Thermodynamics, Transport, and Fluid Mechanics

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Ind. Eng. Chem. Res., **Just Accepted Manuscript** • DOI: 10.1021/acs.iecr.0c02844 • Publication Date (Web): 24 Jul 2020

Experimental and CPA EoS Description of the Key Components in the BTX Separation from Gasolines by Extractive Distillation with Tricyanomethanide-based Ionic Liquids

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Abstract

Two tricyanomethanide-based ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium tricyanomethanide ([C_2C_1im][TCM]) and 1-butyl-4-methylpyridinium tricyanomethanide ([4-C_4C_1py][TCM]) have been recently reported as effective solvents for the BTX extractive distillation from pyrolysis gasoline. The vapor-liquid or vapor-liquid-liquid equilibria (VLE/VLLE) of several {aliphatic + aromatic + [TCM]-based ILs} ternary systems related to pyrolysis gasoline was extensively determined by headspace-gas chromatography (HS-GC), on a wide range of temperatures and solvent-to-feed (S/F) ratios. The Cubic Plus Association Equation of State (CPA EoS) was used to predictively describe the experimental VLE/VLLE from binary interaction parameters regressed from {hydrocarbon + IL} binary systems. Here, the VLE/VLLE related to the separation of the pyrolysis gasoline key components (*n*-octane and benzene) and other aliphatic/aromatic challenging mixtures in terms of aliphatic/aromatic relative volatility is reported. Specifically, the VLE/VLLE data for {*n*-octane + benzene + IL}, {*n*-heptane + benzene + IL} and {*n*-octane + toluene + IL} ternary systems were determined. The CPA EoS accuracy, robustness, and transferability between different systems is verified, with the advantages and limitations shown in previous works. Overall, the results obtained in this work lay the foundation for the implementation of the CPA EoS parametrization in a commercial simulator to rigorously simulate the multicomponent BTX extractive distillation from pyrolysis gasoline with ILs.

Keywords: Ionic liquids; aromatic/aliphatic separation; extractive distillation; Headspace-Gas Chromatography; CPA EoS

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1. Introduction

Extractive distillation is commonly used in the petrochemical industry to separate mixtures that cannot be addressed by conventional distillation due to the presence of close-boiling compounds and azeotropes.[1,2] In these cases, a mass separating agent is added as an additional feed stream to modify the activity coefficients, increasing the relative volatility of the key components in the mixture.[3] One of the main applications of the extractive distillation is the separation of aromatic hydrocarbons, mainly benzene, toluene, and xylenes (BTX), from refinery streams with high-aromatic content, such as pyrolysis gasoline (66.1 wt.%).[1] Current mass separating agents used in conventional BTX extractive distillation processes are organic compounds, namely sulfolane, *N*-methylpyrrolidone or *N*-formylmorpholine, among others. These mass separating agents present several drawbacks, such as their flammability, volatility and toxicity, leading to a negative environmental impact. The conventional BTX extractive distillation processes present high energy consumption and operating costs, owing to the losses and high boiling points of solvents.[4] Therefore, the selection of a suitable solvent is a crucial step to ensure an effective, economical and sustainable extractive distillation process.[5–11]

Lately, ionic liquids (ILs) have received great interest from researchers due to their remarkable characteristics that favor their use as mass separating agents: negligible vapor pressure, broad liquid range[12] and high thermal and chemical stability.[13] Also, ILs can be considered as designer solvents due to the possibility of tuning their extractive and physical properties through the combination of different anions and cations[14] or through carefully planning IL mixtures.[15–18] ILs have been successfully tested as mass agents in extractive distillation processes for the separation of different mixtures,[8,19–26] with special impact in those containing aromatic compounds.[27–35] The promising results have prompted the IL-based extractive distillation as a potential alternative to current extractive distillation processes, reducing energy consumption, and, at the same time, enhancing purity standards in only one piece of equipment.[36–38]

In previous works, tricyanomethanide-based ILs were selected as the most appropriate ILs for the aromatic/aliphatic extractive distillation.[39] This selection was based on the extensive liquid-liquid equilibria data reported to {alkane + aromatic + IL} ternary systems and their relatively low viscosity and high thermal stability.[40] Afterwards, the experimental characterization of the VLE/VLLE for several {aliphatic/aromatic + IL} binary systems and {aliphatic + aromatic + IL} ternary systems was made by headspace-gas chromatography (HS-GC) using the 1-ethyl-3-methylimidazolium tricyanomethanide ($[C_2C_1im][TCM]$) and 1-butyl-4-methylpyridinium

tricyanomethanide ([4-C_4C_1py][TCM]) as mass agents.[41] The CPA EoS was used to model the phase equilibria, and its accuracy and robustness were demonstrated in wide ranges of S/F ratios and temperatures. The transferability of the CPA EoS binary interaction parameters between different systems, and their dependence with molecular weight and temperature were also checked.[41,42]

This work deepens in the study of the BTX separation from pyrolysis gasoline by extractive distillation with tricyanomethanide-based ILs. Taking into account the composition of a pyrolysis gasoline model available in the literature,[1] the light and heavy key components of this gasoline model are *n*-octane and benzene, respectively. Thus, the *n*-octane/benzene separation is the most challenging within the overall separation. Also, *n*-heptane/benzene and *n*-octane/toluene are the other difficult separations in terms of aliphatic/aromatic relative volatility. Taking advantage of the above mentioned background, the VLE/VLLE for {*n*-octane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]}, {*n*-heptane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]}, and {*n*-octane + toluene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]} ternary systems were studied in the whole hydrocarbon composition range for a S/F ratio of 10 at the temperatures of 323.2, 363.2 and 403.2 K. The VLE/VLLE experimental data was also used to validate the CPA EoS model obtained in previous works, confirming its robustness.[41,42] Furthermore, the CPA EoS ability to describe dramatic changes in relative volatility in favor of the aliphatics, the so-called flipping phenomenum,[43] is evaluated, creating the bases for the CPA EoS parameters implementation in a commercial simulator like Aspen Plus.

2. Experimental Section

2.1. Chemicals

The two ILs, namely 1-ethyl-3-methylimidazolium tricyanomethanide, [C_2C_1im][TCM], and 1-butyl-4-methylpyridinium tricyanomethanide, [4-C_4C_1py][TCM], were supplied by Iolitec GmbH with a mass purity of at least 98 %. The ILs were further purified at vacuum conditions (50 Pa) and moderate temperature (313 K) before the measurements. The aliphatic and aromatic hydrocarbons were purchased from Sigma-Aldrich with mass fraction purity greater than 99%. The hydrocarbons were kept in their original vessels over 3 Å molecular sieves and were handled inside a glove box to avoid water absorption from ambient humidity. Specifications of the chemicals are reported in Table 1.

Table 1. Chemicals: Suppliers, Purities and Water Contents

Chemical	Supplier	Purity in wt. %	Water content in ppm
1-ethyl-3-methylimidazolium tricyanomethanide [C_2C_1im][TCM]	Iolitec GmbH	98.0	< 300
1-butyl-4-methylpyridinium tricyanomethanide [4-C_4C_1py][TCM]	Iolitec GmbH	98.0	< 300
n-heptane	Sigma-Aldrich	99.7	Anhydrous
n-octane	Sigma-Aldrich	≥ 99.0	Anhydrous
benzene	Sigma-Aldrich	99.8	Anhydrous
toluene	Sigma-Aldrich	99.5	Anhydrous

[a]Karl Fischer titration method

2.2. Determination of VLE/VLLE

The isothermal VLE and VLLE data were experimentally obtained using an Agilent 7697A headspace injector coupled to an Agilent 7890A gas chromatograph (HS-GC). This technique was widely explained in previous work.[44] Firstly, feed mixtures were gravimetrically prepared in 20 mL glass vials using a Mettler Toledo XS205 balance with a precision of 10^{-5} g. After, the mixtures were stirred inside the oven and allowed to reach the equilibrium, for time never smaller than 2 h.

A sample of the vapor phase was taken by the HS and analyzed by GC to obtain its composition (y_i). Knowing the feed (z_i) and the vapor phase composition (y_i), the overall liquid phase composition (x_i) can be determined by mass balance as follows:

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

where F denotes the molar amount of the feed, V_G is the headspace volume of the vial, R is the ideal gas law constant, N is the number of components and p_i is the partial pressure of the component i calculated as follows:

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

where A_i is the peak areas of the hydrocarbons, A_i^0 the peak areas of each pure hydrocarbon at the same conditions and p_i^0 the vapor pressure of each pure component from the literature.[45]

As explained in previous work,[39] for those assays presenting liquid-liquid phase splitting, an additional vial was prepared to determine the composition of one of the liquid phases. A sample of the IL-rich liquid phase was directly taken with a syringe and analyzed by multiple headspace extraction (MHE). Hence, knowing the composition of the vapor phase (y_i) and the IL-rich liquid phase ($x_{II,i}$), the amount of the liquid phases (L_{II} and L_I) and the composition of IL-free liquid phase ($x_{I,i}$) were determined by mass balance as detailed elsewhere[39].

3. CPA EoS Model

Kontogeorgis et al.[46,47] proposed a simplified CPA EoS version with two terms: a physical contribution term from the Soave Redlich-Kwong (SRK) EoS and an association term that takes into account the specific site-site intermolecular interaction. The CPA EoS approach is expressed in terms of the compressibility factor (Z) as the sum of physical and association contributions:

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} \tag{3}$$

In this work, the parameters from physical (a, b and c_0) and association (β and ε) terms for the hydrocarbons (non-associative compounds) and the tricyanomethanide-based IL (associative compounds) were taken from previous works,[41,42] where the IL non-volatile character was carefully described. The parameters a and b are calculated following the well-known vdW-1f mixing rules:

$$a = \sum_{\text{i}} \sum_{\text{j}} x_{\text{i}} x_{\text{j}} a_{\text{ij}} \;\; ; \;\; a_{\text{ij}} = a_{\text{i}} a_{\text{j}} (1 - k_{\text{ij}}) \tag{4}$$

$$b = \sum_{\text{i}} x_{\text{i}} b_{\text{i}} \tag{5}$$

where k_{ij} are the binary interaction parameters, which were obtained in our previous works, with their dependence on temperature.[41,42] Here, only binary interaction parameters for the new binary hydrocarbon systems, namely {*n*-octane + benzene}, {*n*-heptane + benzene} and {*n*-octane + toluene}, are regressed from binary VLE data.

It is worth mentioning that two different k_{ij} values were used for some {hydrocarbon + IL} systems at 403.2 K, since those regressed from binary VLE data were not capable to describe ternary VLE data at 403.2 K or above.[41,42] In any case, the corrections made in previous works[41,42] for some systems at 403.2 K are maintained here to ensure the transferability in ternary systems. All k_{ij} values are collected in Table S1 in the Supporting Information.

4. Results and Discussion

4.1. VLE for {Aliphatic + Aromatic} Binary Systems: CPA EoS Description of Literature Data

The VLE data for {*n*-octane + benzene}, {*n*-heptane + benzene} and {*n*-octane + toluene} binary systems were taken from literature.[48] These systems were further modeled in the temperature range of (323.2 – 403.2) K with the CPA EoS obtained in previous works.[41,42] The results are depicted in Figure S1 in the Supporting Information. The ability of the CPA EoS to describe these systems, using binary interaction parameters, k_{12}, with a small temperature dependency, is here shown. Binary interaction parameters are depicted in Table S1 in the Supporting Information along with the other binary interaction parameters for this work.

4.2. VLE/VLLE for {Aliphatic + Aromatic + IL} Ternary Systems: Experimental and CPA EoS Description

The VLE/VLLE data for the {aliphatic + aromatic + IL} ternary systems were determined at 323.2, 363.2 and 403.2 K in the whole hydrocarbon composition range and for an S/F of 10, as reported in Tables S2-S7 in the Supporting Information and depicted in Figures 1 - 6 (*y-x* and *p-x,y* phase diagrams). This S/F was selected as the optimal for modelling purposes as discussed previously [39,41,42] It can be noted that liquid-liquid phase splitting is found for all ternary systems, except for the {*n*-heptane + benzene + $[C_2C_1im][TCM]$ or $[4\text{-}C_4C_1py][TCM]$} ternary systems at 403.2 K. In other words, it is not possible to avoid heterogenous equilibrium for the systems containing *n*-octane at the conditions studied in this work. The lower solubility of *n*-octane in the ILs compared with other linear aliphatic hydrocarbons with shorter alkyl chains makes it more difficult to achieve the homogeneity in the liquid phase.[42] Nevertheless, this fact does not imply that the VLE region in the whole composition range could not be found in more favorable conditions, especially taking into account that the *n*-octane mass fraction in the pyrolysis gasoline ($w_{n\text{-octane}} = 0.116$) does not result in a heterogeneous equilibrium. In fact, in a previous work,[36] the COSMO-based/Aspen methodology was used to simulate the BTX extractive distillation from pyrolysis gasoline, finding homogenous extractive distillation along the whole column after properly validating COSMO predictions against experimental data. The $[C_2C_1im][TCM]$ was used as mass agent with a S/F ratio of 5 and the feed was preheated up to its bubble point. Considering the slightly lower BTX solubilities predicted by COSMO, more favorable S/F ratios are expected in an optimized design.[36]

Regarding the effect of temperature, two opposing trends are observed on all {aliphatic + aromatic + IL} ternary systems studied, in accordance with those previously observed for other similar systems. On the one hand, the higher the temperature, the larger the VLE region. On the other hand, the separation effectiveness slightly decreases by the increase in temperature. In addition, the equilibrium pressure for 363.2 and 403.2 K is around atmospheric pressure for all ternary systems studied here. Therefore, the temperature profile in a hypothetical extractive distillation column operating at atmospheric pressure would be not far from the temperatures studied in this work, as well as the aliphatic/aromatic relative volatilities.

The most difficult separation of the overall BTX extractive distillation from pyrolysis gasoline is the *n*-octane/benzene separation, *i.e.* light and heavy key components of the pyrolysis gasoline model, respectively. Considering that *n*-octane/benzene relative volatility without IL is lower than 1, the addition of the IL to this separation is quite remarkable. The highest alkane/aromatic relative volatilities in this work are obtained for the {*n*-heptane + benzene + IL} ternary systems, followed by the {*n*-octane + toluene + IL}, as expected since the flipping phenomenon is not as pronounced as for the {*n*-octane + benzene + ionic liquid} system.

Additionally, to analyze the distribution of the hydrocarbons between the IL-free and IL-rich liquid phases, LLE has been plotted in Figures 7 and 8 at 323.2 and 363.2 K. LLE data are reported in Tables S1-S6 in the Supporting Information together with VLE data. At 403.2 K, the LLE could not be determined due to technical limitations. Accordingly, only homogeneous liquid, VLE region, is available to validate CPA EoS predictions in those cases.

Analyzing the ternary LLE diagrams, the typical wide immiscibility region of IL-containing ternary systems is observed. In these cases, it is larger than in previously studied systems due to the lower solubility of *n*-octane and toluene in the ILs, in comparison with benzene and aliphatic hydrocarbons with shorter alkyl chains.[34,41,42] This region decreases as the temperature increases owing to an increment of the amount of vapor phase and the slight variation of the tie-lines slope. The IL solubility in the hydrocarbon mixture (raffinate) is negligible, whereas the non-aromatic presents very low solubility in the {aromatic + IL} mixture.

The CPA EoS previously proposed for {hydrocarbon + IL} binary systems is here used to describe the {aliphatic + aromatic + IL} ternary systems studied.[41,42] Considering the ternary systems presented here and the ternary systems modeled in previous works, the most representative aliphatic/aromatic separations within the pyrolysis gasoline model were modeled. In Figures 1 - 6 it can be seen the excellent description of the {aliphatic + aromatic +

IL} ternary systems provided by the CPA EoS. The best description of experimental results is obtained at lower temperatures, that is, at 323.2 and 363.2 K. For the highest temperature (403.2 K), the CPA description worsens for the ternary systems. Therefore, slight corrections of the experimental k_{13} and k_{23} at 403.2 K were necessary for an accurate description of the ternary systems, as it was claimed previously.[41,42] It is remarkable that the corrections reported for the {*n*-hexane + benzene + IL}, {*n*-heptane + toluene + IL} and {*n*-octane + *p*-xylene + IL} ternary systems remain effective in this work. The EoS describes the boundary between homogeneous and heterogeneous region, even at 403.2 K, and both *p-x,y* and *y-x* diagrams are well-fitted and the ternary liquid-liquid equilibria is also accurately described.. The model covers the description of hydrocarbons distribution and solubility boundaries, such as the negligible solubility of the ILs in the raffinate phase. Therefore, the ability and robustness of the CPA EoS to describe all these {aliphatic + aromatic + IL} ternary systems, studied in this and prior works, are demonstrated. The lack of LLE equilibrium points at 403.2 K for {*n*-octane + benzene + IL} does not adversely affect the CPA EoS modeling, independently regressed from phase equilibria of binary systems. It is true that we can not explicitly validate LLE described by CPA EoS, but it was done implicitly at 323.2 and 363.2 K.

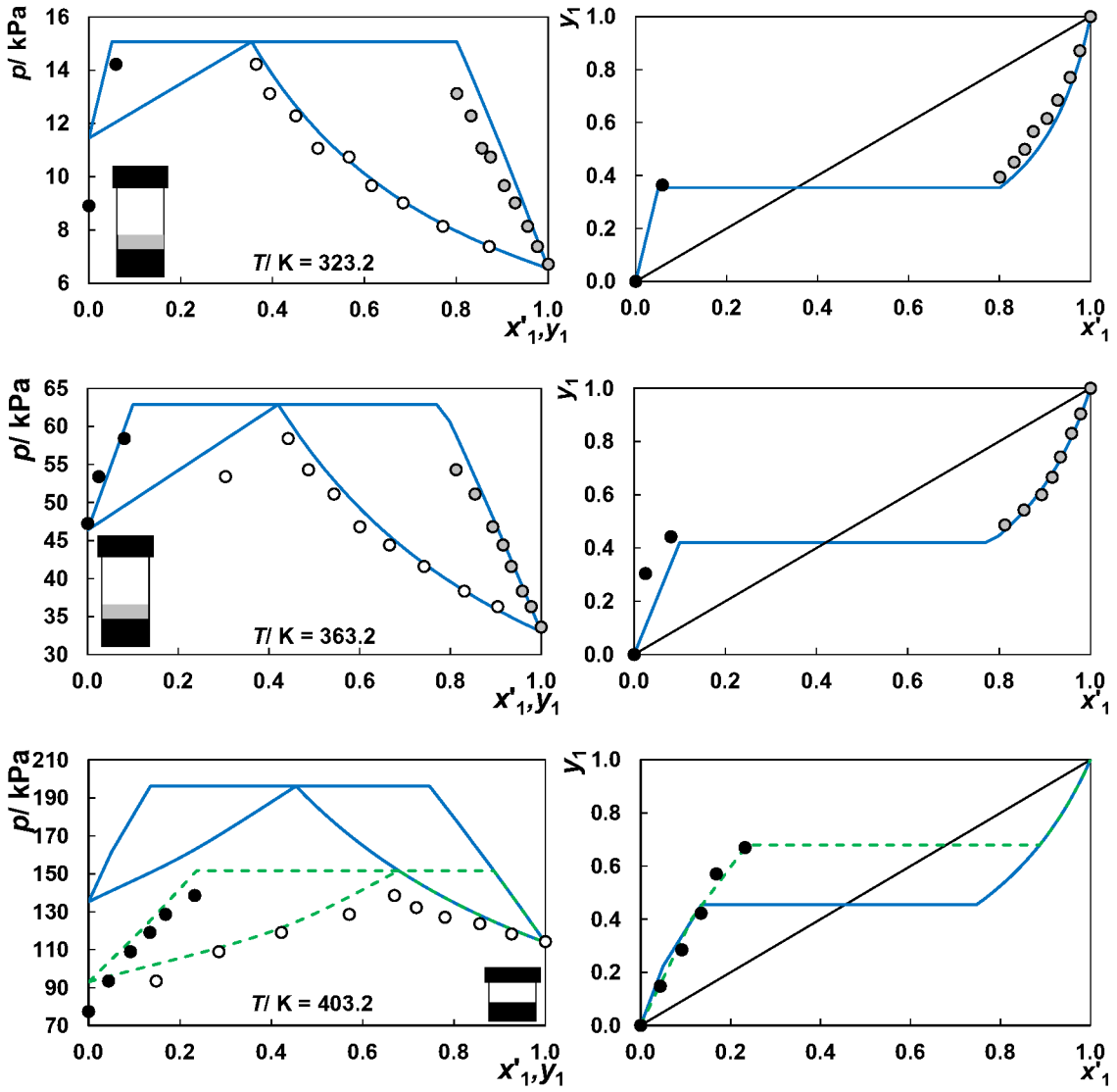

Figure 1. *p-xy* and *y-x* diagrams for the {*n*-octane (1) + benzene (2) + [C_2C_1im][TCM] (3)} ternary system. x_1' refers to the IL-free *n*-octane liquid phase composition. Symbols: black denotes IL-rich liquid phase, grey hydrocarbon-rich liquid phase, and white vapor phase. Lines: solid represents the CPA EoS with binary interaction parameters regressed from binary VLE data and dashed indicates literature corrections for VLE ternary data at 403.2 K.[41,42] The schematic vial shows when VLE or VLLE is observed.

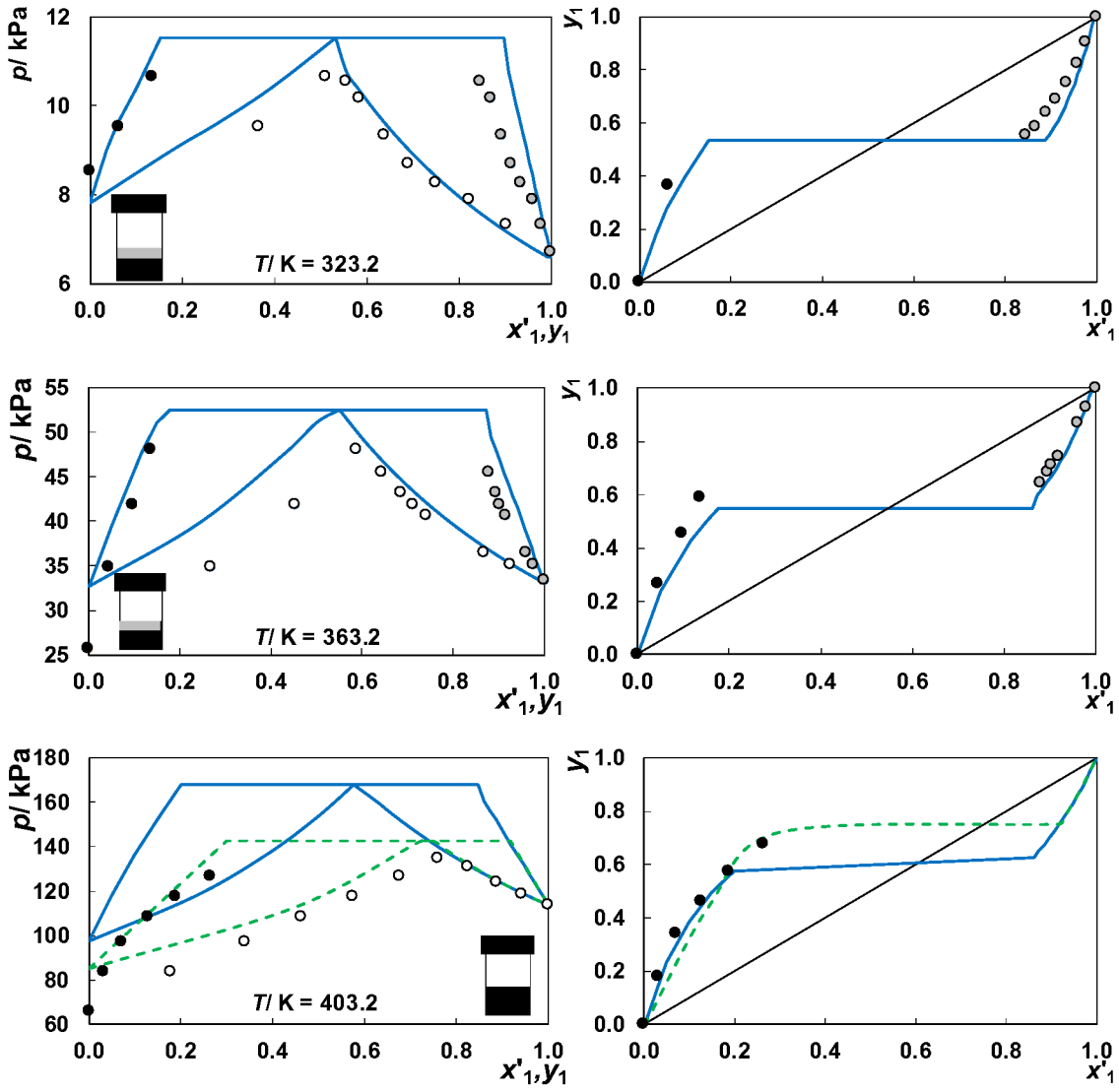

Figure 2. *p-xy* and *y-x* diagrams for the {*n*-octane (1) + benzene (2) + [4-C_4C_1py][TCM] (3)} ternary system. x_1' refers to the IL-free *n*-octane liquid phase composition. Symbols: black denotes IL-rich liquid phase, grey hydrocarbon-rich liquid phase, and white vapor phase. Lines: solid represents the CPA EoS with binary interaction parameters regressed from binary VLE data and dashed indicates literature corrections for VLE ternary data at 403.2 K.[41,42] The schematic vial shows when VLE or VLLE is observed.

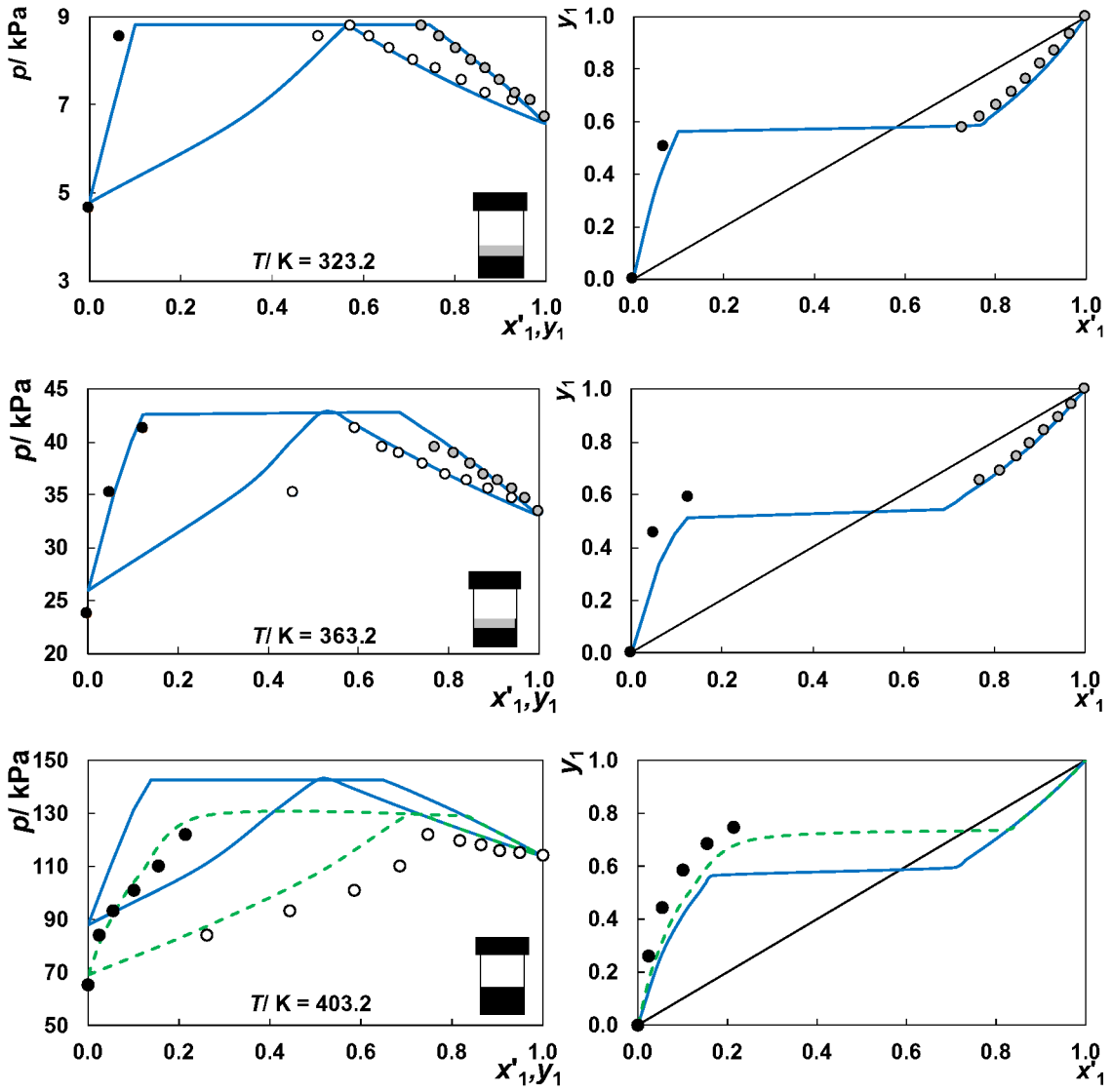

Figure 3. *p-xy* and *y-x* diagrams for the {*n*-octane (1) + toluene (2) + [C_2C_1im][TCM] (3)} ternary system. x_1' refers to the IL-free *n*-octane liquid phase composition. Symbols: black denotes IL-rich liquid phase, grey hydrocarbon-rich liquid phase, and white vapor phase. Lines: solid represents the CPA EoS with binary interaction parameters regressed from binary VLE data and dashed indicates literature corrections for VLE ternary data at 403.2 K.[41,42] The schematic vial shows when VLE or VLLE is observed.

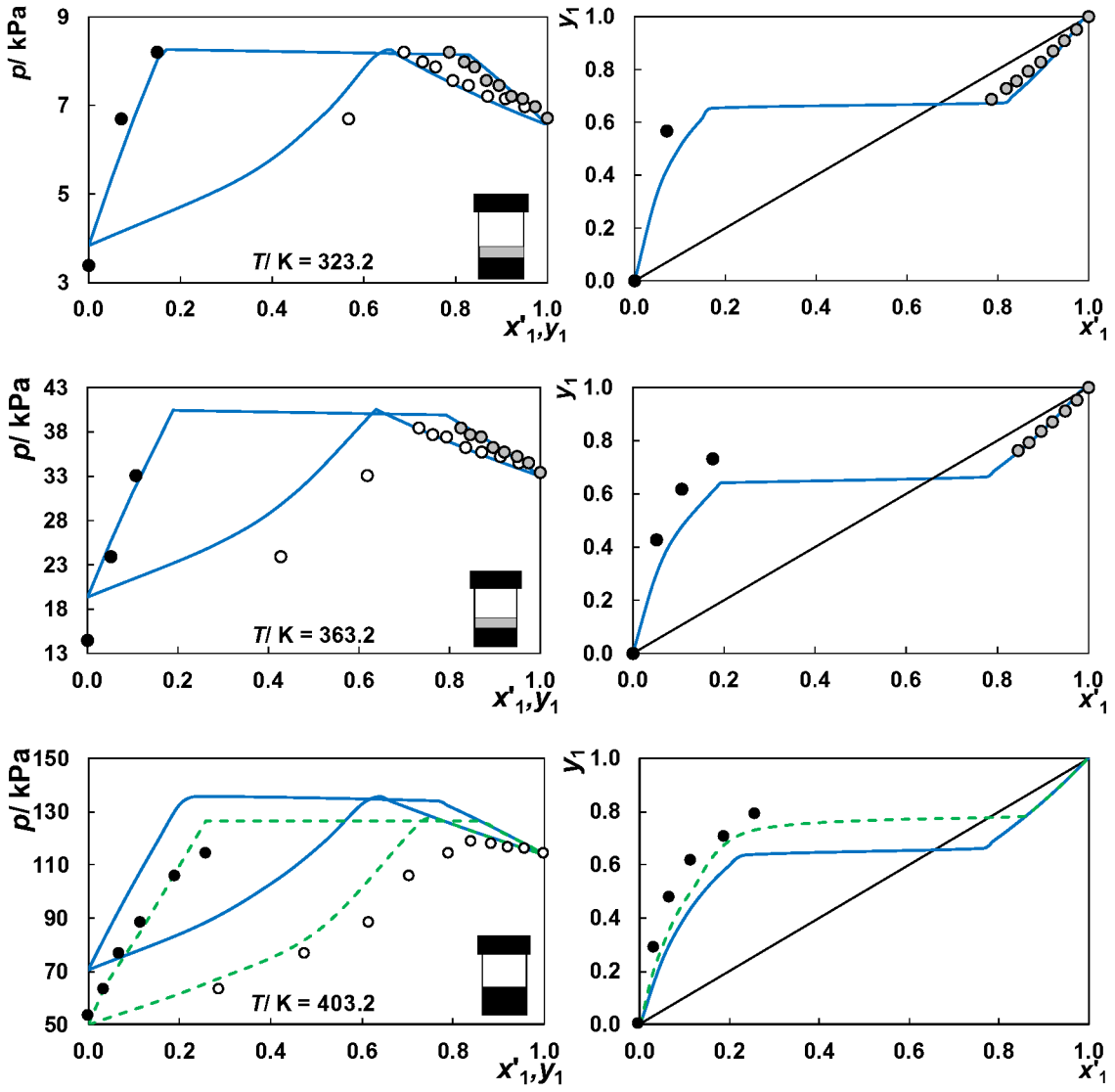

Figure 4. *p-xy* and *y-x* diagrams for the {*n*-octane (1) + toluene (2) + [4-C_4C_1py][TCM] (3)} ternary system. x_1' refers to the IL-free *n*-octane liquid phase composition. Symbols: black denotes IL-rich liquid phase, grey hydrocarbon-rich liquid phase, and white vapor phase. Lines: solid represents the CPA EoS with binary interaction parameters regressed from binary VLE data and dashed indicates literature corrections for VLE ternary data at 403.2 K.[41,42] The schematic vial shows when VLE or VLLE is observed.

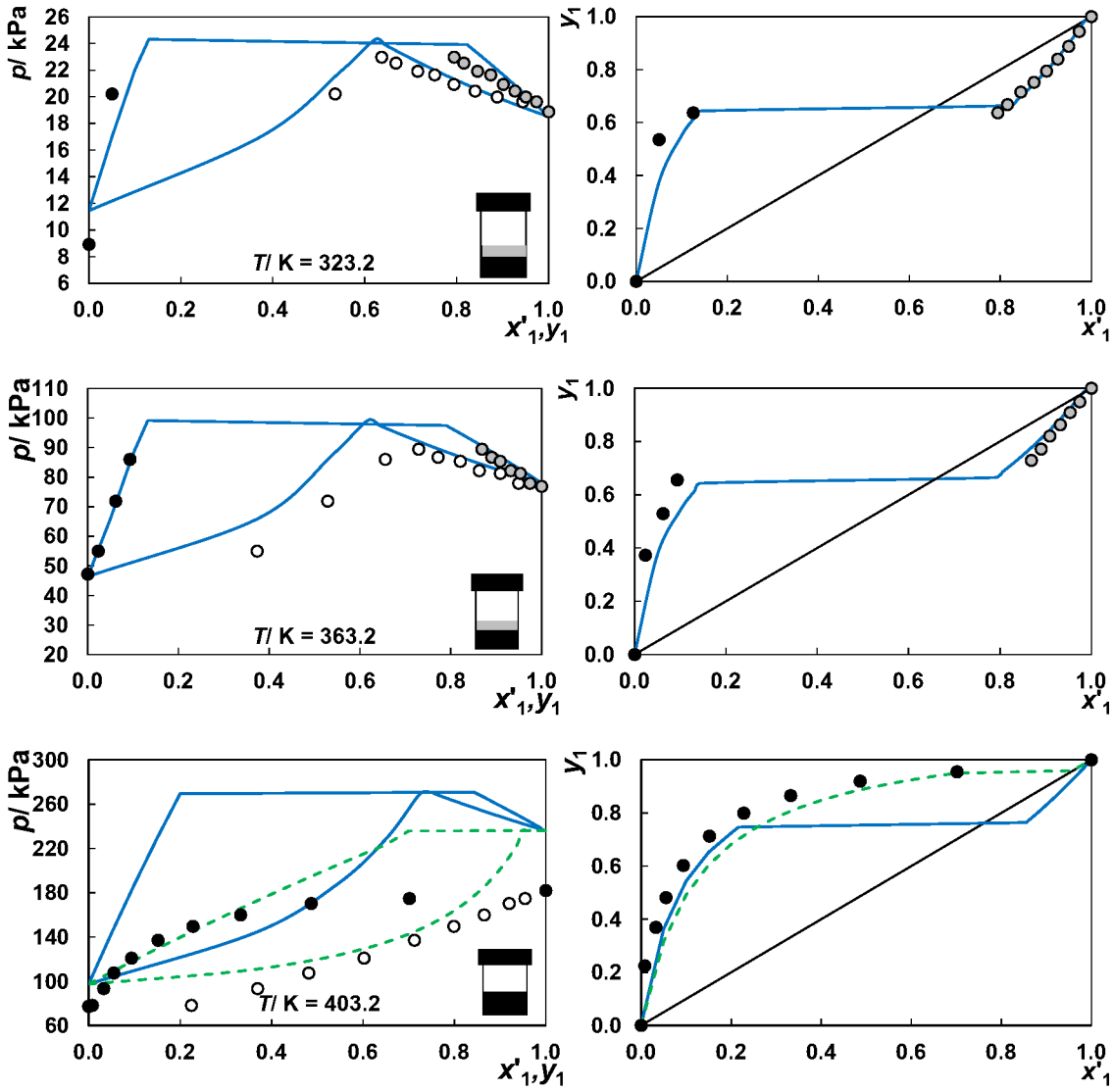

Figure 5. *p-xy* and *y-x* diagrams for the {*n*-heptane (1) + benzene (2) + [C_2C_1im][TCM] (3)} ternary system. x_1' refers to the IL-free *n*-heptane liquid phase composition. Symbols: black denotes IL-rich liquid phase, grey hydrocarbon-rich liquid phase, and white vapor phase. Lines: solid represents the CPA EoS with binary interaction parameters regressed from binary VLE data and dashed indicates literature corrections for VLE ternary data at 403.2 K.[41,42] The schematic vial shows iwhen VLE or VLLE is observed.

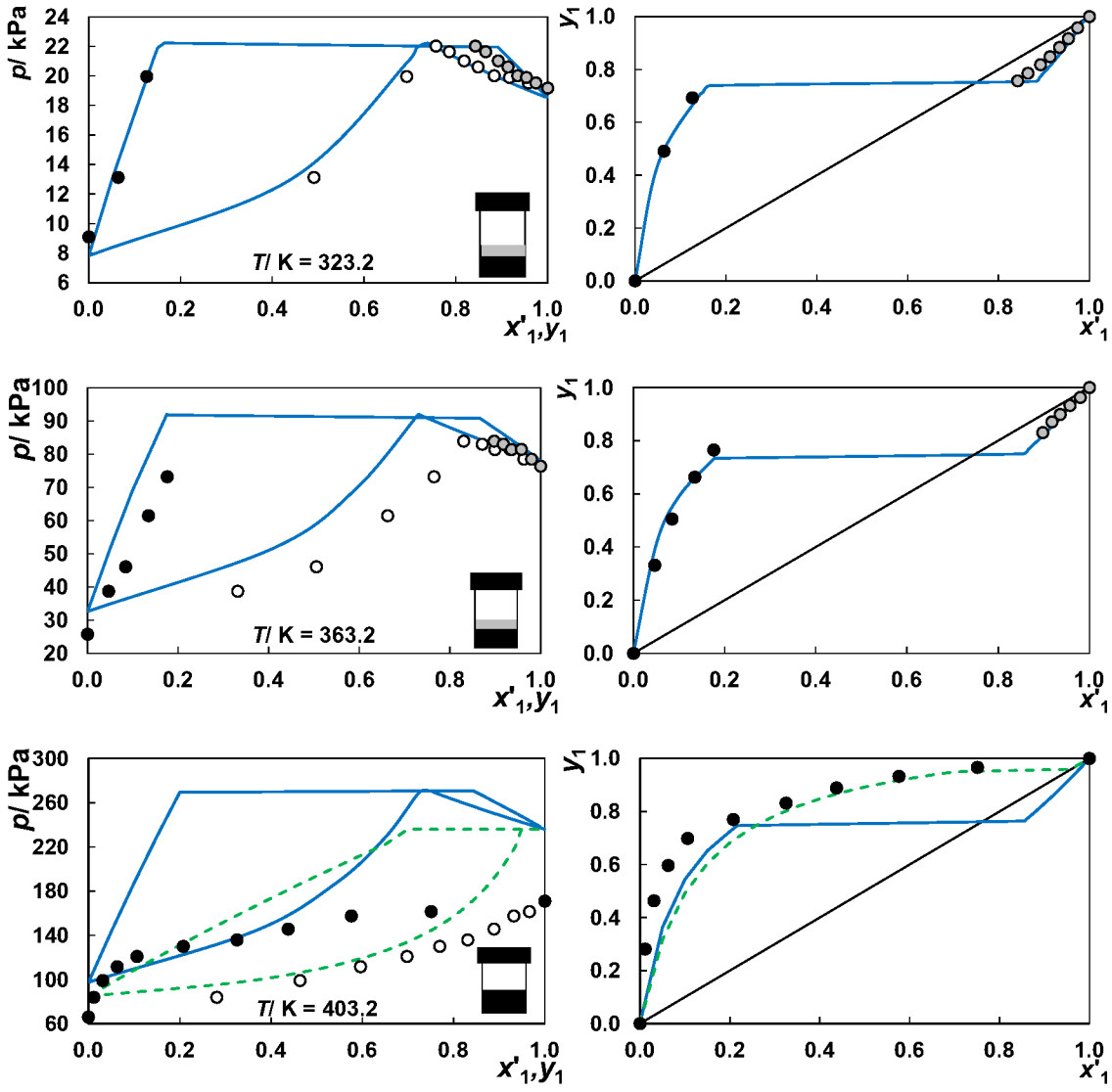

Figure 6. *p-xy* and *y-x* diagrams for the {*n*-heptane (1) + benzene (2) + [4-C_4C_1py][TCM] (3)} ternary system. x_1' refers to the IL-free *n*-heptane liquid phase composition. Symbols: black denotes IL-rich liquid phase, grey hydrocarbon-rich liquid phase, and white vapor phase. Lines: solid represents the CPA EoS with binary interaction parameters regressed from binary VLE data and dashed indicates literature corrections for VLE ternary data at 403.2 K.[41,42] The schematic vial shows when VLE or VLLE is observed.

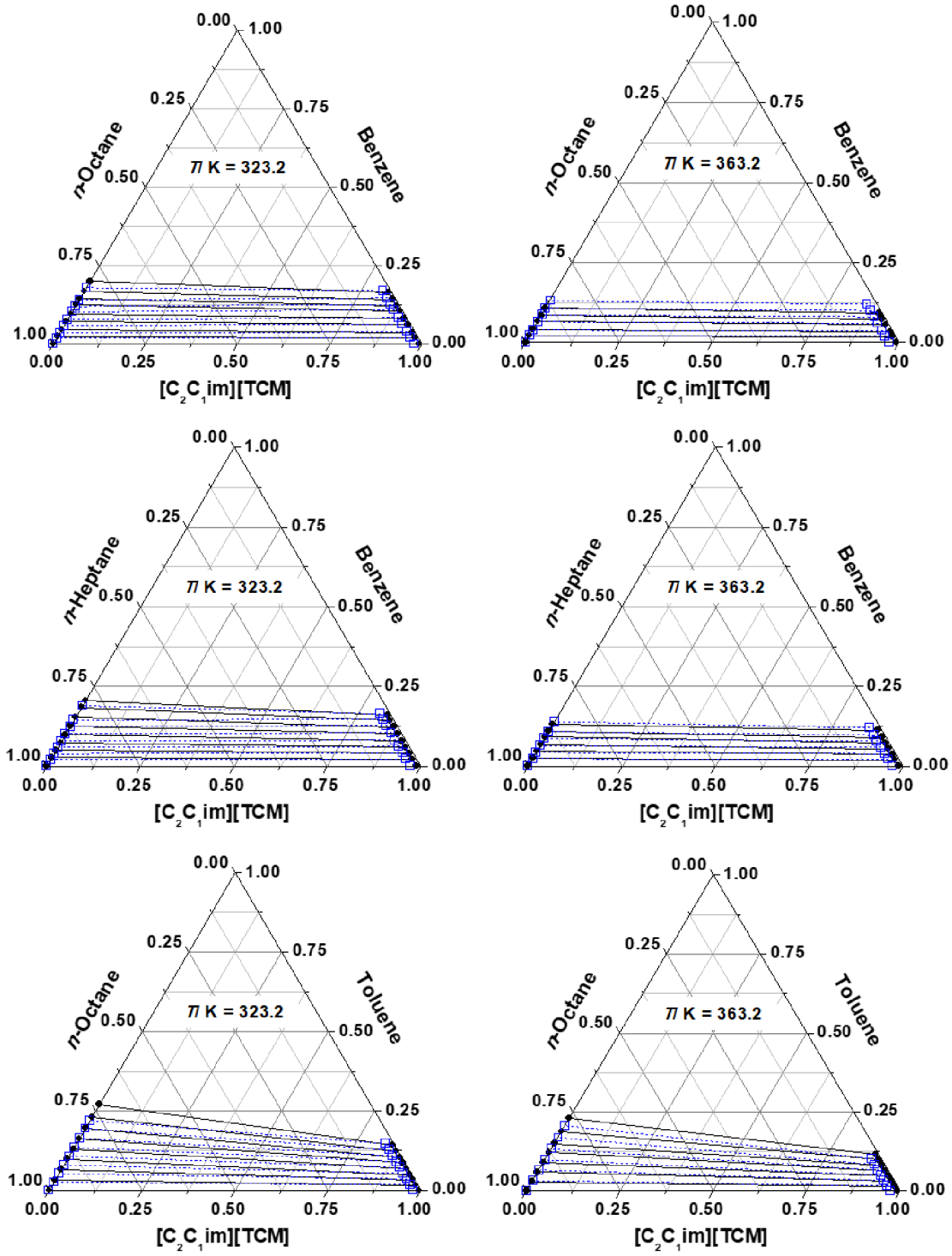

Figure 7. Ternary LLE diagrams from the VLLE data for the {aliphatic + aromatic + $[C_2C_1py][TCM]$} ternary system with S/F = 10. Full symbols and solid lines denote experimental data and empty squares and dashed lines the CPA EoS.

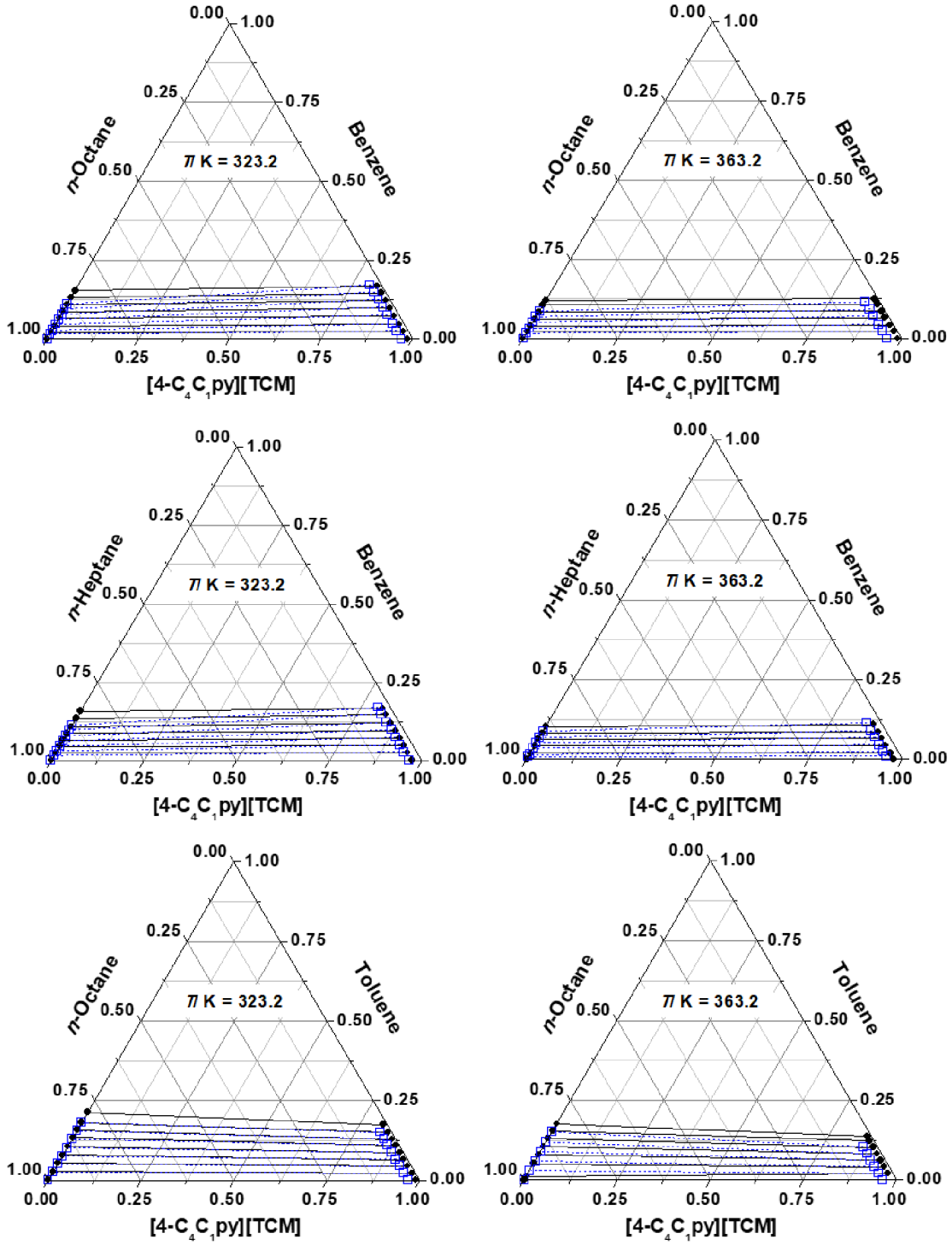

Figure 8. Ternary LLE diagrams from the VLLE data for the {aliphatic + aromatic + [4-C_4C_1py][TCM]} ternary system with S/F = 10. Full symbols and solid lines denote experimental data and empty squares and dashed lines the CPA EoS.

4.3. Analysis of the Aliphatic/Aromatic Relative Volatility

The aliphatic/aromatic relative volatility for each {aliphatic + aromatic + IL} ternary system has been determined from the VLE/VLLE data to quantify the effectiveness of the [TCM]-based ILs for the proposed separation. The values are reported in Tables S1-S6, in the Supporting Information, together with the VLLE data, calculated as follows:

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{y_1 / x_1}{y_2 / x_2} \tag{10}$$

where y_i and x_i denote the molar fraction of component i in the vapor and liquid phases, respectively. The *n*-octane/benzene relative volatility values are depicted in Figure 9 as a function of free-IL hydrocarbon liquid molar fraction. The *n*-heptane/benzene and *n*-octane/toluene relative volatilities as a function of free-IL hydrocarbon molar fraction are reported in Figures S2 and S3 in the Supporting Information. As can be seen in Figure 9, the effectiveness of the [C_2C_1im][TCM] and [4-C_4C_1py][TCM] is quite remarkable. The *n*-octane/benzene relative volatility is reverse for the whole hydrocarbon composition and for all the studied temperatures, achieving values that ensure a feasible separation, values close to up 17 for 363.2 K and up to 9 for 403.2 K. The same effect is observed for the *n*-heptane/benzene and *n*-octane/toluene relative volatility.

Besides comparing the two IL performance, the best results in terms of aliphatic/aromatic relative volatility are obtained with the [4-C_4C_1py][TCM] for all the ternary systems, within the uncertainty, except for the {*n*-heptane + benzene + IL} ternary system at 403.2 K. This ternary system is the only one without heterogeneity and the [C_2C_1im][TCM] shows higher relative volatility than the [4-C_4C_1py][TCM] due to its higher aromatic/aliphatic selectivity, as explained in previous works.[34,39,41,42] In brief, these results show the great potential of the [C_2C_1im][TCM] and [4-C_4C_1py][TCM] ILs as mass agents for the BTX extractive distillation from pyrolysis gasoline.

For the VLLE systems, the aliphatic/aromatic relative volatility remains almost constant for the homogeneous data, while decreases for the heterogeneous ones as free-IL aliphatic molar fraction increases. For the homogeneous ternary systems, *i.e.*, {*n*-heptane + benzene + IL} at 403.2 K, the aliphatic/aromatic relative volatility decreases as the aliphatic molar fraction increases for the whole composition range. These effects are in agreement with those observed for the {*n*-heptane + toluene + IL} ternary systems.[41] As expected, the [4-C_4C_1py][TCM] offers

the best performance when two liquid phases are present due to its higher extraction capacity, while the [C_2C_1im][TCM] stands as a better mass separating agent for homogeneous systems due to its higher selectivity for the aromatic compounds.

These behaviors are well described by the CPA EoS, confirming its great potential as a model to describe the effectiveness of both [C_2C_1im][TCM] and [4-C_4C_1py][TCM] as mass agents in the BTX extractive distillation from pyrolysis gasoline.

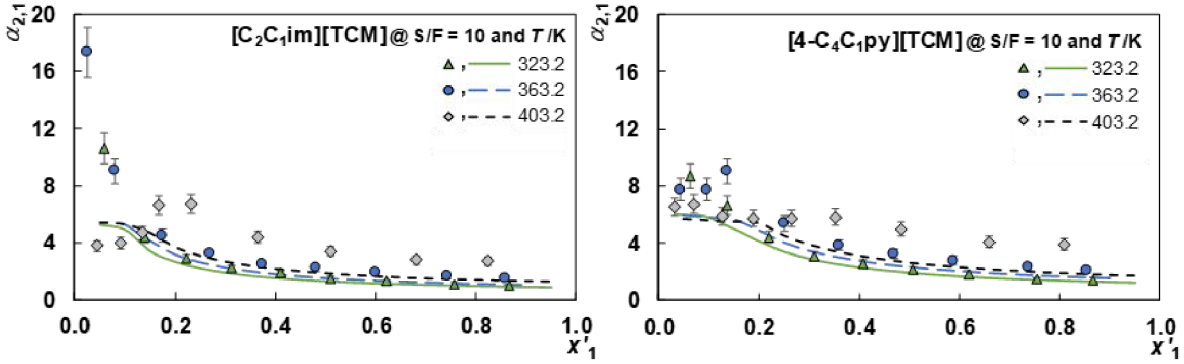

Figure 9. *n*-Octane/benzene relative volatility as a function of the free-IL aliphatic molar fraction for the {*n*-octane + benzene + [C_2C_1im][TCM]/[4-C_4C_1py][TCM]}. Symbols represent the experimental data and the lines the CPA EoS.

Conclusions

In this work the VLE/VLLE for {*n*-octane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]}, {*n*-heptane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]}, and {*n*-octane + toluene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]} ternary systems were determined by HS-GC at 323.2, 363.2 and 403.2 K and for a S/F ratio of 10. The results have shown the great effectiveness of these two ILs for the three aliphatic/aromatic separations. The aliphatic/aromatic relative volatility has been reversed in the whole hydrocarbon composition range for the *n*-octane/benzene separation, *i.e.* the most challenging separation, and the closer ones. Furthermore, the high aliphatic/aromatic relative volatilities obtained suggest a highly favorable BTX recover from pyrolysis gasoline.

The VLE/VLLE data were modeled by the CPA EoS model previously obtained from the VLLE data from different {hydrocarbon + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]} binary systems. The description of the phase equilibria and the transition from the VLE to VLLE region was verified in this work, using the same binary interaction parameters gathered in previous systems and

their small temperature dependency. Moreover, the slight corrections made to describe better the ternary systems previously studied, remain effective for the systems here reported. Therefore, the accuracy and robustness of the modeling proposal were demonstrated. The bases to implement the CPA EoS model on a commercial simulator to rigorously simulate the multicomponent BTX extractive distillation from pyrolysis gasoline with [TCM]-based ILs have been established.

Supporting Information

CPA EoS binary interaction parameters. VLE/VLLE for {*n*-octane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]}, {*n*-heptane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]}, and {*n*-octane + toluene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]} ternary systems. VLE for {*n*-octane + benzene}, {*n*-heptane + benzene} and {*n*-octane + toluene} binary systems. Aliphatic/aromatic relative volatility for *n*-heptane + benzene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]} and {*n*-octane + toluene + [C_2C_1im][TCM] or [4-C_4C_1py][TCM]} ternary systems.

Funding Sources

This work was partly developed in the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. The authors are also grateful to Ministerio de Economía y Competitividad (MINECO) of Spain and Comunidad Autónoma de Madrid for financial support of Projects CTQ2017–85340-R and P2018/EMT-4348, respectively. P.N. and P.J.C. thank FCT for awarding their postdoctoral grant (SFRH/BPD/117084/2016) and contract under the Investigator FCT 2015 (IF/00758/2015), respectively. N.D.-M. and M.A. also thank MINECO for awarding them an FPI grant (BES–2015–072855 and PRE2018-083728, respectively). M.L thanks Ministerio de Eduación, Cultura y Deporte of Spain for awarding him a José Castillejo postdoctoral mobility grant (CAS17/00018). All authors thank Infochem-KBC for the Multiflash program that was used for the CPA EoS calculations.

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Table of Contents