

P, ρ , and *T* Measurements of the Limonene + α -Pinene Mixtures

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S Supporting Information

ABSTRACT: The density of the binary system 1-methyl-4-(1-methylethenyl)-cyclohexene (limonene) + (1*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α -pinene) has been measured for nine different compositions and the pure components at five pressures from (20.0 to 40.0) MPa and six temperatures from (283.15 to 358.15) K with a vibrating-tube densimeter. The experimental uncertainty is estimated to be $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$. The isothermal compressibility and isobaric thermal expansion were derived from the experimental density data. 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.

■ INTRODUCTION

The knowledge of thermophysical properties of oleoresin components from pine species plays an important role in the design and optimization of chemical plants when using raw materials from naval stores industries. Therefore, accurate data are required for an optimal technological and economical design of process plants.

1-Methyl-4-(1-methylethenyl)-cyclohexene (also known as limonene) and (1*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (also known as α -pinene) are two important and very common terpenes that can be found in essential oils of most of the plants. However, they are obtained mainly by fractional distillation from turpentine, which is separated in turn by steam-distillation from pine oleoresin. They are isomers, and their properties are not very different.

Sousa et al.¹ measured the densities of commercial samples of α -pinene, β -pinene, limonene, and two types of turpentine also at atmospheric pressure for temperatures between (293.15 and 313.15) K. Gallis et al.² determined the heat capacity of a crystallized sample of limonene in a range of temperatures between (5 and 250) K. Limonene saturated vapor pressure was obtained by Díaz et al.³ at different temperatures from (223 to 468) K. Sampaio et al.⁴ determined the isobaric heat capacity of commercial samples of α -pinene, β -pinene, limonene, and turpentine at temperatures between (313.15 and 403.15) K. However, there is no experimental work carried out to study the *P*, ρ , and *T* behavior of commercial limonene + pinene isomers binary mixtures at higher pressures. These mixtures are found not only in fractional distillation from turpentine, but also in the supercritical extraction, and subsequent fractionation, of many essential oils.^{5–7}

Taking into account the above-mentioned lack of experimental data, a *P*, ρ , and *T* research of the binary system (limonene + α -pinene) was carried out. This study 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 (20.0, 25.0, 30.0, 35.0, and 40.0) MPa. From these data, isobaric thermal expansivities and isothermal compressibilities were calculated.

Beside the experimental data, the modeling of the thermophysical properties is the nexus between the fundamental knowledge and its later application to develop industrial processes. Therefore, two equations of state, as predictive tools, were tested: the statistical associating fluid theory (SAFT)^{8–10} and perturbed-chain statistical associating fluid theory (PC-SAFT).^{11,12}

■ EXPERIMENTAL SECTION

Chemicals and Samples Preparation. *R*-(+)-Limonene (mole fraction purity > 98) and (–)- α -pinene (mole fraction purity > 98) were supplied by Sigma-Aldrich. Purity of compounds was confirmed by GC-MS. Mixtures were prepared 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 coverage factor *k* = 2.

Apparatus. The measurements were obtained with equipment similar to those used by Sousa et al.¹³ and Steve et al.¹⁴ A detailed description of the apparatus, together with the set up and validation of the equipment, can be found in the literature.¹⁵ 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 of the system was measured with two pressure transmitters (STW-A09), with ± 0.1 % full scale uncertainty of measurement, one operating up to 16 MPa

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Table 1. Density, ρ , as a Function of Temperature, Pressure, and Mole Fraction for Mixtures Limonene (1) + α -Pinene (2)

x_1	ρ				
	$\text{kg} \cdot \text{m}^{-3}$				
	P				
	MPa				
	20.0	25.0	30.0	35.0	40.0
$T = 283.15 \text{ K}$					
0	880.0	883.2	886.3	889.4	892.5
0.0976	878.3	881.4	884.3	887.5	890.4
0.1991	876.4	879.3	882.4	885.4	888.5
0.2983	874.6	877.6	880.5	883.4	886.5
0.3955	872.9	875.8	878.7	881.7	884.7
0.5036	870.9	873.8	876.7	879.7	882.7
0.5967	869.2	872.1	875.1	878.0	880.9
0.7024	867.4	870.3	873.1	876.1	878.9
0.8084	865.3	868.3	871.3	873.9	876.5
0.9060	863.5	866.6	869.2	871.9	874.4
1	862.0	864.9	867.7	870.4	873.3
$T = 298.15 \text{ K}$					
0	868.8	872.1	875.3	878.6	881.9
0.0976	866.9	870.3	873.5	876.7	880.0
0.1991	865.4	868.6	871.7	875.0	878.1
0.2983	863.5	866.8	869.8	873.1	876.3
0.3955	861.7	865.0	868.1	871.3	874.5
0.5036	860.0	863.2	866.3	869.5	872.6
0.5967	858.4	861.6	864.7	867.9	871.0
0.7024	856.9	859.8	862.8	865.9	869.0
0.8084	855.1	858.0	861.0	864.1	867.1
0.9060	853.0	856.1	859.1	862.2	865.2
1	851.5	854.5	857.6	860.9	863.4
$T = 313.15 \text{ K}$					
0	858.0	861.3	864.7	867.9	871.3
0.0976	856.2	859.5	862.8	866.2	869.5
0.1991	854.4	857.7	861.1	864.5	867.8
0.2983	852.6	855.9	859.3	862.6	866.0
0.3955	851.0	854.3	857.6	860.9	864.2
0.5036	849.2	852.5	855.7	858.9	862.2
0.5967	847.6	851.0	854.2	857.4	860.6
0.7024	845.9	849.2	852.4	855.6	858.8
0.8084	844.1	847.4	850.5	853.8	856.9
0.9060	842.4	845.7	848.8	852.0	855.1
1	841.0	844.2	847.2	850.3	853.3
$T = 328.15 \text{ K}$					
0	846.7	850.4	854.0	857.5	861.1
0.0976	845.1	848.7	852.3	855.8	859.4
0.1991	843.4	847.0	850.6	854.0	857.5
0.2983	841.8	845.2	848.8	852.3	855.8
0.3955	840.2	843.6	847.2	850.6	854.1
0.5036	838.4	841.9	845.4	848.8	852.1
0.5967	837.0	840.4	843.9	847.3	850.6
0.7024	835.3	838.6	842.1	845.5	848.8

Table 1. Continued

x_1	ρ				
	$\text{kg} \cdot \text{m}^{-3}$				
	P				
	MPa				
	20.0	25.0	30.0	35.0	40.0
0.8084	833.5	836.9	840.4	843.7	847.1
0.9060	832.0	835.4	838.7	841.9	845.3
1	830.5	833.8	837.2	840.4	843.8
$T = 343.15 \text{ K}$					
0	835.9	839.7	843.8	847.7	851.4
0.0976	834.4	838.1	842.1	846.0	849.6
0.1991	832.8	836.5	840.4	844.2	847.9
0.2983	831.2	834.9	838.8	842.5	846.2
0.3955	829.6	833.4	837.1	840.9	844.5
0.5036	827.9	831.7	835.4	839.1	842.7
0.5967	826.5	830.2	834.0	837.6	841.2
0.7024	824.8	828.4	832.1	835.9	839.5
0.8084	823.1	826.8	830.4	834.1	837.3
0.9060	821.6	825.2	828.8	832.2	835.5
1	820.1	823.7	827.3	831.1	834.6
$T = 358.15 \text{ K}$					
0	825.0	829.2	833.3	837.4	841.5
0.0976	823.5	827.7	831.6	835.7	839.7
0.1991	822.1	826.0	830.0	834.0	838.0
0.2983	820.7	824.6	828.4	832.2	836.2
0.3955	819.3	823.1	826.9	830.7	834.6
0.5036	817.9	821.6	825.3	829.0	832.8
0.5967	816.5	820.2	823.9	827.5	831.2
0.7024	815.1	818.7	822.2	825.8	829.4
0.8084	813.3	816.9	820.6	824.0	827.6
0.9060	811.5	815.3	818.7	822.4	825.9
1	810.2	813.9	817.6	821.3	824.8

and the other one up to 70 MPa. The experimental expanded uncertainty ($k = 2$) in the reported density values was estimated to be $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$.

RESULTS

Densities. 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 (20.0, 25.0, 30.0, 35.0, and 40.0) MPa. Experimental results are given in Table 1.

No previous density data of the studied mixture measured at that pressure and temperature range were found. The most similar research is the one carried out by Sousa et al.,¹⁶ where the densities of commercial samples of α -pinene, β -pinene, limonene and two types of turpentine were measured but at atmospheric pressure at temperatures between (293.15 and 313.15) K. Therefore, no comparisons could be done.

Table 2. Fitting Coefficients of eq 1 for the Pure Liquids and Mixtures Limonene (1) + α -Pinene (2) and Standard Deviations, σ

	$x_1 = 0$	$x_1 = 0.0976$	$x_1 = 0.1991$	$x_1 = 0.2983$	$x_1 = 0.3955$	$x_1 = 0.5036$
$a_0/\text{kg}\cdot\text{m}^{-3}$	874.74	872.81	870.91	869.06	867.40	865.65
$a_1/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	-0.79	-0.78	-0.78	-0.77	-0.77	-0.76
b_0/MPa	204	195	190	183	182	179
$b_1/\text{MPa}\cdot\text{K}^{-1}$	-0.83	-0.77	-0.74	-0.71	-0.71	-0.70
c_0	0.155	0.149	0.145	0.140	0.138	0.135
$\sigma^a/\text{kg}\cdot\text{m}^{-3}$	0.15	0.23	0.13	0.19	0.10	0.29

	$x_1 = 0.5967$	$x_1 = 0.7024$	$x_1 = 0.8084$	$x_1 = 0.9060$	$x_1 = 1$
$a_0/\text{kg}\cdot\text{m}^{-3}$	863.78	862.12	860.13	858.33	857.07
$a_1/\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	-0.75	-0.75	-0.74	-0.74	-0.74
b_0/MPa	179	177	175	174	174
$b_1/\text{MPa}\cdot\text{K}^{-1}$	-0.70	-0.70	-0.70	-0.69	-0.69
c_0	0.135	0.132	0.130	0.128	0.127
$\sigma^a/\text{kg}\cdot\text{m}^{-3}$	0.43	0.33	0.36	0.30	0.23

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

For each composition, the compressed liquid densities were correlated with the modified Tait relationship:¹⁷

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

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

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

and C is assumed to be temperature independent. $\rho(0.1 \text{ MPa}, T)$ 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 $T_0 = 273.15 \text{ K}$ and a_i and b_i are adjustable parameters. The coefficients were obtained using the Marquardt's algorithm and are given in Table 2 along with the standard deviation for each composition.

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

$$\alpha_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (4)$$

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

It is well-known,¹⁸ that analytical differentiation of the Tait equation with respect to pressure is certainly the most direct way to obtain reliable isothermal compressibility data. The calculated isothermal compressibility was estimated to have an expanded uncertainty ($k = 2$) of $\pm 14 \text{ TPa}^{-1}$.

Table 3. Pure Components 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
α -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 ^c	0.313 ^d

^a Reference 23. ^b Reference 24. ^c Reference 25. ^d Reference 26. ^e Reference 27. ^f Reference 28.

Table 4. Pure Components Parameters Used for the Application of the Studied Equations of State

		v^{00} $\text{L}\cdot\text{mol}^{-1}$	u^0/k K
SAFT	m		
α -pinene	5.163	1.4896	242.99
limonene	5.898	1.3278	238.48
PC-SAFT	m_i	σ_i Å	ϵ_i/k K
α -pinene	3.254	4.0359	286.42
limonene	3.704	3.8988	281.49

In a similar way, isobaric thermal expansion data can be determined from analytical calculation following Cerdeir  a et al.¹⁹ and Troncoso et al.²⁰ α_P was evaluated in the studied pressure and temperature ranges 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 Tables S1 and S2, respectively, of the Supporting Information. For this binary system within the considered P and T range and composition range, the isothermal compressibility, as well as the isobaric thermal 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. α_P and κ_T for limonene are slightly lower than α_P and κ_T for α -pinene.

Equation of State (EOS). Two EOS were tested in this work to predict the P , ρ , and T behavior of the fluid mixtures. Both of them are based on the theory of perturbations: SAFT (Huang and Radosz's version)^{8–10} and PC-SAFT.^{11,12} The required properties of pure components were obtained from literature and are gathered in Table 3.

The EOS parameters for limonene and α -pinene were evaluated from vapor–liquid equilibrium data measured by Gil et al.²¹ Liquid densities were extrapolated with eq 1. Vapor pressures for pure components in the studied temperature range were calculated with Antoine equation, using the constants obtained by Rodrigues et al.²² Table 4 shows the parameters obtained for both components, limonene and α -pinene, and for both EOS, SAFT, and PC-SAFT. The absolute average percentage deviation values (AAD) of saturation properties of pure limonene and α -pinene are gathered in Table 5.

To determine the P , ρ , and T behavior 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. SAFT and PC-SAFT were tested with interaction parameters, k_{ij} , from VLE, Gil et al.²¹ at low pressure. No significant

Table 5. Absolute Average Percentage Deviation AAD, for the Correlation of Saturation Properties and Prediction of Compressed Liquid Density^a

compound	EOS	AAD P^{sat}	AAD ρ^{sat}	ΔT_c	ΔP_c	AAD ρ^{comp}
				K	MPa	
limonene	SAFT	0.07	0.97	22.51	4.19	7.73
	PC-SAFT	0.02	0.24	12.78	5.80	2.06
α -pinene	SAFT	0.04	0.79	35.26	8.69	7.80
	PC-SAFT	0.01	0.21	24.91	9.26	2.31

^a AAD = $100 / N \cdot \sum |\rho_{i,\text{EOS}} - \rho_{i,\text{exp}}| / \rho_{i,\text{exp}}$, where N = number of points; $\Delta T_c = T_{c,\text{EOS}} - T_c$ and $\Delta P_c = P_{c,\text{EOS}} - P_c$.

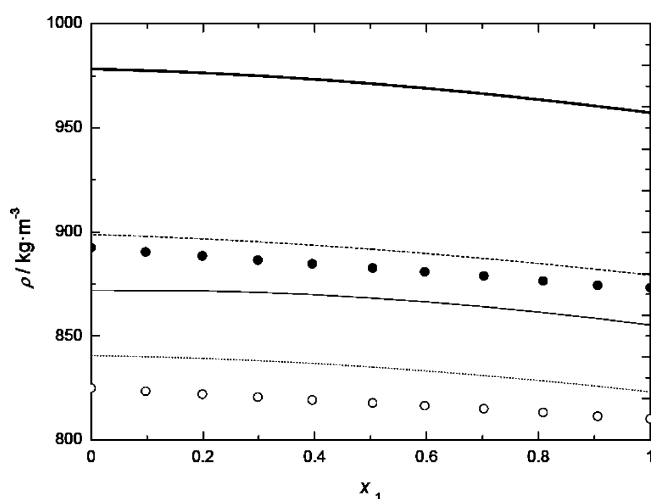


Figure 1. Experimental density, ρ , vs mole fraction of limonene, x_1 , at 283.15 K and 40.0 MPa, ●, and 358.15 K and 20.0 MPa, ○. SAFT prediction at 283.15 K and 40.0 MPa, —, and at 358.15 K and 20.0 MPa, —. PC-SAFT prediction at 283.15 K and 40.0 MPa, ---, and at 358.15 K and 20.0 MPa, ····.

variation of k_{ij} with T and P was found when they were calculated for both theories. k_{ij} for SAFT and PC-SAFT were -0.02080 and -0.1950 , respectively. Density data, predicted with these EOS, are gathered in Table S3. Figure 1 is given as a comparative example of the behavior 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 data than conventional SAFT. The AAD obtained for PC-SAFT was 2.39% and for SAFT 8.12%.

CONCLUSIONS

The density of the pure components and nine compositions for the binary system limonene + α -pinene was measured in the temperature range (283.15 to 358.15) K and from (20.0 to 40.0) MPa with an expanded uncertainty ($k = 2$) of $\pm 0.5 \text{ kg} \cdot \text{m}^{-3}$. Isothermal compressibilities and isobaric thermal expansivities, as well as their dependencies on temperature, pressure and composition were gathered in this work. SAFT and PC-SAFT equations of state were applied to predict the densities of this binary system. Taking into account the results obtained with PC-SAFT, this EOS appears as a valuable tool to predict the P , ρ , and T behavior of mixtures when VLE and pure component saturated density data are available.

ASSOCIATED CONTENT

Supporting Information. 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 isobaric thermal expansivity, α_P , as a function of temperature, pressure, and mole fraction for mixtures limonene (1) + α -pinene (2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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