



P , ρ , and T measurements of the (limonene + β -pinene) mixtures

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ABSTRACT

The density, ρ , and two derived properties, isothermal compressibility, κ_T , and the coefficient of cubic expansion, α_p , were obtained for the mixtures of 1-methyl-4-(1-methylethenyl)-cyclohexene, known as limonene, and (1S,5S)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane, known as β -pinene, for nine different compositions and the pure components at five pressures from 20 MPa to 40 MPa and six temperatures from 283.15 K to 358.15 K. The experimental uncertainty for ρ , κ_T , and α_p were respectively $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$, $\pm 14 \text{ TPa}^{-1}$, and $\pm 0.005 \text{ K}^{-1}$, with $k = 2$ for all of them. Density behaviour with temperature and pressure was as expected. The values of α_p and κ_T increase with temperature and decrease with increasing pressure. Two different equations of state, conventional SAFT and PC-SAFT, were applied to predict the densities of the mixture. The best predictions were achieved with PC-SAFT.

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1. Introduction

Supercritical carbon dioxide is widely known as a green chemistry solvent which allows not only the extraction but also the fractionation of essential oils from plants in order to enriched them in certain compounds, for example limonene and β -pinene. Limonene and β -pinene are two important and very common terpenes that can be found in essential oils from most of the plants [1–3].

For possible industrial application of the supercritical fluid extraction process, it is very important to have an extensive knowledge of the models which allows us to correlate and extrapolate the experimental data. Sovová's model [4], for instance, provides us with a suitable explanation of the experimental supercritical process but it requires, as other models, the knowledge of solute properties, such as the density at the working conditions (usually temperatures and pressures higher than 313.15 K and 10 MPa, respectively).

Limonene, β -pinene, and their mixtures are also found in fractional distillation from turpentine, so a thermodynamic study of this system is always advisable if no undesirable or unexpected results are wanted.

Many scientists worked on the measurement of thermodynamic properties of limonene and β -pinene mixtures, Sousa *et al.* [5], Gallis *et al.*, Diaz *et al.* [6], Sampaio and Nieto de Castro [7] but there is no experimental work carried out to study the P , ρ , and T behaviour of commercial (limonene + β -pinene) binary mixtures at higher pressures. The closest system studied is (limonene + α -pinene), whose density and derived properties were obtained in a previous work at the same P and T conditions by Langa *et al.* [8].

Taking into account the cited lack of experimental data, a P , ρ , and T research of the binary system (limonene + β -pinene) was studied. This work consisted of measuring the density of the mixtures (nine mole fractions and the pure components) at six temperatures (283.15, 298.15, 313.15, 328.15, 343.15, and 358.15) K and at five isobars (20, 25, 30, 35, and 40) MPa. From these data, isobaric thermal expansivities and isothermal compressibilities were 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, were tested: The statistical associating fluid theory (SAFT) [9–11] and perturbed-chain statistical associating fluid theory (PC-SAFT) [12,13].

2. Experimental

2.1. Materials

The R-(+)-limonene (mole fraction purity > 0.98) and (S)-(–)- β -pinene (mole fraction purity > 0.99) were supplied by Sigma-Aldrich, table 1. Purity was confirmed by GC–MS.

Abbreviations: SAFT, statistical associating fluid theory; PC-SAFT, perturbed-chain statistical associating fluid theory; EOS, equation of state; AAD, absolute average percentage deviation; PE, phase equilibria; VLE, (vapour + liquid) equilibrium.

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TABLE 1
Name, purity, and provenance of pure compounds.

Name	Common name	Mole fraction purity	Provenance
1-Methyl-4-(1-methylethenyl)-cyclohexene	R-(+)-limonene	>0.98	Sigma–Aldrich
(1S,5S)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane	(S)-(–)- β -pinene	>0.99	Sigma–Aldrich

Mixtures were set by weighing on a Mettler Toledo AB265-S balance, with a precision of $\pm 10^{-5}$ kg. The expanded uncertainty in the mole fraction was $\pm 1 \cdot 10^{-4}$, using a cover factor $k = 2$.

2.2. Equipment and procedures

The experimental device is similar to those used by Sousa *et al.* [14] and Esteve *et al.* [15].

A detailed description of the apparatus, together with the set up and validation of the equipment, can be looked up in the literature [16]. The measuring principle depends 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 of the system was measured with two pressure transmitters (STW-A09), with $\pm 0.1\%$ 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 $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$ [17].

3. Results

3.1. Density

The experimental densities, ρ , for pure liquids and their binary mixtures were measured at six temperatures (283.15, 298.15, 313.15, 328.15, 343.15, and 358.15) K and at five isobars (20, 25, 30, 35, and 40) MPa. Experimental results are given in table 2.

For each composition, the compressed liquid densities were correlated with modified Tait relationship [18]:

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

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

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

and C is here assumed to be temperature independent. The $\rho(0.1 \text{ MPa}, T)$ is the density at 0.1 MPa, interpolated by the following correlation:

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

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.

No previous density data for the mixtures studied measured at that pressure and temperature range were found, except pure limonene densities, whose values are exactly the same as the ones shown in this work [8]. However, we calculated the density of our mixtures at atmospheric pressure (0.1 MPa) with the Tait coefficients showed in table 3 and compared those densities with the ones from literature in figure 1. There, a good concordance can be observed.

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

x_1	$\rho/(\text{kg} \cdot \text{m}^{-3})$				
	P/MPa				
	20	25	30	35	40
$T/K = 283.15$					
0	891.3	894.2	897.0	899.9	902.6
0.1100	888.1	891.0	893.9	896.7	899.3
0.2008	885.4	888.3	891.0	893.8	896.3
0.2890	882.8	885.7	888.4	891.2	894.0
0.3961	879.6	882.4	885.2	887.9	890.6
0.4938	876.8	879.6	882.5	885.2	887.8
0.5906	873.9	876.8	879.7	882.4	885.1
0.6984	870.9	873.7	876.5	879.3	881.9
0.7993	868.0	870.8	873.6	876.5	879.2
0.9022	864.5	867.8	870.4	873.3	876.0
1	862.0	864.9	867.7	870.4	873.3
$T/K = 298.15$					
0	880.2	883.3	886.3	889.3	892.2
0.1100	877.0	880.1	883.1	886.1	889.0
0.2008	874.1	877.2	880.3	883.5	886.5
0.2890	871.8	874.9	877.9	881.0	883.9
0.3961	868.7	871.8	874.8	877.7	880.7
0.4938	865.8	868.9	871.9	874.9	878.0
0.5906	863.0	866.2	869.2	872.3	875.4
0.6984	859.9	863.1	866.2	869.0	871.9
0.7993	857.2	860.2	863.3	866.5	869.0
0.9022	854.3	857.3	860.3	863.4	866.1
1	851.5	854.5	857.6	860.9	863.4
$T/K = 313.15$					
0	869.3	872.6	875.7	878.8	882.0
0.1100	866.1	869.5	872.6	875.7	878.8
0.2008	863.5	866.8	870.1	873.3	876.7
0.2890	860.9	864.2	867.5	870.6	873.8
0.3961	857.8	861.1	864.3	867.5	870.7
0.4938	854.9	858.1	861.4	864.5	867.8
0.5906	852.4	855.6	858.7	862.0	865.0
0.6984	849.3	852.5	855.7	858.7	861.8
0.7993	846.5	849.8	852.9	856.1	859.1
0.9022	843.7	847.0	849.9	853.0	856.0
1	841.0	844.2	847.2	850.3	853.3
$T/K = 328.15$					
0	858.2	861.7	865.2	868.7	872.2
0.1100	855.3	858.7	862.1	865.5	868.8
0.2008	852.6	856.0	859.5	862.7	866.1
0.2890	850.1	853.5	857.0	860.3	863.7
0.3961	846.9	850.4	853.9	857.2	860.7
0.4938	844.3	847.7	851.2	854.6	857.8
0.5906	841.5	844.9	848.5	851.9	855.3
0.6984	838.9	842.1	845.4	848.7	852.0
0.7993	835.9	839.4	842.7	846.1	849.4
0.9022	833.1	836.4	839.7	843.1	846.8
1	830.5	833.8	837.2	840.4	843.8
$T/K = 343.15$					
0	847.7	851.4	855.0	858.6	862.1
0.1100	844.7	848.4	852.0	855.5	859.0
0.2008	842.1	845.8	849.4	853.1	856.7
0.2890	839.6	843.5	846.9	850.6	854.0
0.3961	836.7	840.3	843.9	847.4	850.8
0.4938	834.0	837.6	841.2	844.8	848.3
0.5906	831.4	834.9	838.6	842.3	845.6
0.6984	828.4	832.0	835.6	839.1	842.4
0.7993	825.7	829.1	832.9	836.7	840.1
0.9022	822.7	826.3	830.0	833.6	837.1

TABLE 2 (continued)

x_1	$\rho/(\text{kg} \cdot \text{m}^{-3})$				
	P/MPa				
	20	25	30	35	40
1	820.1	823.7	827.3	831.1	834.6
$T/K = 358.15$					
0	837.0	840.9	844.8	848.7	852.6
0.1100	834.0	838.0	841.9	845.7	849.6
0.2008	831.4	835.4	839.2	843.0	846.8
0.2890	829.2	833.0	836.8	840.6	844.6
0.3961	826.3	830.1	833.8	837.5	841.4
0.4938	823.7	827.4	831.2	834.9	838.7
0.5906	821.0	824.9	828.6	832.4	836.2
0.6984	818.2	822.0	825.7	829.4	833.1
0.7993	815.6	819.4	823.0	826.8	830.3
0.9022	812.5	816.7	820.0	823.9	827.3
1	810.2	813.9	817.6	821.3	824.8

^a The experimental expanded uncertainty ($k = 2$) in the reported density values was estimated to be $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$.

3.2. Derived properties: coefficient of cubic expansion, α_p , and isothermal compressibility, κ_T

Differentiating equation (1) with respect to temperature and pressure, the coefficient of cubic expansion, α_p , and the isothermal compressibility, κ_T , can be evaluated taking into account their definitions:

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

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

It is well known, that analytical differentiation of the Tait equation with respect to pressure is certainly the most direct way to obtain reliable isothermal compressibility data [19]. The calculated isothermal compressibility was estimated to have an expanded uncertainty ($k = 2$) of $\pm 14 \text{ TPa}^{-1}$.

In a similar way, coefficient of cubic expansion data can be determined from analytical calculation following Cerdeiriña *et al.* [20] and Troncoso *et al.* [21]. The α_p was evaluated for the pressure and temperature range studied finding an expanded uncertainty, $k = 2$, of $\pm 0.005 \text{ K}^{-1}$. The calculated values of α_p and κ_T are given in Appendix A, tables A1 and A2, respectively. figures 2 and 3 offer 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

TABLE 3

Fitting coefficients of equation (1) for the pure liquids and mixtures {limonene (1) + β -pinene (2)} and standard deviations σ .

	$x_1 = 0$	$x_1 = 0.1100$	$x_1 = 0.2008$	$x_1 = 0.2890$	$x_1 = 0.3961$	$x_1 = 0.4938$
$a_0/(\text{kg} \cdot \text{m}^{-3})$	886.65	883.60	880.23	877.97	874.72	871.91
$a_1/(\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-1})$	-0.78	-0.78	-0.77	-0.77	-0.77	-0.77
b_0/MPa	196	191	189	186	183	181
$b_1/(\text{MPa} \cdot \text{K}^{-1})$	-0.82	-0.80	-0.78	-0.77	-0.76	-0.74
C	0.138	0.135	0.134	0.133	0.132	0.131
$\sigma/(\text{kg} \cdot \text{m}^{-3})$	0.11	0.11	0.25	0.13	0.13	0.17
	$x_1 = 0.5906$	$x_1 = 0.6984$	$x_1 = 0.7993$	$x_1 = 0.9022$	$x_1 = 1$	
$a_0/(\text{kg} \cdot \text{m}^{-3})$	868.99	866.29	863.11	860.11	857.07	
$a_1/(\text{kg} \cdot \text{m}^{-3} \cdot \text{K}^{-1})$	-0.76	-0.76	-0.76	-0.75	-0.74	
b_0/MPa	180	179	179	175	174	
$b_1/(\text{MPa} \cdot \text{K}^{-1})$	-0.73	-0.73	-0.72	-0.70	-0.69	
C	0.130	0.130	0.130	0.128	0.127	
$\sigma/(\text{kg} \cdot \text{m}^{-3})$	0.14	0.31	0.23	0.25	0.23	

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

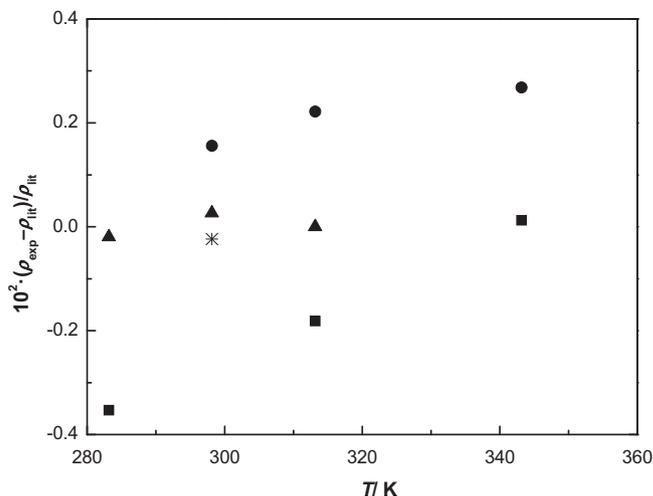


FIGURE 1. Comparison of the densities through the function $10^2 \cdot (\rho_{\text{exp}} - \rho_{\text{lit}}) / \rho_{\text{lit}}$ at atmospheric pressure calculated with Tait coefficients reported in this paper (exp) and those from the literature (lit) obtained by (■) Clará *et al.* [26], (*) Steele *et al.* [27] for pure Limonene and by (●) Gomes-Medeiros *et al.* [28], and (▲) Langa *et al.* [29] for pure β -pinene.

coefficient of cubic expansion, increases, as usual, with increasing temperature and decreases with increasing pressure. For the pure components, no significant variation in these calculated properties was observed, as expected due to they are isomers.

4. Predictive theories. Equation of state (EOS)

Two EOS were tested in this work to predict the P , ρ , and T behaviour of the fluid mixtures. Both of them are based on the theory of perturbations: the statistical associated fluid theory (SAFT, Huang, and Radosz's version) [9–11] and the perturbed chain-statistical associated fluid theory (PC-SAFT) [12,13]. The computations were performed using the phase equilibria (PE 2000, version 2.9.9a) software [22]. The required properties of pure components are gathered in table 4. These parameters were obtained from literature [23,30–34] and were used to create the input files for the programme PE.

The EOS parameters for limonene and β -pinene were evaluated from (vapour + liquid) equilibrium data determined by Bernardo-Gil *et al.* [24]. Liquid densities were extrapolated with equation (1). Vapour pressures for pure components within the temperature range studied were calculated with the Antoine equation, using the constants obtained by Rodrigues *et al.* [25]. Table 5 shows the

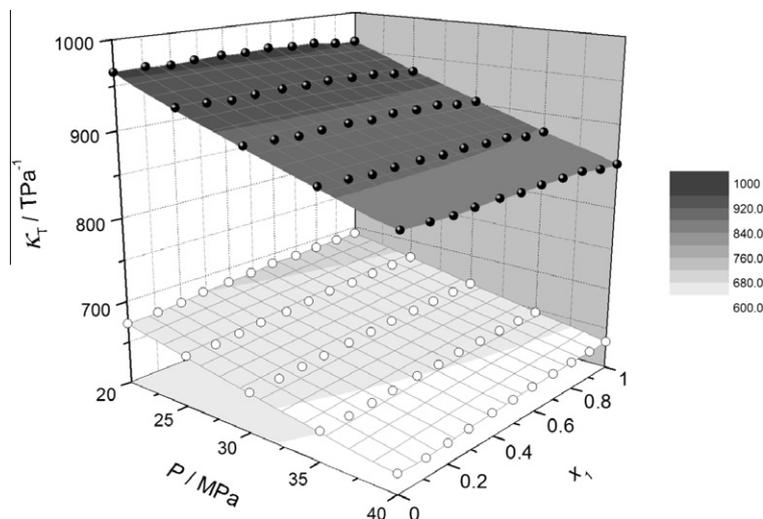


FIGURE 2. Isothermal compressibility, κ_T , vs mole fraction of limonene, x_1 , and pressure at (o) $T = 283.15$ K and (●) 358.15 K. Contour plots appear at the bottom of the figure.

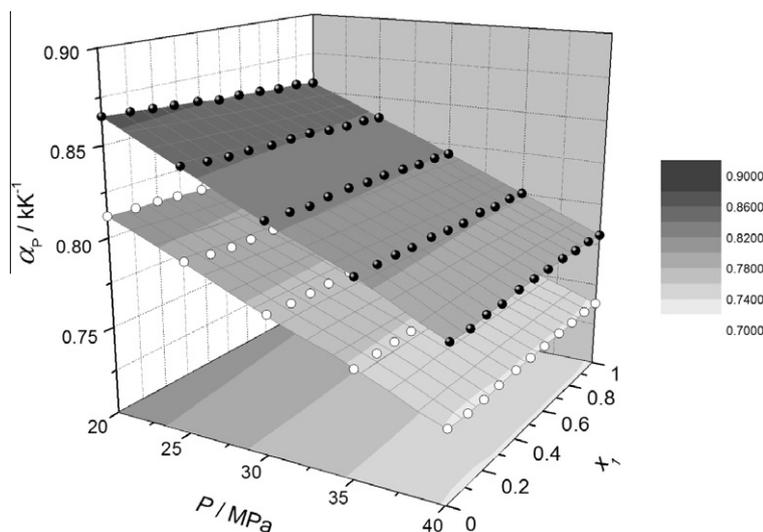


FIGURE 3. Coefficients of cubic expansion, α_p , vs mole fraction of limonene, x_1 , and pressure at (o) $T = 283.15$ K and (●) 358.15 K. Contour plots appear at the bottom of the figure.

TABLE 4

Pure component parameters used for the application of the studied equations of state.

	$M_w / (\text{g} \cdot \text{mol}^{-1})$	T_c / K	P_c / MPa	T_b / K	ω
β -Pinene	136.24 ^a	620 ^b	2.5 ^b	428.75 ^c	0.2862 ^e
Limonene	136.24 ^a	655 ^f	2.8 ^f	450.65 ^g	0.313 ^d

^a Reference [30].

^b Reference [31].

^c Reference [23].

^d Reference [32].

^e Reference [33].

^f Reference [34].

^g Reference [23].

parameters obtained for both components, limonene, and β -pinene, and for both EOS, SAFT, and PC-SAFT. The absolute average percentage deviation values (AAD) of saturation properties of pure limonene and β -pinene are gathered in table 6.

To determine the P , ρ , and 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

TABLE 5

Pure component parameters used for the application of the studied equations of state.

	SAFT	m	$v^{00} / (\text{dm}^3 \cdot \text{mol}^{-1})$	$(u^0/k)/\text{K}$	$(\varepsilon/k)/\text{K}$
β -Pinene		4.893	1.5656	257.39	10
Limonene		5.898	1.3278	238.48	10
	PC-SAFT	m_i	$\sigma_i / \text{\AA}$	$(\varepsilon_i/k)/\text{K}$	
β -Pinene		3.099	4.0832	302.43	
Limonene		3.704	3.8988	281.49	

all cases. SAFT and PC-SAFT were tested as predictive models and the binary interaction parameters, were optimized and were not set to zero. No significant variation of interactions parameters with temperature was found when they were calculated for SAFT EOS, being this value 0.0173. The same behaviour was observed when the interaction parameter was obtained for PC-SAFT, being this value 0.0333. Density data, predicted with these EOS, are gathered in Appendix A, table A3. Figure 4 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

TABLE 6

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

Compound	EOS	AAD ρ^{sat}	AAD ρ^{sat}	$\Delta T_c/\text{K}$	$\Delta P_c/\text{MPa}$	AAD ρ^{comp}
Limonene	SAFT	0.07	0.97	22.51	4.19	7.73
	PC-SAFT	0.02	0.24	12.78	5.80	2.06
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

AAD $\zeta = 100/N \cdot \sum |\zeta_{i,\text{EOS}} - \zeta_{i,\text{exp}}| / \zeta_{i,\text{exp}}$ where ζ is ρ^{sat} , ρ^{sat} , or ρ^{comp} and $N =$ number of points; $\Delta T_c = T_{c,\text{EOS}} - T_c$ and $\Delta P_c = P_{c,\text{EOS}} - P_c$.

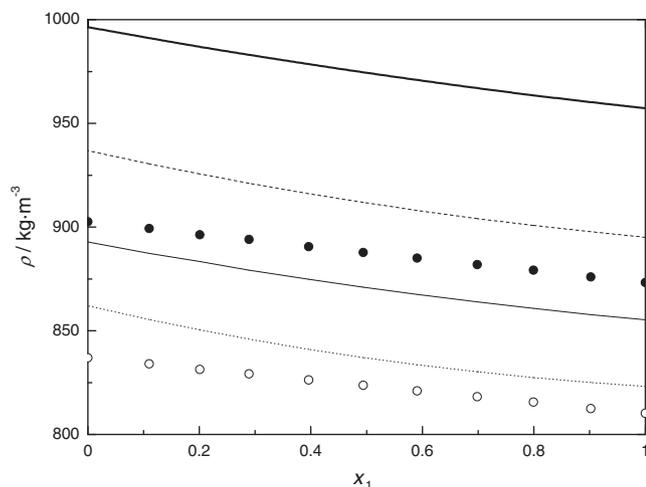


FIGURE 4. Experimental density, ρ , vs mole fraction of limonene, x_1 , at, ●, $T = 283.15$ K and 40 MPa and, ○, 358.15 K and 20 MPa. SAFT prediction at, —, 283.15 and 40 MPa and at, ---, 358.15 K and 20 MPa. PC-SAFT prediction at, —, 283.15 K and 40 MPa and at, ···, 358.15 K and 20 MPa.

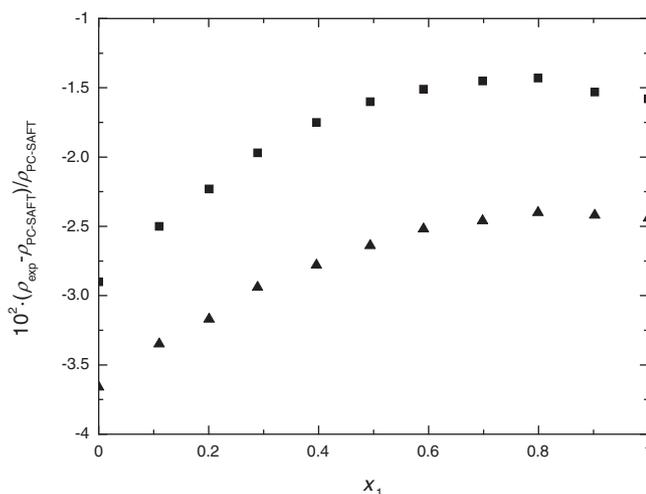


FIGURE 5. Relative errors for density calculated with PC-SAFT, $10^2 \cdot (\rho_{\text{exp}} - \rho_{\text{PC-SAFT}}) / \rho_{\text{PC-SAFT}}$, vs mole fraction of limonene, x_1 , at (▲) 40 MPa and $T = 283.15$ K, highest density conditions, and (■) 20 MPa and $T = 358.15$ K, lowest density conditions.

experimental conditions). As can be seen, PC-SAFT predicts more accurately the experimental data than conventional SAFT, although PC-SAFT disagree to some extent with the experimental points, as shown in figure 5, where relative errors for PC-SAFT vs x_1 at 40 MPa and $T = 283.15$ K, highest density conditions, and at 20 MPa and $T = 358.15$ K, lowest density conditions, are offered. The AAD ρ^{comp}

obtained for PC-SAFT was 2.40% and for SAFT 8.04%, which is coherent with figure 4.

5. Conclusions

After measuring the density of nine compositions for the binary system (limonene + β -pinene) within the temperature range (283.15 to 358.15) K and from (20 to 40) MPa, we can be assured that an unexpected behaviour of the density of this mixtures with temperature and pressure is unlikely to be found, whatever the P - T conditions may be. Density, as well as isothermal compressibility and isobaric thermal expansivity dependency on temperature and pressure were as expected for these mixtures. The PC-SAFT provided us with better results, AAD ρ^{comp} of 2.40%, so for future density predictions of mixtures like that, when VLE and pure component saturated density data are available, conventional SAFT will be rejected. The PC-SAFT is a very good tool to predict the density of mixtures when it is needed for other purposes, for example modelling of supercritical fluid extraction or fractionation.

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Appendix A. Supplementary data

Density, ρ , as a function of temperature, pressure, and mole fraction calculated with SAFT and PC-SAFT; isothermal compressibility, κ_T , as a function of temperature, pressure, and mole fraction; and the coefficient of cubic expansion, α_p as a function of temperature, pressure, and mole fraction for mixtures { α -pinene (1) + β -pinene (2)} is given in Appendix A. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2011.12.013.

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