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Experimental screening towards developing ionic liquid-based extractive distillation in the dearomatization of refinery streams

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Abstract

Ionic liquids (ILs) are potential neoteric solvents to design new advanced separation processes. Among several separation cases studied so far, the good performance of ILs regarding the dearomatization of liquid fuels, i.e. pyrolysis and reformer gasolines, has received especially attention. Indeed, a wide number of works has been done to characterize the phase equilibria for {aliphatic + aromatic + ILs} systems as well as the IL thermophysical properties, concluding in the development of a liquid-liquid extraction process. However, this technology seems not to be enough to fulfill current aromatic commercial standards nor potential incoming restrictions for aromatic content in liquid fuels as a result of its low separation effectiveness for extreme aliphatic and aromatic purification. Extractive distillation with ILs stands as a new process configuration to overcome these limitations by enhancing the aliphatic/aromatic relative volatilities. In this work, an IL experimental screening in the *n*-heptane/toluene separation was done to further develop this new IL-based technology. Nine ILs were tested as mass agents in a wide range of conditions, i.e. solvent to feed (S/F) ratios from 1 to 10 and temperatures from 323.2 to 403.2 K. The required vapor-liquid-liquid equilibria (VLLE) data were obtained by an experimental procedure based on headspace gas chromatography (HS-GC) developed in the framework of this work. Although all pre-selected ILs have shown good performance, tricyanomethanide-based ILs have been the most promising mass agents.

Keywords: Ionic liquids; aromatic/aliphatic separation; vapor-liquid-liquid equilibrium; extractive distillation

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1. Introduction

ILs are non-conventional salts that are liquid under 373 K and have negligible vapor pressure, showing an interesting liquid range of use [1]. Among other purposes, ILs have been successfully used in a high number of separation cases as solvents in liquid-liquid extraction processes or as mass agents in vapor-liquid separation technologies [2-11]. Liquid-liquid extraction processes using ILs have been designed to eliminate non-desirable compounds in final streams (i.e. aromatics or drugs) or to recover high-valuable substances (i.e. metals, proteins, nucleic acids, lipids or amino-acids) from waste streams [12-18]. As mass agents, ILs have been mainly proved in homogeneous {alcohol + water + IL} systems [19-22].

Focusing the attention in the dearomatization of hydrocarbon streams, which is one of the most prolific and hopeful research lines using ILs [23], several remarks can be given from the wide majority of the published works until now. It is important to mention that all these works were aimed in designing a liquid-liquid extraction process with ILs. From the liquid-liquid equilibrium (LLE) data referring to {aliphatics + aromatics + ILs} systems, it is possible to highlight the suitability of cyano-based and bis(trifluoromethylsulfonyl)imide-based ILs as can be seen in the recent review on the aromatic/aliphatic separation topic by Canales and Brennecke or in previous works based on both experimental data or COSMO-RS prediction studies [23-26]. Thiocyanate-based and dicyanamide-based ILs have shown aromatic/aliphatic selectivities quite higher than those for conventional organic solvents [27-29], whereas tricyanomethanide-based and bis(trifluoromethylsulfonyl)imide-based ILs displayed comparable or even higher aromatic distribution ratios in mass basis in comparison with those exhibited by the conventional solvents such as sulfolane [26-27, 30]. In addition to this, all of these ILs present low viscosities and enough densities to ensure two liquid phases splitting [26]. Therefore, by using these pure ILs or a well-selected binary mixture of them in the aromatic extraction from aromatic main sources, i.e. pyrolysis and reformer gasolines, the extractor efficiencies and size would be similar to that in the Sulfolane process and the aromatic purity in the extract stream would be increased [31]. However, further purification is mandatory in the extract stream to achieve a commercial purity of aromatics. In fact, Meindersma (2005) has advised years ago that an IL with an unrealistic toluene/*n*-heptane selectivity of 440 was necessary to avoid additional purifications [32]. Thus, the feasibility of the liquid-liquid extraction process is completely dependent on the efficiencies in the recovery section destined to selectively separate the aromatics from the extract stream.

To properly design this recovery section, our research group has been focused on determining the vapor-liquid equilibria (VLE) data regarding extract stream compositions [33]. The best process configuration obtained so far for the aromatic recovery section involved three flash distillation units; the first two flashes destined to selectively remove the aliphatics and the third to separate the aromatics from the IL-based solvent [12,34]. Other options as a lower number of flash distillation units or an stripping column were planned in the literature, but aromatic purity was far for commercial grade because it is essential to tune temperature and pressure in each equilibrium step [35]. Flash distillation units were selected to solve the aromatic purification and hydrocarbon remove from the solvent as a result of the high aliphatic/aromatic relative volatility shown in the extract stream compositions and the aforementioned non-volatile character of ILs. The commercial aromatic purities (99.9 wt. %) obtained after the recovery section, working at temperatures below the maximum operating temperature (MOT) estimated for the ILs, support the technical feasibility of the process [34].

Nevertheless, there are some limitations that IL-based liquid-liquid extraction technology seems not to be able to solve. Dearomatized gasolines showed a residual amount of aromatics that can vary between 1 – 2 wt. % [31, 36]. These values are slightly higher than current restrictions for benzene and toluene in liquid fuels [37] and can limit the uses of the outcome gasoline. Liquid-liquid extraction technology is not capable to reduce this residual aromatic content in the raffinate stream because ILs and commercial solvents have shown tie-lines with very low slope in the {aliphatic + aromatic + IL} ternary systems at low aromatic concentration [23]. Hence, the search of a new process configuration is necessary to achieve better aliphatic purities.

On the other hand, the values of aromatic purity obtained in the extract stream range from 97.2 to 98.4 wt. % [31, 36]. Although this was solved by a series of flashes as mention above, the recovery section has required very low vacuum conditions (near 5 kPa) at temperatures up to 393.2 K [34]. Taking into consideration that the MOTs for the potential ILs in the aromatic/aliphatic separation are below 500 K [29-30, 38-39], the recovery section for the extract stream irreparably implies high vacuum costs independently of the nature of the IL. In addition to this, the aromatic purification also implies recycling stream to the extractor, fact that implies a higher IL consumption [35]. Therefore, it is important to develop an IL-based technologies that can avoid additional separation steps in the way of process intensification and taking also into account that coming directives will probably strengthen impurity limits and future technologies must deal with even lower impurities.

IL-based extractive distillation can overcome the aforementioned limitations by enhancing the aliphatic/aromatic relative volatilities, as previously suggested [40-41]. Extractive distillation takes advantage of the good performance seen in liquid-liquid extraction technology with ILs together with the volatility difference as an additional driving force to separate aromatics from gasolines and jointly purify aromatic-rich and aliphatic-rich streams [41].

In this work, an experimental screening for nine ILs as mass agents in the toluene/*n*-heptane separation by extractive distillation is presented. ILs were selected by their highlighted extractive properties in the toluene separation from *n*-heptane and also by their low viscosity [23]. The VLLE data have been determined by HS-GC in {*n*-heptane + toluene + IL} ternary systems. The {*n*-heptane + toluene} binary system was fixed to a toluene content of 66 wt. % due to the typical aromatic content in the pyrolysis gasoline [42], whereas the S/F ratio was studied from 1 to 10 within the (323.2 to 403.2) K temperature range. S/F ratio has been evaluated in this range to include both the values that were used in previous publications and those used currently at industrial scale [40, 42].

2. Experimental section

2.1. Chemicals

The nine ILs, namely 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]), 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]), 1-butyl-3-methylimidazolium tricyanomethanide ([bmim][TCM]), 1-butyl-4-methylpyridinium tricyanomethanide ([4bmpy][TCM]), 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf₂N]), and 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4bmpy][Tf₂N]), were acquired from Iolitec GmbH with purities higher than 98 wt. % for cyano-based ILs and higher than 99 wt. % for bis(trifluoromethylsulfonyl)imide-based ILs. They have been used as received without further purification and handled into a glove box under an inert atmosphere of dry nitrogen. Hydrocarbons (toluene and *n*-heptane) were supplied by Sigma-Aldrich with purities higher than 99.5 wt. % and were kept into their original vessels over molecular sieves. Additional details for the chemicals used in this work can be found in Table 1.

Table 1 Specifications of chemicals

Chemical	Source	Analysis method	Purity in wt. %	Water content in ppm
[emim][SCN]	Iolitec GmbH	NMR ^a , IC ^b	98	1678
[bmim][SCN]	Iolitec GmbH	NMR ^a , IC ^b	98	1831
[emim][DCA]	Iolitec GmbH	NMR ^a , IC ^b	98	1121
[bmim][DCA]	Iolitec GmbH	NMR ^a , IC ^b	98	1760
[emim][TCM]	Iolitec GmbH	NMR ^a , IC ^b	98	537
[bmim][TCM]	Iolitec GmbH	NMR ^a , IC ^b	98	153
[4bmpy][TCM]	Iolitec GmbH	NMR ^a , IC ^b	98	304
[4empy][Tf ₂ N]	Iolitec GmbH	NMR ^a , IC ^b	99	76
[4bmpy][Tf ₂ N]	Iolitec GmbH	NMR ^a , IC ^b	99	48
<i>n</i> -heptane	Sigma-Aldrich	GC ^c	99.7	-
toluene	Sigma-Aldrich	GC ^c	99.5	-

^a Nuclear Magnetic Resonance

^b Ion Chromatography

^c Gas Chromatography

2.2. Vapor-liquid-liquid equilibrium procedure

The determination of VLLE data was solved by HS-GC technique, similar to that applied to determine the VLE for mixtures containing an aliphatic, an aromatic, and an IL [43]; only the essential information is displayed in this paper to understand the background of the technique and the novelty for the VLLE case.

The feed was prepared by mass using a Mettler Toledo XS205 balance with a precision of $\pm 10^{-5}$ g. Two sample vials were filled with a controlled volume of the mixture; one for characterizing the vapor phase and the other to characterize the IL-rich phase. Fig. 1 shows the schematic representation of the three phases in the vial. The vapor phase characterization leads to know the overall liquid molar amount and compositions, whereas the IL-rich liquid (liquid phase II) characterization permits to indirectly calculate the same information for the IL-free liquid (liquid phase I).

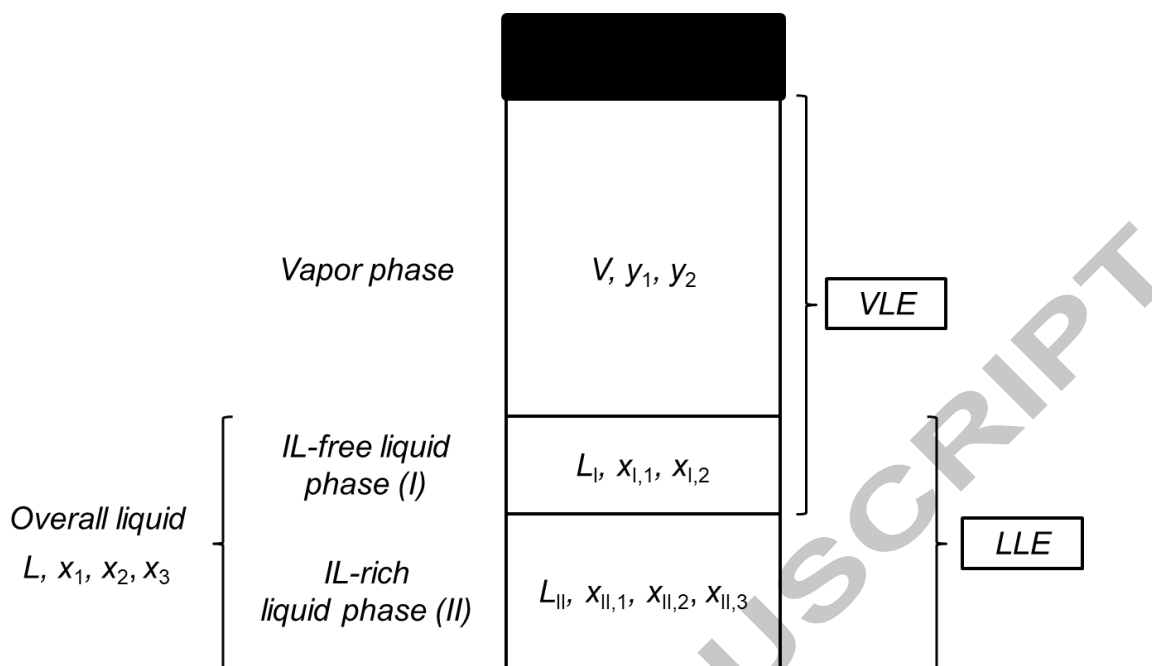


Fig. 1. VLE vial scheme for an $\{n\text{-heptane (1)} + \text{toluene (2)} + \text{IL (3)}\}$ system.

To characterize the vapor phase in the first vial, the equipment used to reach and analyze the equilibrium was an Agilent 7697A Headspace injector coupled to an Agilent 7890A GC. After two hours of equilibration, the vapor phase was analyzed by GC using the response factor method to correct the compositions. Thus, the overall liquid mole fractions (x_i), involving both IL-rich and IL-free liquid phases, can be recalculated with the feed compositions (z_i) and the hydrocarbon amount that goes to the vapor phase:

$$x_i = \frac{z_i \cdot F - (P_i \cdot V_G / RT)}{\sum_{i=1}^3 (z_i \cdot F - (P_i \cdot V_G / RT))} \quad (1)$$

where F denotes the molar amount of the feed, V_G is the headspace volume of the vial, and R is the ideal gas law constant. Partial pressures of n -heptane and toluene (P_i) were also calculated using the relationship between the peak areas of the hydrocarbons in the VLE experiments determined by HS-GC (A_i) and the peak areas developed by each hydrocarbon alone in the same conditions (A_i^0) [44]:

$$P_i = \frac{P_i^0 \cdot A_i}{A_i^0} \quad (2)$$

where P_i^0 refers to the vapor pressure of each pure hydrocarbon from literature [45]. Thus, the total pressure was calculated as the sum of the partial pressures.

The second vial was introduced in a Labnet Vortemp 1550 shaking incubator for 2 h to reach the equilibrium at the same temperature used in the HS-GC oven. After phase splitting, a sample from the liquid phase II was directly taken with a syringe and analyzed by multiple headspace extraction (MHE) technique. The details and background of the MHE method are widely explained in our previous work [27]. By knowing the mole fractions of the liquid phase II ($x_{II,i}$) and taking into account that the IL is only presented in this phase, the molar amounts of the two liquid phases (L_I and L_{II}) are calculated as follows:

$$L_{II} = \frac{L \cdot x_3}{x_{II,3}} \quad (3)$$

$$L_I = L - L_{II} \quad (4)$$

After that, the mole fractions of the liquid phase I ($x_{I,1}$ and $x_{I,2}$) can be calculated as:

$$x_{I,1} = \frac{L \cdot x_1 - L_{II} \cdot x_{II,1}}{L_I} \quad (5)$$

$$x_{I,2} = \frac{L \cdot x_2 - L_{II} \cdot x_{II,2}}{L_I} \quad (6)$$

The validation of the experimental proposal is here presented. As can be noticed, it is clear that vapor and liquid phase I must satisfy VLE, whereas liquid phase I and II must be in LLE. Figure 2 shows the percentage difference for the equilibrium pressure and the vapor mole fraction obtained in the comparison between the VLE data from the VLLE experiments (excluding the IL-rich liquid phase) and the VLE for the $\{n\text{-heptane} + \text{toluene}\}$ binary mixture at the same temperature previously reported [43]. As can be inferred from Fig. 2, there is a good agreement with the literature VLE with a mean relative deviation of 2.3 % for n -heptane mole fraction and 1.9 % for equilibrium pressure.

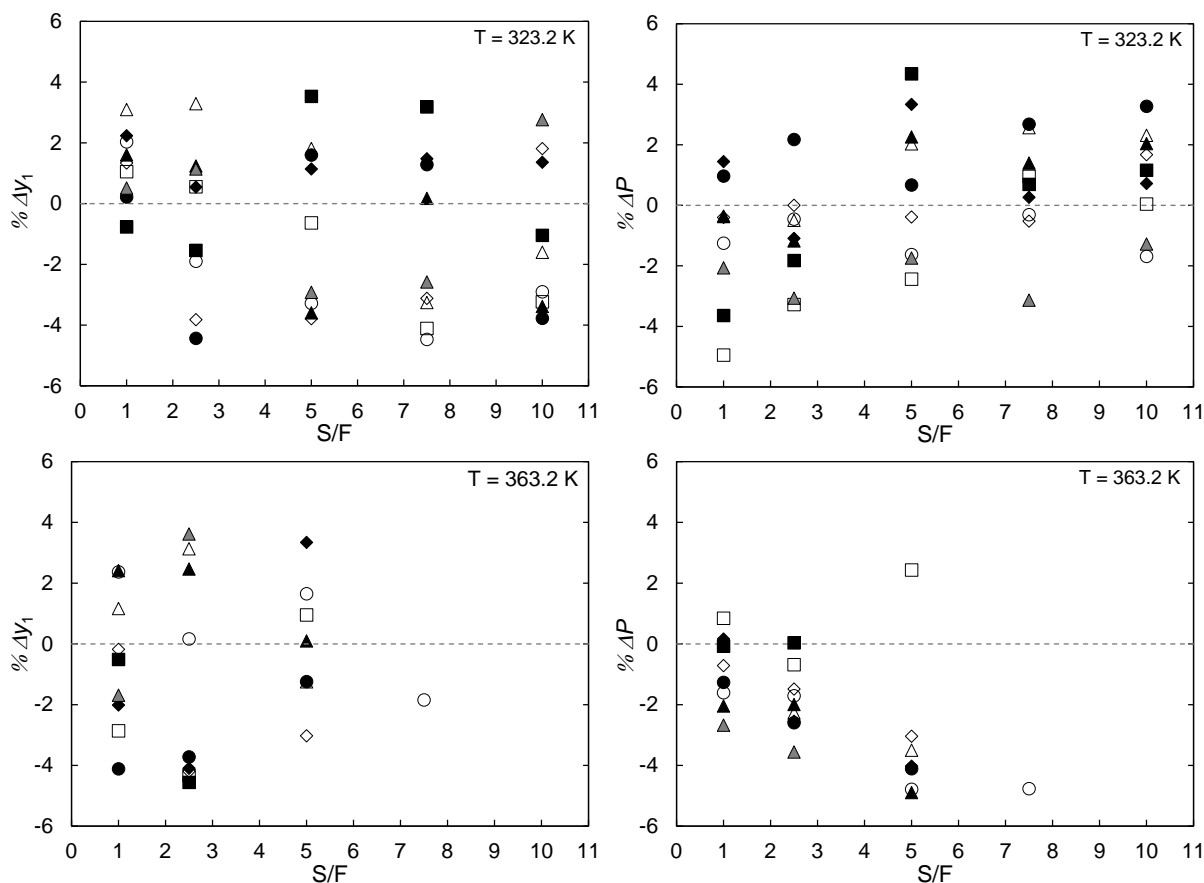


Fig. 2. Percentage difference for *n*-heptane mole fraction and equilibrium pressure in the comparison between VLE for {*n*-heptane + toluene} regarding new experimental VLLE and literature (Ref. 43) as a function of temperature. ILs: [emim][SCN], ○; [bmim][SCN], ●; [emim][DCA], ◇; [bmim][DCA], ◆; [emim][TCM], △; [bmim][TCM], ▲; [4bmpy][TCM], ▲; [4empy][Tf₂N], □; [4bmpy][Tf₂N], ■.

On the other hand, the extractive properties were calculated from the experimental LLE results and compared in Table 2 with those previously reported in similar conditions [27-28, 30, 46-47, 48]. Mass-based hydrocarbons distribution ratios (D_i) and toluene/*n*-heptane selectivities ($S_{2,1}$) were calculated using the following equations:

$$D_i \left(\frac{g}{g} \right) = \frac{w_i^{\text{II}}}{w_i^{\text{I}}} \quad (7)$$

$$S_{2,1} = \frac{D_2}{D_1} \quad (8)$$

where w_i are the mass fraction of each component, superscript I refers to liquid phase I, and superscript II indicates liquid phase II. As seen, there is a good agreement between experimental and literature data.

Table 2. Experimental (exptl, 323.2 K) and literature (lit, 313.2 K) toluene distribution ratios (D_2) and toluene/ n -heptane selectivities ($S_{2,1}$) for the LLE in the $\{n$ -heptane + toluene + IL} systems

IL	D_2 (exptl)/ g·g ⁻¹	D_2 (lit)/ g·g ⁻¹	$S_{2,1}$ (exptl)	$S_{2,1}$ (lit)	Ref.
[emim][SCN]	0.12	0.12	52.0	58.6	[28]
[bmim][SCN]	0.19	0.20	26.1	25.2	[28]
		0.192*		24.3*	[48]
[emim][DCA]	0.15	0.17	35.7	39.2	[27]
[bmim][DCA]	0.23	0.24	17.4	22.0	[27]
		0.232*		24.5*	[48]
[emim][TCM]	0.31	0.32	25.2	26.4	[27]
[bmim][TCM]	0.36	0.36	14.7	16.5	[30]
[4bmpy][TCM]	0.47	0.45	16.8	19.9	[30]
[4empy][Tf ₂ N]	0.30	0.36	9.4	12.2	[46]
[4bmpy][Tf ₂ N]	0.36	0.43	4.9	5.1	[47]

*Extractive properties at 328.2 K.

3. Results and discussion

3.1. VLLE data for $\{n$ -heptane + toluene + IL} systems within (323.2 to 363.2) K and with S/F ratios from 1 to 10

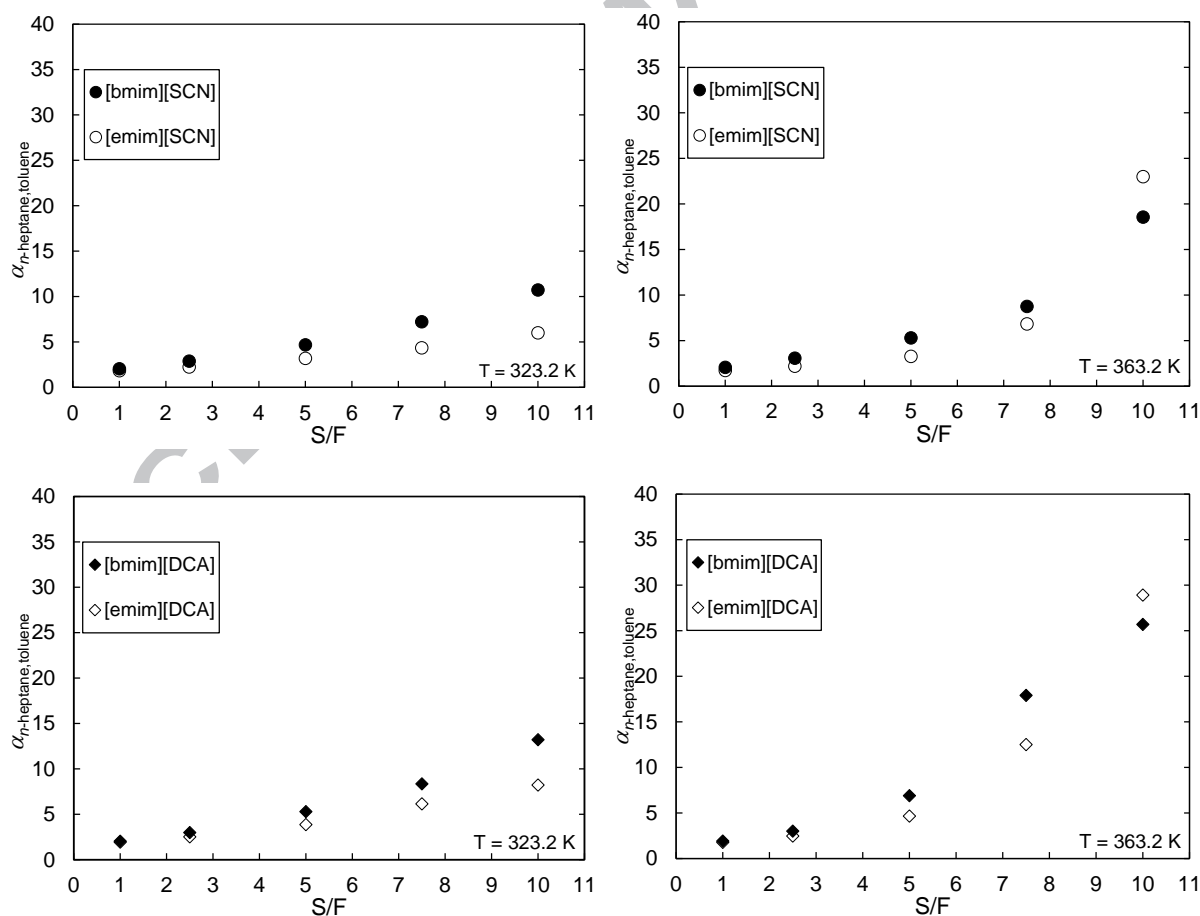
In this work the VLLE have been determined for $\{n$ -heptane + toluene + IL} ternary mixtures at temperatures of 323.2 K and 363.2 K. The composition of the binary mixture of hydrocarbons (feed) was fixed for a toluene mass fraction of 0.66, whereas the concentration of the IL (solvent) was studied for S/F ratios from 1 to 10. The VLLE data are listed in Tables S1 to S4 in the Supplementary Material. The IL effectiveness was evaluated by calculating the n -heptane (1) relative volatility from toluene (2) as follows:

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} \quad (9)$$

where K is the K -value for each volatile compound, y denotes the vapor mole fractions and x represents the overall liquid mole fractions. The values of n -heptane/toluene relative volatility are listed in Table S1 to S4 in the Supplementary Material together with the experimental compositions and are also graphically shown in Fig. 3 for all ILs as a function of both temperature and S/F ratio. The n -heptane/toluene relative volatility increases with an increase of S/F ratio because higher amounts of the hydrocarbons, preferably toluene, are retained in the liquid phase II, enriching in n -heptane the liquid phase I and, consequently, the vapor phase.

On the other hand, increasing the value of temperature negatively impacts on the amount of liquid phase I in favor to the vapor phase with a negligible impact on the *n*-heptane/toluene relative volatility at S/F ratios lower than 5 but with an important increase at higher IL concentrations. In fact, the highest *n*-heptane/toluene relative volatility is observed at 363.2 K and with an S/F ratio of 10, showing also a homogeneous VLE system. Then, high S/F ratios are required to ensure a good separation effectiveness and deal with homogeneous extractive distillation.

However, temperature has shown a hardly effect on *n*-heptane/toluene relative volatility in the {*n*-heptane + toluene + [4bmpy][TCM] / [4bmpy][Tf₂N]} ternary systems at S/F ratio of 10. This is explained by the high hydrocarbon solubilities in these ILs [30,47], fact that combined to a high S/F ratio drastically reduces aromatic content in vapor and IL-free liquid phases even at low temperatures. Then, increasing the temperature in these systems does not lead to significant changes in the three phases composition neither in the *n*-heptane/toluene relative volatility.



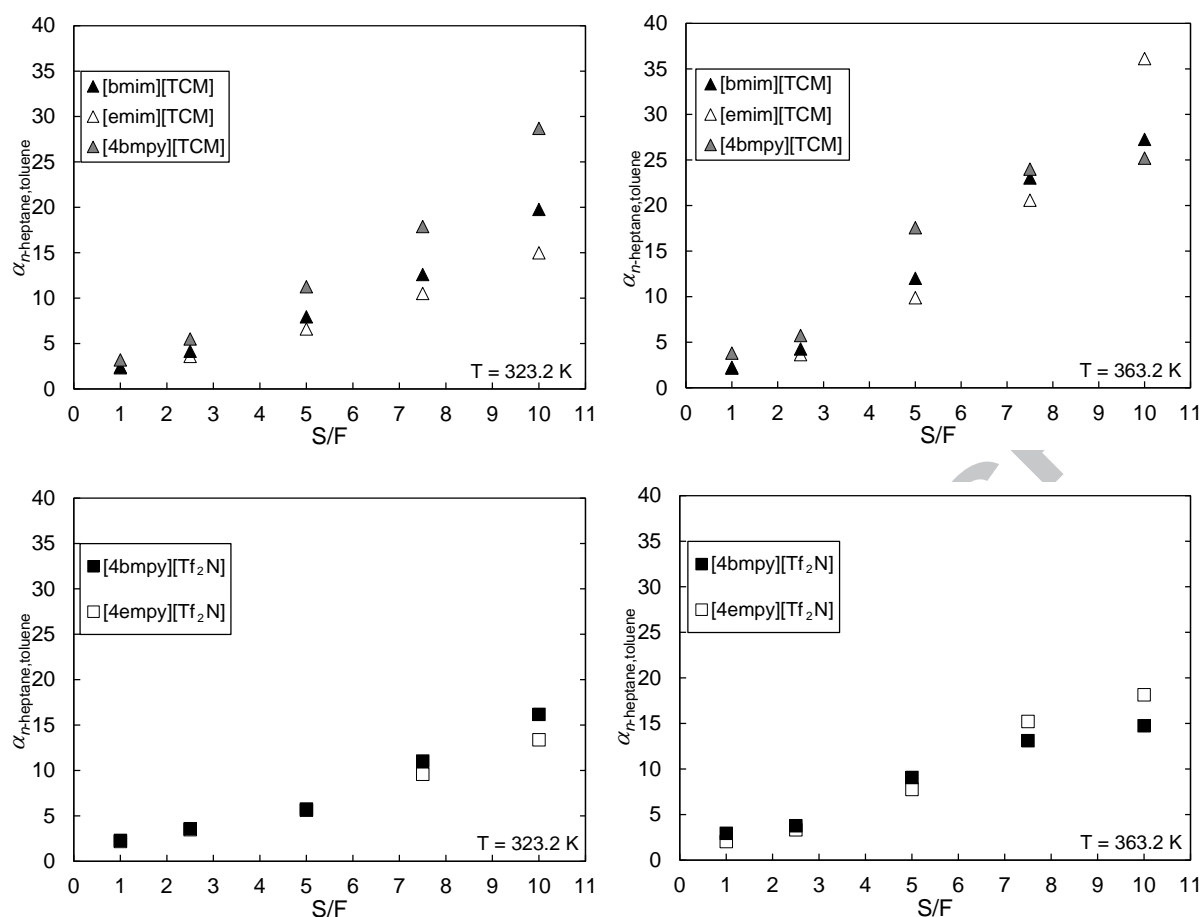


Fig. 3. Relative volatility of *n*-heptane from toluene as a function of S/F and temperature for several ILs.

As the differences between ILs are higher at S/F ratio of 10, the comparison between ILs was done only at this IL concentration. Tricyanomethanide-based ILs have revealed themselves as the most effective mass agents in separating *n*-heptane and toluene at the two temperatures tested. Among the others, bis(trifluoromethylsulfonyl)imide-based ILs have shown higher *n*-heptane/toluene relative volatility than dicyanamide and thiocyanate-based ILs at 323.2 K, whereas the opposite trend was found at 363.2 K. In addition to this, those ILs with butyl groups in the cation instead of ethyl substituents, for imidazolium and pyridinium cases, have led to achieve higher *n*-heptane/toluene relative volatilities at 323.2 K; however, the opposite behavior was observed at 363.2 K. Moreover, the comparison between [4bmpy][TCM] and [bmim][TCM] has set that pyridinium instead of imidazolium cation improves *n*-heptane/toluene relative volatility at 323.2 K but slightly deteriorates it at 363.2 K. These trends are supported by the IL extractive properties, shown in Fig. 4. Thiocyanate and dicyanamide-based ILs show high values of toluene/*n*-heptane selectivity, whereas bis(trifluoromethylsulfonyl)imide-based ILs have much larger toluene distribution ratios and quite lower selectivities. Tricyanomethanide-based ILs show an intermediate behavior that

implies almost the same toluene distribution ratios as bis(trifluoromethylsulfonyl)imide-based ILs and slightly lower selectivities than dicyanamide-based ILs.

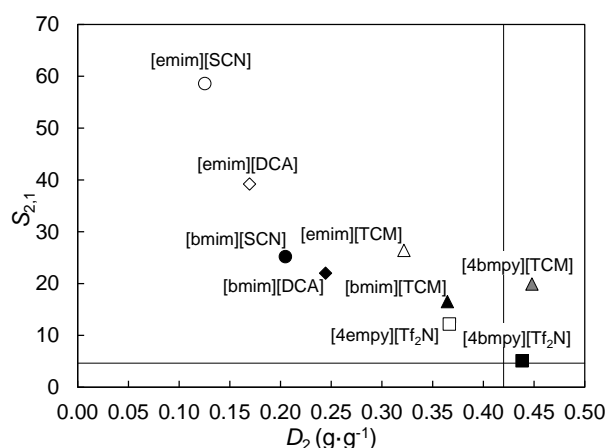


Fig. 4. Toluene/*n*-heptane selectivities vs toluene mass-based distribution ratios at 313.2 K in the LLE of toluene from mixtures with *n*-heptane with an approximate mass fraction of toluene of 0.66 taken from Refs. 27, 28, 30, 46, 47. Solid lines represent sulfolane values at the same conditions used as benchmark and taken from Ref. 16.

Correlating the *n*-heptane/toluene relative volatilities trends with the IL extractive properties, it was found that temperature sets the dominant extractive property as depicted in Fig. 5 for the three most representative ILs. At 323.2 K, the IL with the highest distribution ratio ([4bmpy][TCM]) has shown the higher values of *n*-heptane/toluene relative volatility, whereas the ILs with the high toluene/*n*-heptane selectivity ([emim][SCN]) or intermediate extractive properties ([emim][TCM]) have enhanced the values of *n*-heptane/toluene relative volatility at 363.2 K.

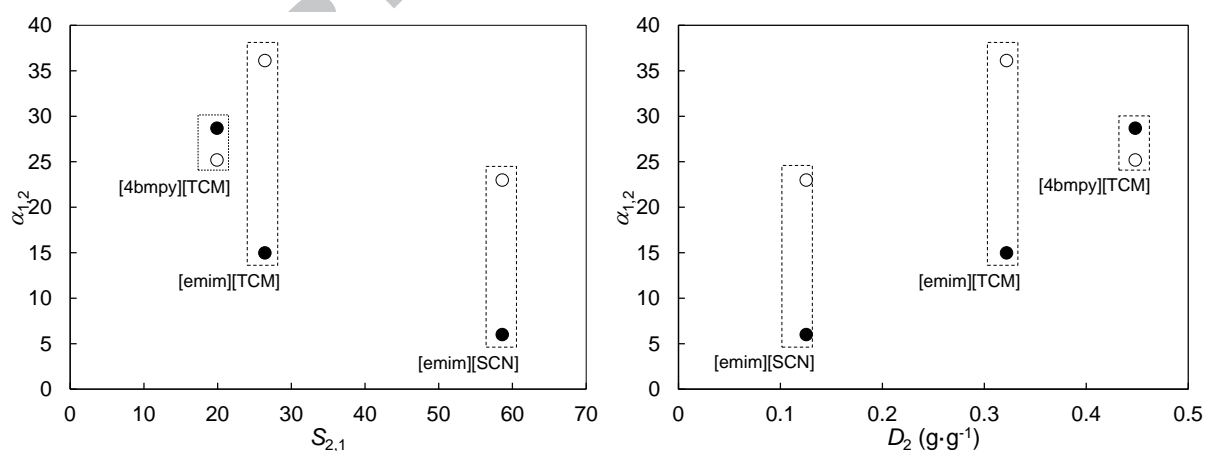


Fig 5. Relative volatility of *n*-heptane from toluene ($\alpha_{1,2}$) at 323.2 K (full symbols) and 363.2 K (empty symbols) and S/F ratio of 10 vs toluene/*n*-heptane selectivities ($S_{2,1}$) and toluene distribution ratios (D_2) at 313.2 K with the same hydrocarbon feed.

3.2. VLLE data for {*n*-heptane + toluene + [emim][SCN] or [emim][TCM] or [4bmpy][TCM]} up to 403.2 K

The evolution of *n*-heptane/toluene relative volatility with temperature for the three aforementioned ILs within (323.2 to 363.2) K has demanded to increase temperature and inspect its impact on the *n*-heptane/toluene relative volatility. Additional VLLE were obtained for {*n*-heptane + toluene + [emim][SCN] / [emim][TCM] / [4bmpy][TCM]} up to 403.2 K. Results are summarized in Tables S5 to S7 in the Supporting Information. From these values, as depicted in Fig. S1 in the Supporting Information, it is clear that the best results were obtained with an S/F ratio of 10 for the three ILs even at higher temperatures. For this reason, Fig. 6 shows the evolution of *n*-heptane/toluene relative volatility with temperature within (323.2 to 403.2) K to discuss cross-effects between the IL extractive properties and temperature. In addition to this, it is also clear that increasing temperature does not permit to obtain high enough values of *n*-heptane/toluene relative volatilities with S/F ratios lower than those studied for liquid-liquid extraction (S/F ratio near to 5) to ensure complete separation and purification [31, 36].

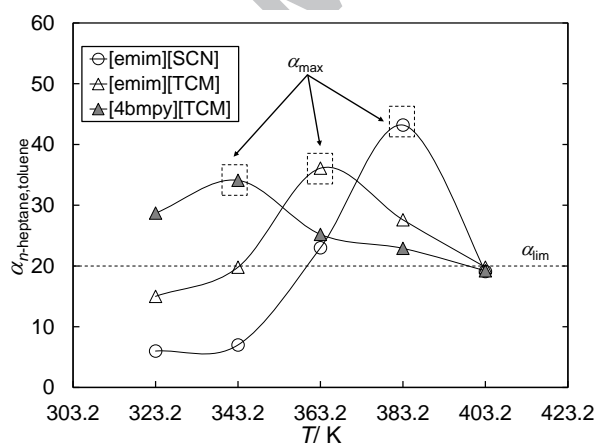


Fig. 6. Relative volatility of *n*-heptane from toluene with S/F = 10 for [emim][SCN], [emim][TCM], and [4bmpy][TCM] as a function of temperature. Highlighted zones denote maximum *n*-heptane/toluene relative volatility for each IL (α_{\max}) and the approximate limit seen for the three ILs at 403.2 K ($\alpha_{\lim} = 20$)

As seen, [4bmpy][TCM] has shown the best performance at 323.2 K and 343.2 K, whereas [emim][TCM] and [emim][SCN] have presented the higher *n*-heptane/toluene relative volatility at 363.2 K and 383.2 K, respectively. Therefore, it is possible to claim that higher toluene distribution ratio ([4bmpy][TCM] ($0.45 \text{ g}\cdot\text{g}^{-1}$) > [emim][TCM] ($0.32 \text{ g}\cdot\text{g}^{-1}$) > [emim][SCN] ($0.12 \text{ g}\cdot\text{g}^{-1}$)) enhances higher *n*-heptane/toluene relative volatility at 323.2 K, whereas higher toluene/*n*-heptane selectivity ([emim][SCN] (58.6) > [emim][TCM] (26.4) > [4bmpy][TCM] (19.9)) leads to achieved higher *n*-heptane/toluene relative volatility at higher

temperatures (383.2 K). In other words, there are two driving forces regarding the use of a mass agent: capacity and selectivity; capacity works preferably for low solubility cases (heterogeneous) and selectivity is the essential property of a mass agent for high solubility (homogeneous) cases. As temperature decreases the insolubilized liquid amount, low temperature can be related to well-performance zone for high capacity ILs, whereas high temperatures imply better results with high selectivity mass agents. Finally, a final decrease of all ILs effectiveness is expected increasing temperature over the boiling point of the compounds to be separated because the IL interaction with the hydrocarbons is lower as temperature increases; thus, IL effectiveness as function of temperature describes a maximum. Hence, it is important to fully cover a wide range of temperature prior to select an IL as mass agent in the *n*-heptane/toluene relative volatility. In order to analyze the implications of this trend with temperature, certain parameters are depicted in Table 3 along with IL key properties: thermal stability and viscosity.

Table 3. Key parameters and properties for the three ILs to be used as mass agents in the *n*-heptane separation from toluene at S/F ratio of 10

IL	α_{\max}	α_{mean}	$T_{\text{range},20}$ / K	MOT/ K	μ / mPa·s (323.2 K)
[emim][SCN]	43.2 (383.2 K)	19.7	358 – 403	360 [30]	11.7 [28]
[emim][TCM]	36.1 (363.2 K)	23.7	343 – 403	452 [30]	7.7 [27]
[4bmpy][TCM]	34.1 (343.2 K)	26.0	323 – 403	447 [37]	14.1 [37]

α_{\max} , maximum *n*-heptane/toluene relative volatility
 α_{mean} , mean *n*-heptane/toluene relative volatility in the temperature range of (323.2 to 403.2) K
 $T_{\text{range},20}$, temperature range that assays an *n*-heptane/toluene relative volatility of 20 (see Figure 6 for details)
MOT, maximum operation temperature
 μ , dynamic viscosity

It is clear that maximum *n*-heptane/toluene relative volatility (α_{\max}) is not enough to establish the IL suitability as mass agent, whereas α_{mean} and $T_{\text{range},20}$ permit to evaluate the real potential of the IL since the extractive distillation column will work showing a temperature profile and the IL effectiveness must cover it. Thus, both tricyanomethanide-based ILs seem to be the most promising mass agents according to the wider effectiveness temperature range and better performance within (323.2 to 403.2) K.

In addition, [emim][TCM] and [4bmpy][TCM] show comparable dynamic viscosity at 323.2 K to the values of ethylene glycol, 10.4 mPa·s [49], and sulfolane, 6.4 mPa·s [27]. Finally, [emim][TCM] is the nearest IL to N-methylpyrrolidone, 1.2 mPa·s [50]. Then, considering mass transfer, [emim][TCM] would require the same or even lower stages in a hypothetical extractive distillation column in comparison with [4bmpy][TCM].

4. Conclusions

The use of ILs as mass agents has been evaluated in the aromatic/aliphatic separation by extractive distillation. An experimental screening has been performed selecting the most promising IL proved so far as solvents in the liquid-liquid extraction of aromatics from aliphatics. In addition to evaluate the anion, the cation, and the length of the cation substituents, both S/F ratio and temperature have been also analyzed in the ranges of 1 to 10 and (323.2 to 403) K, respectively.

Extractive distillation stands as a promise unit operation in the aromatic/aliphatic separation with ionic liquid as a result of the high *n*-heptane/toluene relative volatility (6 – 43) values obtained in this work using an S/F ratio of 10. At low temperatures, the capacity of extraction has played the dominant role, whereas increasing temperature gives higher importance to the toluene/*n*-heptane selectivity of the IL. Accordingly, an IL with high and compensate extractive properties is the best option to design an effective extractive distillation process to isolate the aromatics from pyrolysis gasoline. Among the ILs analyzed, the use of tricyanomethanide-based ILs seems to enhance *n*-heptane/toluene relative volatility values using an S/F ratio of 10 (15 – 36), offering also a quite flexible operating range of temperatures in the extractive distillation column with high effectiveness. Considering also mass transfer properties, [emim][TCM] is probably the best candidate to further inspect this new separation technology using ILs.

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**Experimental screening towards developing ionic
liquid-based extractive distillation in the
dearomatization of refinery streams**

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SUPPLEMENTARY MATERIAL

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Table S1 Experimental VLLE or VLE data^a for several {*n*-heptane (1) + toluene (2) + IL (3)} systems at different temperatures and S/F ratio. Thiocyanate-based ILs

IL	<i>T</i> / K	S/F	<i>P</i> / kPa	Vapor phase		Overall liquid			Liquid II			Liquid I		$\alpha_{1,2}$
				<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
[emim][SCN]	323.2	1.0	15.8	0.4603	0.5397	0.1997	0.4305	0.3698	0.0014	0.1355	0.8631	0.349	0.651	1.8
		2.5	16.1	0.5053	0.4947	0.1262	0.2781	0.5957	0.0017	0.1094	0.8889	0.380	0.620	2.3
		5.0	16.3	0.5790	0.4210	0.0745	0.1730	0.7525	0.0019	0.1031	0.8950	0.460	0.540	3.2
		7.5	16.9	0.6359	0.3641	0.0513	0.1280	0.8207	0.0022	0.0903	0.9075	0.520	0.480	4.4
		10.0	17.0	0.6880	0.3120	0.0367	0.1001	0.8632	0.0026	0.0809	0.9165	0.597	0.403	6.0
	363.2	1.0	66.2	0.4392	0.5608	0.1908	0.4223	0.3869	0.0022	0.1561	0.8417	0.349	0.651	1.7
		2.5	67.0	0.4806	0.5194	0.1107	0.2625	0.6268	0.0022	0.1277	0.8701	0.386	0.614	2.2
		5.0	66.5	0.5357	0.4643	0.0559	0.1586	0.7855	0.0024	0.1109	0.8867	0.461	0.539	3.3
		7.5	67.8	0.6155	0.3845	0.0262	0.1118	0.8620	0.0027	0.0973	0.9000	0.532	0.468	6.8
		10.0	59.7	0.6601	0.3399	0.0076	0.0901	0.9023	-	-	-	-	-	23.0
[bmim][SCN]	323.2	1.0	16.2	0.4856	0.5144	0.2095	0.4536	0.3369	0.0050	0.2243	0.7707	0.369	0.631	2.0
		2.5	16.8	0.5634	0.4366	0.1354	0.3032	0.5614	0.0062	0.1874	0.8064	0.433	0.567	2.9
		5.0	17.4	0.6587	0.3413	0.0787	0.1911	0.7302	0.0063	0.1609	0.8328	0.598	0.402	4.7
		7.5	18.1	0.7278	0.2722	0.0531	0.1436	0.8033	0.0064	0.1301	0.8635	0.684	0.316	7.2
		10.0	18.3	0.7784	0.2216	0.0377	0.1150	0.8473	0.0067	0.1057	0.8876	0.698	0.302	10.7
	363.2	1.0	66.7	0.4796	0.5204	0.1991	0.4474	0.3535	0.0067	0.2250	0.7683	0.361	0.639	2.1
		2.5	67.7	0.5555	0.4445	0.1162	0.2866	0.5972	0.0069	0.2023	0.7908	0.449	0.551	3.1
		5.0	68.7	0.6328	0.3672	0.0597	0.1836	0.7567	0.0069	0.1578	0.8353	0.556	0.444	5.3
		7.5	64.3	0.6786	0.3214	0.0323	0.1339	0.8338	-	-	-	-	-	8.8
		10.0	61.4	0.7293	0.2707	0.0152	0.1046	0.8802	-	-	-	-	-	18.6

^a Standard uncertainty (u) are $u(y) = 0.001$, $u(x) = 0.001$, $u(x_1) = 0.02$, $u(x_{II}) = 0.002$, $u(P) = 0.02$, and $u(T) = 0.1$ K.

Table S2 Experimental VLLE or VLE data^a for several {*n*-heptane (1) + toluene (2) + IL (3)} systems at different temperatures and S/F ratio. Dicyanamide-based ILs

IL	<i>T</i> / K	S/F	<i>P</i> / kPa	Vapor phase		Overall liquid			Liquid II			Liquid I		$\alpha_{1,2}$
				<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
[emim][DCA]	323.2	1.0	16.0	0.4716	0.5284	0.1992	0.4301	0.3707	0.0026	0.1674	0.8300	0.359	0.641	1.9
		2.5	16.3	0.5314	0.4686	0.1280	0.2836	0.5884	0.0030	0.1359	0.8611	0.399	0.601	2.5
		5.0	16.8	0.6204	0.3796	0.0760	0.1797	0.7443	0.0036	0.1261	0.8703	0.507	0.493	3.9
		7.5	17.3	0.7012	0.2988	0.0487	0.1275	0.8238	0.0037	0.1059	0.8904	0.611	0.389	6.1
		10.0	18.0	0.7401	0.2599	0.0365	0.1054	0.8581	0.0040	0.0956	0.9004	0.704	0.296	8.2
	363.2	1.0	66.7	0.4449	0.5551	0.1924	0.4273	0.3803	0.0040	0.1460	0.8500	0.343	0.657	1.8
		2.5	67.2	0.5042	0.4958	0.1117	0.2707	0.6176	0.0041	0.1414	0.8545	0.388	0.612	2.5
		5.0	68.5	0.5990	0.4010	0.0532	0.1661	0.7807	0.0043	0.1325	0.8632	0.504	0.496	4.7
		7.5	66.6	0.6809	0.3191	0.0196	0.1152	0.8652	-	-	-	-	-	12.5
		10.0	64.4	0.7092	0.2908	0.0080	0.0945	0.8975	-	-	-	-	-	28.9
[bmim][DCA]	323.2	1.0	16.4	0.4847	0.5153	0.2136	0.4623	0.3241	0.0094	0.2668	0.7238	0.380	0.620	2.0
		2.5	16.5	0.5716	0.4284	0.1388	0.3109	0.5503	0.0110	0.2308	0.7582	0.479	0.521	3.0
		5.0	18.0	0.6844	0.3156	0.0828	0.2018	0.7154	0.0123	0.1789	0.8088	0.627	0.373	5.3
		7.5	17.8	0.7544	0.2456	0.0551	0.1497	0.7952	0.0122	0.1406	0.8472	0.719	0.281	8.3
		10.0	18.1	0.8054	0.1946	0.0355	0.1133	0.8512	0.0103	0.1093	0.8804	0.783	0.217	13.2
	363.2	1.0	67.5	0.4619	0.5381	0.2025	0.4538	0.3437	0.0107	0.2128	0.7765	0.353	0.647	1.9
		2.5	67.4	0.5436	0.4564	0.1188	0.2997	0.5815	0.0105	0.2110	0.7785	0.433	0.567	3.0
		5.0	69.9	0.6628	0.3372	0.0545	0.1911	0.7544	0.0108	0.1791	0.8101	0.628	0.372	6.9
		7.5	67.6	0.7209	0.2791	0.0204	0.1415	0.8381	-	-	-	-	-	17.9
		10.0	55.3	0.7450	0.2550	0.0126	0.1109	0.8765	-	-	-	-	-	25.7

^a Standard uncertainty (*u*) are *u*(*y*) = 0.001, *u*(*x*) = 0.001, *u*(*x*₁) = 0.02, *u*(*x*₁₁) = 0.002, *u*(*P*) = 0.02, and *u*(*T*) = 0.1 K.

Table S3 Experimental VLLE or VLE data^a for several {*n*-heptane (1) + toluene (2) + IL (3)} systems at different temperatures and S/F ratio. Tricyanomethanide-based ILs

IL	<i>T</i> / K	S/F	<i>P</i> / kPa	Vapor phase		Overall liquid			Liquid II			Liquid I		$\alpha_{1,2}$
				<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
[emim][TCM]	323.2	1.0	16.4	0.5171	0.4829	0.2087	0.4535	0.3378	0.0079	0.3417	0.6504	0.427	0.573	2.3
		2.5	17.0	0.6136	0.3864	0.1356	0.3060	0.5584	0.0082	0.2623	0.7295	0.554	0.446	3.6
		5.0	18.0	0.7254	0.2746	0.0784	0.1959	0.7257	0.0083	0.1815	0.8102	0.685	0.315	6.6
		7.5	18.2	0.7907	0.2093	0.0518	0.1441	0.8041	0.0081	0.1346	0.8573	0.718	0.282	10.5
		10.0	18.4	0.8262	0.1738	0.0372	0.1172	0.8456	0.0086	0.1128	0.8786	0.779	0.221	15.0
	363.2	1.0	68.5	0.4871	0.5129	0.2132	0.4844	0.3024	0.0080	0.3605	0.6315	0.399	0.601	2.2
		2.5	69.4	0.5833	0.4167	0.1147	0.2984	0.5869	0.0081	0.2561	0.7358	0.529	0.471	3.6
		5.0	70.5	0.7071	0.2929	0.0460	0.1881	0.7659	0.0083	0.1792	0.8125	0.644	0.356	9.9
		7.5	67.6	0.7654	0.2346	0.0160	0.1400	0.8440	-	-	-	-	-	28.6
		10.0	55.3	0.7737	0.2263	0.0106	0.1124	0.8770	-	-	-	-	-	36.1
[bmim][TCM]	323.2	1.0	16.4	0.5250	0.4750	0.2190	0.4761	0.3049	0.0193	0.3817	0.5990	0.427	0.573	2.4
		2.5	17.0	0.6457	0.3543	0.1448	0.3294	0.5258	0.0215	0.3025	0.6760	0.579	0.421	4.1
		5.0	18.0	0.7573	0.2427	0.0863	0.2195	0.6942	0.0217	0.2072	0.7711	0.675	0.325	7.9
		7.5	18.2	0.8142	0.1858	0.0577	0.1659	0.7764	0.0216	0.1628	0.8156	0.782	0.218	12.6
		10.0	18.4	0.8548	0.1452	0.0387	0.1300	0.8313	0.0221	0.1279	0.8500	0.794	0.206	19.8
	363.2	1.0	67.5	0.4964	0.5036	0.2078	0.4731	0.3191	0.0231	0.3805	0.5964	0.418	0.582	2.2
		2.5	70.2	0.6126	0.3874	0.1208	0.3256	0.5536	0.0233	0.3024	0.6743	0.560	0.440	4.3
		5.0	70.2	0.7344	0.2656	0.0497	0.2159	0.7344	0.0232	0.2135	0.7633	0.688	0.312	12.0
		7.5	64.1	0.7598	0.2402	0.0219	0.1593	0.8188	-	-	-	-	-	23.0
		10.0	51.5	0.7617	0.2383	0.0141	0.1205	0.8654	-	-	-	-	-	27.3

^a Standard uncertainty (u) are $u(y) = 0.001$, $u(x) = 0.001$, $u(x_1) = 0.02$, $u(x_{11}) = 0.002$, $u_r(P) = 0.02$, and $u(T) = 0.1$ K.

Table S3 Continued

IL	T/ K	S/F	P/ kPa	Vapor phase		Overall liquid			Liquid II			Liquid I		$\alpha_{1,2}$
				y_1	y_2	x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	
[4bmpy][TCM]	323.2	1.0	16.4	0.5912	0.4088	0.2160	0.4740	0.3100	0.0239	0.4391	0.5370	0.478	0.522	3.2
		2.5	17.0	0.7035	0.2965	0.1449	0.3383	0.5168	0.0275	0.3359	0.6366	0.651	0.349	5.5
		5.0	17.6	0.8120	0.1880	0.0844	0.2242	0.6914	0.0287	0.2218	0.7495	0.748	0.252	11.5
		7.5	17.5	0.8585	0.1415	0.0563	0.1719	0.7718	0.0316	0.1712	0.7972	0.808	0.192	18.5
		10.0	17.6	0.8904	0.1096	0.0383	0.1351	0.8266	0.0338	0.1350	0.8312	0.903	0.097	28.7
	363.2	1.0	70.0	0.6106	0.3894	0.1999	0.4916	0.3085	0.0284	0.5231	0.4485	0.574	0.426	3.8
		2.5	70.4	0.6696	0.3304	0.1182	0.3348	0.5470	0.0299	0.3319	0.6382	0.639	0.361	5.7
		5.0	70.4	0.7834	0.2166	0.0465	0.2256	0.7279	-	-	-	-	-	17.6
		7.5	55.9	0.7999	0.2001	0.0270	0.1652	0.8078	-	-	-	-	-	24.5
		10.0	42.6	0.7992	0.2008	0.0210	0.1330	0.8460	-	-	-	-	-	25.2

^a Standard uncertainty (u) are $u(y) = 0.001$, $u(x) = 0.001$, $u(x_1) = 0.02$, $u(x_{II}) = 0.002$, $u(P) = 0.02$, and $u(T) = 0.1$ K.

Table S4 Experimental VLE or VLE data^a for several {*n*-heptane (1) + toluene (2) + IL (3)} systems at different temperatures and S/F ratio. Bis(trifluoromethylsulfonyl)imide-based ILs

IL	<i>T</i> / K	S/F	<i>P</i> / kPa	Vapor phase		Overall liquid			Liquid II			Liquid I		$\alpha_{1,2}$
				<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
[4empty][Tf ₂ N]	323.2	1.0	15.5	0.5037	0.4963	0.2557	0.5526	0.1917	0.0330	0.4705	0.4965	0.397	0.603	2.2
		2.5	16.4	0.6103	0.3897	0.1916	0.4272	0.3812	0.0372	0.4058	0.5570	0.528	0.472	3.5
		5.0	17.0	0.7035	0.2965	0.1318	0.3127	0.5555	0.0381	0.3023	0.6596	0.636	0.364	5.6
		7.5	17.9	0.7872	0.2128	0.0951	0.2468	0.6581	0.0379	0.2417	0.7204	0.706	0.294	9.6
		10.0	17.9	0.8261	0.1739	0.0729	0.2053	0.7218	0.0402	0.2032	0.7566	0.762	0.238	13.4
	363.2	1.0	68.2	0.4770	0.5230	0.2452	0.5490	0.2058	0.0419	0.4089	0.5491	0.365	0.635	2.0
		2.5	69.3	0.5735	0.4265	0.1727	0.4380	0.3893	0.0428	0.3838	0.5734	0.465	0.535	3.4
		5.0	74.9	0.6947	0.3053	0.0910	0.3103	0.5987	0.0445	0.3087	0.6468	0.647	0.353	7.8
		7.5	69.4	0.7577	0.2423	0.0504	0.2454	0.7042	-	-	-	-	-	15.2
		10.0	58.0	0.7708	0.2292	0.0376	0.2027	0.7597	-	-	-	-	-	18.1
[4bmpy][Tf ₂ N]	323.2	1.0	15.7	0.5155	0.4845	0.2621	0.5676	0.1703	0.0706	0.5205	0.4089	0.400	0.600	2.3
		2.5	16.6	0.6158	0.3842	0.2059	0.4607	0.3334	0.0751	0.4512	0.4737	0.519	0.481	3.6
		5.0	18.4	0.7047	0.2953	0.1403	0.3386	0.5211	0.0793	0.3393	0.5814	0.674	0.326	5.8
		7.5	18.2	0.8061	0.1939	0.1007	0.2675	0.6318	0.0821	0.2688	0.6491	0.802	0.198	11.0
		10.0	18.3	0.8456	0.1544	0.0753	0.2224	0.7023	0.0815	0.2217	0.6968	0.808	0.192	16.2
	363.2	1.0	69.9	0.5576	0.4424	0.2086	0.4877	0.3037	0.0845	0.4712	0.4443	0.473	0.527	2.9
		2.5	70.3	0.5962	0.4038	0.1748	0.4522	0.3730	0.0851	0.4319	0.4830	0.490	0.510	3.8
		5.0	67.4	0.7170	0.2830	0.0947	0.3392	0.5661	-	-	-	-	-	9.1
		7.5	52.7	0.7592	0.2408	0.0640	0.2659	0.6701	-	-	-	-	-	13.1
		10.0	46.6	0.7619	0.2381	0.0485	0.2235	0.7280	-	-	-	-	-	14.8

^a Standard uncertainty (u) are $u(y) = 0.001$, $u(x) = 0.001$, $u(x_1) = 0.02$, $u(x_{II}) = 0.002$, $u(P) = 0.02$, and $u(T) = 0.1$ K.

Table S5 Experimental VLLE or VLE data^a for {*n*-heptane + toluene + [emim][SCN]} to study the cross influences of temperature and S/F ratio

<i>T</i> / K	<i>S</i> / <i>F</i>	<i>P</i> / kPa	<i>Vapor phase</i>		<i>Overall liquid</i>			<i>Liquid II</i>			<i>Liquid I</i>		$\alpha_{1,2}$
			<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
323.2	1.0	15.8	0.4603	0.5397	0.1997	0.4305	0.3698	0.0014	0.1355	0.8631	0.349	0.651	1.8
343.2	1.0	33.4	0.4596	0.5404	0.1959	0.4286	0.3755	0.0016	0.1455	0.8529	0.349	0.651	1.8
363.2	1.0	66.2	0.4392	0.5608	0.1908	0.4223	0.3869	0.0022	0.1561	0.8417	0.349	0.651	1.8
383.2	1.0	124.8	0.4391	0.5609	0.1727	0.4087	0.4186	0.0022	0.1346	0.8632	0.333	0.667	1.9
403.2	1.0	167.4	0.4344	0.5656	0.1644	0.4028	0.4328	0.0026	0.1428	0.8546	0.330	0.670	1.9
323.2	5.0	16.3	0.5790	0.4210	0.0745	0.1730	0.7525	0.0019	0.1031	0.8950	0.460	0.540	3.2
343.2	5.0	30.0	0.5623	0.4377	0.0670	0.1655	0.7675	0.0023	0.1046	0.8931	0.463	0.537	3.2
363.2	5.0	66.5	0.5357	0.4643	0.0559	0.1586	0.7855	0.0024	0.1109	0.8867	0.461	0.539	3.3
383.2	5.0	122.5	0.5355	0.4645	0.0276	0.1382	0.8342	0.0023	0.1103	0.8874	0.424	0.576	8.8
403.2	5.0	161.4	0.5304	0.4696	0.0079	0.1245	0.8676	0.0020	0.1136	0.8844	0.311	0.689	17.7
323.2	10.0	16.0	0.6880	0.3120	0.0367	0.1001	0.8632	0.0026	0.0809	0.9165	0.597	0.403	6.0
343.2	10.0	32.8	0.6703	0.3297	0.0287	0.0991	0.8722	0.0025	0.0821	0.9154	0.581	0.419	7.0
363.2	10.0	59.7	0.6601	0.3399	0.0076	0.0901	0.9023	-	-	-	-	-	23.0
383.2	10.0	81.6	0.6265	0.3735	0.0033	0.0856	0.9111	-	-	-	-	-	43.2
403.2	10.0	111.1	0.4853	0.5147	0.0030	0.0616	0.9354	-	-	-	-	-	19.1

^a Standard uncertainty (*u*) are *u*(*y*) = 0.001, *u*(*x*) = 0.001, *u*(*x*₁) = 0.02, *u*(*x*₁₁) = 0.002, *u*(*P*) = 0.02, and *u*(*T*) = 0.1 K.

Table S6 Experimental VLLE or VLE data^a for {*n*-heptane + toluene + [emim][TCM]} to study the cross influences of temperature and S/F ratio

<i>T</i> /K	<i>S</i> / <i>F</i>	<i>P</i> /kPa	<i>Vapor phase</i>		<i>Overall liquid</i>			<i>Liquid II</i>			<i>Liquid I</i>		$\alpha_{1,2}$
			<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
323.2	1.0	16.4	0.5171	0.4829	0.2087	0.4535	0.3378	0.0079	0.3417	0.6504	0.427	0.573	2.3
343.2	1.0	29.5	0.4907	0.5093	0.2047	0.4494	0.3459	0.0092	0.3396	0.6512	0.426	0.574	2.2
363.2	1.0	68.5	0.4871	0.5129	0.2132	0.4844	0.3024	0.0080	0.3605	0.6315	0.399	0.601	2.2
383.2	1.0	123.6	0.4805	0.5195	0.1785	0.4421	0.3794	0.0106	0.3232	0.6662	0.400	0.600	2.3
403.2	1.0	169.4	0.4799	0.5201	0.1661	0.4373	0.3966	0.0094	0.3219	0.6687	0.394	0.606	2.4
323.2	5.0	18.0	0.7254	0.2746	0.0784	0.1959	0.7257	0.0083	0.1815	0.8102	0.685	0.315	6.6
343.2	5.0	31.8	0.7217	0.2783	0.0663	0.1902	0.7435	0.0099	0.1789	0.8112	0.687	0.313	7.4
363.2	5.0	70.5	0.7071	0.2929	0.0460	0.1881	0.7659	0.0083	0.1792	0.8125	0.644	0.356	9.9
383.2	5.0	101.2	0.6440	0.3560	0.0237	0.1740	0.8023	-	-	-	-	-	13.3
403.2	5.0	122.8	0.6113	0.3887	0.0162	0.1652	0.8186	-	-	-	-	-	16.1
323.2	10.0	16.9	0.8262	0.1738	0.0372	0.1172	0.8456	0.0086	0.1128	0.8786	0.779	0.221	15.0
343.2	10.0	33.3	0.8090	0.1910	0.0257	0.1198	0.8545	0.0079	0.1131	0.8790	0.787	0.213	19.8
363.2	10.0	56.2	0.7737	0.2263	0.0106	0.1124	0.8770	-	-	-	-	-	36.1
383.2	10.0	67.9	0.6687	0.3313	0.0074	0.1012	0.8914	-	-	-	-	-	27.6
403.2	10.0	89.3	0.5780	0.4220	0.0061	0.0885	0.9054	-	-	-	-	-	19.8

^a Standard uncertainty (*u*) are *u*(*y*) = 0.001, *u*(*x*) = 0.001, *u*(*x*₁) = 0.02, *u*(*x*₁₁) = 0.002, *u*(*P*) = 0.02, and *u*(*T*) = 0.1 K.

Table S7 Experimental VLLE or VLE data^a for {*n*-heptane + toluene + [4bmpy][TCM]} to study the cross influences of temperature and S/F ratio

<i>T</i> /K	<i>S</i> / <i>F</i>	<i>P</i> /kPa	<i>Vapor phase</i>		<i>Overall liquid</i>			<i>Liquid II</i>			<i>Liquid I</i>		$\alpha_{1,2}$
			<i>y</i> ₁	<i>y</i> ₂	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	
323.2	1.0	16.4	0.5912	0.4088	0.2160	0.4740	0.3100	0.0239	0.4391	0.5370	0.478	0.522	3.2
343.2	1.0	33.9	0.6074	0.3926	0.2110	0.4812	0.3078	0.0240	0.4668	0.5092	0.497	0.503	3.5
363.2	1.0	70.0	0.6106	0.3894	0.1999	0.4916	0.3085	0.0284	0.5231	0.4485	0.574	0.426	3.8
383.2	1.0	124.5	0.6093	0.3907	0.1712	0.4906	0.3382	0.0288	0.5117	0.4595	0.568	0.432	4.6
403.2	1.0	167.1	0.5875	0.4125	0.1566	0.4901	0.3533	0.0268	0.5128	0.4604	0.585	0.415	4.6
323.2	5.0	17.6	0.8120	0.1880	0.0844	0.2242	0.6914	0.0287	0.2218	0.7495	0.748	0.252	11.5
343.2	5.0	30.5	0.8065	0.1935	0.0725	0.2216	0.7059	0.0290	0.2225	0.7485	0.792	0.208	12.7
363.2	5.0	70.4	0.7834	0.2166	0.0465	0.2256	0.7279	-	-	-	-	-	17.6
383.2	5.0	88.4	0.7146	0.2854	0.0260	0.2107	0.7633	-	-	-	-	-	20.3
403.2	5.0	120.4	0.6208	0.3792	0.0152	0.1908	0.7940	-	-	-	-	-	20.5
323.2	10.0	17.6	0.8904	0.1096	0.0383	0.1351	0.8266	0.0338	0.1350	0.8312	0.903	0.097	28.7
343.2	10.0	30.6	0.8650	0.1350	0.0255	0.1359	0.8386	-	-	-	-	-	34.1
363.2	10.0	42.6	0.7992	0.2008	0.0210	0.1330	0.8460	-	-	-	-	-	25.2
383.2	10.0	56.4	0.7133	0.2867	0.0137	0.1262	0.8601	-	-	-	-	-	22.9
403.2	10.0	73.1	0.6297	0.3703	0.0100	0.1128	0.8772	-	-	-	-	-	19.2

^a Standard uncertainty (*u*) are *u*(*y*) = 0.001, *u*(*x*) = 0.001, *u*(*x*₁) = 0.02, *u*(*x*₁₁) = 0.002, *u*(*P*) = 0.02, and *u*(*T*) = 0.1 K.

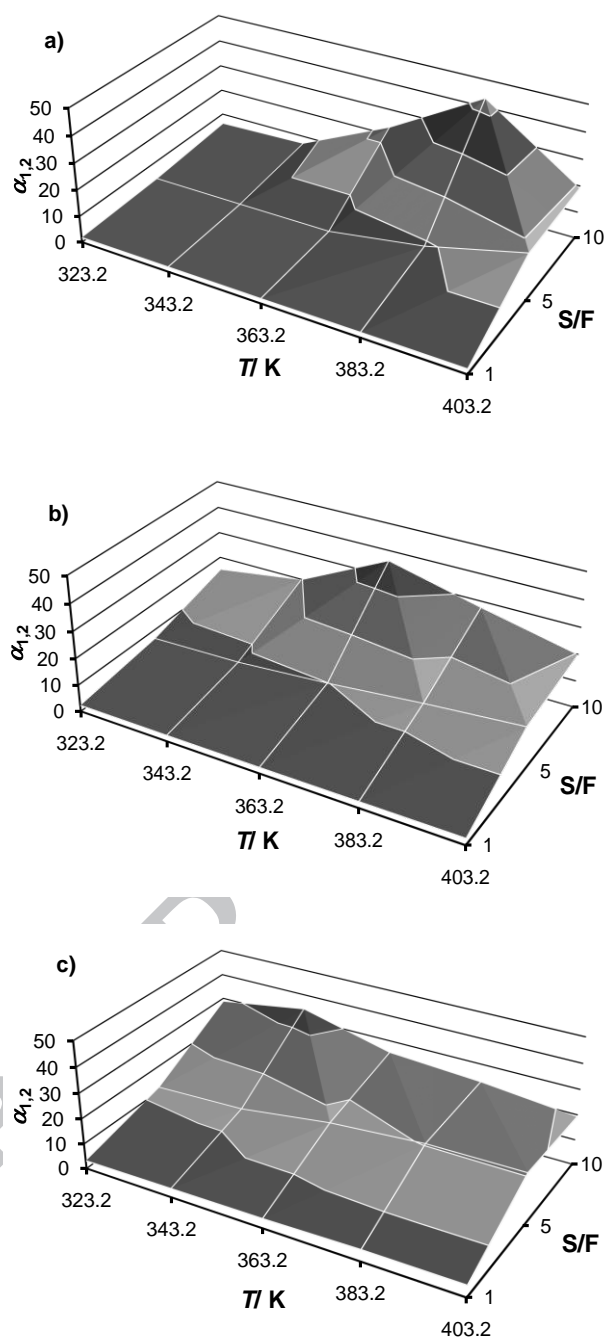


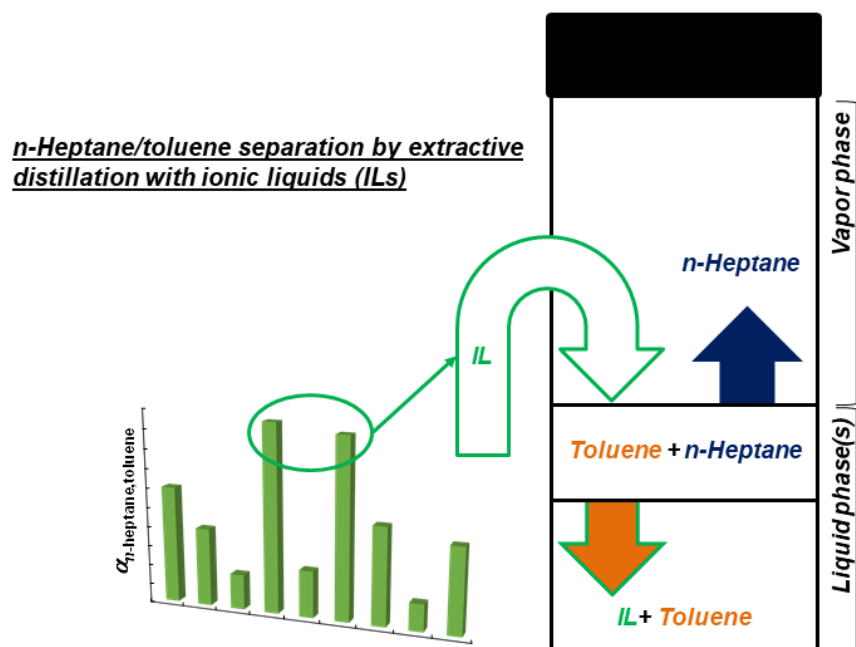
Fig. S1. Maps of *n*-heptane/toluene relative volatility as a function of S/F ratio and temperature for the ILs: (a), [emim][SCN]; (b), [emim][TCM]; (c), [4bmpy][TCM].

Highlights

- VLLE were determined by a novel HS-GC procedure for *n*-heptane + toluene + IL systems.
- Nine ILs were tested with S/F ratios from 1 to 10 in the range of 323.2 to 403.2 K.
- Extractive distillation with ILs is suitable to separate aromatics from gasolines.
- Tricyanomethanide-based ILs were revealed as the most promising mass agents.

ACCEPTED MANUSCRIPT

Graphical abstract



ACCEPT