyl-4-methylimidazolium tetrafluoroborate [bmim]BF₄ (≥ 97.0 wt. %) and 1-methyl-3-octylimidazolium tetrafluoroborate [omim]BF₄ (≥ 97.0 wt. %) were obtained from Fluka. They were purified by heating under a vacuum (100 mbar, 353 K) for 24 h to remove trace of any volatile components including water.

2.2 Experimental procedure

The LLE runs were carried out in 8 mL vials with screw caps providing hermetic sealing. 2 mL of toluene/heptane feed with a composition of 10.5 molar % toluene were transferred to tared vials. After reweighing the vials, the solvent (sulfolane, pure IL or a binary mixture of ILs in specific ratios) was gravimetrically added to the feed. In all cases, the molar solvent-to-feed ratios were fixed to 0.9. The vials were then introduced in a shaking incubator (Vortemp 1550, LabNet) at 313 K with a shaking speed of 800 rpm for 5 hours to reach the thermodynamic equilibrium. Finally, they were left to settle down overnight to ensure complete phase separation at a constant temperature of 313 K in a dry bath (AccuBlock Digital Dry Bath, LabNet). All of the weights involved in the

experimental work were carried out in a Mettler Toledo AB104 balance, with a precision of $\pm 1 \cdot 10^{-4}$ g. The uncertainty of temperature measurements was ± 0.1 K.

2.3 Analysis

Samples from the lower and upper layers were carefully taken with disposable Pasteur micropipettes and analyzed by a Bruker Avance 500 MHz NMR Spectrometer. Three samples of each phase were taken, dissolved in deuterated acetone (99.9 atom % D) supplied by Aldrich and placed in NMR tubes, then running ^1H -NMR experiments for all samples and integrating in the spectra the selected areas for the compositional analysis. The estimated uncertainties in the molar phase compositions are shown in Table 1.

3. Results and Discussion

The experimental LLE data for the system {heptane (1) + toluene (2) + [bmim]BF₄ (3) + [omim]BF₄ (4)} at 313 K and atmospheric pressure are given in Table 1, together with the toluene distribution ratio (D_2) and the toluene/heptane selectivity (S) calculated from the experimental data as follows:

$$D_2 = \frac{x_2^{II}}{x_2^I} \quad (1)$$

$$S = \frac{x_2^{II} x_1^I}{x_2^I x_1^{II}} \quad (2)$$

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

As can be seen from Table 1, it was found that the upper layers (heptane-rich phase) are totally free of ILs. It is also clear from the data shown in Table 1 that toluene has a much higher affinity toward heptane (upper layer) than solvents (lower layer) because the values of distribution ratio are always less than 1, but the values of selectivity are greater than 1 for all solvents; thus the extraction will be always possible.

Figure 1 summarizes the effects of the solvent composition on toluene distribution ratio and toluene/heptane selectivity. These results are compared with those of sulfolane which was used as a benchmark for this comparison and also with those calculated from heptane and toluene solubilities in ideal mixed IL solutions defined as follows:

$$x_{i,ideal}^{I \text{ or } II} = \sum_j \phi_j x_{i,j}^{I \text{ or } II} \quad (3)$$

where x is the molar fraction, ϕ is the solvent composition, superscripts I and II refer to the heptane-rich and IL-rich phases, subscript i to heptane and toluene and subscript j to the pure ILs in the binary solvent mixture.

Table 1. LLE data for the system {heptane (1) + toluene (2) + [bmim]BF₄ (3) + [omim]BF₄ (4)} at 313 K and atmospheric pressure (10.5 molar % toluene in the hydrocarbon feed and molar solvent-to-feed ratio of 0.9)*

[bmim]BF ₄ in solvent (molar basis)	IL-rich phase (lower layer)				Heptane-rich phase (upper layer)		<i>D</i> ₂	<i>S</i>
	<i>x</i> ₁ ^{II}	<i>x</i> ₂ ^{II}	<i>x</i> ₃ ^{II}	<i>x</i> ₄ ^{II}	<i>x</i> ₁ ^I	<i>x</i> ₂ ^I		
1.00	0.0055	0.0270	0.9675		0.9184	0.0816	0.331	55.5
	<i>0.0002</i>	<i>0.0002</i>	<i>0.0004</i>		<i>0.0014</i>	<i>0.0014</i>	<i>0.006</i>	<i>1.9</i>
0.80	0.0108	0.0323	0.7583	0.1986	0.9248	0.0752	0.429	36.7
	<i>0.0004</i>	<i>0.0004</i>	<i>0.0001</i>	<i>0.0000</i>	<i>0.0013</i>	<i>0.0013</i>	<i>0.010</i>	<i>1.7</i>
0.60	0.0284	0.0367	0.5573	0.3776	0.9284	0.0716	0.513	16.8
	<i>0.0023</i>	<i>0.0007</i>	<i>0.0015</i>	<i>0.0010</i>	<i>0.0036</i>	<i>0.0036</i>	<i>0.027</i>	<i>1.6</i>
0.40	0.0468	0.0411	0.3674	0.5447	0.9334	0.0666	0.617	12.3
	<i>0.0009</i>	<i>0.0004</i>	<i>0.0002</i>	<i>0.0003</i>	<i>0.0014</i>	<i>0.0014</i>	<i>0.014</i>	<i>0.4</i>
0.20	0.0719	0.0448	0.1766	0.7066	0.9365	0.0635	0.706	9.2
	<i>0.0003</i>	<i>0.0004</i>	<i>0.0001</i>	<i>0.0003</i>	<i>0.0013</i>	<i>0.0013</i>	<i>0.016</i>	<i>0.2</i>
0.00	0.1076	0.0478		0.8446	0.9396	0.0604	0.791	6.9
	<i>0.0031</i>	<i>0.0009</i>		<i>0.0030</i>	<i>0.0019</i>	<i>0.0019</i>	<i>0.029</i>	<i>0.3</i>

* The figures in italic type represent the standard deviations of the upper data which are the average of three replicates. The standard deviations of *D*₂ and *S* were calculated from the uncertainties estimates in the LLE data using the rule of propagation of uncertainties.

As can be seen from Figure 1, the IL [bmim]BF₄ has a value of selectivity greater than sulfolane but a less distribution ratio, whereas the IL [omim]BF₄ has a value of selectivity less than sulfolane but a greater distribution ratio. Therefore, none of these two pure ILs present simultaneously values of distribution ratio and selectivity greater than those of sulfolane. On the other hand, it can be seen that all of the IL mixtures present values of distribution ratio and selectivity above the predicted by the ideal mixing defined by eq. 3. The most prominent departure from ideality is observed for selectivity. A significant maximum excess of selectivity results at a solvent composition of 80 molar % [bmim]BF₄. At that solvent composition, this IL mixture presents values of distribution ratio and selectivity nearly equal to those of sulfolane.

On the basis of the experimental results, we can confidently postulate that for the mixed IL extraction system considered in this study, synergistic behaviors in distribution ratio and selectivity are found. Thus, this mixed IL solvent system appears to be more efficient for the extraction of aromatic from aliphatic hydrocarbons than the pure ILs. This result is a demonstration that mixing ILs may be a viable approach in the design and modification of IL based solvents with improved properties.

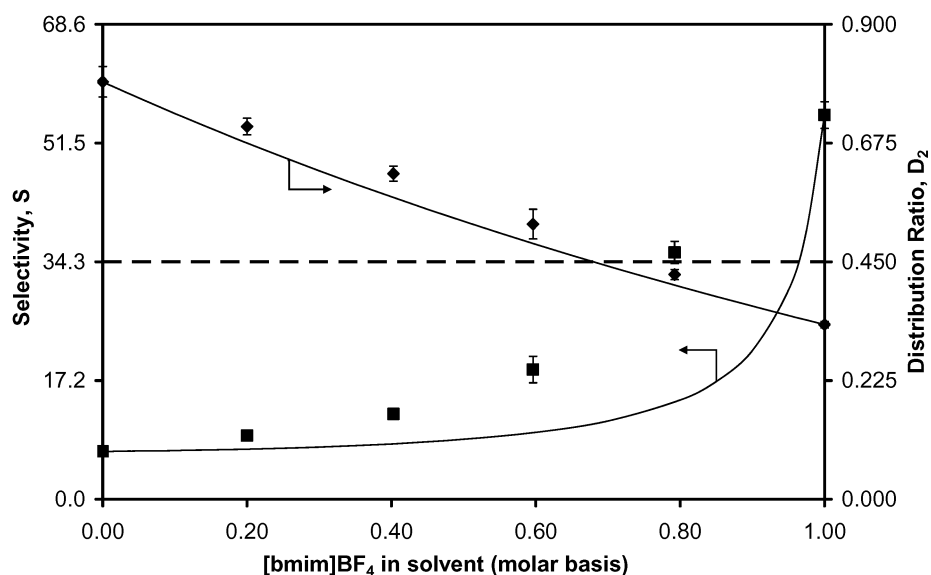


Figure 1. Selectivity (■) and distribution ratio (◆) for the system {heptane (1) + toluene (2) + [bmim]BF₄ (3) + [omim]BF₄ (4)} at 313 K and atmospheric pressure (10.5 molar % toluene in the hydrocarbon feed and molar solvent-to-feed ratio of 0.9). The dashed line represents the selectivity and distribution ratio of sulfolane at the same conditions. The solid lines represent the selectivities and distribution ratios for the mixed IL solvents following the ideal behaviour defined by eq. 3.

4. Conclusions

Liquid-liquid extraction of toluene from heptane at 313 K and atmospheric pressure with binary mixtures of the ILs 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄ and 1-methyl-3-octylimidazolium tetrafluoroborate [omim]BF₄ as solvents have been reported.

Our results suggest that mixing some ILs may be a viable approach to obtain a good compromise between distribution ratio and selectivity. By preparing mixed IL solutions of two or more different ILs (varying the cation, anion or both), the components, or latent properties thereof, may confer on the mixture improved distribution ratio and/or selectivity for aromatic extraction.

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