

Comparative Evaluation of [Imidazolium][Tf₂N] and [Pyridinium][Tf₂N] Ionic Liquids for the Liquid-liquid Extraction of Aromatics

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The distribution ratios and separation factors for the four ternary systems heptane + toluene + [C₂mim][Tf₂N], or [C₄mim][Tf₂N], or [3-mC₂py][Tf₂N], or [3-mC₄py][Tf₂N] were determined at 313.2 K and atmospheric pressure. The four ionic liquids (ILs) show values of distribution ratio larger than those of sulfolane in the whole range of the toluene mole fractions in the heptane-rich phase. The pyridinium-based ILs clearly show the best values of toluene distribution ratio. However, there were really few differences between the separation factors of the pyridinium-based and imidazolium-based ILs with the same alkyl side chains in the cations. Just the use of the [3-mC₂py][Tf₂N] leads to higher values of separation factor in the whole range of compositions than those of sulfolane. Therefore, it was concluded that only the [3-mC₂py][Tf₂N] ionic liquid could reach better aromatic extraction results than sulfolane.

1. Introduction

The liquid-liquid extraction of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) from C₄–C₁₀ aliphatic hydrocarbons has traditionally been one of the most challenging tasks in the refinery process (Meindersma et al., 2005). Typical solvents used are polar compounds having a selective high-affinity for the aromatic hydrocarbons. In the year 2000, ionic liquids (ILs) were proposed for the first time as environmentally friendly replacements for conventional organic solvents in the extraction of aromatics (Selvan et al., 2000). Since then a large number of papers have been published dealing with this topic (Meindersma et al., 2010). Some 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_nmim][Tf₂N]) ILs have previously shown better extractive separation of benzene and hexane than sulfolane, which is the most common organic solvent in current liquid-liquid extraction processes of aromatics (Arce et al., 2007). Moreover, ILs containing the [Tf₂N] anion have a significantly lower viscosity than those ILs with other anions (Jacquemim et al., 2006). Bearing these aspects in mind and the fact that a 3-methyl-N-alkylpyridinium ([3-mC_npy]) cation could provide capacity and selectivity superior to that of the [C_nmim] cation because of its higher aromaticity, here we compare aromatic distribution ratios and separation factors for the four ternary systems heptane + toluene + [C₂mim][Tf₂N], or [C₄mim][Tf₂N], or [3-mC₂py][Tf₂N], or [3-mC₄py][Tf₂N] at T = 313.2 K and atmospheric pressure.

2. Experimental

2.1 Chemicals

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. Four ILs based on the cations 1-ethyl-3-methylimidazolium ([C₂mim]), 1-butyl-3-methylimidazolium ([C₄mim]), 3-methyl-N-ethylpyridinium P([3-mC₂py]), and 3-methyl-N-butylpyridinium ([3-mC₄py]), all with the anion bis(trifluoromethylsulfonyl)imide ([Tf₂N]), were provided by Iolitec GmbH with quoted mass fraction purities greater than 0.99, and halides and water mass fractions less than 0.0001. 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

The liquid-liquid equilibrium experiments were performed in 8 mL vials with screw caps providing hermetic sealing. Mixtures of known masses of heptane/toluene feed were transferred to tared vials. After the vials were reweighed, the IL ([C₂mim][Tf₂N], or [C₄mim][Tf₂N], or [3-mC₂py][Tf₂N], or [3-mC₄py][Tf₂N]) 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 to reach the thermodynamic equilibrium. Finally, to ensure complete phase separation, the vials were left to settle overnight at a constant temperature of 313.2 K in a dry bath. Every weighing involved in the experimental work was carried out on a Mettler Toledo AB104 balance with a precision of ± 0.0001 g. The uncertainties in the temperature measurements were ± 0.1 K.

2.3 Analysis

Samples from the upper layers (heptane-rich phases) were analyzed using a Bruker Avance 500 MHz NMR spectrometer. The ¹H NMR spectra showed no detectable signals arising from any of the ILs, so the IL mole fractions in the heptane-rich phases appear to be negligible. Thus, gas chromatographic (GC) analyses of each layer plus an overall mass balance on hydrocarbons in the mixture were done to determine the phase compositions. A more detailed description of the GC method can be found elsewhere (García et al., 2010a)

An area normalization method with response factors was carried out to determine the hydrocarbon concentration ratio in each layer. The gas chromatography response factors for the hydrocarbons were calculated by using standard mixture samples of pure 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 set as the standard, and its response factor was set to 1.0. The response factor for heptane was then calculated using the renormalization 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 here reported. The estimated uncertainties in the hydrocarbon molar compositions in the heptane-rich phase and IL-rich phase were less than 0.001.

3. Results and Discussion

The potential use of the four ILs as solvents for the extraction of toluene from heptane at different concentrations of toluene in the feed has been evaluated by the toluene distribution ratio (β) and the separation factor (S), calculated from the experimental data as follows

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

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

where x is the mole fraction, superscripts I and II refer to the heptane-rich and IL-rich phases, respectively, and subscripts 1 and 2 to heptane and toluene, respectively. The mole fraction compositions for the heptane-rich phase (raffinate) and IL-rich phase (extract) for the ternary systems heptane + toluene + [C₂mim][Tf₂N], or [C₄mim][Tf₂N], or [3-mC₂py][Tf₂N], or [3-mC₄py][Tf₂N] can be found elsewhere (García et al., 2010a, 2010b, and 2011).

The values of distribution ratio and separation factor for the four ternary systems as functions of the toluene mole fractions in the heptane-rich phase (x_2^{I}) are plotted in Figures 1 and 2. Comparison with literature data for the ternary system heptane + toluene + sulfolane at 313.2 K is also made (Meindersma et al., 2006). A second-order polynomial equation was used to correlate the data with a good degree of accuracy.

The results of β for all the four ILs (Figure 1) are higher than that of sulfolane in the whole range of compositions. The best results are for the pyridinium-based ILs, surely due to their higher aromatic character. It can also be seen that β for all the four ILs grows with decreasing values of x_2^{I} , whereas it decreases for sulfolane. According to Hansmeier et al. (2010), ILs and aromatic solutes organize in a sandwich structure, where the IL cations and the aromatic solutes interact in an alternating structure through π - π interactions with the IL anion arranged around this complex. With increasing aromatics content the distance between aromatic solutes and cations becomes larger, reducing the strength of interaction and thereby the distribution coefficient. Additionally, the increased aromatics content of the IL increases the aliphatic distribution coefficient by enabling the aliphatic components to arrange themselves between the molecules.

As can be seen from Figure 2, S decreases with increasing values of x_2^{I} for all the four ILs. Just the [3-mC₂py][Tf₂N] IL shows values of S higher than that of sulfolane in the whole range of x_2^{I} . There are really few differences between the results shown by the pyridinium-based and imidazolium-based ILs when they have the same alkyl side chains in the cations. The main difference seems to be that pyridinium-based ILs tend to show higher values of S at low values x_2^{I} than imidazolium-based ILs, whereas at high values of x_2^{I} the pyridinium-based ILs show lower values of S than the imidazolium-based ILs.

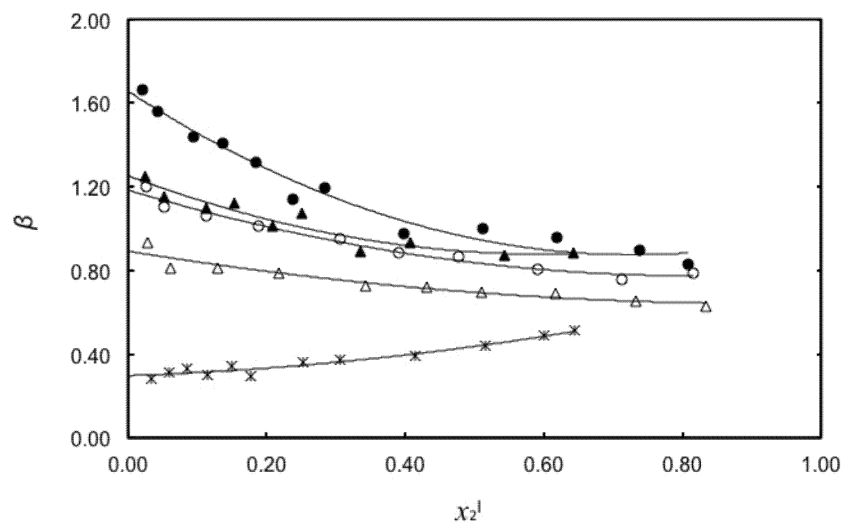


Figure 1: Toluene distribution ratio (β) for the ternary systems heptane + toluene + IL at $T = 313.2$ K: Δ , $[C_2mim][Tf_2N]$; \circ , $[C_4mim][Tf_2N]$; \blacktriangle , $[3-mC_2py][Tf_2N]$; \bullet , $[3-mC_4py][Tf_2N]$; $*$, sulfolane from Meindersma et al. (2006). The solid lines correspond to regressions according to a second-order polynomial equation.

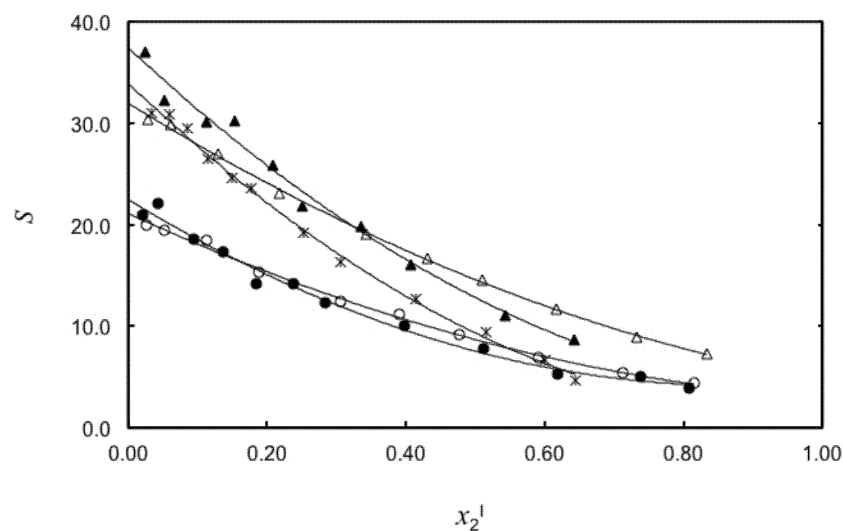


Figure 2: Toluene separation factor (S) for the ternary systems heptane + toluene + IL at $T = 313.2$ K: Δ , $[C_2mim][Tf_2N]$; \circ , $[C_4mim][Tf_2N]$; \blacktriangle , $[3-mC_2py][Tf_2N]$; \bullet , $[3-mC_4py][Tf_2N]$; $*$, sulfolane from Meindersma et al. (2006). The solid lines correspond to regressions according to a second-order polynomial equation.

In Figure 3, the plot of the extrapolated values of the toluene distribution ratio and the separation ratio at infinite dilution against sulfolane and the four ILs is shown. As can be seen, the values of the distribution ratio and separation factor at infinite dilution increase from the imidazolium-based ILs to the pyridinium-based ILs when ILs with the same alkyl side chains in the imidazolium or pyridinium cations are compared. All the four ILs show higher values of the toluene distribution ratio at infinite dilution than those of sulfolane. However, only the use of the [3-mC₂py][Tf₂N] IL leads to higher separation factor value at infinite dilution than that of sulfolane.

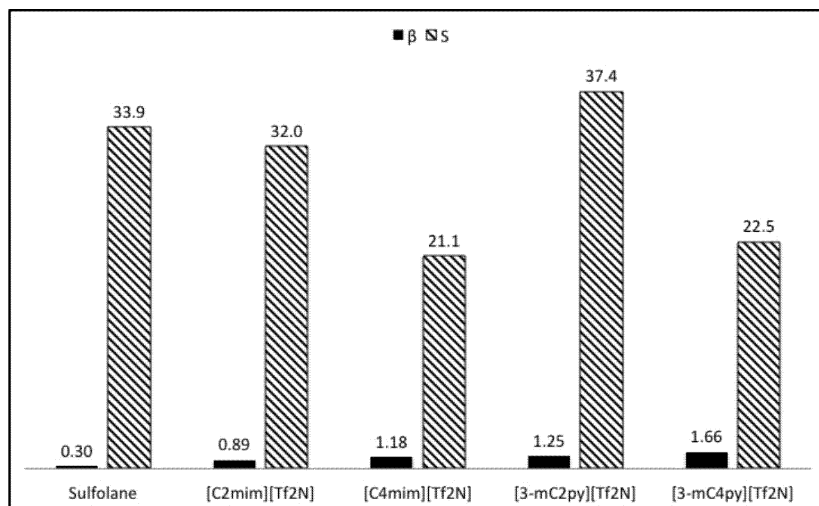


Figure 3: Extrapolated values of the distribution ratio (β) and separation factor (S) at infinite dilution for the heptane + toluene + (sulfolane or IL) ternary systems.

4. Conclusions

A comparative evaluation for the liquid-liquid extraction of toluene from heptane with the ionic liquids [C₂mim][Tf₂N], [C₄mim][Tf₂N], [3-mC₂py][Tf₂N], and [3-mC₄py][Tf₂N]) in terms of their distribution ratios and separation factors has been done. The four ILs show values of the distribution ratio larger than those of sulfolane in the whole range of the toluene mole fractions in the heptane-rich phase. Moreover, in contrast with sulfolane the distribution ratios for the four ILs increase with decreasing values of the toluene mole fractions in the heptane-rich phase. The pyridinium-based ionic liquids clearly show the best values of the toluene distribution ratio. However, there were really few differences between the separation factors shown by the pyridinium-based and imidazolium-based ionic liquids when they have the same alkyl side chains in the cations. Nevertheless, pyridinium-based ionic liquids tend to show slightly better values of separation factors at low toluene mole fractions in the heptane-rich phase than those of imidazolium-based ionic liquids. Therefore, in view of the experimental results, it can be concluded that only the [3-mC₂py][Tf₂N] can reach better aromatic extraction results than sulfolane.

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