



## Separation of benzene from methylcycloalkanes by extractive distillation with cyano-based ionic liquids: Experimental and CPA EoS modelling

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### ABSTRACT

The aromatic/aliphatic separation using ionic liquids (ILs) has been proposed as an enhanced technology when compared to conventional liquid-liquid extraction and extractive distillation processes. Some ILs show extractive properties (distribution ratios and selectivities) greater than those of conventional solvents, like sulfolane and *N*-methylpyrrolidone, positioning these solvents to address challenging separations. Methylcycloalkanes and benzene are close-boiling mixtures in the petrochemical industry, presented at the hydrogenated pyrolysis naphtha where benzene is at a high concentration (ca. 70 wt%). Aiming to tackle this separation, cyano-based ILs were tested as mass agents in the benzene separation from methylcycloalkanes. A complete phase equilibria characterization with the most promising ILs, [C<sub>2</sub>C<sub>1</sub>im][DCA] and [C<sub>2</sub>C<sub>1</sub>im][SCN], were done, using a recently developed experimental-modelling strategy. Isothermal vapour-liquid equilibria for binary, ternary and quaternary systems was measured by Headspace Gas-Chromatography (HS-GC) and modelled using the Cubic Plus Association (CPA) Equation of State (EoS). The presence of the ILs improved the methylcycloalkane/benzene relative volatilities by one order of magnitude, whereas homogeneous and heterogeneous regions were determined by HS-GC, leading to a consistent model.

### 1. Introduction

The separation of aromatics hydrocarbons from linear and cyclic aliphatic hydrocarbons presents several challenges due to the proximity of their boiling points. Concentrations of aromatic hydrocarbons in the feedstock determine the technology of separation to be selected. Liquid-liquid extraction is used when aromatic contents are between 20 and 65 wt%, whereas the extractive distillation is selected for aromatic contents between 65 and 90 wt% [1]. The main sources of aromatic hydrocarbons are the reformer and pyrolysis gasolines with aromatic contents of 55 wt% and 66 wt%, respectively [2]. However, other feedstocks with higher aromatic contents can be found in a refinery, such as the hydrogenated pyrolysis naphtha or benzole from coal carbonization [3]. Although these industrial streams are not the principal sources of aromatic hydrocarbons, they constitute a considerable opportunity to explore additional resources.

In the last decade, ILs have received great interest as alternatives solvents in a wide variety of separation processes, owing to their tunable physicochemical and extractive properties by the simple

combination of widely different anions and cations [4–11]. Applications range from the recovery of valued-product from water streams with hydrophobic ILs [4,9] to hydrocarbon separations [5,6,10,11] and biological and pharma separations [7,8].

Among others, their negligible vapor pressure, high thermal and chemical stability, and wide liquidus range are their most outstanding properties [12,13]. ILs have been successfully evaluated as solvents to extract aromatics and olefins from alkanes [14–23]. Aromatic/aliphatic separation was studied by experimental [15,16] and computational approaches [17] in simplified *n*-heptane/toluene systems to narrow down the most effective solvents, whereas multicomponent streams were evaluated by approximate simulations [18,20] and pilot plant studies [23]. In these studies, ILs allowed to achieve high aromatic/aliphatic selectivity and higher capacities than those reported for conventional solvents, such as sulfolane or *N*-methylpyrrolidone [24], evidencing a real applicability. Scarce explored, the alkane/alkene separation is being developed in the recent years with interesting interactions but more limited extractive properties [19,21,22]. In a previous work the suitability of the extractive distillation with ILs to separate

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**Table 1**  
Compound description, supplier, mass fraction purity and water content.

Chemical	Supplier	Mass fraction purity/wt.%	Water content/ppm
1-ethyl-3-methylimidazolium thiocyanate [C <sub>2</sub> C <sub>1</sub> im][SCN]	Iolitec GmbH	98	< 300
1-ethyl-3-methylimidazolium dicyanamide [C <sub>2</sub> C <sub>1</sub> im][DCA]	Iolitec GmbH	98	< 300
1-ethyl-3-methylimidazolium tricyanomethanide [C <sub>2</sub> C <sub>1</sub> im][TCM]	Iolitec GmbH	98	< 300
1-butyl-4-methylpyridinium tricyanomethanide [4-C <sub>4</sub> C <sub>1</sub> py][TCM]	Iolitec GmbH	98	< 300
bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate [C <sub>2</sub> C <sub>1</sub> im] <sub>2</sub> [Co(SCN) <sub>4</sub> ]	Iolitec GmbH	99	< 300
bis(1-butyl-3-methylimidazolium) tetrathiocyanatocobaltate [C <sub>4</sub> C <sub>1</sub> im] <sub>2</sub> [Co(SCN) <sub>4</sub> ]	Iolitec GmbH	99	< 300
Methylcyclopentane	Sigma-Aldrich	≥ 99.0	Anhydrous
Methylcyclohexane	Sigma-Aldrich	≥ 99.0	Anhydrous
Benzene	Sigma-Aldrich	99.8	Anhydrous

**Table 2**  
Mass basis composition of the hydrogenated pyrolysis naphtha.

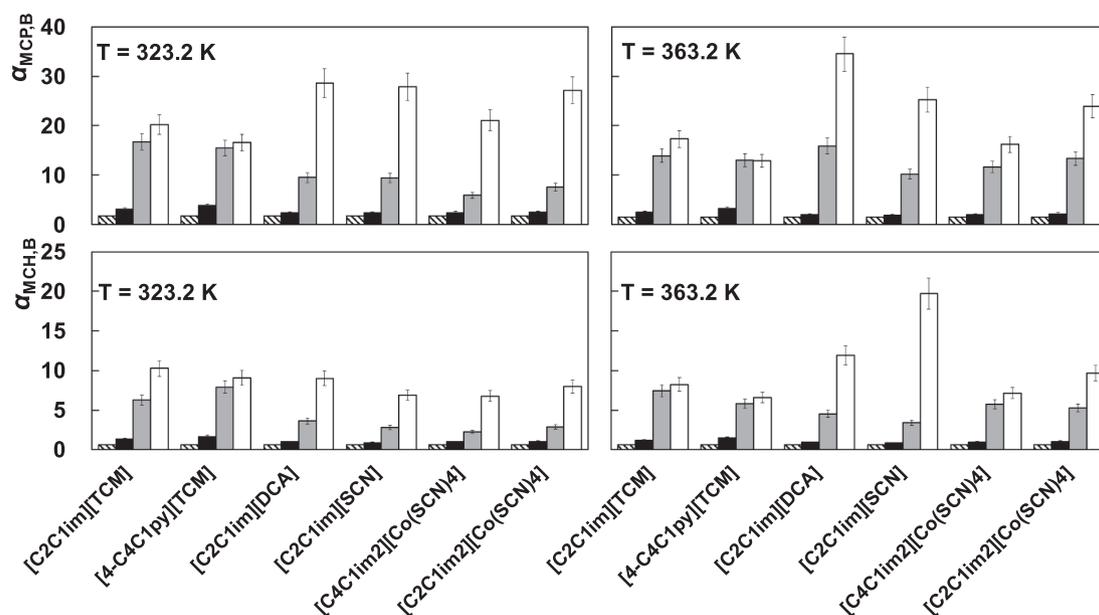
Chemical	wt.%
Methylcyclopentane	24.0
Methylcyclohexane	4.0
Benzene	72.0

toluene and *n*-heptane was evaluated [25,26], highlighting the notably grown interest on the extractive distillation to overcome the inherent limitations to liquid-liquid extraction, showing enhanced relative volatility of the key components to be separated; the standards of purity are obtained in only one equipment and further purification steps at high vacuum were not needed as detailed in the literature for liquid-liquid extraction [27–31].

Aiming at evaluating the use of ILs and extractive distillation for these challenging separations more complex and industrially relevant mixtures must be addressed. The benzene/methylcyclopentane mixture is one of the most difficult separations in the oil industry context

because its relative volatility is close to unity and the formation of an azeotrope of minimum boiling temperature ( $T = 333.2$  K;  $Y_{\text{methylcyclopentane}} = 0.861$ ) [32]. This mixture presents great interest in the hydrogenated pyrolysis naphtha where methylcyclohexane also has a non-negligible presence [30,33]. Methylcyclohexane/benzene relative volatility is near unity at high benzene concentration, which is the case of interest, making also difficult the separation of benzene from its binary mixture with methylcyclohexane. Regarding the ternary mixture involving both methylcycloalkanes and benzene, boiling point is just in the middle, making a real challenge the benzene separation. Therefore, an effective process to separate the benzene from these cycloalkanes could suppose an additional source of this aromatic compound to the petrochemical industry.

The separation of benzene from methylcyclopentane or methylcyclohexane by extractive distillation with ILs is studied in this work. Firstly, a screening of six cyano-based ILs, namely 1-ethyl-3-methylimidazolium thiocyanate ([C<sub>2</sub>C<sub>1</sub>im][SCN]), 1-ethyl-3-methylimidazolium dicyanamide ([C<sub>2</sub>C<sub>1</sub>im][DCA]), 1-ethyl-3-methylimidazolium tricyanomethanide ([C<sub>2</sub>C<sub>1</sub>im][TCM]), 1-butyl-4-methylpyridinium tricyanomethanide ([4-C<sub>4</sub>C<sub>1</sub>py][TCM]), bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate ([C<sub>2</sub>C<sub>1</sub>im]<sub>2</sub>[Co(SCN)<sub>4</sub>]) and bis(1-

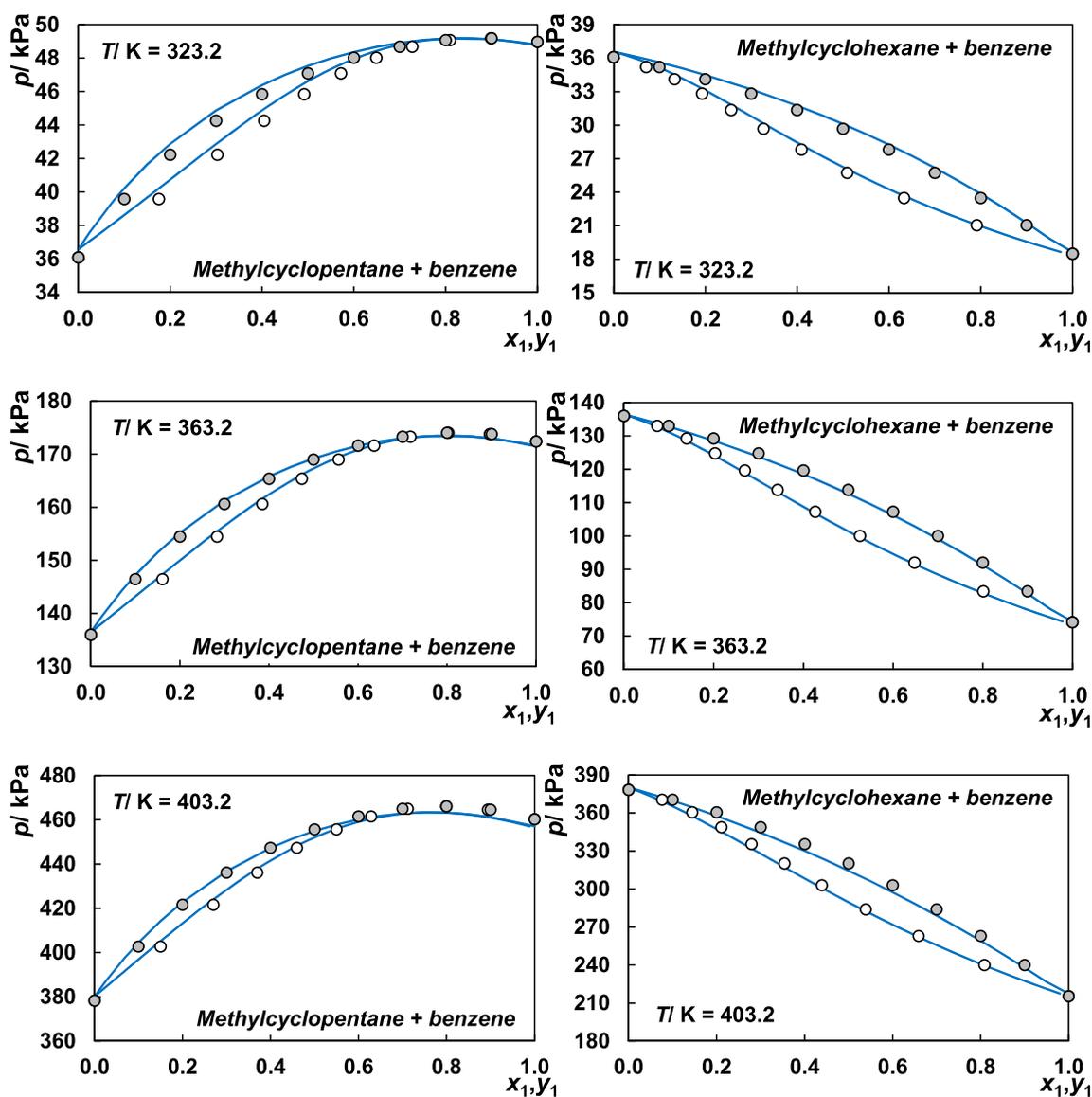


**Fig. 1.** Cyano-based IL screening in the methylcycloalkane separation from benzene (MCP: methylcyclopentane; MCH: methylcyclohexane; B: benzene). Diagonal stripes are the methylcycloalkane/benzene relative volatility used as benchmark, black bars denote  $S/F = 1$ , grey bars denote  $S/F = 5$  and white bars denote  $S/F = 10$ . Free solvent content of benzene in the feed was 80 wt%.

**Table 3**  
CPA EoS molecular parameters, deviations for  $\Delta$ ,  $C_p$  and critical properties for the  $[C_2C_1im][DCA]$  and  $[C_2C_1im][SCN]$  ILs.

IL	$[C_2C_1im][SCN]$	$[C_2C_1im][DCA]$
<i>Molecular parameters</i>		
$a_0/Pa \cdot m^6 \cdot mol^{-2}$	6.79	9.31
$10^4 b/m^3 \cdot mol^{-1}$	1.46	1.56
$c_1$	1.16	0.84
$10^2 \beta$	2.79	2.79
$10^4 \epsilon/kJ \cdot mol^{-1}$	1.51	1.51
<i>ARD/%</i>		
$\rho(0.1 MPa)$	0.690	0.714
$C_p$	19.0	0.631
<i>IL volatility</i>		
$p^0(443 K)/kPa$	0.001	0.001
<i>Critical properties [44]</i>		
$T_c/K$	1013.6	999.0
$p_c/MPa$	22.3	29.1
$\omega$	0.3931	0.7661

butyl-3-methylimidazolium) tetrathiocyanatocobaltate ( $[C_4C_1im]_2[Co(SCN)_4]$ ), was made. The choice of these ILs is based on the good performance in the toluene/*n*-heptane separation, with these ILs presenting the best combination of toluene/*n*-heptane selectivity and toluene distribution ratio. Indeed, the  $[Co(SCN)_4]^{2-}$  anion-based ionic liquids were chosen because the presence of transition salts improves the aromatic separation from alkanes, as reported in previous works [25,34]. The corresponding isothermal vapor-liquid or vapor-liquid-liquid equilibria (VLE/VLLE) was evaluated for the {methylcyclopentane/methylcyclohexane + benzene + IL} ternary systems with 80 wt% of benzene in the binary hydrocarbon mixture, at 323.2 K and 363.2 K, and with solvent to feed ratios (S/F) of 1, 5 and 10 in mass basis. Then the  $[C_2C_1im][SCN]$  and  $[C_2C_1im][DCA]$  impact on the methylcycloalkane/benzene separation was analyzed. The isothermal VLE/VLLE for {methylcycloalkane + benzene +  $[C_2C_1im][DCA]$  or  $[C_2C_1im][SCN]$ } binary and ternary systems were experimentally determined on a wide temperature range (323.2–403.2 K). Ternary systems were evaluated along the whole hydrocarbon concentrations, fixing a S/F mass ratio of 10 aiming at defining the heterogeneous and homogeneous extractive distillation boundaries. In addition, the



**Fig. 2.** VLE data for {methylcycloalkane (1) + benzene (2)} binary systems. Symbols denote data from Ref. [48] and solid lines the CPA EoS with  $k_{12}$  reported in Table 4.

**Table 4**  
CPA EoS binary interaction parameters ( $k_{ij}$ ) for the cycloalkane (1) + benzene (2) + IL (3) systems.

T/K	$k_{12}$	$k_{13}$		$k_{23}$	
		[C <sub>2</sub> C <sub>1</sub> im] [DCA]	[C <sub>2</sub> C <sub>1</sub> ] [SCN]	[C <sub>2</sub> C <sub>1</sub> im] [DCA]	[C <sub>2</sub> C <sub>1</sub> im] [SCN]
323.2–403.2	0.023	−0.02	−0.02	−0.09	−0.07
323.2–403.2	0.015	−0.02	−0.02	−0.09	−0.07

isothermal VLE/VLLE for a representative model of a real hydrogenated naphtha [30], involving the two methylcycloalkanes and benzene, and the corresponding IL were determined at S/F mass ratio of 10.

The VLLE was modelled with CPA EoS. This equation of state has been previously used in similar systems containing hydrocarbons and ILs, showing great robustness and accuracy in describing homogeneous and heterogeneous extractive distillation [26]. New molecular parameters for [C<sub>2</sub>C<sub>1</sub>im][DCA] and [C<sub>2</sub>C<sub>1</sub>im][SCN] were regressed from the compounds densities and heat capacities reported in the literature [35–37] and independently from VLLE, whereas temperature-independent binary interaction parameters ( $k_{ij}$ ) were regressed from binary systems and successfully transferred to describe the ternary systems. Thus, a robust and accurate model was developed to describe a potential alternative process to isolate benzene from unconventional sources.

## 2. Experimental section

### 2.1. Chemicals

The six cyano-based ILs used in this work, [C<sub>2</sub>C<sub>1</sub>im][SCN], [C<sub>2</sub>C<sub>1</sub>im][DCA], [C<sub>2</sub>C<sub>1</sub>im][TCM], [4-C<sub>4</sub>C<sub>1</sub>py][TCM], [C<sub>2</sub>C<sub>1</sub>im]<sub>2</sub>[Co(SCN)<sub>4</sub>] and [C<sub>4</sub>C<sub>1</sub>im]<sub>2</sub>[Co(SCN)<sub>4</sub>], were acquired from Iolitec GmbH. Prior to use,

the ILs were dried under vacuum (0.1 Pa) and mild temperature (313 K) conditions. The hydrocarbons, namely benzene, methylcyclopentane and methylcyclohexane, were purchased from Sigma Aldrich and were used as received, without further purification. Additional details, such as mass purity and water content after drying are reported in Table 1.

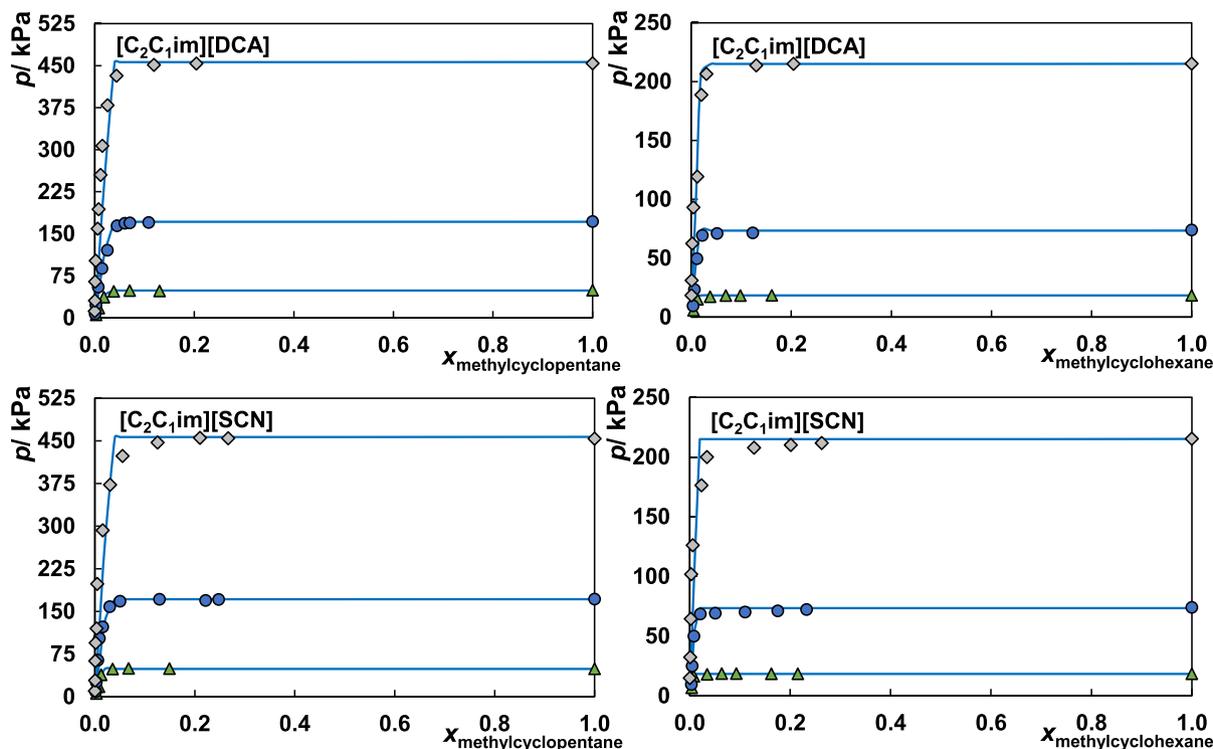
### 2.2. Determination of VLE/VLLE

The isothermal VLE/VLLE data was determined through the coupling of an Agilent 7697A headspace (HS) injector and an Agilent 7890A gas chromatograph. This technique, as well as the equipment, are extensively described in previous works [38,39]. Beforehand, feed mixtures are prepared analytically using a Mettler Toledo XS205 balance with a precision of 10<sup>−5</sup> g. In the case of the multicomponent mixtures, a hydrogenated pyrolysis naphtha model, taken from literature, was used and its mass composition is reported in Table 2 [30]. These mixtures were prepared in the headspace vials that were then hermetically closed. The equilibrium was reached in the HS injector after 2 h. Then the vial vapor phase was sampled and transferred to the gas chromatograph to be analyzed. The molar composition of the overall liquid phase ( $x_i$ ), integrating IL-rich and IL-free phases, was calculated by mass balance from the knowledge of the feed composition ( $z_i$ ) and the molar hydrocarbon amounts present in the vapor phase:

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

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. The partial pressure of each hydrocarbon,  $p_i$ , were determined, using the relationship between the peak areas of the hydrocarbons ( $A_i$ ) and the peak areas of each pure hydrocarbon at the same conditions ( $A_i^0$ ).

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



**Fig. 3.** VLE/VLLE data for the {methylcycloalkane + IL} binary systems. Symbols denote experimental data:  $\triangle$ , 323.2 K;  $\circ$ , 363.2 K;  $\diamond$ , 403.2 K and the solid lines the CPA EoS with  $k_{13}$  listed in Table 4.

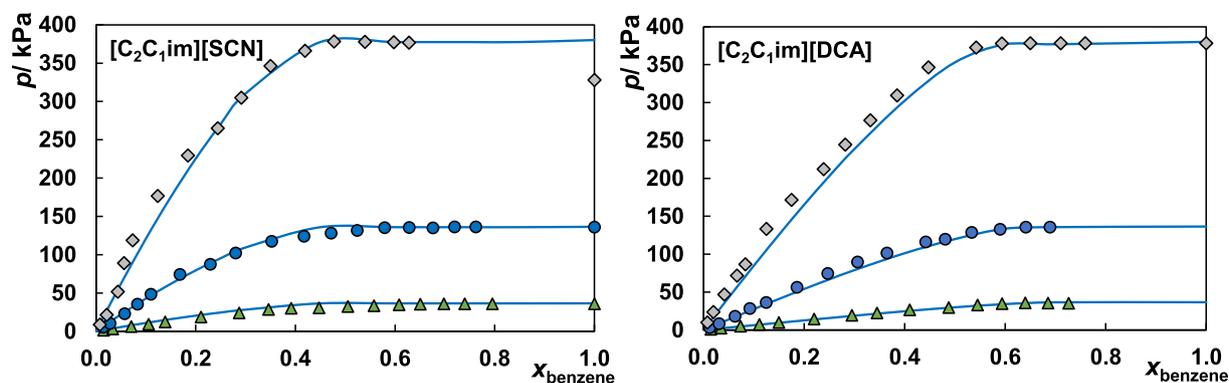


Fig. 4. VLE/VLE data for the {benzene + IL} binary systems. Symbols denote experimental data:  $\triangle$ , 323.2 K;  $\circ$ , 363.2 K;  $\diamond$ , 403.2 K and the solid lines the CPA EoS with  $k_{i3}$  listed in Table 4.

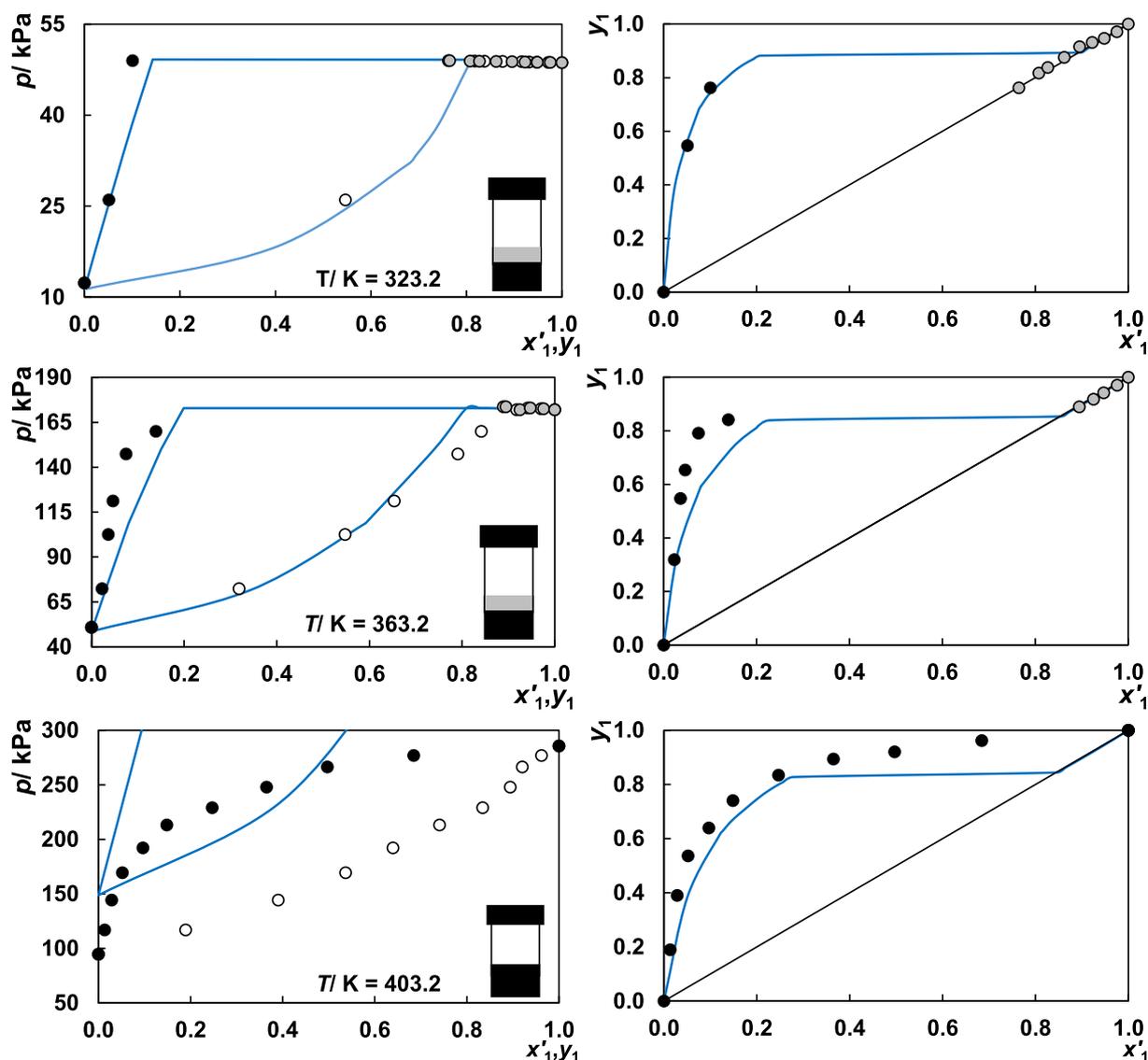


Fig. 5. VLE p-xy and y-x diagrams for the {methylcyclopentane (1) + benzene (2) +  $[C_2C_1im][DCA]$  (3)} ternary system with S/F = 10. Symbols: black denotes IL-rich liquid phases, grey refers to hydrocarbon-rich liquid phases, and white represents vapor phases. Lines: solid represents the CPA EoS with  $k_{i3}$  reported in Table 4.

where  $p_i^0$  refers to the vapor pressure of each pure hydrocarbon, taken from the literature [40]. Thus, the total pressure was calculated as the sum of the partial pressures.

When a VLE is observed, additional experiments were required because the hydrocarbon distribution between the two liquid phases

cannot be determined. In these cases, a second vial with identical compositions was prepared to determine the IL-rich liquid phase composition. The mixtures were allowed to reach equilibrium in a Labnet Vortemp 1550 during 2 h. After phase separation, a sample of the IL-rich liquid phase was taken, weighted and analyzed by means of

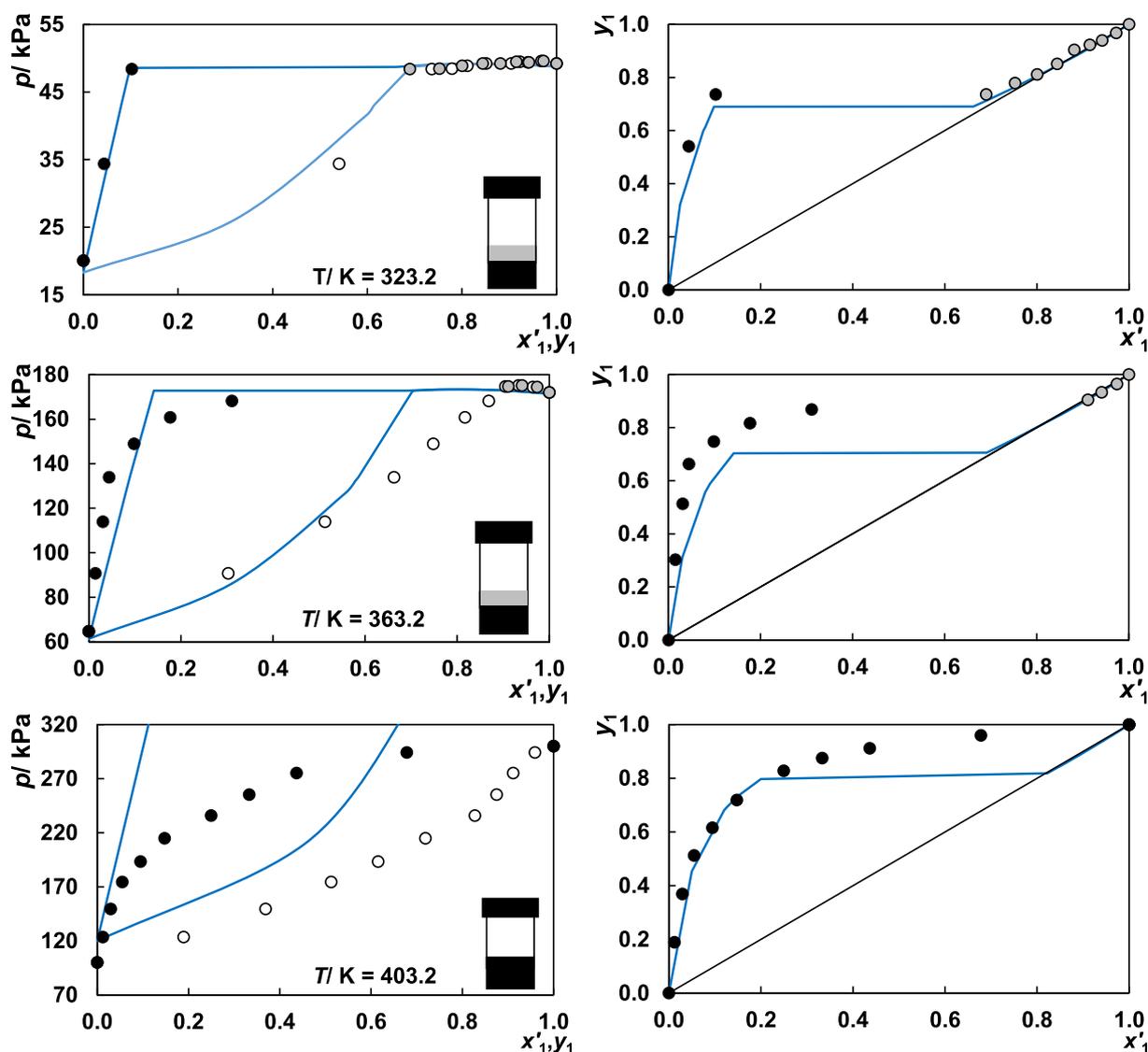


Fig. 6. VLE p-xy and y-x diagrams for the {methylcyclopentane (1) + benzene (2) + [C<sub>2</sub>C<sub>1</sub>im][SCN] (3)} ternary system with S/F = 10. Symbols: black denotes IL-rich liquid phases, grey refers to hydrocarbon-rich liquid phase, and white represents vapor phases. Lines: solid represents the CPA EoS with  $k_{13}$  from Table 4.

multiple headspace extraction technique (MHE), as described in prior works [20,35]. Finally, the IL-free liquid phase composition is calculated by mass balance. This experimental methodology has been validated and is explained in detail elsewhere [25,26].

### 3. CPA EoS

A simplified CPA EoS model, proposed by Konteorgis et al. [41,42] was selected to describe the cycloalkane/benzene extractive distillation with cyano-based ILs. Only the essential information is given in this work since a more exhaustive description can be found elsewhere for the *n*-heptane/toluene close-related case [26]. Hereunder, the CPA EoS is expressed in terms of compressibility factor ( $Z$ ) as the sum of physical and association contributions:

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} \quad (3)$$

Firstly, to obtain the three parameters from the physical term the hydrocarbons have been considered as non-associative compounds, while the ILs are considered as associative compounds with two association sites (2B association scheme).

The physical term parameters of the hydrocarbons ( $a$ ,  $b$  and  $c_0$ ) were taken from the literature where they were regressed from their vapor

pressures and densities [43]. Since the ILs present negligible vapor pressure and non-measurable saturated liquid densities, the parameters of these compounds have been determined from the regression of the atmospheric density and heat capacity data, as proposed in a previous work [26], using the following objective function:

$$\%AARD = \left( \frac{|\rho^{\text{calc}} - \rho^{\text{exp}}|}{\rho^{\text{exp}}} + \frac{|C_p^{\text{calc}} - C_p^{\text{exp}}|}{C_p^{\text{exp}}} \right) \cdot 100 \quad (4)$$

Furthermore, the associative term parameters ( $\beta^{\text{Aibj}}$  and  $\epsilon^{\text{Aibj}}$ ) are obtained in the same regression, selecting Scheme 2B, which accounts the existence of two association sites: cation and anion charges.

As the aim of this work lies in the modeling of binary, ternary and quaternary mixtures,  $a$  and  $b$  are calculated following the well-known vdW-1f mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij}; \quad a_{ij} = a_i a_j (1 - k_{ij}) \quad (5)$$

$$b = \sum_i x_i b_i \quad (6)$$

where  $k_{ij}$  are the binary interaction parameters, which were the only adjustable binary parameters used in this work.

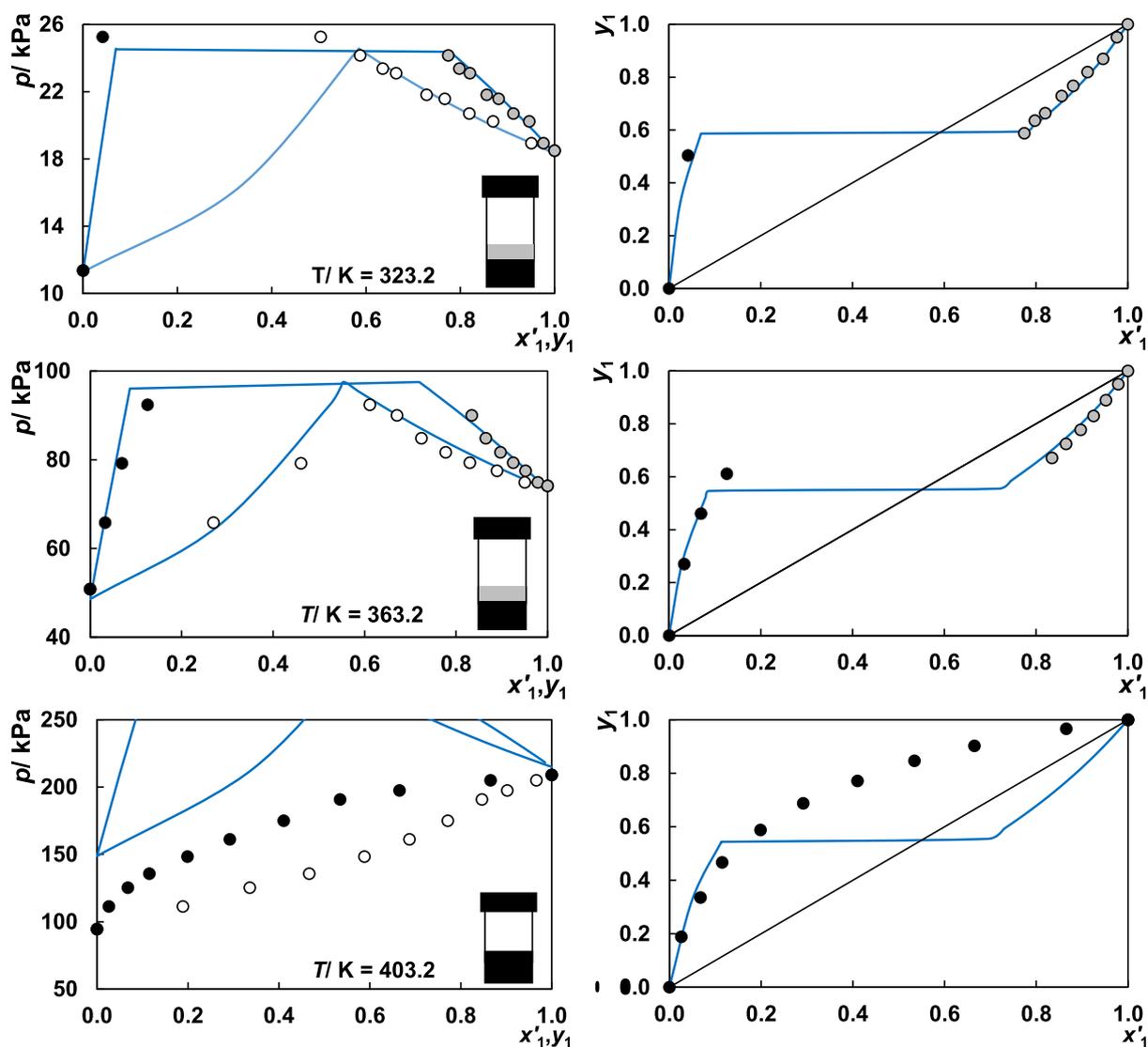


Fig. 7. VLE  $p$ - $x$ y and  $y$ - $x$  diagrams for the {methylcyclohexane (1) + benzene (2) + [C<sub>2</sub>C<sub>1</sub>im][DCA] (3)} ternary system with  $S/F = 10$ . Symbols: black denotes IL-rich liquid phases, grey refers to hydrocarbon-rich liquid phases, and white represents vapor phases. Lines: solid represents the CPA EoS with  $k_{13}$  from Table 4.

## 4. Results and discussion

### 4.1. Experimental screening

Systematic measurements for {methylcycloalkane + benzene + IL} ternary systems were carried at 323.2 and 363.2 K for all ILs. The benzene content in the binary hydrocarbon mixture was set at 80 wt% to represent the relative content of benzene to methylcyclopentane in the real hydrogenated pyrolysis naphtha [30]. Meanwhile, the solvent-to-feed ratio in mass basis was varied from 1 to 10, a range previously tested in similar systems and in line with the current solvent-to-feed ratios used in the petrochemical industry for this kind of separations [3,25,26]. The criterion to evaluate the operating conditions and the ILs was to maximize the methylcycloalkane/benzene relative volatility, calculated as follows:

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} \quad (7)$$

where  $K$  is the  $K$ -value, and  $y_i$  and  $x_i$  denote the vapor and overall liquid phase mole fractions of component  $i$ , respectively. The methylcycloalkane/benzene relative volatility values as a function of  $S/F$  mass ratio and temperature are collected in Table S1 in the Supplementary

Information and depicted in Fig. 1 for all ILs.

As shown in Fig. 1, the methylcycloalkane/benzene relative volatility is enhanced by the addition of the ILs, even reversing the methylcyclohexane/benzene relative volatility. An increase of the solvent-to-feed ratio provides an increment of the methylcycloalkane/benzene relative volatility in all cases since the ILs retain greater amounts of both hydrocarbons, but preferably benzene, thus, enriching the IL-free phases in methylcycloalkane.

On the other hand, the temperature impact on the methylcycloalkane/benzene relative volatility shows similar trends to those previously observed for the  $n$ -heptane/toluene extractive distillation with ILs [25]. Cross effects between IL extractive properties and temperature have been noted. The systems studied in this work present relatively high solubility of the non-aromatic compound compared to those related to linear alkanes. Then, the crucial property is the IL selectivity towards the aromatic compound, especially at higher temperatures when the low distribution ratios can be compensated, enhancing the separation. Indeed, for a solvent-to-feed ratio of 10, only for the ILs with the highest benzene/methylcycloalkane selectivities – [C<sub>2</sub>C<sub>1</sub>im][SCN] and [C<sub>2</sub>C<sub>1</sub>im][DCA] –, an increase of temperature has a positive effect on the methylcycloalkane/benzene relative volatility. Conversely, for a solvent-to-feed ratio of 5, the methylcycloalkane/benzene relative volatility increases when temperature increases for

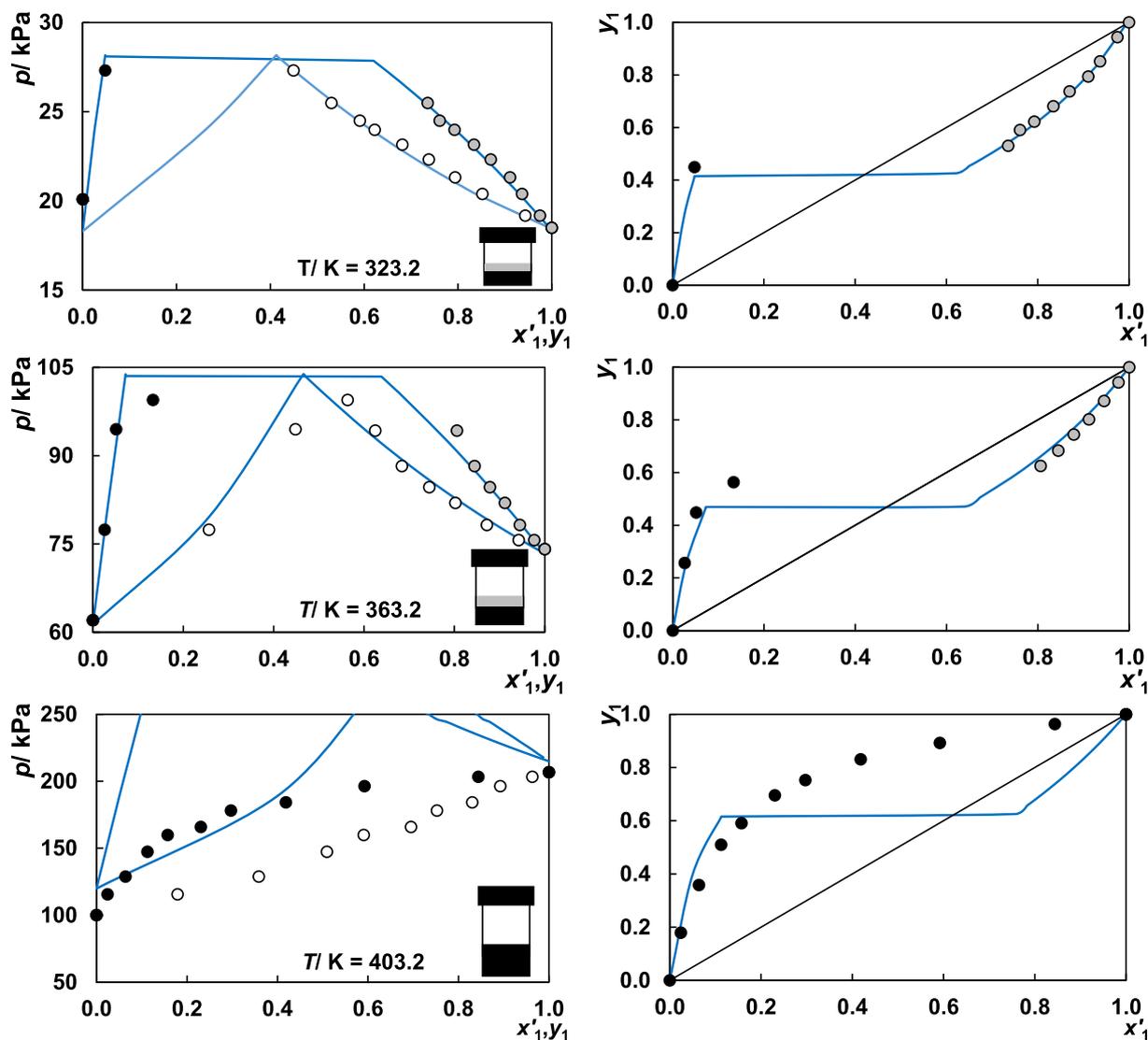


Fig. 8. VLE p-xy and y-x diagrams for the {methylcyclohexane (1) + benzene (2) +  $[C_2C_1im][SCN]$  (3)} ternary system with S/F = 10. Symbols: black denotes IL-rich liquid phases, grey refers to hydrocarbon-rich liquid phases, and white represents vapor phases. Lines: solid represents the CPA EoS with  $k_{13}$  from Table 4.

both separations except for the  $[4-C_4C_1py][TCM]$ , which is the IL with the lowest selectivity and the highest benzene distribution ratio. By contrast, when an inefficient solvent-to-feed ratio of 1 is used, the temperature has shown a slightly negative effect on methylcycloalkane/benzene relative volatility.

Overall, the best candidates for this separation are  $[C_2C_1im][DCA]$  and  $[C_2C_1im][SCN]$ , since competitive S/F mass ratios indicate that selective ILs are preferable to maximize methylcycloalkane/benzene relative volatility in the temperature range at which atmospheric extractive distillation can occur.

#### 4.2. CPA EoS molecular parameters for $[C_2C_1im][DCA]$ and $[C_2C_1im][SCN]$ ILs

As in a previous work [26], molecular parameters for  $[C_2C_1im][DCA]$  and  $[C_2C_1im][SCN]$  ILs were regressed using their atmospheric densities and heat capacities taken from the literature [35–37]. The new parameters together with the absolute relative deviations, vapor pressures and critical properties are depicted in Table 3.

As seen, these new parameters describe density and heat capacities properly with deviations similar to those reported in the literature [26], except for  $[C_2C_1im][SCN]$ ; however, one must remind that heat capacity is a very sensitive property to determine experimentally as well as

difficult to describe by EoS-based models [45]. In addition, the well-known non-volatile character of the ILs is properly addressed, being similar to reported vapor pressures for imidazolium-based ILs ranging 0.05–0.2 kPa at 450 K [46,47]. Comparing CPA EoS parameters of  $[C_2C_1im][DCA]$  and  $[C_2C_1im][SCN]$  with those reported to  $[C_2C_1im][TCM]$  [26], association parameters are maintained constant (same cation with the same association scheme), whereas parameter  $b$ , which is related to the molar volume, followed the expectable trend:  $[C_2C_1im][SCN] < [C_2C_1im][DCA] < [C_2C_1im][TCM]$ .

#### 4.3. Phase equilibria for {methylcycloalkane/benzene + IL} binary systems: Experimental and CPA EoS modelling

The VLE for the {methylcycloalkane + benzene} binary systems at 323.2, 363.2 and 403.2 K were taken from the literature [48] and are depicted in Fig. 2 together with the CPA EoS description, using the  $k_{12}$  values reported in Table 4. It is clear the ability of the CPA EoS to describe these systems in the temperature range studied using a temperature independent binary interaction parameter.

The VLE/VLEE for the {hydrocarbon +  $[C_2C_1im][SCN]$  /  $[C_2C_1im][DCA]$ } binary systems were then determined from 323.2 to 403.2 K. The VLE/VLEE data are represented in Figs. 3 and 4 and reported in Table S2 and S3, in the Supporting Information. As expected, two

regions are observed in the  $pTx$  phase diagrams: (i) a growing pressure zone until the maximum of solubility of the hydrocarbon in the IL is reached and (ii) a constant pressure zone with the same value of the pure hydrocarbon vapor pressure. As can be inferred, methylcyclopentane is slightly more soluble in the ILs than the methylcyclohexane, denoting that the increase of the volume has a negative effect on solubility [49]. In addition, the temperature hardly affects the hydrocarbon solubility in the IL, in agreement with previous works [26,50–52]. Finally, the CPA EoS was successfully used to describe these binary systems with the  $k_{i3}$  binary interaction parameters reported in Table 4.

#### 4.4. Phase equilibria for {methylcycloalkane + benzene + IL} ternary systems: Experimental and CPA EoS modelling

The VLE/VLLE for {methylcycloalkane + benzene + IL} ternary systems were determined at 323.2, 363.2 and 403.2 K, in the whole hydrocarbon composition range and with a solvent-to-feed ratio of 10. The data are reported in Tables S4–S7, in the Supporting Information, and the  $y-x$  and  $p-x,y$  diagrams are shown in Figs. 5–8.

Regarding the effect of the IL in both separations, in Figs. 5–8 it can be observed that the methylcycloalkane/benzene relative volatility is highly improved by the addition of these mass agents. On the one hand, the methylcyclopentane/benzene relative volatility is much higher compared to that without IL, with especial relevance at cycloalkane concentrations higher than the azeotrope. On the other hand, taking into account that methylcyclohexane is less volatile than benzene, the effectiveness of these two solvents is demonstrated since the methylcyclohexane/benzene relative volatility is reversed and presents values close to 20 (see Tables S4–S7 in the Supplementary Material). This is crucial because methylcyclohexane and benzene are the light and heavy

key components, respectively, in the benzene separation from both cycloalkanes considering a more realistic naphtha model.

Nonetheless, a boundary between homogeneous and heterogeneous extractive distillation conditions is found at 323.2 and 363.2 K, coexisting both VLE and VLLE regions. Comparing the two separations, higher VLLE region is found for the {methylcyclohexane + benzene + IL} systems since methylcyclohexane is less soluble than methylcyclopentane in the ILs as aforementioned. A similar behavior is observed contrasting the ILs;  $[C_2C_1im]$  [DCA] has a higher extraction capacity, so the VLE/VLLE transition is produced for a higher methylcycloalkane molar liquid fraction than for the  $[C_2C_1im]$  [SCN].

In spite of the heterogeneity described below 363.2 K, homogeneous conditions are achieved at 403.2 K throughout the whole hydrocarbon composition. A similar behavior was previously reported for the  $n$ -heptane/toluene separation with [TCM]-based ILs [26]. Here, despite the systematically lower aromatic extraction capacity of the  $[C_2C_1im]$  [SCN] and  $[C_2C_1im]$  [DCA] compared to the [TCM]-based ILs values [24,35,36] and the lower vapor pressure of methylcyclohexane compared to that of the  $n$ -heptane [40], the higher solubility of branched-chain and cyclic alkanes is the crucial parameter [53].

In addition, ternary liquid-liquid phase diagrams are represented in Fig. 9 for those systems in which VLLE was identified. Firstly, it is observed that the amount of IL in the hydrocarbon-rich phase is negligible. In the same line, the high benzene/methylcycloalkane selectivity implies that a low amount of methylcycloalkane is found in the IL-rich phase. Therefore, it can be concluded that liquid-liquid extraction effectively separates benzene from methylcycloalkanes with high purity and negligible losses of IL. As known, the immiscibility region decreases as the temperature increases for the same feed because of the higher amount that goes to the vapor phase. In any case, the ILs

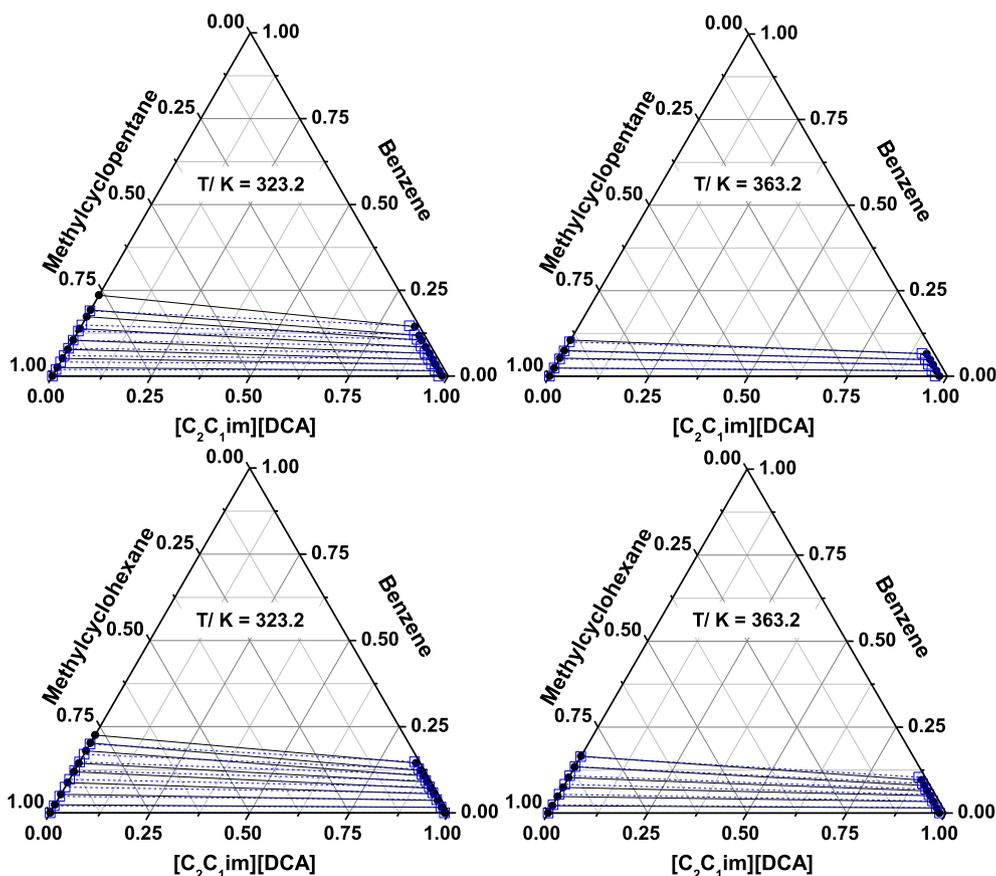


Fig. 9. Ternary LLE diagrams from the VLLE data of {methylcycloalkane + benzene + IL} ternary system with  $S/F = 10$ . Full symbols and solid lines denote experimental data and empty squares and dashed lines are the CPA EoS.

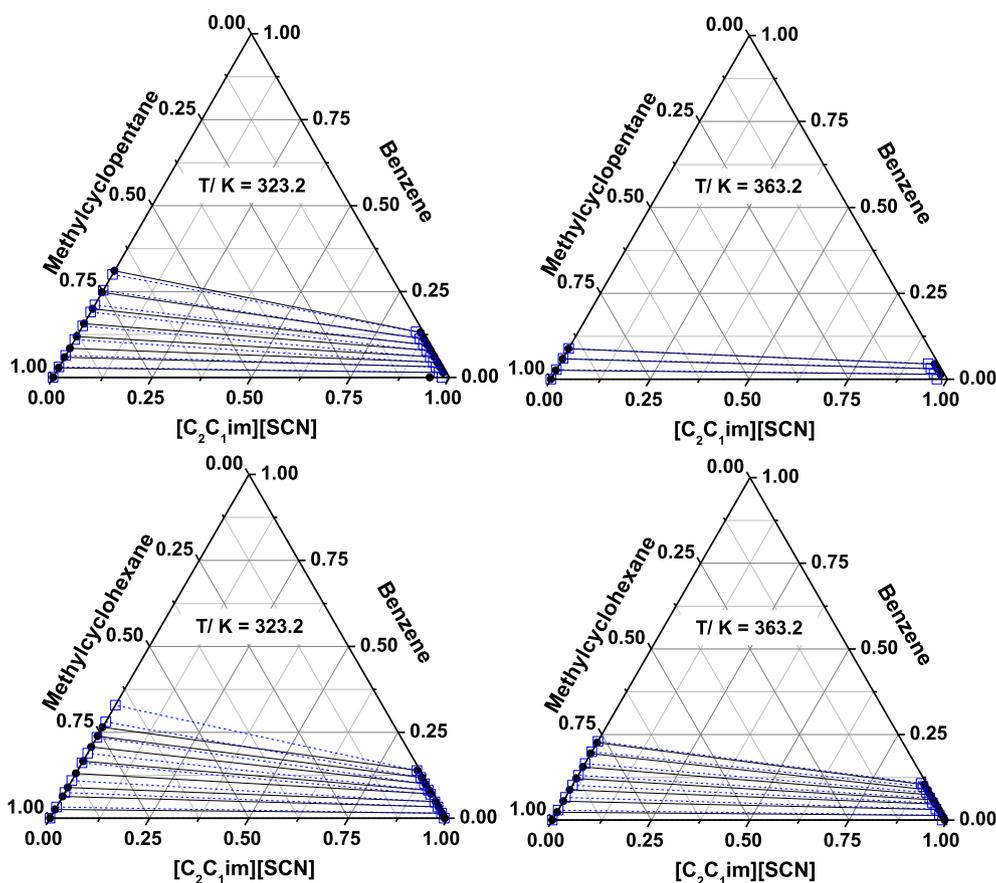


Fig. 9. (continued)

extractive properties hardly change.

The ternary phase diagrams were described by CPA EoS using the binary interaction parameters reported in Table 4. In Figs. 5–9 it can be observed the accuracy of the model, especially at low temperatures, avoiding the use of temperature-dependent binary interaction parameters. In the {methylcyclohexane + benzene + IL} case, the model describes better the experimental results than for the {methylcyclopentane + benzene + IL} system, owing to its higher accuracy when temperatures are below hydrocarbon boiling points [26]. Only at 403.2 K, the model presents significant deviations when describing the  $p$ - $x,y$  diagram; however, even then, the  $y$ - $x$  diagram is accurately represented for high aromatic concentration.

In a hypothetical extractive distillation column operating at atmospheric pressure, 403.2 K is located in the benzene-rich region near the reboiler; thus, the observed deviation of the model will underestimate the reboiler temperature and close-near stages. Furthermore, this divergence of the model is expected to be less significant in terms of temperature than for pressure due to the well-known Arrhenius correlation between pressure and temperature. In any case, more remarks on temperature underestimation are given in the last section of this work. The results here reported show that a robust, reliable and simple model was successfully developed to describe the phase behavior in the separation of benzene from these two methylcycloalkanes.

#### 4.5. Phase equilibria for {methylcyclopentane + methylcyclohexane + benzene + IL} quaternary systems: Experimental and CPA EoS modelling

Once the effectiveness of  $[C_2C_1im][DCA]$  and  $[C_2C_1im][SCN]$  ILs as mass agents to isolate benzene independently from methylcyclopentane and methylcyclohexane was evidenced, these ILs were tested in a more realistic multicomponent mixture containing both methylcycloalkanes

to represent the typical hydrogenated pyrolysis naphtha composition (see Table 2). Then, the corresponding methylcycloalkanes/benzene relative volatilities and total pressures are graphically presented in Fig. 10 as a function of temperature together with the CPA EoS description of the phase equilibria, whereas VLE/VLE data is depicted in Tables S8 and S9 in the Supplementary Material. It should be highlighted that this is the first work involving experimental and CPA EoS modelling of the VLE/VLE in a quaternary system containing ILs.

As inferred from Fig. 10, both ILs are still effective to isolate benzene from a complex mixture, indicating that the benzene isolation from the hydrogenated pyrolysis naphtha is feasible by extractive distillation with ILs. Regarding CPA EoS, although there is a loss on the quality of the phase equilibria description, at atmospheric pressure, as the temperature increases, the IL effectiveness is still properly represented, although underestimated, providing a useful model for further explore extractive distillation ILs at atmospheric pressure from a process simulation point of view.

## 5. Conclusions

In this work, the use of cyano-based ILs as mass agents in the benzene separation from a hydrogenated pyrolysis naphtha model was studied to find new aromatic sources for the oil industry. After screening the most promising species reported in the literature, the mass agents were narrowed down to  $[C_2C_1im][DCA]$  and  $[C_2C_1im][SCN]$  ILs due to their high cycloalkane/benzene relative volatility. Binary, ternary and quaternary systems involving methylcyclopentane, methylcyclohexane, benzene and the IL were characterized in a wide temperature range with a S/F mass ratio of 10 that allowed to describe homogeneous and heterogeneous extractive distillation boundaries. Overall, the enhanced methylcycloalkane/benzene relative volatilities suggest the feasibility of separating benzene from this new refinery

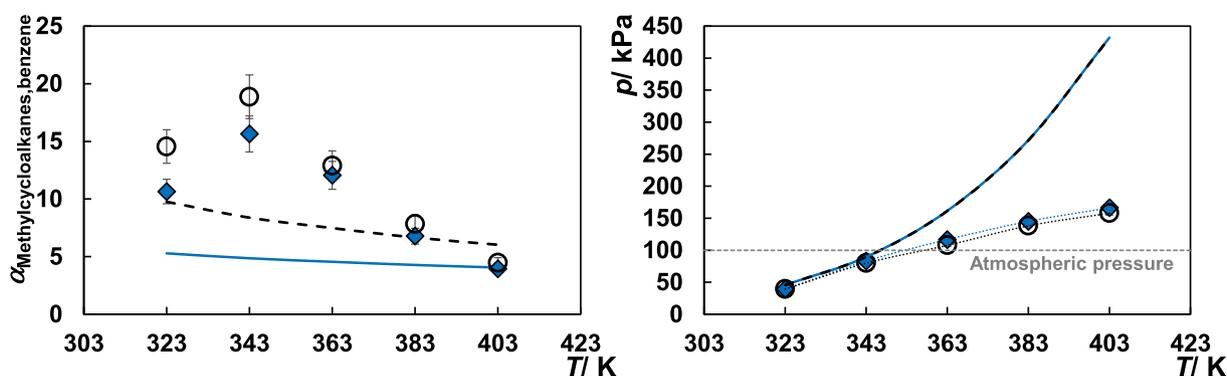


Fig. 10. Methylcycloalkanes/benzene relative volatility and equilibrium pressure as a function of temperature for the benzene separation from a multicomponent model representing the hydrogenated pyrolysis naphtha by extractive distillation. Symbols denote the experimental data (○, [C<sub>2</sub>C<sub>1</sub>im][DCA]; ◇, [C<sub>2</sub>C<sub>1</sub>im][SCN]) and the dashed and solid lines are the CPA EoS for [C<sub>2</sub>C<sub>1</sub>im][DCA] and [C<sub>2</sub>C<sub>1</sub>im][SCN], respectively. Dotted lines are guides to the eyes within the experimental data trend.

stream using an ILs as mass agents.

The complexity of the phase equilibria on the systems studied, simultaneously showing VLE and VLLE, imposed a hard task in the modelling of these systems. Nonetheless, CPA EoS has been revealed as a suitable approach to accurately describe vapor and liquid streams as well as the distribution of the compounds between the liquid phases when heterogeneous extractive distillation takes place. Overall, this work reports extensive experimental evidence and an accurate model to further explore the extractive distillation with ILs as a powerful technology to separate difficult hydrocarbon mixtures with industrial interest, such as methylcycloalkane/benzene.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.116128>.

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