P, ρ, T and heat capacity measurements of (α-pinene + β-pinene) mixtures over the temperature range 283.15 K to 358.15 K and pressures up to 40 MPa: Experiments and modelling

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ABSTRACT

The density and isobaric heat capacity of the binary system {α-pinene (4,7,7-trimethylbicyclo[3.1.1]hept-3-ene (1), CAS Number 7785-26-4) + β-pinene (6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane (2), CAS Number 127-91-3)} has been measured for eleven different compositions. The density was determined at five pressures from (20 MPa to 40 MPa) and temperatures from (283.15 K to 358.15 K) and the isobaric heat capacity at atmospheric pressure and temperatures from (313.15 K to 418.15 K). Density was measured with an experimental uncertainty estimated to be ± 0.5 kg·m^{-3}. The isothermal compressibility and isobaric thermal expansion were derived from the experimental density data. The isobaric heat capacity was determined with a DSC calorimeter being the experimental uncertainty lower than 1.5%. Isobaric heat capacity behaviour was as expected for both pure compounds and for mixtures. Two different equations of state, conventional SAFT and PC-SAFT, were applied to calculate the densities of the mixture, being the best predictions achieved with PC-SAFT equation.

1. Introduction

Thermodynamic properties such as P, ρ, T and isobaric heat capacity, Cp, of pure fluids and their binary mixtures are very important for the design of chemical process plants [1,2]. Since there is not a suitable molecular theory for complex fluid mixtures, most of the studies performed so far have an experimental nature.

Pinene mixtures are found not only in fractional distillation from turpentine, but also in the supercritical extraction and subsequent fractionation of many essential oils [3–5]. Only few data on pure pinenes and their mixtures are available in the literature, which will be described briefly here.

Sousa et al. [6] studied the density at atmospheric pressure and temperatures between 293.15 K and 313.15 K of several mixtures rich in (1S,5S)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene(CAS 7785-26-4, also known as α-pinene) and (1S,5S)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (CAS 127-91-3, also known as β-pinene), prepared by the continuous enrichment of different fractions and obtained during the distillation of very impure α-pinene and β-pinene coming from turpentine from Pinus pinaster. Later Sousa and Nieto de Castro [7] measured the densities of commercial samples of α-pinene, β-pinene, limonene and two

types of turpentine also at atmospheric pressure at temperatures between 293.15 K and 313.15 K. Gomes-Medeiros et al. [8] studied densities and kinematic viscosities of mixtures containing α-pinene + β-pinene at temperatures between 298.15 K and 363.15 K. These terpenes were obtained once again by distillation from turpentine. Hawkings and Amstrong [9] measured the vapour pressures of α-pinene (between 292.6 K and 428.91 K) and β-pinene (between 291.87 K and 413.15 K). Densities and speed of sound of pure β-pinene were studied by E. Langa et al. [10] within the temperature range from 283.15 K to 313.15 K. Sampaio and Nieto de Castro [11] determined the isobaric heat capacity of commercial samples of α-pinene, β-pinene, limonene and turpentine at temperatures between 313 K and 403 K. However, there is no experimental work on P, ρ, T behaviour of (α-pinene + β-pinene) at high pressures, nor Cp of their mixtures at ambient pressure. Taking into account the lack of these experimental data for pinene mixtures, we have started an experimental programme involving pinene binary mixtures, from which the systems (limonene + α-pinene) and (limonene + β-pinene) were recently reported [12,13].

The present paper reports P, ρ, T and Cp measurements of the binary system (α-pinene + β-pinene). This study consisted of measuring the density of the mixtures (eleven mole fractions) at six temperatures (283.15, 298.15, 313.15, 328.15, 343.15, and 358.15) K and at five pressures (20, 25, 30, 35, and 40) MPa and

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Cp at atmospheric pressure at those mole fractions and over the temperature range from (313.16 K to 418.15 K). From these data, values of the isobaric thermal expansivity and isothermal compressibility were also calculated.

Beside the experimental data, the modelling of the thermophysical properties is the nexus between the fundamental knowledge and its later application to develop industrial processes. To this extent, two equations of state, as predictive models, were tested: The Statistical Associating Fluid Theory (SAFT) [14–16] and Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [17,18].

2. Experimental

2.1. Chemicals and samples preparation

The (1S,5S)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene or α-pinene (mole fraction purity > 0.98) and (5S)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane or β-pinene (mole fraction purity > 0.99) were supplied by Sigma-Aldrich. The purity of the compounds was confirmed by GC-MS (see table1). Mixtures were prepared by weighing using a Mettler Toledo AB265-S balance, with a precision of ±10⁻⁵ kg. The expanded uncertainty in the mole fraction was calculated using the Guide to the Expression of Uncertainty in Measurements (GUM) [19] was ±1·10⁻⁴, using a coverage factor $k = 2$. Details of its application to density measurement using vibrating tube densimeters can be found in the work of Lampreia and Nieto de Castro [20].

2.2. Apparatus

The densimeter is similar to those used by Sousa *et al.* [21] and Esteve *et al.* [22]. Its detailed description, together with construction and validation, can be found in the literature [23]. The measuring principle lays on the determination of the oscillation period of a U-shaped tube that contains the sample.

Temperature was measured with a platinum resistance thermometer with an uncertainty ±0.01 K. The pressure was determined with two pressure transmitters (STW-A09), with ±0.1% full scale uncertainty of measurement, one operating up to 16 MPa and the other one up to 70 MPa. The experimental expanded uncertainty ($k = 2$) in the reported density values was estimated to be ±0.5 kg·m⁻³.

A differential scanning calorimeter (DSC-111, from Setaram, France) previously described [11,24] was used in order to measure the isobaric heat capacity. This calorimeter is a heat flux DSC, operating on the Tian–Calvet principle, and using a cylinder type measuring system composed by two sintered alumina cylindrical tubes set parallel and symmetrically in the heating furnace. The sensing part in this calorimeter is the central portion of the alumina cylinders, which are surrounded by thermocouple-carrying heat flux transducers (thermopiles) wrapped around the central part of the tubes. Details of the calibration by the Joule effect with a resistive probe and the temperature calibration using Hg, In, Sn and Pb (LGC, UK certified reference materials) can be found in reference [24] and

TABLE 1
Name, purity and provenance of pure compounds.

Name	Common name	Mole fraction purity	Provenance
4,7,7-trimethylbicyclo[3.1.1] hept-3-ene	––α-pinene	>0.98	Sigma-Aldrich
6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane	S–––β-pinene	>0.99	Sigma-Aldrich

shall not be repeated here. The mass of the samples was confirmed after each run to confirm possible weight losses. The uncertainty of the temperature measurement is 0.1 K. From the data represented in table 2 of reference [11], it can be seen that the average deviation for the heat capacity of sapphire is 0.7% and for toluene 1.1%. It can be claimed that the uncertainty of the measurements is smaller than 1.5 %, at a 95% confidence level. Details of the uncertainty estimation can be found in [11,24].

3. Results

3.1. Densities

The density, ρ, for the pure liquids and their binary mixtures was measured at six temperatures (283.15, 298.15, 313.15, 328.15, 343.15, and 358.15) K and at five pressures (20, 25, 30, 35, and 40) MPa, for several compositions. Experimental results are given in table 2.

No previous density data of these pinene isomers mixtures measured at these pressure and temperature ranges were found for comparison. The most similar research is that of Sousa and Nieto de Castro [7] and Gomes-Medeiros *et al.* [8], where the densities of samples of α-pinene, β-pinene, limonene, and two types of turpentine were measured at atmospheric pressure and temperatures between 293.15 K and 313.15 K [7], and mixtures of α-pinene +β-pinene, for temperatures between 298.15 K and 363.15 K [8]. The purity of the α-pinene samples was very high, 99.85 %, as commercial samples were distilled in a packed column, with 100 theoretical plates. However, the purity of the β-pinene-was smaller, 94.01 %, the main impurities being α-pinene, myrcene and limone and no further purification was possible. The purity of the limonene samples was 96.59 %, the main impurities being p-cymene and α-terpeniol. In the work of Medeiros *et al.* [8], the purity of α-pinene, β-pinene, was respectively, 99.88 % and 98.14 % and the β-pinene was purified by fractional distillation under vacuum. Langa *et al.* [9] also measured the density of β-pinene at three temperatures, between 283.15 K and 313.15 K, using 99% purity commercial samples, without further purification.

For each composition, the compressed liquid densities were correlated with the modified Tait relationship [25]:

$$\rho(P,T)/\text{kg} \cdot \text{m}^{-3} = \rho(0.1 \text{ MPa}, T)/\text{kg} \cdot \text{m}^{-3}(1 - C(T)$$
$$\times \ln \frac{B(T)/\text{MPa} + P/\text{MPa}}{B(T)/\text{MPa} + 0.1\text{MPa}})^{-1}, \quad (1)$$

where $C(T)$ and $B(T)$ are temperature dependent functions. In this work the following expression for B is used:

$$B/\text{MPa} = b_0 + b_1(T - T_0/\text{K}) + b_2(T - T_0/\text{K})^2, \quad (2)$$

while C is assumed to be temperature independent, as reported in previous studies [12,13]. Moreover ρ (0.1 MPa, T) has the following dependence on the temperature:

$$\rho(0.1 \text{ MPa}, T)/\text{kg} \cdot \text{m}^{-3} = a_0 + a_1(T - T_0/\text{K}), \quad (3)$$

where $T_0 = 273.15$ K and a_i and b_i have been considered as adjustable parameters. The coefficients were obtained using the Marquardt′s algorithm and are given in table 3 along with the standard deviation for each composition.

Figure 1 shows the densities and the fitted surfaces of (α-pinene + β-pinene) *vs* mole fraction of α-pinene, x_1, and P at $T = 283.15$ K and 358.15 K.

Using Eq. (3) with the coefficients given in table 3 for α-pinene and β-pinene, and those for limonene from our previous work, Langa *et al.* [12] (table 3), the values of the density for "pure" α-pinene, limonene and β-pinene, now obtained, can be compared with the data at atmospheric pressure by Sousa and Nieto de

TABLE 2
Density, ρ, as a function of temperature, pressure, and mole fraction for mixtures {α-pinene (1) + β-pinene (2)}.

x_1	ρ/kg·m^{-3}				
	P/MPa				
	20	25	30	35	40
		T/K = 283.15			
0.0000	891.3	894.2	897.0	899.9	902.6
0.1044	890.1	893.1	896.0	898.9	901.7
0.1926	889.0	891.9	894.8	897.7	900.6
0.3036	887.9	890.9	893.7	896.7	899.4
0.3949	886.9	889.9	892.9	895.8	898.6
0.5020	885.7	888.7	891.6	894.7	897.5
0.6052	884.7	887.8	890.7	893.7	896.6
0.7022	883.4	886.6	889.3	892.5	895.3
0.7983	882.3	885.4	888.5	891.6	894.6
0.9028	881.1	884.3	887.4	890.3	893.5
1.0000	880.0	883.2	886.3	889.4	892.5
		T/K = 298.15			
0.0000	880.2	883.3	886.3	889.3	892.2
0.1044	879.6	882.5	885.3	888.3	891.1
0.1926	878.2	881.3	884.2	887.3	890.2
0.3036	876.9	880.0	883.0	886.1	889.1
0.3949	875.8	879.0	882.0	885.1	888.0
0.5020	874.6	877.8	880.8	884.0	887.1
0.6052	873.4	876.7	879.7	882.9	886.0
0.7022	872.3	875.6	878.8	882.0	885.1
0.7983	871.2	874.5	877.6	880.8	884.0
0.9028	870.0	873.3	876.4	879.7	882.9
1.0000	868.8	872.1	875.3	878.6	881.9
		T/K = 313.15			
0.0000	869.3	872.6	875.7	878.8	882.0
0.1044	868.0	871.4	874.6	877.8	881.1
0.1926	867.0	870.3	873.5	876.7	879.9
0.3036	865.9	869.2	872.4	875.5	878.7
0.3949	864.9	868.2	871.4	874.6	877.8
0.5020	863.6	867.0	870.2	873.4	876.6
0.6052	862.6	865.8	869.1	872.3	875.5
0.7022	861.4	864.7	868.0	871.2	874.5
0.7983	860.3	863.6	866.9	870.2	873.5
0.9028	859.0	862.4	865.7	869.1	872.4
1.0000	858.0	861.3	864.7	867.9	871.3
		T/K = 328.15			
0.0000	858.2	861.7	865.2	868.7	872.2
0.1044	857.2	860.6	864.1	867.5	870.8
0.1926	855.9	859.5	863.1	866.6	870.0
0.3036	855.0	858.3	862.0	865.4	868.9
0.3949	853.7	857.2	860.8	864.3	867.7
0.5020	852.5	856.1	859.6	863.1	866.6
0.6052	851.3	854.9	858.5	861.9	865.5
0.7022	850.2	853.8	857.4	860.9	864.3
0.7983	849.1	852.7	856.3	859.8	863.4
0.9028	847.9	851.5	855.1	858.6	862.1
1.0000	846.7	850.4	854.0	857.5	861.1
		T/K = 343.15			
0.0000	847.7	851.4	855.0	858.6	862.1
0.1044	846.7	850.5	854.2	857.7	861.3
0.1926	845.5	849.3	853.0	856.6	860.2
0.3036	844.3	848.1	851.9	855.5	859.1
0.3949	843.2	847.0	850.9	854.5	858.1
0.5020	841.9	845.7	849.6	853.3	857.0
0.6052	840.7	844.6	848.5	852.2	855.9
0.7022	839.4	843.3	847.2	851	854.7
0.7983	838.3	842.1	846.2	850	853.7
0.9028	837.0	840.9	844.9	848.7	852.4
1.0000	835.9	839.7	843.8	847.7	851.4
		T/K = 358.15			
0.0000	837.0	840.9	844.8	848.7	852.6
0.1044	835.9	839.8	843.7	847.6	851.5
0.1926	834.6	838.6	842.5	846.4	850.4
0.3036	833.3	837.4	841.3	845.2	849.1
0.3949	832.2	836.3	840.3	844.2	848.2
0.5020	831.0	835.0	839.0	843.0	847.1
0.6052	829.8	833.9	838.0	841.8	846.0
0.7022	828.5	832.7	836.7	840.7	844.8

TABLE 2 (continued)

x_1	ρ/kg·m^{-3}				
	P/MPa				
	20	25	30	35	40
0.7983	827.3	831.5	835.6	839.6	843.8
0.9028	826.1	830.3	834.4	838.4	842.6
1.0000	825.0	829.2	833.3	837.4	841.5

The experimental expanded uncertainty (k = 2) in the reported density values was estimated to be ±0.5 kg·m^{-3}.

Castro [7] and Gomes-Medeiros et al. [8] and Langa et al. [10]. Figure 2 shows the results obtained as deviations, in per cent, from Eq. (1). It can be seen that for α-pinene, the agreement is within the mutual uncertainty, up to T = 320 K as it is for the β-pinene samples of Gomes-Medeiros et al. [8] and Langa et al. [10]. The deviations from Gomes-Medeiros et al. [8] are of the order of -0.2 % up to T = 323.15 K, increasing to −0.36 at the higher temperature, values that are commensurate with the mutual uncertainty of the different sets of data, as the purities of the samples are always greater than 98 %. Regarding the deviations from and Langa et al. [10], they are negligible. However, for the β-pinene and limonene samples of Sousa et al. [7], the deviations are always systematic, being around +0.4 % for the limonene sample and −0.5 % for the β-pinene sample, a result that demonstrates the influence of lower purity in the samples. Therefore it can be concluded that for samples with stated impurities greater than 98 %, the results of this work (and of Langa et al. [13]) agree within their mutual uncertainties, in spite of the necessary extrapolation of the current data from 20 MPa to atmospheric pressure. This fact also guarantees the accuracy of the Tait equation for extrapolation to lower pressures and the fitting algorithm used.

3.1.1. Derived properties: isobaric thermal expansion, α_P, and isothermal compressibility, κ_T.

Differentiating Eq. (1) with respect to temperature and pressure, the isobaric thermal expansion, α_P, and the isothermal compressibility, κ_T, can be evaluated taking into account their definitions:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p, \tag{4}$$

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T. \tag{5}$$

It is well known [26] that analytical differentiation of the Tait equation with respect to pressure is certainly the most direct way to obtain reliable isothermal compressibility data. The isothermal compressibility obtained was estimated to have an expanded uncertainty (k = 2) [19] of ±14 TPa^{-1}. In a similar way, isobaric thermal expansion data can be determined from analytical calculation following Cerdeiriña et al. [27] and Troncoso et al. [28]. The α_P was evaluated over the pressure and temperature ranges studied resulting in an expanded uncertainty (k = 2) of ±0.005 kK^{-1}. The calculated values of α_P and κ_T are given in tables S1 and S2, respectively, of the Supplementary Information. Figures 3 and 4 show the calculated values for these properties at the highest and lowest density. For this binary system within the considered P–T range and composition, the isothermal compressibility, as well as the isobaric thermal expansion, increases, as usual, with temperature and decreases with increasing pressure. For pure components, no significant change in these calculated properties was observed, as expected, since they are isomers. In addition, the values of α_P and κ_T for β-pinene are slightly lower than the α_P and κT for α-pinene.

TABLE 3
Fitting coefficients of Eq. (1) for the pure liquids and {α-pinene (1) + β-pinene (2)} and standard deviations σ.

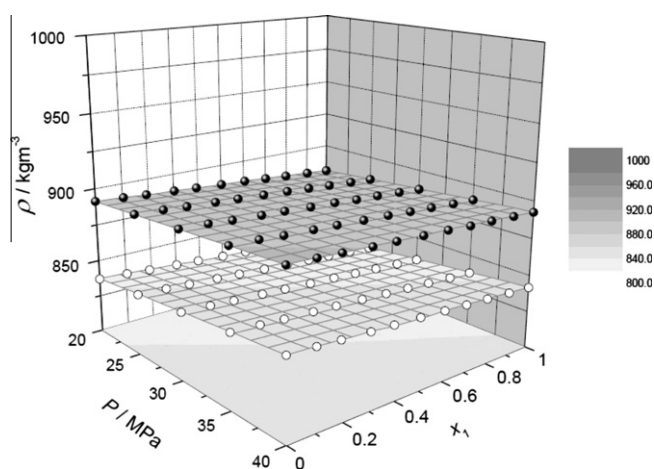|	$x_1 = 0$	$x_1 = 0.1044$	$x_1 = 0.1926$	$x_1 = 0.3036$	$x_1 = 0.3949$	$x_1 = 0.5020$
a_0/kg·m^{-3}	886.65	885.61	884.12	883.16	882.08	880.74
a_1/kg·m^{-3} K^{-1}	−0.78	−0.78	−0.78	−0.78	−0.79	−0.79
b_0/ MPa	196	196	198	202	203	204
b_1/MPa·K^{-1}	−0.82	−0.82	−0.82	−0.82	−0.83	−0.83
c_0	0.138	0.139	0.141	0.145	0.146	0.149
σ/kg·m^{-3}	0.11	0.22	0.17	0.17	0.33	0.23
	$x_1 = 0.6052$	$x_1 = 0.7022$	$x_1 = 0.7983$	$x_1 = 0.9028$	$x_1 = 1$	
a_0/kg·m^{-3}	879.84	878.40	877.16	875.98	874.74	
a_1/kg·m^{-3} K^{-1}	−0.79	−0.79	−0.79	−0.79	−0.79	
b_0/MPa	204	204	204	204	204	
b_1/MPa K^{-1}	−0.83	−0.83	−0.83	−0.83	−0.83	
c_0	0.152	0.154	0.154	0.155	0.155	
σ/kg·m^{-3}	0.35	0.33	0.18	0.27	0.15	

$\sigma = [\sum_{i=1} N(\rho_i,\exp \leftarrow \rho_i,cal)^2/(N - P)]^{1/2}$, where N = number of experimental points and P = number of adjustable parameters.

FIGURE 1. Experimental density, ρ, and Tait surfaces vs mole fraction of α-pinene, x_1, ●, at T = 283.15 K and, o, 358.15 K. Contour plots appear at the bottom of the figure.

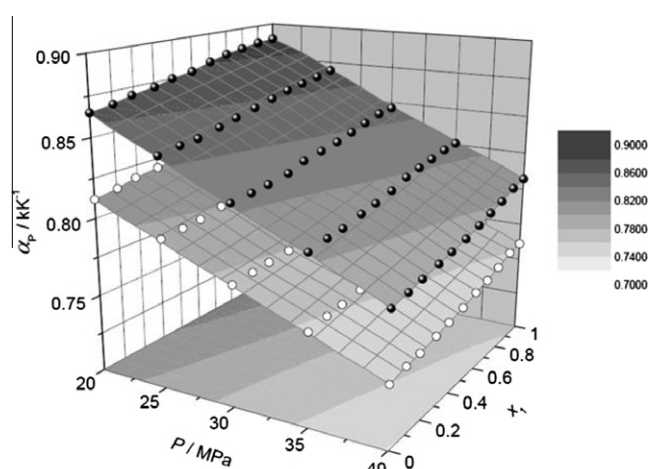**FIGURE 3.** Isobaric thermal expansion, α_P, vs mole fraction of α-pinene, x_1, and pressure at, o, T = 283.15 K, and, ●, 358.15 K,. Contour plots appear at the bottom of the figure.
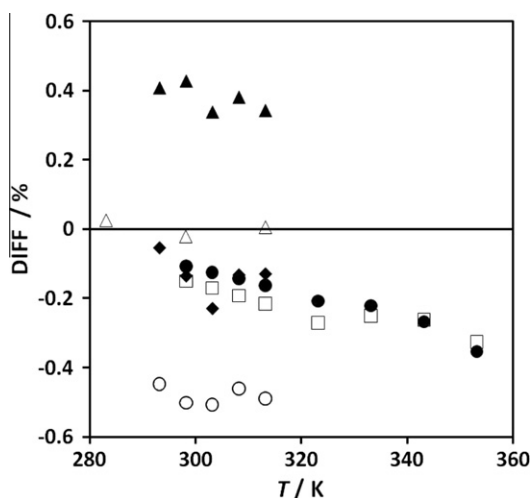

FIGURE 2. Comparison of the densities of α-pinene, β-pinene and limonene reported in this paper and by Langa et al. [13], with previous works ([7,8]. DIFF is given by $DIFF = (\rho_{Lit} - \rho_{pw})/\rho_{pw} \times 100$; ♦, −α-pinene [7]; ●, α-pinene [8]; ○, β-pinene [7]; □, β-pinene [8]; △, β-pinene [7]; ▲, limonene [7].

FIGURE 4. Isothermal compressibility, κ_T, vs mole fraction of α-pinene, x_1, and pressure at, o, T = 283.15 K and, ●, 358.15 K. Contour plots appear at the bottom of the figure.

3.1.2. Equation of state (EOS)

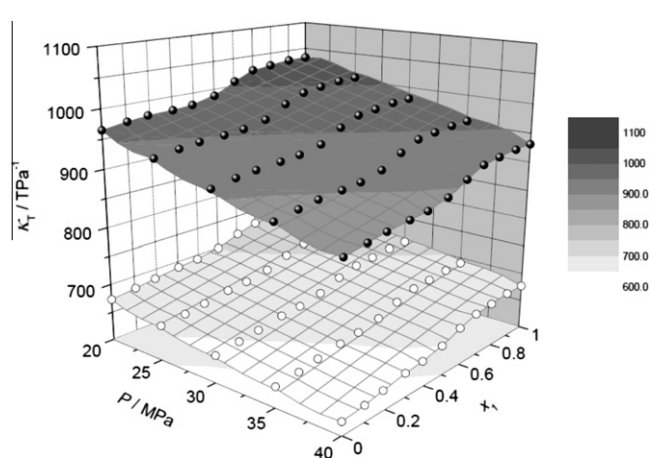Two EOS were applied in this work to predict the P, ρ, T behaviour of the fluid mixtures, and to conclude on the best equation for these type of systems. Both of them are based on the theory of perturbations: the Statistical Associated Fluid Theory (SAFT, Huang and Radosz version) [14–16] and the Perturbed Chain-Statistical Associated Fluid Theory (PC-SAFT) [17–18]. The required properties of pure components obtained from literature are gathered in table 4.

TABLE 4
Pure components parameters used for the application of the studied equations of state.

	$M_w/\text{g·mol}^{-1}$	T_c/K	P_c/MPa	T_b/K	ω
α-pinene	136.24[a]	620[b]	2.5[b]	428.75[c]	0.2862[e]
β-pinene	136.24[a]	635[b]	2.5[b]	439.15[d]	0.3252[e]

[a] Reference [33].
[b] Reference [34].
[c] Reference [35].
[d] Reference [36].
[e] Reference [37].

TABLE 5
Pure components parameters used for the application of the studied equations of state.

SAFT	m	$v^{00}/\text{dm}^3\text{·mol}^{-1}$	$(u^0/k)/\text{K}$	κ	$\varepsilon/k/\text{K}$
α-pinene	5.163	1.4896	242.99	0	10
β-pinene	4.893	1.5656	257.39	0	10
PC-SAFT	m_i	σ_i/nm	$\varepsilon_i/k/\text{K}$	κ^{AiBi}	$\varepsilon^{AiBi}/k)/\text{K}$
α-pinene	3.254	0.40359	286.42	0	0
β-pinene	3.099	0.40832	302.43	0	0

TABLE 6
Absolute average percentage deviation, AAD, for the correlation of saturation properties and prediction of compressed liquid density.

Compound	EOS	AADP^{sat}	AADρsat	ΔT_c / K	ΔP_c / MPa	AADρcomp
α-pinene	SAFT	0.04	0.79	35.26	8.69	7.83
	PC-SAFT	0.01	0.21	24.91	9.26	2.31
β-pinene	SAFT	0.05	3.53	43.49	10.72	8.65
	PC-SAFT	0.01	3.75	32.10	11.06	3.39

AADP^{sat} = $100/N·\Sigma|P_{i,EOS} - P_{i,exp}|/P_{i,exp}$, and AAΔρsat = $100/N·\Sigma|\rho_{i,EOS} - \rho_{i,exp}|/\rho_{i,exp}$ where N = number of points; $\Delta T_c = T_{c,EOS} - T_c$ and $\Delta P_c = P_{c,EOS} - P_c$.

The EOS parameters for α- and β-pinene can be evaluated by adjusting the model to the high pressure density results or from vapour + liquid equilibrium data. We preferred to use this latter independent method to test the predictive power of the two models over the range studied. Therefore VLE data measured by M. G. Bernardo-Gil and A. Barreiros [29] were applied. Liquid densities were extrapolated with Eq (1). Vapour pressures for pure components over the temperature range studied were calculated through the Antoine equation, using the constants obtained by Rodrigues and Bernardo-Gil [30]. Table 5 contains the parameters obtained for both components, α- and β-pinene, and for modles EOS, SAFT and PC-SAFT. The absolute average percentage deviation values (AAD) of saturation properties of pure α- and β-pinene are gathered in table 6.

To determine the P, ρ, T behaviour of the binary mixture, the van der Waals one-fluid mixing rules were used and classical quadratic combining rules for the cross-terms were selected in all cases. The SAFT and PC-SAFT equations were tested with interaction parameters, k_{ij}, from VLE, Bernardo-Gil et al. [28] at low pressure. No significant variation of k_{ij} with T and P was found when they were calculated for both models. The k_{ij} was $3.5 \cdot 10^{-3}$ for SAFT and $-1.8 \cdot 10^{-3}$ for PC-SAFT. Density data, predicted with these EOS, are gathered in table S3. Figure 5 is given as a comparative example of the behaviour of both EOS at the highest and lowest density conditions (very similar results were obtained with the other experimental conditions). As it can be seen, PC-SAFT predicts more accurately the experimental values than conventional SAFT.
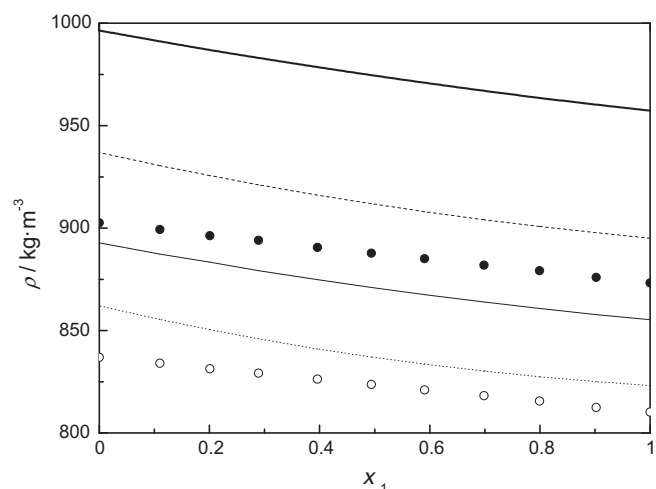

FIGURE 5. Experimental density, ρ, vs mole fraction of α-pinene, x_1, at, ●, T = 283.15 K and 40 MPa and, o, 358.15 K and 20 MPa. SAFT prediction at, —, 283.15 and 40 MPa and at, –, 358.15 K and 20 MPa. PC-SAFT prediction at,······, 283.15 K and 40 MPa and at, ········, 358.15 K and 20 MPa.
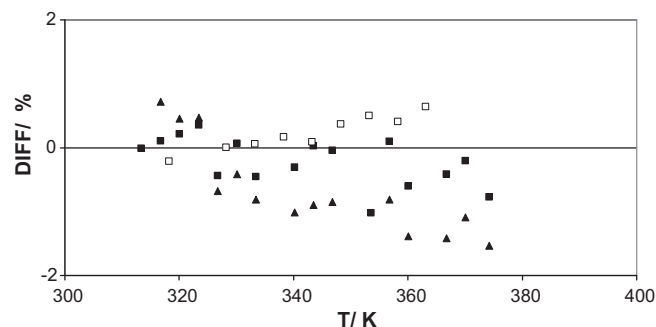

FIGURE 6. Deviations, DIFF, calculated as($Cp_{lit} - Cp_{pw}$)·$100/Cp_{pw}$, as a function of temperature for sapphire, ■, and toluene, □, related to references [31,32], respectively, and sapphire, ▲, and toluene, Δ, related to reference [11].

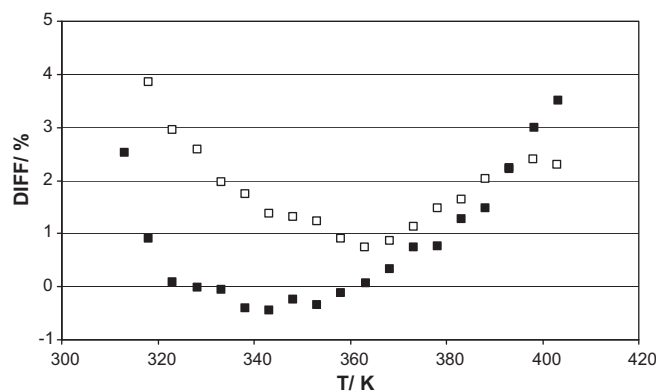**FIGURE 7.** Deviations, DIFF, calculated as ($Cp_{lit} - Cp_{pw}$)·$100/Cp_{pw}$, as a function of temperature for α-pinene, ■, and β-pinene, □. Values of Cp_{ref} were obtained from reference [11].

The AAD obtained for PC-SAFT was 2.99 % and for SAFT 8.55 %, which is coherent with figure 5.

3.2. Heat capacity

The heat capacity, Cp, of sapphire and toluene was measured and compared to those from literature data [31,32], also shown

TABLE 7
Experimental heat capacities, Cp, mole fractions, x, and temperatures for {α-pinene (1) + β-pinene (2)}.

	$Cp/J \cdot K^{-1} \cdot g^{-1}$										
x_1 T/K	1	0.9002	0.7987	0.7026	0.5907	0.5012	0.3922	0.2997	0.2041	0.1002	0
313.16	1.84	1.86	1.85	1.84	1.83	1.84	1.85	1.84	1.84	1.83	1.83
318.16	1.85	1.87	1.86	1.86	1.85	1.86	1.86	1.85	1.85	1.85	1.85
323.16	1.88	1.88	1.87	1.88	1.87	1.87	1.88	1.88	1.87	1.88	1.87
328.22	1.89	1.90	1.88	1.90	1.89	1.88	1.90	1.89	1.88	1.89	1.89
333.22	1.91	1.91	1.89	1.91	1.92	1.90	1.91	1.90	1.90	1.91	1.91
338.19	1.94	1.93	1.92	1.93	1.93	1.93	1.93	1.93	1.92	1.94	1.93
343.18	1.96	1.95	1.94	1.94	1.96	1.95	1.95	1.96	1.95	1.96	1.95
348.15	1.98	1.97	1.96	1.96	1.97	1.98	1.97	1.98	1.97	1.98	1.97
353.18	2.00	1.98	1.98	1.98	2.00	2.00	1.99	2.00	2.00	2.01	1.99
358.15	2.02	2.00	1.99	2.00	2.02	2.02	2.01	2.01	2.01	2.02	2.01
363.18	2.04	2.02	2.02	2.01	2.04	2.04	2.03	2.03	2.03	2.04	2.04
368.17	2.05	2.04	2.03	2.03	2.06	2.06	2.05	2.05	2.05	2.05	2.06
373.21	2.07	2.05	2.06	2.05	2.07	2.07	2.07	2.07	2.07	2.08	2.08
378.20	2.09	2.07	2.07	2.06	2.09	2.09	2.09	2.09	2.08	2.09	2.09
383.17	2.11	2.09	2.08	2.09	2.11	2.10	2.11	2.11	2.10	2.11	2.11
388.20	2.14	2.11	2.10	2.12	2.13	2.13	2.14	2.13	2.12	2.14	2.13
393.17	2.15	2.12	2.12	2.14	2.14	2.15	2.16	2.15	2.14	2.15	2.15
398.20	2.16	2.15	2.15	2.16	2.16	2.17	2.18	2.16	2.17	2.16	2.17
403.19	2.18	2.16	2.17	2.17	2.18	2.19	2.20	2.18	2.19	2.18	2.20
408.16	2.20	2.18	2.19	2.20	2.20	2.22	2.23	2.20	2.21	2.20	2.22
413.19	2.21	2.20	2.20	2.21	2.21	2.24	2.24	2.21	2.22	2.21	2.23
418.19	2.23	2.22	2.23	2.23	2.22	2.25	2.25	2.23	2.24	2.23	2.25

The uncertainty of the values is estimated to be smaller than 1.5% (the ISO definition, with a coverage factor $k = 2$ is used).

in figure 6. As it can be observed, DIFF values are always within ±1.5 % for sapphire and toluene.

Sampaio and Nieto de Castro [11] also measured pinene mixtures, as mentioned in the introduction of the present work. However their compounds α-pinene and β-pinene were not pure, but distilled from turpentine. So their purities were different from those of our pinene compounds. In figure 7, DIFF values for our pinene Cp compared with those from Sampaio and Nieto de Castro [11]. Deviations between the two sets of data are well within their mutual uncertainty.

Pure pinene and (α-pinene + β-pinene) Cp were measured at atmospheric pressure over the entire the composition range and at temperatures from 313.15 K to 418.15 K, and are shown in table 7. The values of Cp for α-pinene are very similar to the values for β-pinene as expected because they are isomers. For a given mole fraction, Cp increases with temperature. At a given temperature, the dependence of the heat capacity of the binary mixture on composition is almost negligible, and therefore the regression line to interpolate in temperature was considered composition independent, and given by:

$$C_P/(J \cdot K^{-1} \cdot mol^{-1}) = b_1 + b_2(T/K) + b_3(T/K)^2, \qquad (6)$$

with $b_1 = -6.80726$; $b_2 = 1.046295$; $b_3 = -0.00073$. The root mean square deviation associated with the fit is $0.6747 J \cdot K^{-1} \cdot mol^{-1}$, always smaller than 0.24%, a value that gives an idea of the reproducibility of the measurements. The uncertainty of the values, is estimated to be smaller than 1.5% (the ISO definition, with a coverage factor $k = 2$ is used).

Excess isobaric heat capacities, C_p^E, were calculated but their values were lower than the uncertainty, demonstrating the ideal behaviour of this mixture of two isomers, as expected.

4. Conclusions

The density and the isobaric heat capacity of nine compositions for the binary system (α-pinene + β-pinene) was measured. Density was determined over the temperature range (283.15 K to 358.15 K) and pressures from (20 MPa to 40 MPa) with an expanded uncertainty ($k = 2$) of ±0.5 kg·m^{-3}. The isobaric heat capac-

ity was measured at atmospheric pressure and within the temperature range (313.15 K to 418.15 K) with an experimental uncertainty lower than 1.5%. Isothermal compressibilities and isobaric thermal expansivities, as well as their dependencies on temperature, pressure and composition, were gathered in this work. The SAFT and PC-SAFT equations of state were applied to predict the densities of this binary system. Taking into account the results (ADD of 2.99%), the PC-SAFT equation appears as a valuable tool to predict the P, ρ, T behaviour of mixtures when VLE and pure component saturated density data are available.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2012.09.012.

References

[1] D. Zudkevitch, Encyclopedia of Chemical Processing and Design, Marcel Dekker, New York, 1992. pp 431.
[2] G.C. Straty, A.M.F. Palavra, J. Res. Natl. Bur. Stand. 89 (5) (1984) 375–383.
[3] O. Prakash, S. Joshi, A.K. Pant, C.S. Chanotiya, C.S. Mathela, J. Essential Oil Res. 19 (5) (2007) 407–409.
[4] J. Torras, M.D. Gran, J.F. López, F.X.C. de las Heras, J. Sci. Food Agric. 87 (12) (2007) 2327–2333.
[5] B. Tepe, D. Daferera, A.S. Tepe, M. Polission, A. Sokmen, Food Chem. 103 (4) (2007) 1358–1367.
[6] A.C.T. Sousa, C.A. Nieto de Castro, J.A. Lourenço, High Temp. – High Pressure 21 (1989) 149–156.
[7] A.T. Sousa, C.A. Nieto de Castro, Int. J. Thermophys. 13 (2) (1992) 295–301.
[8] A.M.F. Gomes-Medeiros, A.T. Sousa, C.A. Nieto de Castro, High Temp. – High Pressure 26 (1994) 257–266.
[9] J.E. Hawkins, G.T. Armstrong, J. Am. Chem. Soc. 76 (14) (1954) 3756–3758.

[10] E. Langa, A.M. Mainar, J.I. Pardo, J.S. Urieta, J. Chem. Eng. Data 50 (4) (2005) 1255–1261.
[11] M.B.O. Sampaio, C.A. Nieto de Castro, Fluid Phase Equil. 150 (151) (1998) 789–796.
[12] E. Langa, A. Palavra, C.A. Nieto de Castro, Ana Mainar, J. Chem. Eng. Data 56 (2011) 1709–1713.
[13] E. Langa, A. Palavra, C.A. Nieto de Castro, Ana Mainar, J. Chem. Thermodyn. 48 (2012) 175–180.
[14] S.H. Huang, M. Radosz, Ind. Eng. Chem. Res. 29 (1990) 2284–2294.
[15] S.H. Huang, M. Radosz, Ind. Eng. Chem. Res. 30 (1991) 1994–2005.
[16] S.H. Huang, M. Radosz, Ind. Eng. Chem. Res. 32 (4) (1993). 762-762.
[17] J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (1) (2001) 244–1260.
[18] J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 41 (2002) 5510–5515.
[19] Working Group 1 of the Joint Committee for Guides in Metrology. JCGM 100:2008. Evaluation of the measurement data: guide to the expression of uncertainty in measurement. JCGM:2008.
[20] I.M.S. Lampreia, C.A. Nieto de Castro, J. Chem. Thermodyn. 43 (2011) 537–545.
[21] A.T. Sousa, C.N. de Castro, R. Tufeu, B. Le Neindre, High Temp. – High Pressure 24 (1992) 185–194.
[22] X. Esteve, A. Conesa, A.J. Coronas, Chem. Eng. Data. 48 (2003) 392–397.
[23] J.M. Lasarte, L. Martín, E. Langa, J.S. Urieta, A.M. Mainar, J. Chem. Eng. Data 53 (6) (2008) 1393–1400.
[24] C.A. Nieto de Castro, M.J.V. Lourenço, M.B.O. Sampaio, Thermochim. Acta 347 (2000) 85–91.
[25] I. Cibulka, L. Hdnedkovsky, J. Chem. Eng. Data 41 (1996) 657–668.
[26] J.S. Rowlinson, F.L. Swinton, Liquid and Liquid Mixtures, Butterworths, London, 1982.
[27] C.A. Cerdeiriña, C.A. Tovar, D. González-Salgado, E. Carballo, L. Romaní, Phys. Chem. Chem. Phys. 3 (2001) 5230–5236.
[28] J. Troncoso, D. Bessières, C.A. Cerdeiriña, E. Carballo, L. Romaní, Fluid Phase Equlib. 208 (2003) 141–154.
[29] M.G. Bernardo-Gil, A. Barreiros, Fluid Phase Equilib. 100 (1994) 283–291.
[30] M.F. Rodrigues, M.G. Bernardo-Gil, J. Chem. Eng. Data 40 (6) (1995) 1193–1195.
[31] NIST/PICT Standard Reference Database 14, Heat Capacities of Liquid Hydrocarbons, Version 1.00, 1993.
[32] R.D. Goodwin, J. Phys. Chem. 18 (1989) 1565–1635.
[33] NIST Chemistry Web Book. http://webbook.nist.gov/chemistry.
[34] ESDU, ESDU International – Engineering Sciences Data – Physical Data, Chemical Engineering, vol 1 - General – Melting points, boiling points and critical properties; ESDU International plc., 1987; 87028 (Rc 1.2).
[35] M.H. Nadais, M.G. Bernardo-Gil, Fluid Phase Equilib. 91 (1993) 321–330.
[36] M.G. Bernardo-Gil, M.A. Ribeiro, Fluid Phase Equilib. 85 (1993) 153–160.
[37] R. Reich, V. Sanhueza, J. Chem. Eng. Data 38 (1993) 341–343.

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