

Highly Selective Extraction of Toluene from n-Heptane using [emim][SCN] Pure Ionic Liquid and its Mixtures with Several Transition Metal Salts

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In this work, we have studied the liquid–liquid extraction of toluene from toluene/n–heptane mixtures with 10 % of toluene in mass basis at 313.2 K and atmospheric pressure using 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]) ionic liquid (IL) as extraction solvent. Also, we have employed as extraction solvents binary mixtures of [emim][SCN] with AgBF_4 , AgNO_3 , Co(SCN)_2 , CuSCN , and AgSCN in a transition metal salt concentration of 0.5 M, to evaluate the influence of adding metal salts to the IL on the extraction efficiency. To perform a comparative analysis of extractive properties of the IL-based solvents and those of sulfolane, toluene distribution ratios and toluene/n-heptane selectivities were calculated from the liquid-liquid equilibrium (LLE) data. Dynamic viscosities of the solvents were also measured at the temperature range from 293.2 to 353.2 K. Pure [emim][SCN] IL could be considered as an alternative to organic solvents, since this IL has shown adequate physical and extractive properties. By contrast, salt addition caused an important increase in the dynamic viscosity of the IL, and the extractive properties of these mixtures were quite similar to the results obtained with pure [emim][SCN].

1. Introduction

An ionic liquid is a salt composed of an anion and a cation with a melting point below 373 K, and the most remarkable property of ILs is their practically negligible vapor pressure. Physicochemical properties of ILs can be modified by changing the structure of the anion, the cation, or both, and for this reason ILs are usually described as designer solvents (Rogers and Seddon, 2003).

Liquid–liquid extraction of aromatic hydrocarbons is currently performed using organic compounds as solvent, such as sulfolane, at industrial scale. The replacement of these organic solvents by ILs would reduce environmental impact, energy consumption, and process steps of the aromatic separation process, as a result of their non-volatile behavior. Among pure ILs and binary IL mixtures studied until now only a small number has shown proper physical and extractive properties to be considered as alternative solvents (Meindersma et al., 2010; García et al., 2011a; García et al., 2012; Larriba et al., 2013).

The main drawback of ILs compared to conventional organic compounds used in aromatic extraction is their high viscosity (Meindersma and de Haan, 2012). Therefore, we have selected in this work the 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]), since the [emim] cation has a high aromatic character and this IL has a viscosity substantially lower than that of ILs studied so far in the extraction of aromatics.

On the other hand, several authors concluded that the addition of transition metal salts to ILs increases the olefins/parafins selectivity (Azhin et al. 2008; Galán Sánchez et al. 2009; Li et al. 2012). Because of this, we have analyzed the effect on aromatic/aliphatic selectivity and on toluene distribution ratio of adding the following salts in a concentration of 0.5 M to pure [emim][SCN]: AgSCN , CuSCN , Co(SCN)_2 , AgNO_3 , and AgBF_4 . Salt concentration was the same in all cases to allow a quantitative comparison of the effect of salts, and the value of 0.5 M was selected to ensure a complete dissolution of the salts in the IL.

The aim of this work was to evaluate the potential of [emim][SCN] and its mixtures with five transition metal salts to be used as solvents in aromatic extraction. For this purpose, we have made a comparative analysis between extractive properties and viscosities of these solvents and those of sulfolane.

2. Experimental

2.1 Chemicals

Toluene and n-heptane over molecular sieves were purchased from Sigma-Aldrich with mass fraction purities greater than 0.995 and 0.997, respectively. 1-Ethyl-3-methylimidazolium thiocyanate ([emim][SCN]) IL was supplied by Iolitec GmbH with mass fraction purity higher than 0.98, and water and halides mass fractions less than 0.002 and 0.02, respectively. The following transition metal salts were also purchased from Sigma-Aldrich: silver tetrafluoroborate (AgBF_4), silver nitrate (AgNO_3), Cobalt (II) thiocyanate ($\text{Co}(\text{SCN})_2$), copper (I) thiocyanate (CuSCN), and silver thiocyanate (AgSCN) with mass fraction purity higher than 0.99. All chemicals were used as received without further purification. To avoid water absorption, chemicals were stored in a desiccator in their original tightly closed bottles and the handling of the IL was made in a glove box filled with dry nitrogen.

2.2 Experimental procedure

Liquid-liquid equilibrium experiments were gravimetrically carried out in 8 mL vials with screw caps using a Mettler Toledo XS 205 balance with a precision of $\pm 1 \cdot 10^{-5}$ g. Firstly, 2 mL of a toluene/n-heptane binary mixture with 10 % of toluene in mass basis was added. Subsequently, the same volume of {pure [emim][SCN], ([emim][SCN] + AgBF_4 0.5 M), ([emim][SCN] + AgNO_3 0.5 M), ([emim][SCN] + $\text{Co}(\text{SCN})_2$ 0.5 M), ([emim][SCN] + CuSCN 0.5 M), or ([emim][SCN] + AgSCN 0.5 M)} was gravimetrically added. The LLE was reached using a Labnet Vortemp 1550 shaking incubator at (313.2 ± 0.1) K for 5 h at 800 rpm. Afterwards, vials were left to settle in a Labnet Accublock dry bath during 12 h at (313.2 ± 0.1) K.

On the other hand, dynamic viscosities of the pure [emim][SCN] and its mixtures with transition salts were determined at temperatures between 293.2 and 353.2 K. Viscosities were measured in an Anton Paar Automated Micro Viscometer (AMVn) based on the falling ball principle. Experimental uncertainty of dynamic viscosities was estimated to be less than ± 0.9 %. A complete description of this measurement method can be found in Larriba et al. (2011 and 2012).

2.3 Analysis

The compositions of the raffinate (n-heptane rich phase) were measured using an Agilent 7890A Gas Chromatograph (GC). Three samples from n-heptane-rich phases were injected three times using an autosampler Agilent 7693, and the results shown in this paper are the average compositions. To determine the composition, we employed an area normalization method using gravimetrically prepared binary mixtures of toluene and n-heptane, and toluene was used as standard. Estimated uncertainties in toluene and n-heptane mass compositions in the raffinate phases were less than 0.0008. Solubility of ILs in the hydrocarbon rich-phase is usually considered negligible (García et al., 2011b). This fact was checked analyzing samples from the n-heptane rich phases using a Bruker Avance 500 MHz NMR spectrometer. In the ^1H NMR spectra, signals corresponding to ILs were not observed, and therefore, the mass fraction of the ILs in the raffinate was assumed to be zero.

The technique of multiple headspace extraction (MHE) was employed to determine the composition of the extract (IL-rich phase). In this quantitative technique, consecutive extractions from the headspace of the same vial are made to determine the amount of volatile analytes in the sample as the sum of the peak areas obtained. Three samples from extract phases were analyzed using an Agilent 7890A Gas Chromatograph equipped with a Headspace Sampler Agilent 7697A. Samples from the IL-rich phase were added to 20 mL tared vials, and the exact amount was determined using the balance described previously. Tightly sealed vials were introduced to the oven of the headspace sampler at 393.2 K during 1 h with a shaking speed of 100 rpm to promote the evaporation of the hydrocarbons. In this technique, the IL is not introduced to the chromatographic column due to its non-volatile behavior, and this fact is an important advantage compared to the usual technique of GC. The mass fraction of IL in the IL-rich phase can be easily estimated as the difference between the mass of the sample added to the vial and the weight of toluene and n-heptane determined by the MHE technique. The estimated uncertainty in the toluene mass fractions in the extract phase was less than 0.0011, whereas that of n-heptane was estimated to be lower than 0.0004. A more detailed overview of GC and HSGC analysis methods is published in Larriba et al. (2013), and a full description of the MHE technique can be found in Kolb and Ettre (1997).

3. Results and Discussion

Experimental compositions of the heptane-rich (raffinate) and IL-rich (extract) phases in equilibrium for the ternary systems {heptane (1) + toluene (2) + ([emim][SCN], ([emim][SCN] + AgBF_4 0.5 M), ([emim][SCN] + AgNO_3 0.5 M), ([emim][SCN] + $\text{Co}(\text{SCN})_2$ 0.5 M), ([emim][SCN] + CuSCN 0.5 M), or ([emim][SCN] + AgSCN 0.5 M)) (3)} at 313.2 K and atmospheric pressure are listed in Table 1.

Table 1: Experimental LLE data on mass fraction (w_i), distribution ratios (D_i), and toluene/n-heptane selectivities ($\alpha_{2,1}$) for the ternary systems {heptane (1) + toluene (2) + extraction solvent (3)} with 10 % in weight basis of toluene in feed and at 313.2 K.

Extraction Solvent	n-Heptane rich phase			Ionic liquid-rich phase			D_1	D_2	$\alpha_{2,1}$
	w_1	w_2	w_3	w_1	w_2	w_3			
[emim][SCN]	0.9174	0.0826	0.0000	0.0011	0.0095	0.9894	0.0012	0.115	97.7
[emim][SCN] + AgBF ₄ 0.5 M	0.9166	0.0834	0.0000	0.0008	0.0084	0.9908	0.0010	0.100	104.9
[emim][SCN] + AgNO ₃ 0.5 M	0.9161	0.0839	0.0000	0.0009	0.0083	0.9908	0.0010	0.099	99.7
[emim][SCN] + Co(SCN) ₂ 0.5 M	0.9209	0.0791	0.0000	0.0013	0.0103	0.9884	0.0014	0.130	95.6
[emim][SCN] + CuSCN 0.5 M	0.9178	0.0822	0.0000	0.0010	0.0092	0.9898	0.0011	0.112	101.9
[emim][SCN] + AgSCN 0.5 M	0.9158	0.0842	0.0000	0.0009	0.0083	0.9908	0.0010	0.098	103.2

To study the potential employment of the [emim][SCN] IL and its mixtures with transition metal salts in an aromatics extraction process at industrial scale, their extractive and physical properties must be studied. Firstly, extractive capacity of these solvents was evaluated by calculating the n-heptane and toluene distribution ratios (D_i). On the other hand, the purity of the toluene extracted from the toluene/n-heptane mixture is related to the selectivity ($\alpha_{2,1}$). These parameters were calculated employing the following expressions from the LLE data:

$$D_1 = \frac{w_1^{II}}{w_1^I} \quad (1)$$

$$\alpha_{2,1} = \frac{w_2^I w_1^{II}}{w_2^{II} w_1^I} = \frac{D_2}{D_1} \quad (2)$$

where w_i is the mass fraction of the compound, whereas subscripts 1 and 2 refer to n-heptane and toluene, respectively. The superscript I denotes the raffinate (n-heptane-rich phase) and the superscript II the extract (IL-rich phase). Toluene and n-heptane distribution ratios and selectivities of the extraction solvents used here are shown in Table 1 along with the LLE experimental data.

As we have explained in the introduction section, sulfolane is the most commonly employed solvent in aromatic extraction processes, and because of this, it must be used as a benchmark. In Figure 1, toluene distribution ratios of the solvent studied in this work are shown together with the published data for the sulfolane under the same conditions ($T = 313.2$ K and 10 % of toluene in mass basis in toluene/n-heptane feed) (Meindersma et al., 2006). As can be observed, toluene distribution ratios of the pure [emim][SCN] and of its mixtures with inorganic salts were substantially lower than the sulfolane values. This aspect could imply a higher solvent-to-feed ratio and bigger extraction and regeneration units replacing sulfolane by the solvents studied (Meindersma and de Haan, 2012).

In Figure 2, toluene/n-heptane selectivity of the IL-based solvents and that of sulfolane are graphically shown. As can be seen, selectivities using [emim][SCN] and its mixtures with salts as solvents were approximately three times higher than that employing sulfolane. Therefore, toluene extracted by the IL-based solvents has a higher purity than that obtained with sulfolane. A higher purity of the solute would facilitate the purification of hydrocarbons extracted and it would reduce operating costs.

Comparing the results obtained for mixtures of transition metal salts and [emim][SCN] with those of the pure IL, we have not observed significant changes in values of toluene distribution ratio and toluene/n-heptane selectivity. Thus, the addition of transition metal salts appears not to cause an improvement in the liquid-liquid extraction of toluene from toluene/n-heptane mixtures with [emim][SCN] as solvent.

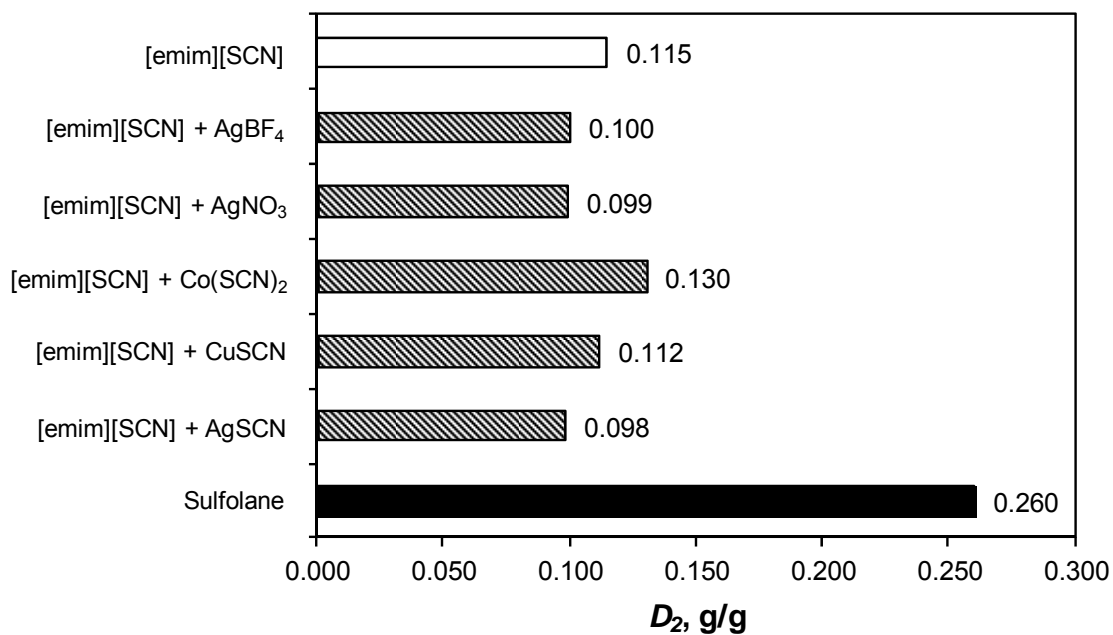


Figure 1: Mass-based toluene distribution ratios (D_2) at $T=313.2$ K in the liquid-liquid extraction of toluene from toluene/*n*-heptane mixtures with 10% of toluene in mass basis. Salt concentration in the ionic liquid was 0.5 M in all cases. Sulfolane data from Meindersma et al. (2006).

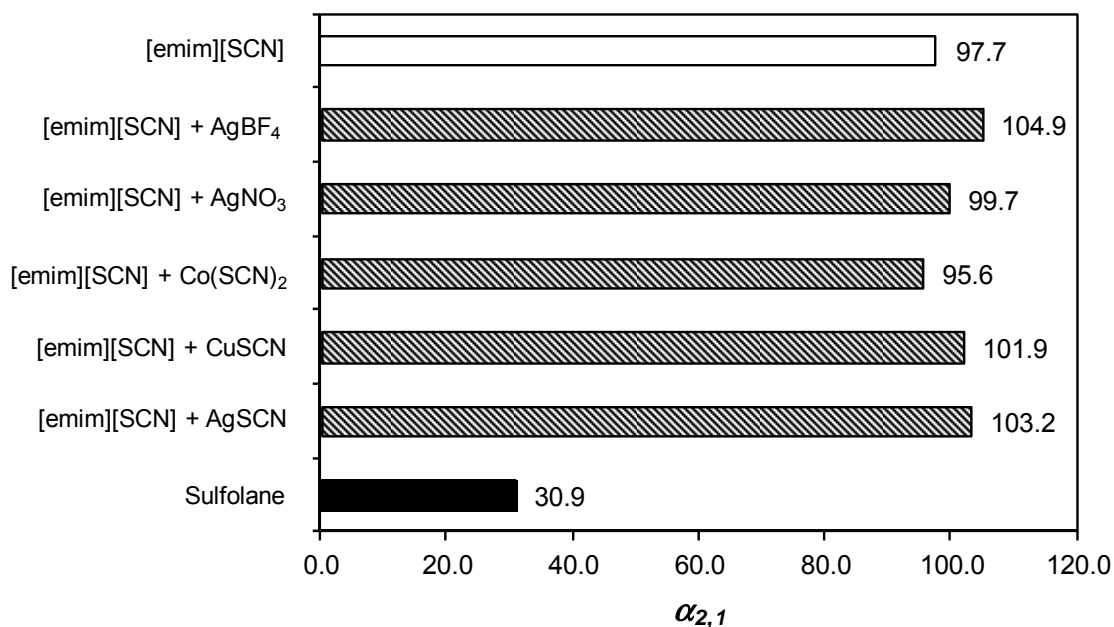


Figure 2: Toluene/*n*-heptane selectivity ($\alpha_{2,1}$) at $T=313.2$ K in the liquid-liquid extraction of toluene from toluene/*n*-heptane mixtures with 10% of toluene in mass basis. Salt concentration in the ionic liquid was 0.5 M in all cases. Sulfolane data from Meindersma et al. (2006).

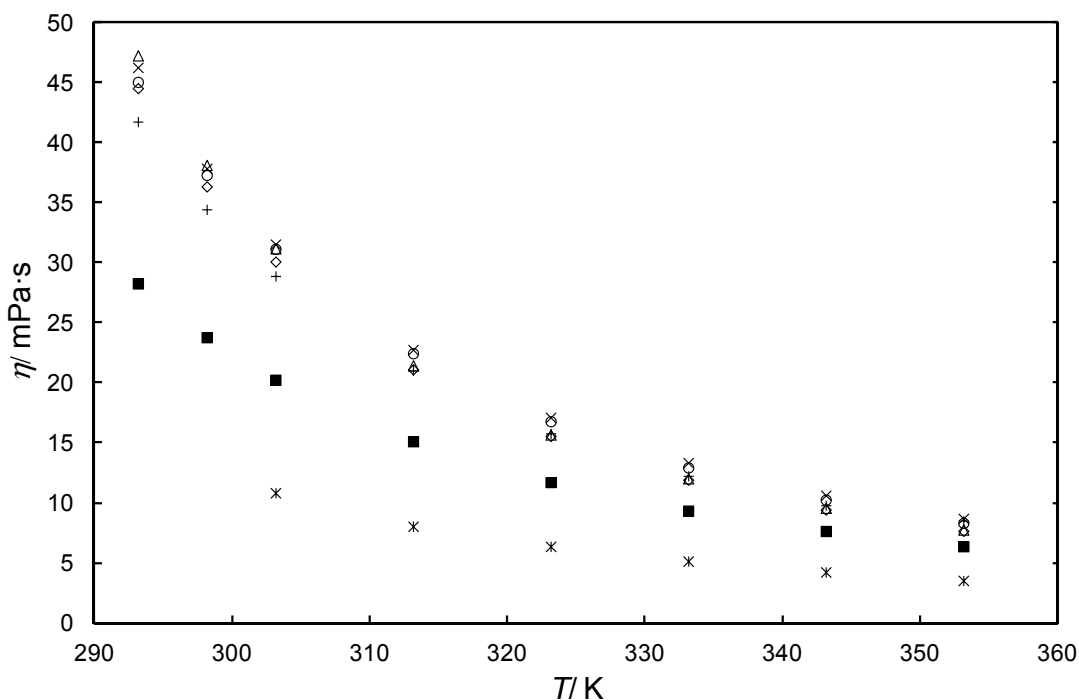


Figure 3: Dynamic viscosities as a function of temperature: ■, [emim][SCN]; +, [emim][SCN] + AgBF₄ 0.5 M; ×, [emim][SCN] + AgNO₃ 0.5 M; Δ, [emim][SCN] + Co(SCN)₂ 0.5 M; ◇, [emim][SCN] + CuSCN 0.5 M; ○, [emim][SCN] + AgSCN 0.5 M; *, sulfolane from Kelayeh et al. (2011).

As explained in the introduction section, IL-based solvents has a higher viscosity compared to organic solvents and it could imply an increase in mixing and pumping costs of the aromatic extraction unit. In Figure 3, dynamic viscosities of [emim][SCN] and of its mixtures with five transition metal salts are represented against temperature together with the published viscosity of sulfolane. As seen, the viscosity of pure [emim][SCN] is approximately twice than the sulfolane value. Despite this difference, the viscosity of [emim][SCN] (15.2 mPa·s at 313.2 K) is substantially lower than that of other promising ILs in aromatic extraction such as [4bmpy][BF₄] (92.4 mPa·s at 313.2 K) (Meindersma et al. 2011), or [emim][EtSO₄] (50.1 mPa·s at 313.2 K) (González et al. 2007).

Rosol et al. (2009) studied the influence of adding lithium salts to pure ILs, and they concluded that salt addition causes a substantial increase in dynamic viscosity. As can be seen in Figure 3, the same effect was observed in metal transition salts mixtures with [emim][SCN] IL. These mixtures shown viscosities between 21.0 and 22.4 mPa·s at 313.2 K, which means an increase of approximately 50 % with respect to the viscosity of pure [emim][SCN].

4. Conclusions

In this paper, we have studied the liquid-liquid extraction of toluene from toluene/n-heptane mixtures with 10 % of toluene in mass basis in feed using as extraction solvents pure [emim][SCN] IL and its mixtures with AgBF₄, AgNO₃, Co(SCN)₂, CuSCN, AgSCN in a salt concentration of 0.5 M. The performance of the solvents has been evaluated by calculating the values of toluene/n-heptane selectivity and toluene distribution ratio.

Pure [emim][SCN] has shown a toluene/n-heptane selectivity more than three times higher than the sulfolane value, and a toluene distribution ratio significantly lower than that of sulfolane. Therefore, toluene extracted using [emim][SCN] has much higher purity than that obtained with the organic solvent, but a higher solvent-to-feed ratio would be needed. This IL can be considered as an alternative to currently used solvents since [emim][SCN] has also shown proper dynamic viscosities.

On the other hand, the addition of metal transitions salts to [emim][SCN] has not increased appreciably the extraction efficiency compared to pure [emim][SCN]. In addition, the mixtures of [emim][SCN] with these salts have exhibited dynamic viscosities considerably higher than that of pure IL. Hence, the metal salts dissolution in ILs should not be considered as a further alternative in the field of research of ILs as aromatic extraction solvents.

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