



High pressure density of tricyanomethanide-based ionic liquids: Experimental and PC-SAFT modelling

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ABSTRACT

Tricyanomethanide-based ionic liquids (ILs) are, probably, the most interesting ILs for separation purposes considering their low viscosity and high thermal stability, but mainly due to their enhanced performance in a wide number of applications. However, the scarce high pressure density data (ρpT) limits the development of robust models for process simulation implementation and consequently process development. In this work, high pressure density data of 1-ethyl-3-methylimidazolium tricyanomethanide ($[C_2C_1im][TCM]$) and 1-butyl-4-methylpyridinium tricyanomethanide ($[4-C_4C_1py][TCM]$) are reported in a wide range of temperature (283–363) K and pressure (0.1–95) MPa. The new ρpT data and its derivative properties, namely isothermal compressibility (k_T) and isobaric thermal expansivity (α_p), of the studied ILs and that reported for the 1-butyl-3-methylimidazolium tricyanomethanide ($[C_4C_1im][TCM]$), were successfully modelled using the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT). New molecular parameters for the tricyanomethanide-based ILs are here proposed allowing a good description of the studied properties while assessing the well-known non-volatile character of the ILs.

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1. Introduction

Ionic liquids (ILs) are non-conventional solvents with melting points below 373 K that, due to their negligible vapor pressures and the possibility of tuning physical and extractive properties, by modifying cation or anion structures, are presented as designer solvents in a wide variety of applications [1–4].

IL-based liquid-liquid extraction processes and extractive distillation are being proposed as separation processes in which ILs are outselling common organic compounds. Such high performance calls for better models to evaluate the feasibility of the ILs at process scale [5–7].

Tricyanomethanide-based ILs stand out as a real potential alternative to replace volatile organic compounds (VOCs) due to their low viscosities, high thermal stability, and their high capacity of extraction combined with a selective interaction in a wide variety of separations [5–13]. In fact, low viscosity values, ranging

from 7.7 to 14.1 mPa s at 323.2 K, can be found for 1-alkyl-3-methylimidazolium and 1-alkyl-4-butylpyridinium cation-based ILs with short substituents (ethyl and butyl) [12,13]; viscosities that are similar to the now-used VOCs, like ethylene glycol or sulfolane (with viscosities of 10.4 and 6.4 mPa s, at the same temperature, respectively) [12,14]. Concerning thermal stability, the aforementioned tricyanomethanide-based ILs have shown maximum operating temperatures around 450 K [11,13]. Finally, the suitability of tricyanomethanide-based ILs are found in several separations, like the dearomatization and desulfuration of liquid fuels or in the sweetening of natural gas, among others [5–12].

Nevertheless, the molecular description of these ILs is still poor. Although molecular parameters for 1-butyl-3-methylimidazolium tricyanomethanide ($[C_4C_1im][TCM]$) and 1-butyl-4-butylpyridinium tricyanomethanide ($[4-C_4C_1py][TCM]$) were reported by Lukoshko et al. [9], the reduced literature data at high pressure, like density, hampers the development of more robust models. Here, the high pressure density for $[C_2C_1im][TCM]$ and $[4-C_4C_1py][TCM]$ was determined in the 283–363 K temperature range and in the 0.1–95 MPa pressure range. The studied ILs allow to study the

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influence of the alkyl chain length and the cation family change, from imidazolium to pyridinium. The high pressure density data and the derivative properties, namely isothermal compressibility (k_T) and isobaric thermal expansivity (α_p), were further modelled by the Perturbed-Chain Statistic Association Fluid Theory (PC-SAFT).

2. Experimental and modelling

2.1. Chemicals

The 1-ethyl-3-methylimidazolium tricyanomethanide, [C₂C₁im][TCM], and the 1-butyl-4-methylpyridinium tricyanomethanide, [C₄C₁py][TCM], ILs were acquired from Iolitec GmbH with mass fraction purities higher than 98%. Aiming at reducing to negligible values both water and volatile compounds the ILs were further dried under vacuum (1 Pa), moderate temperature (313 K) and continuous stirring for a minimum of 48 h prior to the measurements. The ILs water content was determined with a Metrohm 831 Karl Fischer coulometer (using the HydranalCoulomat AG from Riedel-de Haens as analyte) and their purity checked by ¹H and ¹³C NMR. The full name, CAS number, molecular weight, average water content, mass fraction purity, and supplier of each IL are reported in Table 1.

2.2. High pressure density measurements

The ILs high pressure density was determined in the 283–363 K and 0.1–95 MPa temperature and pressure ranges, respectively, using an Anton Paar high pressure density meter (DMA-HPD) coupled to an mPDS 5 unit. The density standard uncertainty was found to be $5 \cdot 10^{-4} \text{ g cm}^{-3}$, as reported in previous publications [15,16]. A Julabo MC circulator and a silicon piezoresistive transducer from Kulite (HEM 375) placed directly in a 1/4 in stainless steel line, between the measuring cell and the movable piston to minimize dead volumes, were used to thermostatize the cell and measure the system pressure, with uncertainties in temperature and pressure of 0.1 K and 0.2%, respectively. A detailed description of the apparatus and methodology can be found elsewhere [15,16].

2.3. PC-SAFT modelling

Gross and Sadowski developed the PC-SAFT equation of state [17], which can be written, in terms of the residual Helmholtz energy, as the sum of a hard-chain energy contribution (a_{hc}), a dispersive energy contribution (a_{disp}) and an association interaction energy (a_{assoc}):

$$a_{res} = a_{hc} + a_{disp} + a_{assoc} \quad (1)$$

For non-associative fluids, three parameters are required, namely the segment number (m), the segment diameter (σ), and the dispersive energy between segments (ϵ), whereas association

compounds have two additional parameters related to the volume (k^{HB}) and energy (ϵ^{HB}) of the association sites. Tricyanomethanide-based ILs were considered as associating fluids as reported in the literature [9,18]. Ayad et al. [18] and Lukoshko et al. [9] considered a symmetric 3 + 3 association scheme due to the three lone pairs present on the anion, independently of the nature of the cation, i.e. imidazolium, pyridinium or piperidinium. This scheme accounts for the three negative association sites regarding the delocalization charge in the anion and the three positive association sites on the cation, namely delocalization of charge, electrostatic interactions concerning alkyl substituents of the cation and also acid proton for the imidazolium ring and the acid region of the pyridinium ring.

3. Results and discussion

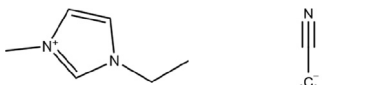
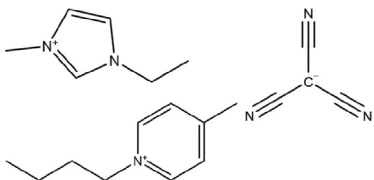
The studied ILs densities have been reported by several authors [11,12,19–24] only at 0.1 MPa and temperatures ranging between (273–373) K. As depicted in Fig. 1, a good agreement between the literature data and that measured here is observed, with absolute average relative deviation ($\%AARD = \frac{|\rho_{lit} - \rho_{exp}|}{\rho_{lit}} 100$) of 0.026% and 0.062% for the [C₂C₁im][TCM] and [4-C₄C₁py][TCM], respectively [11,12,21–24].

Higher deviations are observed against the data reported by Souckova et al. [19] and Krolikowski et al. [20], with %AARD of 0.40% and 0.20% respectively.

The ρpT data was measured for the two tricyanomethanide-based ILs in the temperature and pressure ranges of (283–363) K and (0.1–95) MPa, respectively. The experimental data are depicted in Fig. 2, along with literature data from Gardas et al. [25] for [C₄C₁im][TCM], and reported in Tables 2 and 3. As shown, the cation alkyl chain size, from ethyl to butyl, imposes a decrease on the ILs density and inherently an increase on the compounds molar volume. Being additive, the molecular weight increase of the pyridinium cation also leads to higher molar volumes of the IL, compared to the other ILs.

As mentioned in the PC-SAFT modelling section, the tricyanomethanide-based ILs were modelled with a symmetric 3 + 3 association scheme. PC-SAFT EoS pure-component parameters for [C₄C₁im][TCM] and [4-C₄C₁py][TCM] were reported by Ayad et al. [18] and later revised by Lukoshko et al. [9]. Then, the authors proposed the ILs' compounds molecular parameters by fitting the EoS against isothermal vapor–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE) data thus, when used to describe the pure compounds density, measure here, the EoS failed to describe the pressure influence on the density, with average relative deviation (%ARD) of 0.8%, 74.6% and 12.5% for ρ , k_T , α_p , respectively, as depicted in Fig. 3. Thus, new molecular parameters, reported in Table 4, were determined following the regressions of the experimental ρpT data by minimizing the following objective function (OF):

Table 1
Chemical structure, compound description, supplier, mass fraction purity and water mass fraction content of the studied ILs.

Compound	Structure
1-ethyl-3-methylimidazolium tricyanomethanide [C ₂ C ₁ im][TCM] CAS Reg. No. 666823-18-3; Mw = 201.23 g mol ⁻¹ ; w _{H2O} < 100 ppm; wt% = 98% ^a ; acquired from IoLiTec GmbH	
1-butyl-4-methylpyridinium tricyanomethanide [4-C ₄ C ₁ py][TCM] CAS Reg. No. 1312925-66-8; Mw = 240.30 g mol ⁻¹ ; w _{H2O} < 100 ppm; wt% = 98% ^a ; acquired from IoLiTec GmbH	

^a Reported by the supplier and verified by Nuclear Magnetic Resonance and Ion Chromatography.

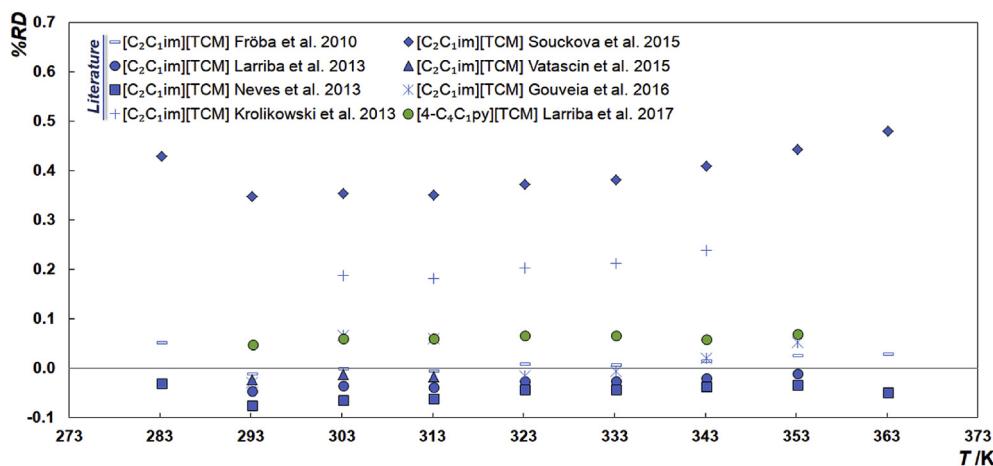


Fig. 1. Relative deviation (%RD) as a function of temperature between experimental and literature density data for the $[C_2C_1im][TCM]$ and $[4-C_4C_1py][TCM]$ ILs, at 0.1 MPa [11,12,19–24].

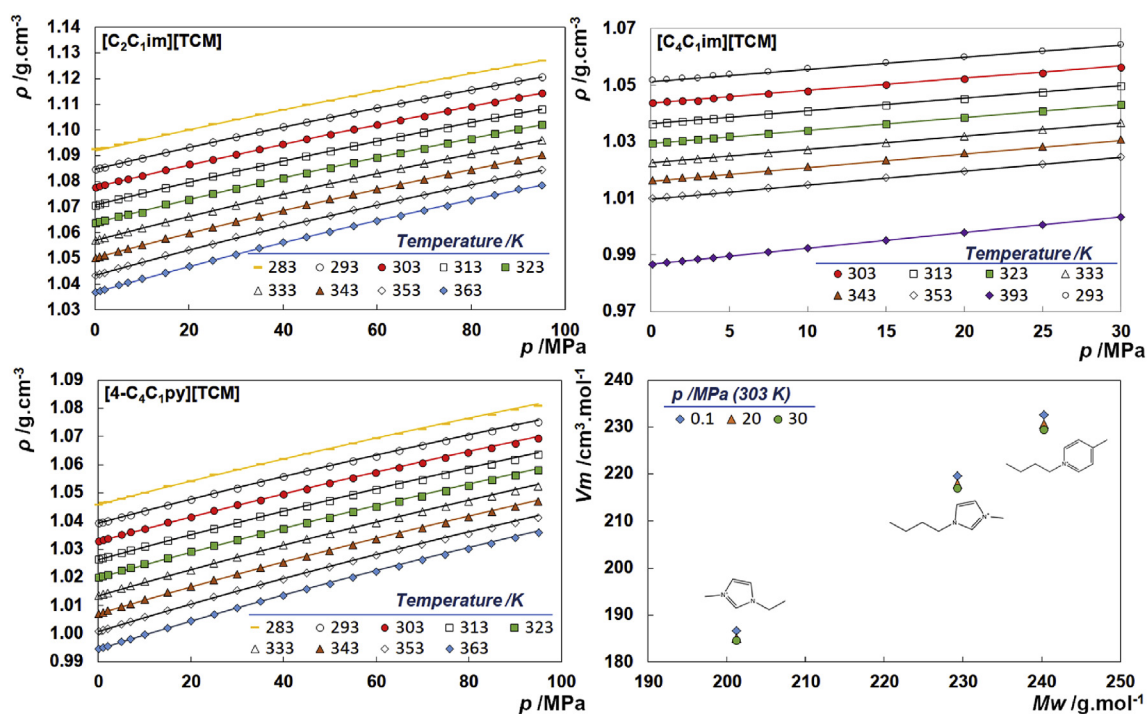


Figure 2. ρpT data for the studied tricyanomethanide-based ILs. Data for $[C_4C_1im][TCM]$ was taken from literature [25]. The solid lines represent the Tait Equation fit to the experimental data (Table S1).

$$OF = \frac{1}{N} \sum_{i=1}^N \left[0.8(\rho_{exp} - \rho_{calc})_i + 0.1(\alpha_{P,exp} - \alpha_{P,calc})_i + 0.1(k_{T,exp} - k_{T,calc})_i \right] \quad (2)$$

where N is the number of data points. As reported in Table 4, the new set of molecular parameters present percentage average relative deviation ($\%ARD = \frac{100}{N} \sum_{i=1}^N \frac{|\rho_{exp,i} - \rho_{calc,i}|}{\rho_{exp,i}}$) of 0.099%, 7.46% and 8.60% for the ρ , k_T , α_P , respectively (relative deviations between experimental and calculated data, as function of temperature and pressure, are depicted in Figures S1 through S3 in the Supporting Information). Although the σ and m parameters are similar to those reported by the authors, the energy parameter (ϵ/k_B), the

association volume (K_{AB}) and energy (ϵ_{AB}/k_B) are higher, which translates in vapor pressures reasonably more realistic to those expected for ILs. In fact, using the reported molecular parameters one would obtain vapor pressures of 6471 and 1755 Pa, at 500 K, for the ILs convening ILs as volatile compounds, which inherently will have an important impact on any VLE separation process. The molecular parameters proposed here addresses the well-known non-volatile character of ILs [26,27], with ILs vapor pressures of $3.6 \cdot 10^{-2}$, $1.4 \cdot 10^{-5}$ and $1.89 \cdot 10^{-4}$ Pa for the $[C_2C_1im][TCM]$, $[C_2C_1im][TCM]$ and $[4-C_4C_1py][TCM]$, respectively, while allowing a good description of the compounds' properties, as reported in Table 4 and depicted in Fig. 3.

As seen in Fig. 3, PC-SAFT properly describes the behavior of density as a function of temperature and pressure, starting to present small deviations at pressures above 30 MPa and

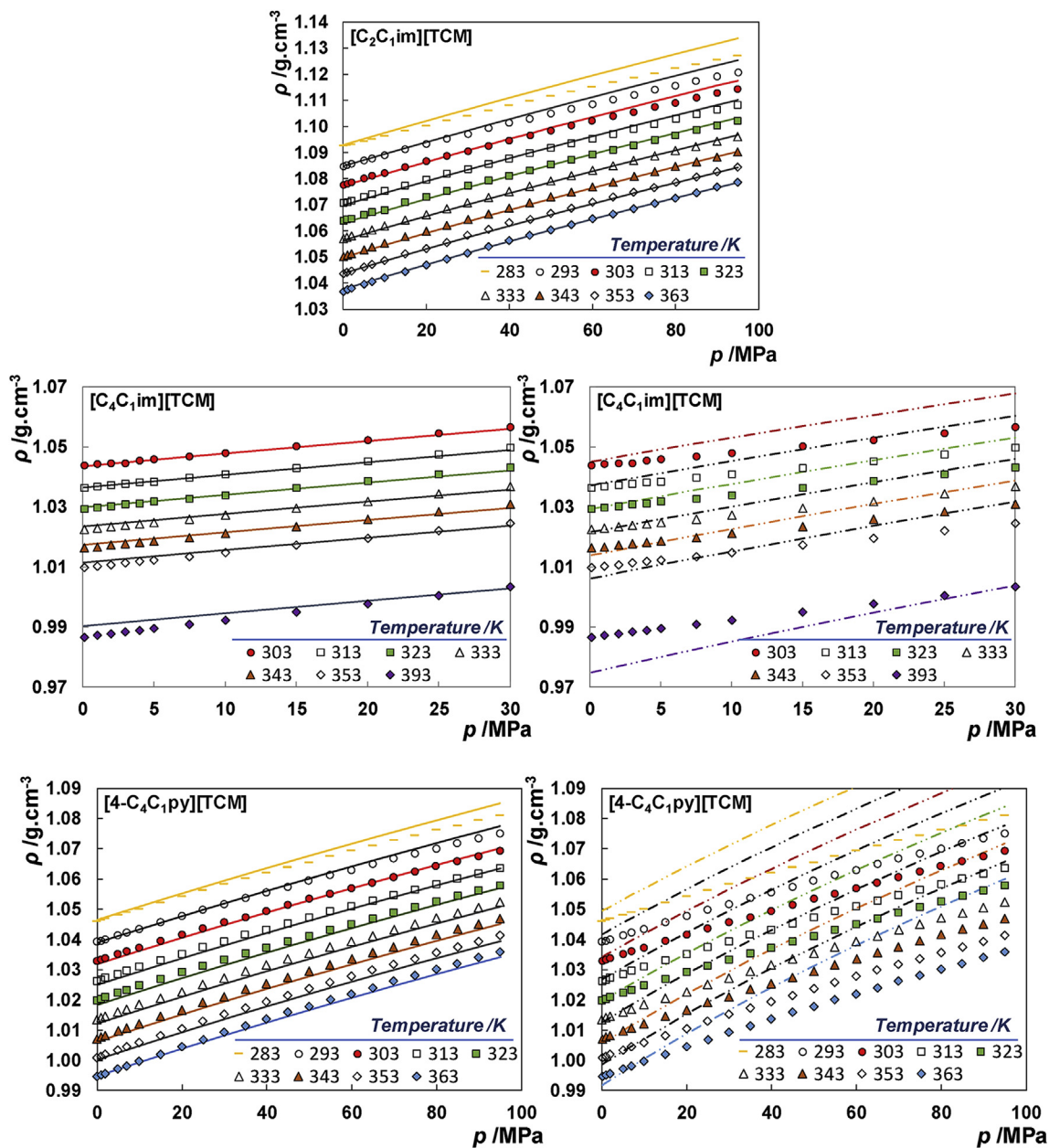


Figure 3. ρpT data for the tricyanomethanide-based ILs studied. Experimental and PC-SAFT modelling (full lines, this work; dot and dashed lines, literature [25]).

Table 4

PC-SAFT molecular parameters and deviations for high pressure density and derivative properties for $[C_2C_1im][TCM]$, $[C_4C_1im][TCM]$ and $[4-C_4C_1py][TCM]$ ILs.

	$[C_2C_1im][TCM]$		$[C_4C_1im][TCM]$		$[4-C_4C_1py][TCM]$	
	This work	Literature [18]	This work	Literature [18]	This work	Literature [18]
<i>Vapor pressure (p^0) and molecular parameters</i>						
p^0 (500 K)/Pa	$3.6 \cdot 10^{-2}$	6417	$1.4 \cdot 10^{-5}$	1755	$1.89 \cdot 10^{-4}$	3.428
$\sigma/\text{\AA}$	3.61	3.60	3.607	3.878	3.0722	3.428
$\epsilon/k_B/K$	357	233.40	360.00	265.46	307.22	307.22
m	6.23	6.864	7.49	5.972	8.94	8.94
K_{AB}	0.0780	0.0514	0.0780	0.0514	0.0780	0.0780
ϵ_{AB}/k_B (K)	3785	1816	3785	1816	3785	3785
%ARD						
ρpT	0.094	0.408	0.078	1.212	0.125	0.125
k_T	7.26	78.51	10.58	71.20	4.55	4.55
α_p	9.23	16.51	4.19	8.52	12.39	12.39

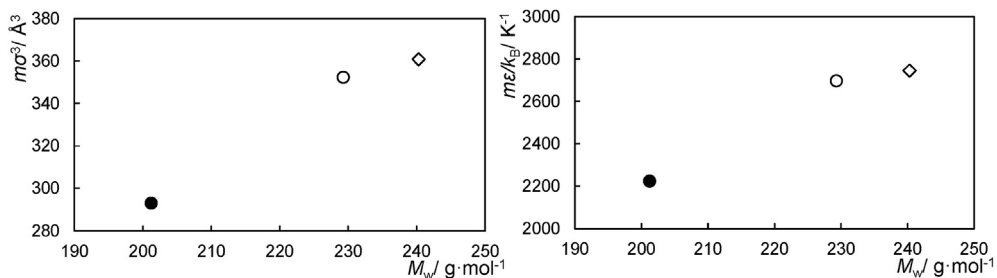


Figure 4. $m\sigma^3$ and $m\varepsilon/k_B$ as a function of molecular weight for the $[C_2C_1im][TCM]$ (●), $[C_4C_1im][TCM]$ (○) and $[4-C_4C_1py][TCM]$ (◇) ILs.

molecular weight of the ILs. The association parameters, on the other hand, remain constant for the three ILs; small changes lead to negligible improvements while losing the well-known transferability of the parameters.

Density derivative properties, namely isothermal compressibility (k_T) and isobaric thermal expansivity (α_p), were further calculated through the $\ln \rho$ dependency with pressure, at constant temperature, and temperature, at constant pressure, respectively,

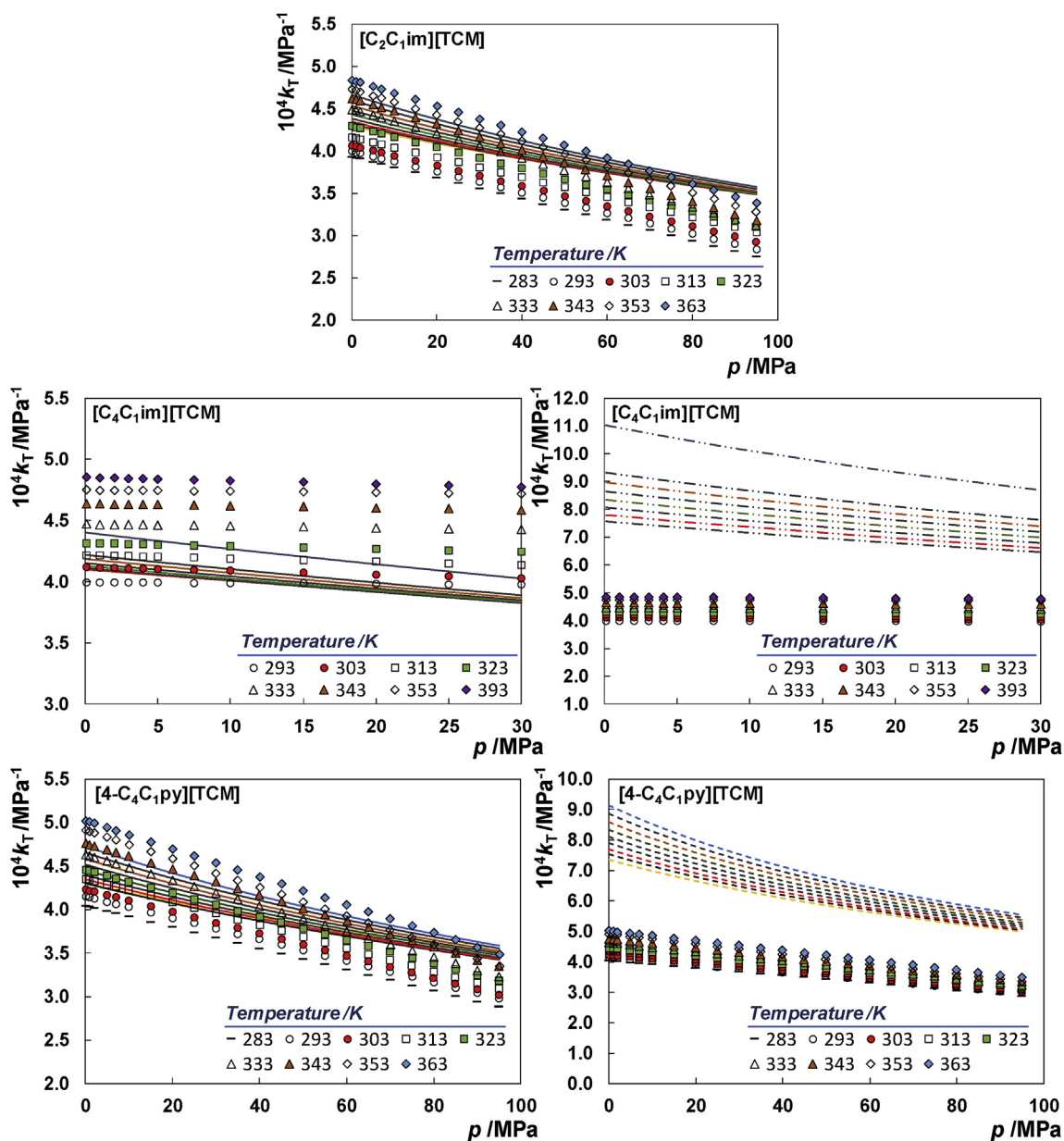


Figure 5. k_T as a function of pressure for the three tricyanomethanide-based ILs studied. Solid lines represent the proposed molecular parameters and the dashed lines those reported in the literature [25].

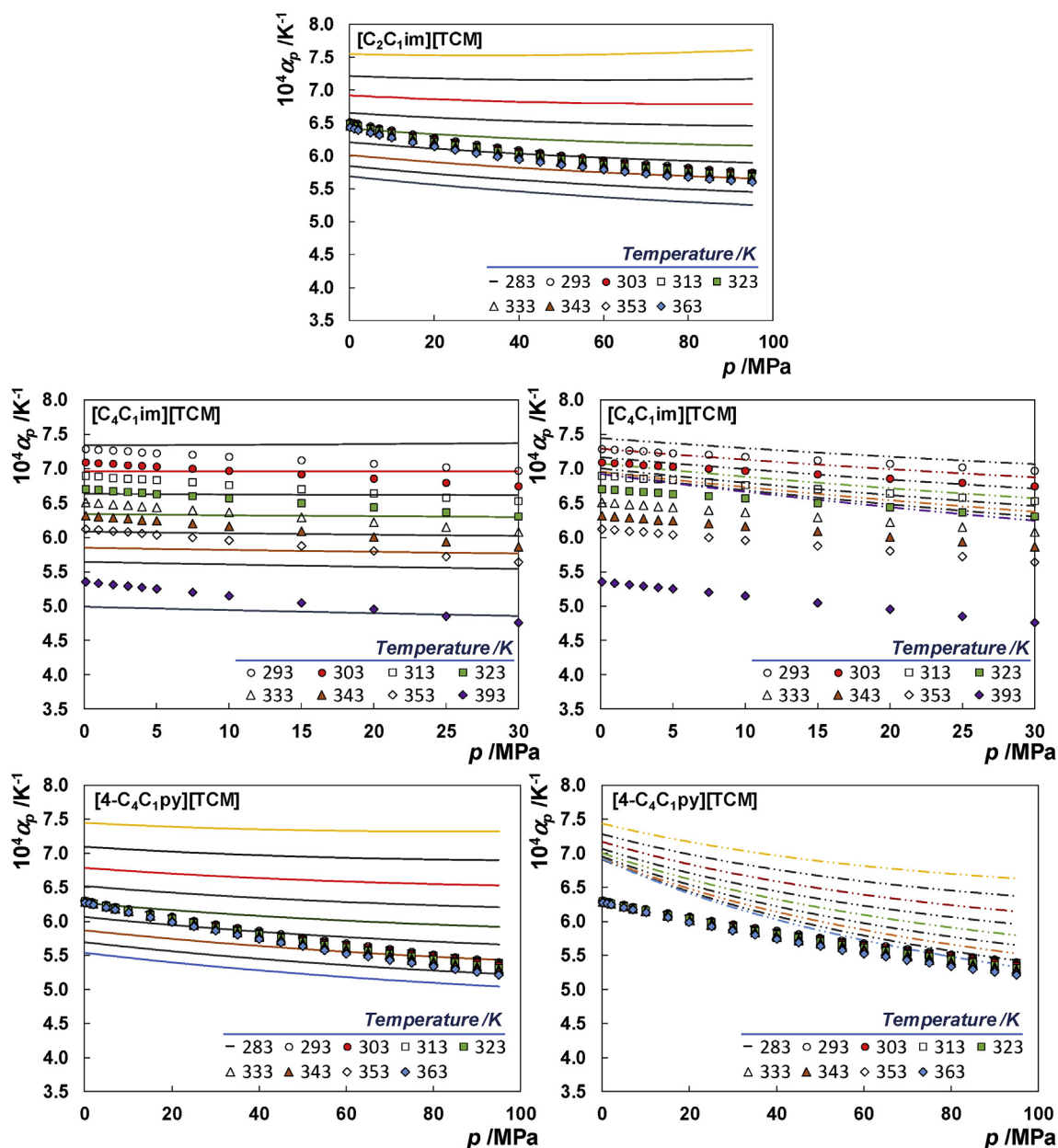


Figure 6. α_p as a function of pressure for the three tricyanomethane-based ILs studied. Solid lines represent the proposed molecular parameters and the dashed lines those reported in the literature [25].

and are depicted in Figs. 5 and 6. The isothermal compressibility is a measure of the variation of the IL volume with pressure and can be described as the change in density with pressure at constant temperature, while the isobaric thermal expansivity is a measure of the change in density with temperature at constant pressure.

$$k_T = \left(\frac{\partial \ln \rho}{\partial p} \right)_T \quad (4)$$

$$\alpha_p = - \left(\frac{\partial \ln \rho}{\partial T} \right)_p \quad (5)$$

As can be seen, the proposed PC-SAFT molecular parameters allow an adequate description of both properties with the average relative deviations reported in Table 4, below or close to 10%, for the three ILs studied here. Overall, PC-SAFT correctly describes k_T but, for the three data collections, underestimates the temperature

effect on this derivative property, especially for $[C_4C_1im][TCM]$ for which the densities present a smaller pressure dependency than that of the studied compounds. The smaller pressure dependency reported for the $[C_4C_1im][TCM]$ translates into almost no volume change with pressure, which PC-SAFT is not able to describe.

For α_p , on the other hand, although PC-SAFT is able to describe the small pressure impact on the density correctly, the data reported for the $[C_4C_1im][TCM]$ still presents smaller dependency with pressure than that measured for the remaining ILs.

4. Conclusions

High pressure density data for $[C_2C_1im][TCM]$ and $[4-C_4C_1py][TCM]$ was determined in wide ranges of temperature (283–363 K) and pressure (0.1–95 MPa). These data and that reported in the literature for $[C_4C_1im][TCM]$, along with their derivative properties, namely isothermal compressibility and isobaric thermal

expansivity, were further determined and modelled with PC-SAFT. New molecular parameters are proposed allowing correctly description of not only the high pressure density and the derivative properties, but also the well-known non-volatile character of ILs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Pablo Navarro: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft. **André M. Palma:** Data curation, Formal analysis, Investigation, Writing - review & editing. **Julián García:** Funding acquisition, Project administration, Resources, Writing - review & editing. **Francisco Rodríguez:** Funding acquisition, Project administration, Resources, Writing - review & editing. **João A.P. Coutinho:** Funding acquisition, Project administration, Resources, Software, Writing - review & editing. **Pedro J. Carvalho:** Conceptualization, Data curation, Formal analysis, Methodology, Software, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fluid.2020.112652>.

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