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PρT Measurements of the (Ethanol + Linalool), (Propan-1-ol + Linalool), and (Propan-2-ol + Linalool) Mixtures: Cubic and Statistical Associating Fluid Theory-Based Equation of State Analyses

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The density of the asymmetrical binary systems (ethanol + linalool), (propan-1-ol + linalool), and (propan-2-ol + linalool) has been measured (660 points) for nine different compositions including the pure compounds at four temperatures in the range (283.15 to 328.15) K and 5 isobars up to 20 MPa with a vibrating-tube densimeter. The experimental expanded uncertainty is estimated to be ± 0.5 $\mathrm{kg \cdot m^{-3}}$. The isothermal compressibility, the isobaric thermal expansion, and the excess molar volume were derived from the experimental density data, revealing that a volume contraction occurs for these binary mixtures. Three different equations of state (EOS's), Peng−Robinson (PR), statistical associating fluid theory (SAFT), and perturbed-chain statistical associating fluid theory (PC-SAFT), were applied to predict the volumetric behavior of the alkanolic mixtures. The best predictions were achieved with the PC-SAFT equation of state.

Introduction

Experimental knowledge of thermophysical properties of organic liquids and their mixtures is of great interest for both industrial and theoretical purposes. Information about pressure and temperature dependencies of such properties allows thermodynamic modeling based on equations of state (EOS's) and statistical mechanics to be checked. The rationalization of high-pressure methods permits the development of green, environmentally friendly processes such as supercritical extraction processes (SCE), which are being applied successfully.

The present work involves the experimental and theoretical study of three binary mixtures made up of (±)-3,7-dimethyl-1,6-octadien-3-ol, also known as (±)-linalool, and ethanol, propan-1-ol, or propan-2-ol. All of the solvents here used are considered as friendly compounds in a green chemistry context, and they are destined to improve the cosolvent-assisted SCE of valuable substances contained in vegetable matrix.[1] Linalool is the main component in extracts of a great number of vegetable species such as coriander, basil, and orange blossom among others. Its minimal toxicity for humans and its use as a chemical intermediate (e.g., vitamin E) make linalool one of the substances most common in cosmetic, food, and pharmacology industries.

The pressure and temperature ranges of measurement, (0.1 to 20) MPa and (283.15 to 328.15) K, were selected due to the experimental conditions employed in our laboratory[2] when extracting volatile oils containing linalool using supercritical CO_2 and alcohols as entrainers. The study also includes isobaric thermal expansivities and isothermal compressibilities, as well as the excess volumes.

Besides the experimental data, the modeling of the thermophysical properties is the nexus between the fundamental knowledge and its later application to develop industrial processes. To this extent, three EOS's, as predictive, were tested: Peng−Robinson (PR),[3] the statistical associating fluid theory (SAFT),[4−6] and the perturbed-chain statistical associating fluid theory (PC-SAFT).[7,8]

Figure 1. Molecule of *R*-(−)-linalool enantiomer.

Experimental Section

Chemicals and Preparation of Samples. (±)-Linalool (purity, mole fraction > 0.982) and ethanol (purity, mole fraction > 0.999) were supplied from Aldrich. Propan-1-ol (purity, mole fraction > 0.999) and propan-2-ol (purity, mole fraction > 0.999) were from Scharlab (Barcelona, Spain). The stated purities of the chemicals were checked by gas chromatography analysis. All liquids were used without further purification. Figure 1 shows the more stable conformation of the *R*-(−)-enantiomer of linalool obtained by a method of molecular mechanics force field (MM2).

Mixtures were set by weighing on a Mettler Toledo AB265-S balance, whose precision is ± 10^{-5} kg. They were prepared in 11 mL airtight glass vials. The expanded uncertainty (coverage factor, $k = 2$) in the mole fraction was ± 0.0001.

Experimental Device. The experimental device used is similar to others previously used by Sousa et al.[9] and Esteve et al.[10] A detailed description of the apparatus, together with the setup

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Table 1. Density, ρ, as a Function of Temperature, Pressure, and Mole Fraction for Mixtures (Ethanol + Linalool), (Propan-1-ol + Linalool), and (Propan-2-ol + Linalool)

	ρ/kg·m^{-3}									
	p/MPa					p/MPa				
x_1	0.1	5	10	15	20	0.1	5	10	15	20
Ethanol (1) + Linalool (2)										
			T/K = 283.15					T/K = 298.15		
0	869.2	872.3	875.2	878.2	881.0	856.9	860.1	863.5	866.6	869.6
0.1129	866.8	869.9	872.9	875.9	878.8	854.5	857.8	861.1	864.3	867.4
0.1935	865.6	868.7	871.7	874.8	877.6	853.4	856.7	860.0	863.2	866.3
0.3049	862.7	866.0	869.0	872.1	874.9	850.5	853.9	857.2	860.5	863.6
0.4023	859.9	863.1	866.1	869.2	872.1	847.6	851.0	854.4	857.7	860.8
0.5121	855.3	858.5	861.6	864.8	867.7	843.0	846.5	850.0	853.2	856.4
0.6055	850.3	853.5	856.8	860.1	862.9	838.0	841.4	845.1	848.4	851.7
0.7008	843.1	846.5	849.7	853.0	856.1	830.9	834.6	838.2	841.6	844.9
0.8009	832.7	836.3	839.6	843.1	846.3	820.6	824.4	828.1	831.7	835.1
0.9009	818.2	822.0	825.5	829.2	832.5	805.9	809.9	813.9	817.7	821.3
1	797.7	801.8	805.6	809.6	813.1	784.9	789.3	793.6	797.7	801.6
			T/K = 313.15					T/K = 328.15		
0	844.1	847.8	851.3	854.8	858.1	831.3	835.2	839.1	842.7	846.3
0.1129	841.7	845.4	849.0	852.5	855.8	828.9	832.9	836.9	840.5	844.1
0.1935	840.6	844.4	847.9	851.4	854.8	827.8	831.8	835.8	839.4	843.0
0.3049	837.8	841.6	845.2	848.7	852.1	824.9	828.9	832.9	836.6	840.3
0.4023	834.7	838.6	842.3	845.8	849.2	821.8	825.9	829.9	833.7	837.3
0.5121	830.2	834.1	837.8	841.4	844.9	817.3	821.4	825.5	829.3	833.0
0.6055	825.3	829.3	833.1	836.7	840.2	812.3	816.6	820.6	824.5	828.4
0.7008	818.0	822.3	826.1	829.8	833.4	805.2	809.5	813.9	817.8	821.6
0.8009	807.9	812.1	816.1	820.0	823.7	794.9	799.4	803.9	808.0	811.9
0.9009	793.2	797.7	801.9	806.0	809.8	780.2	784.9	789.6	793.9	798.1
1	771.9	776.8	781.3	785.7	789.9	758.6	763.8	768.9	773.6	778.1
Propan-1-ol (1) + Linalool (2)										
			T/K = 283.15					T/K = 298.15		
0	869.5	872.6	875.7	878.7	881.5	857.3	860.6	863.9	867.0	870.0
0.1070	867.0	870.2	873.1	876.2	879.0	854.8	858.1	861.4	864.6	867.7
0.2060	864.9	868.1	871.0	874.1	876.9	852.7	856.0	859.4	862.6	865.6
0.3066	862.1	865.4	868.3	871.4	874.4	849.9	853.3	856.6	859.9	863.0
0.4064	859.0	862.2	865.2	868.3	871.3	846.8	850.2	853.6	856.8	859.9
0.5010	855.4	858.6	861.6	864.8	867.7	843.2	846.7	850.1	853.3	856.5
0.6034	850.3	853.6	856.7	859.9	862.8	838.2	841.7	845.2	848.5	851.6
0.7055	843.7	847.0	850.0	853.3	856.3	831.6	835.1	838.7	842.0	845.2
0.7985	835.9	839.3	842.4	845.8	848.8	824.0	827.7	831.2	834.6	837.9
0.8980	825.2	828.8	832.0	835.5	838.6	813.4	817.2	820.8	824.4	827.8
1	810.9	814.7	818.1	821.7	824.9	799.0	803.0	806.9	810.6	814.1
			T/K = 313.15					T/K = 328.15		
0	844.5	848.2	851.6	855.0	858.4	831.7	835.6	839.5	843.1	846.7
0.1070	842.1	845.8	849.3	852.8	856.1	829.4	833.3	837.2	840.9	844.4
0.2060	840.1	843.8	847.3	850.8	854.1	827.3	831.2	835.2	838.8	842.4
0.3066	837.3	841.1	844.6	848.1	851.5	824.5	828.5	832.5	836.2	839.8
0.4064	834.1	837.9	841.5	845.1	848.4	821.3	825.3	829.3	833.0	836.7
0.5010	830.5	834.4	838.0	841.5	844.9	817.7	821.8	825.8	829.5	833.2
0.6034	825.6	829.5	833.2	836.7	840.2	812.8	816.9	821.0	824.8	828.5
0.7055	819.1	823.1	826.8	830.4	833.9	806.3	810.5	814.7	818.5	822.3
0.7985	811.6	815.6	819.4	823.2	826.7	799.0	803.3	807.5	811.4	815.2
0.8980	801.2	805.3	809.2	813.1	816.7	788.7	793.1	797.5	801.5	805.3
1	786.8	791.2	795.3	799.3	803.1	774.5	779.1	783.7	787.8	791.9
Propan-2-ol (1) + Linalool (2)										
			T/K = 283.15					T/K = 298.15		
0	869.5	872.6	875.7	878.7	881.5	857.3	860.6	863.9	867.0	870.0
0.1031	866.3	869.5	872.5	875.5	878.5	854.1	857.4	860.8	864.0	867.0
0.2049	862.7	865.9	869.0	872.1	875.0	850.5	853.9	857.3	860.5	863.6
0.3054	858.7	861.9	864.9	868.1	870.9	846.3	849.8	853.2	856.5	859.6
0.4056	854.1	857.4	860.5	863.7	866.7	841.7	845.2	848.7	852.0	855.2
0.5022	848.8	852.2	855.3	858.6	861.6	836.4	839.9	843.5	846.9	850.1
0.6050	842.3	845.7	848.9	852.2	855.3	829.7	833.3	837.0	840.4	843.7
0.7008	834.6	838.1	841.4	844.9	848.0	821.9	825.6	829.4	832.9	836.4
0.7981	824.5	828.2	831.6	835.1	838.4	812.0	815.9	819.7	823.4	826.9
0.9092	809.3	813.1	816.6	820.4	823.7	796.8	800.9	804.9	808.8	812.4
1	793.7	797.5	801.3	805.2	808.9	781.2	785.5	789.7	793.8	797.6
			T/K = 313.15					T/K = 328.15		
0	844.5	848.2	851.6	855.0	858.4	831.7	835.6	839.5	843.1	846.7
0.1031	841.4	845.1	848.6	852.1	855.4	828.5	832.5	836.4	840.1	843.6
0.2049	837.7	841.5	845.1	848.6	852.0	824.8	828.8	832.8	836.5	840.2
0.3054	833.4	837.3	840.9	844.5	847.9	820.4	824.5	828.6	832.3	836.0
0.4056	828.7	832.6	836.3	840.0	843.5	815.5	819.7	823.9	827.8	831.5
0.5022	823.2	827.2	831.0	834.8	838.3	809.9	814.2	818.4	822.3	826.1
0.6050	816.4	820.6	824.4	828.2	831.8	802.8	807.2	811.6	815.6	819.5
0.7008	808.5	812.8	816.8	820.6	824.4	794.9	799.4	803.9	808.0	812.0
0.7981	798.6	803.0	807.1	811.1	814.9	784.8	789.5	794.2	798.4	802.6
0.9092	783.6	788.2	792.5	796.7	800.7	769.8	774.8	779.7	784.1	788.4
1	768.1	773.0	777.5	781.9	786.1	754.4	759.6	764.8	769.5	774.0

and validation of the equipment, was also done in the literature.[11] The measuring principle lays on the determination of the oscillation period of an U-shaped tube that contains the sample. The uncertainty in the control of temperature is ± 0.01 K. The pressure of the system was controlled by two pressure transmitters (STW-A09), with ± 0.1 % full scale uncertainty of measurement, one operating up to 16 MPa and the other up to 70 MPa. The overall experimental expanded uncertainty ($k = 2$) in the reported density values was estimated to be ± 0.5 $\text{kg}\cdot\text{m}^{-3}$.

Results

Densities. The experimental densities, ρ, for pure liquids and binary mixtures alkanol + linalool were measured at four temperatures (283.15, 298.15, 313.15, and 328.15) K and several pressures from (0.1 to 20) MPa in steps of 5 MPa. The experimental results appear in Table 1.

Figure 2a shows the relative deviation between experimental and bibliographic data for ethanol (< 0.1 %).[12−20] Figure 2b,c includes the relative deviations for propan-1-ol and propan-2-ol between our experimental results and interpolated values from the literature.[21−24] The absolute differences are lower than 0.2 %.

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

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

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

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

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

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

where $T_0 = 273.15$ K in all cases. The coefficients were obtained using the Marquardt's algorithm and are given in Table 2 along with the standard deviation for each composition. Figure 3 presents the experimental densities and the fitted surfaces of alkanol (1) + linalool (2) versus x_1 and P at (283.15 and 328.15) K.

Derived Properties: Isobaric Thermal Expansion, α_P, Isothermal Compressibility, κ_T, and Excess Molar Volume, V_m^E. 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 definition:

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

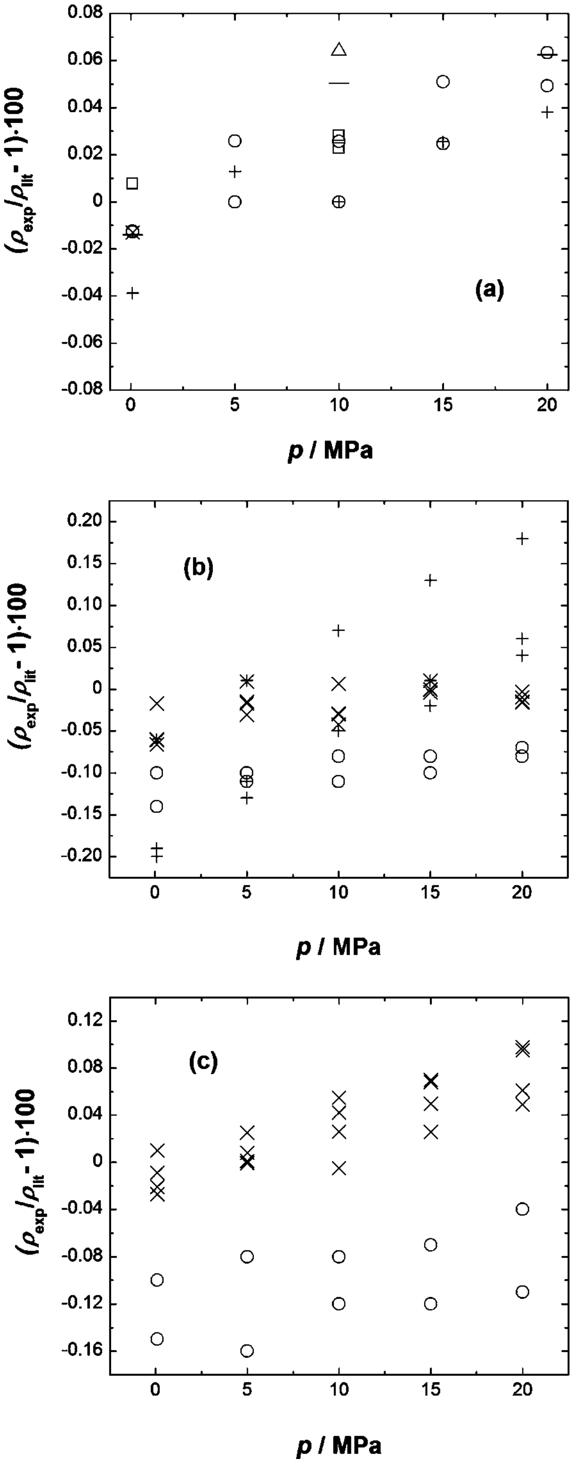

Figure 2. Comparison of densities for pure compounds vs pressure shown as the deviation ($\rho_{\text{exp}}/\rho_{\text{lit}} - 1$) between experimental values of this work and literature values. (a) Differences for ethanol: △, ref 17 at 313.15 K; —, ref 16 at 298.15 K; +, ref 20 at 313.15 K; ○, ref 15 at (283.15 and 313.15) K; □, ref 19 at (298.15 and 313.15) K; ×, ref 18 at 313.15 K. Differences between experimental values of this work and interpolated values from literature: (b) propan-1-ol: ×, ref 21 at (283.15, 298.15, 313.15, and 328.15) K; ○, ref 23 at (313.15 and 328.15) K; +, ref 24 at (298.15, 313.15, and 328.15) K; (c) propan-2-ol: ×, ref 22 at (283.15, 298.15, 313.15, and 328.15) K; ○, ref 23 at (313.15 and 328.15) K.

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

It is well-known[26] that analytical differentiation of the Tait equation with respect to pressure is certainly the most direct

Table 2. Fitting Coefficients of Equation 4 for the Pure Liquids and Mixtures (Ethanol + Linalool), (Propan-1-ol + Linalool), and (Propan-2-ol + Linalool) and Standard Deviations s^a

Ethanol (1) + Linalool (2)

	$x_1 = 0$	$x_1 = 0.1129$	$x_1 = 0.1935$	$x_1 = 0.3049$	$x_1 = 0.4023$	$x_1 = 0.5121$
a_0/kg·m^{-3}	877.781	875.330	874.153	871.349	868.534	863.910
a_1/kg·m^{-3}·K^{-1}	−0.8433	−0.8420	−0.8401	−0.8420	−0.8473	−0.8450
b_0/MPa	134.5	120.0	128.2	125.1	114.8	121.5
b_1/MPa·K^{-1}	−1.3311	−1.1148	−1.252	−1.2515	−1.234	−1.270
b_2/MPa·K^{-2}	0.00931	0.00735	0.00877	0.00908	0.00941	0.00959
c_0	0.08747	0.08059	0.08553	0.08478	0.07818	0.08447
s/kg·m^{-3}	0.098	0.096	0.12	0.12	0.12	0.12

	$x_1 = 0.6055$	$x_1 = 0.7008$	$x_1 = 0.8009$	$x_1 = 0.9009$	$x_1 = 1$
a_0/kg·m^{-3}	858.870	851.703	841.328	826.827	806.523
a_1/kg·m^{-3}·K^{-1}	−0.8432	−0.8431	−0.8401	−0.8447	−0.8698
b_0/MPa	121.1	97.77	107.2	103.5	88.7
b_1/MPa·K^{-1}	−1.258	−1.048	−1.114	−1.007	−0.7919
b_2/MPa·K^{-2}	0.00958	0.00797	0.00855	0.00719	0.00458
c_0	0.08671	0.07317	0.08422	0.08840	0.08584
s/kg·m^{-3}	0.14	0.15	0.16	0.14	0.12

Propan-1-ol (1) + Linalool (2)

	$x_1 = 0$	$x_1 = 0.1070$	$x_1 = 0.2060$	$x_1 = 0.3066$	$x_1 = 0.4064$	$x_1 = 0.5010$
a_0/kg·m^{-3}	878.103	875.529	873.435	870.635	867.551	863.931
a_1/kg·m^{-3}·K^{-1}	−0.8415	−0.8370	−0.8366	−0.8360	−0.8385	−0.8376
b_0/MPa	128.7	131.8	124.5	129.4	119.0	116.8
b_1/MPa·K^{-1}	−1.068	−1.182	−1.198	−1.161	−1.251	−1.171
b_2/MPa·K^{-2}	0.00624	0.00771	0.00841	0.00760	0.00890	0.00867
c_0	0.08656	0.08839	0.08342	0.08888	0.08834	0.08114
s/kg·m^{-3}	0.13	0.10	0.11	0.11	0.12	0.14

	$x_1 = 0.6034$	$x_1 = 0.7055$	$x_1 = 0.7985$	$x_1 = 0.8980$	$x_1 = 1$
a_0/kg·m^{-3}	858.841	852.154	844.285	833.491	819.137
a_1/kg·m^{-3}·K^{-1}	−0.8343	−0.8308	−0.8202	−0.8112	−0.8102
b_0/MPa	111.3	111.9	113.4	105.1	92.7
b_1/MPa·K^{-1}	−1.121	−1.186	−1.170	−1.008	−0.8204
b_2/MPa·K^{-2}	0.00829	0.00896	0.0089	0.00730	0.00526
c_0	0.07917	0.08032	0.08434	0.08336	0.08005
s/kg·m^{-3}	0.14	0.14	0.14	0.13	0.090

Propan-2-ol (1) + Linalool (2)

	$x_1 = 0$	$x_1 = 0.1031$	$x_1 = 0.2049$	$x_1 = 0.3054$	$x_1 = 0.4056$	$x_1 = 0.5022$
a_0/kg·m^{-3}	878.103	874.875	871.338	867.374	862.894	857.761
a_1/kg·m^{-3}·K^{-1}	−0.8415	−0.8401	−0.8434	−0.8513	−0.8584	−0.8669
b_0/MPa	128.7	120.2	125.07	116.4	121.9	121.0
b_1/MPa·K^{-1}	−1.068	−1.098	−1.210	−1.155	−1.253	−1.288
b_2/MPa·K^{-2}	−0.00624	0.00750	0.00869	0.00808	0.00905	0.00962
c_0	0.08658	0.08176	0.08566	0.08093	0.08587	0.08701
s/kg·m^{-3}	0.13	0.13	0.14	0.12	0.15	0.15

	$x_1 = 0.6055$	$x_1 = 0.7008$	$x_1 = 0.7981$	$x_1 = 0.9092$	$x_1 = 1$
a_0/g·cm^{-3}	851.295	843.643	833.698	818.359	802.614
a_1/g·cm^{-3}·K^{-1}	−0.8770	−0.8822	−0.8833	−0.8766	−0.8702
b_0/MPa	117.3	113.7	111.2	99.22	104.8
b_1/MPa·K^{-1}	−1.399	−1.278	−1.347	−1.240	−1.168
b_2/MPa·K^{-2}	0.0115	0.01010	0.0112	0.01045	0.01035
c_0	0.08510	0.08693	0.08751	0.08356	0.09464
s/kg·m^{-3}	0.19	0.17	0.23	0.23	0.24

[a]

$$s = \sqrt{\sum_{i=1}^{N} (\rho_{i,\mathrm{exp}} - \rho_{i,\mathrm{calc}})^2/(N - P)}$$

where N = number of experimental points and P = number of adjustable parameters.

way to obtain reliable isothermal compressibility data. The calculated isothermal compressibility was estimated to have an expanded uncertainty ($k = 2$) 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] α_P was evaluated in the investigated pressure and temperature ranges finding an expanded uncertainty ($k = 2$) of ± 0.005 kK^{-1}. Uncertainties for isothermal compressibility and isobaric expansion were obtained following the statistical method of propagation of uncertainty. The calculated values of κ_T and α_P are given respectively in Tables S1 and S2 of Supporting Information. Figure 3 shows the calculated values of these properties for the alkanol (1) + linalool (2) mixtures versus x_1 and P at (283.15 and 328.15) K.

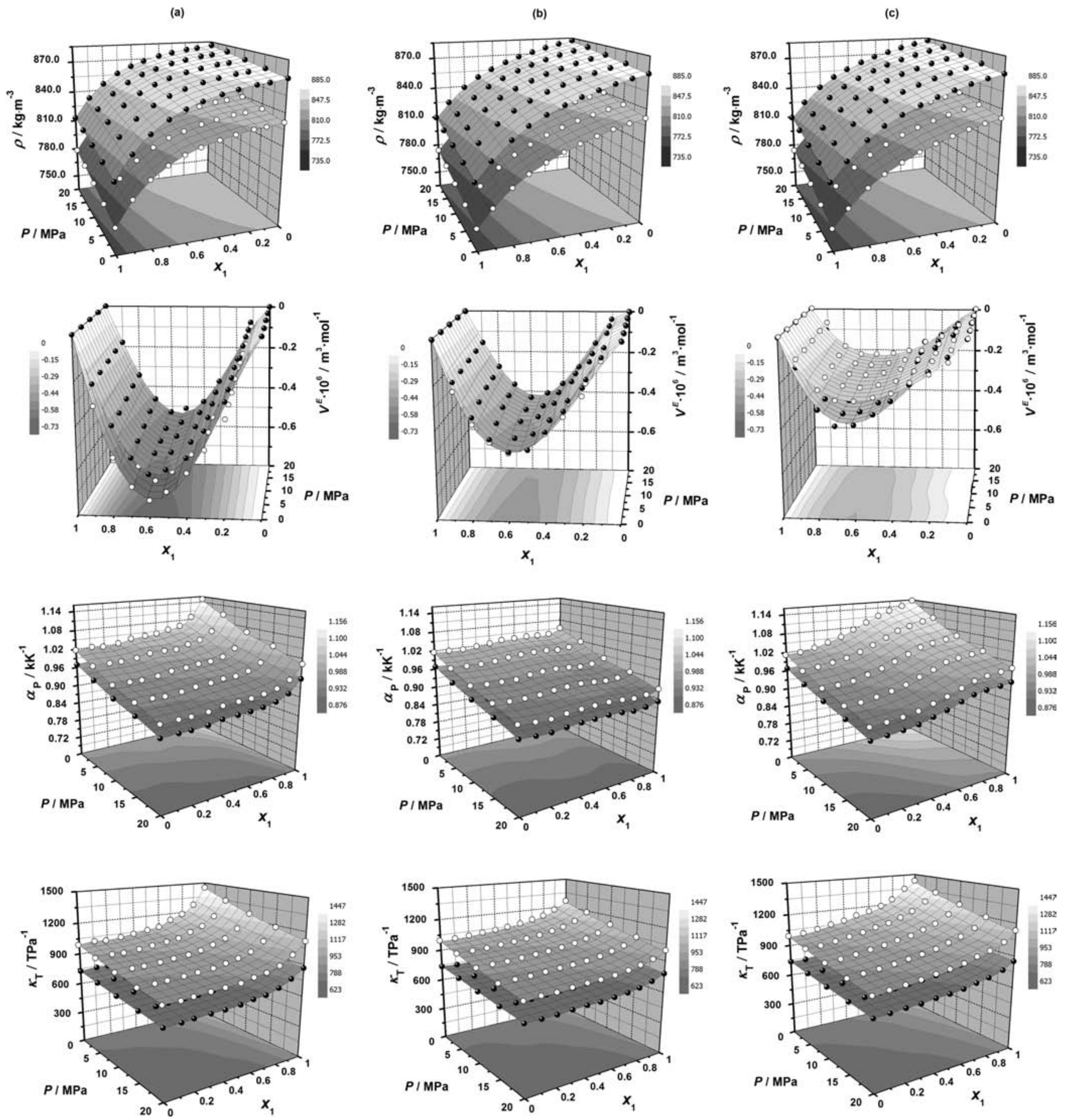

Figure 3. Experimental density, ρ, excess molar volume, V_m^E, and fitted surfaces, calculated isobaric thermal expansion, α_P, and calculated isothermal compressibility, κ_T, for the mixtures: (a) ethanol (1) + linalool (2); (b) propan-1-ol + linalool (2); and (c) propan-2-ol (1) + linalool (2) vs mole fraction and pressure at ●, 283.15 K and ○, 328.15 K. Contour plots appear at the bottom of the figures.

For the three binary systems within the considered T, P range and composition, the isothermal compressibility, as well as the isobaric thermal expansion, increases, as usually, with increasing temperature and decreases with increasing pressure.

The pure compounds in the conditions of this work exhibit the following sequences:

$$\alpha_P(\text{ethanol}) \approx \alpha_P(\text{propan-2-ol}) > \alpha_P(\text{propan-1-ol}) \approx \alpha_P(\text{linalool})$$

$$\kappa_T(\text{ethanol}) \approx \kappa_T(\text{propan-2-ol}) > \kappa_T(\text{propan-1-ol}) > \kappa_T(\text{linalool})$$

These series could help us to explain the behavior of both derived properties among a binary mixture. As it can be observed for the three systems, the isothermal compressibility shows a monotonically increasing behavior as a function of the alcohol concentration, x_1. Similar results are found for the isobaric thermal expansion coefficient in relation with the ethanol + linalool and propan-2-ol + linalool systems. In

Table 3. Fitting Coefficients of Equation 7 for the Mixtures (Ethanol + Linalool), (Propan-1-ol + Linalool), and (Propan-2-ol + Linalool) and Standard Deviations s at the Given (p, T) Conditions[a]

	P/MPa					P/MPa				
	0.1	5	10	15	20	0.1	5	10	15	20
Ethanol (1) + Linalool (2)										
			T/K = 283.15					T/K = 298.15		
$A_1 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−2.400	−2.299	−2.244	−2.183	−2.096	−2.566	−2.470	−2.391	−2.293	−2.247
$A_2 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−0.767	−0.718	−0.680	−0.621	−0.562	−0.925	−0.863	−0.827	−0.787	−0.714
$A_3 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.969	0.907	0.959	0.965	0.831	0.722	0.730	0.820	0.721	0.767
$s \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02
			T/K = 313.15					T/K = 328.15		
$A_1 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−2.683	−2.596	−2.514	−2.419	−2.349	−2.795	−2.662	−2.535	−2.457	−2.364
$A_2 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−1.02	−1.02	−0.892	−0.881	−0.836	−1.14	−1.07	−0.966	−0.936	−0.902
$A_3 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.644	0.6663	0.673	0.648	0.664	0.344	0.380	0.344	0.411	0.404
$s \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02
Propan-1-ol (1) + Linalool (2)										
			T/K = 283.15					T/K = 298.15		
$A_1 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−1.862	−1.814	−1.713	−1.672	−1.642	−1.898	−1.852	−1.791	−1.745	−1.704
$A_2 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−0.822	−0.707	−0.805	−0.765	−0.706	−0.903	−0.871	−0.788	−0.767	−0.695
$A_3 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.717	0.809	1.046	0.918	1.016	0.593	0.579	0.657	0.606	0.610
$s \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.009	0.009	0.009	0.01	0.01	0.01	0.009	0.01	0.01	0.01
			T/K = 313.15					T/K = 328.15		
$A_1 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−1.916	−1.864	−1.829	−1.800	−1.717	−1.878	−1.822	−1.753	−1.718	−1.676
$A_2 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−0.847	−0.820	−0.765	−0.686	−0.705	−0.807	−0.800	−0.765	−0.734	−0.698
$A_3 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.336	0.347	0.477	0.752	0.491	0.139	0.342	0.329	0.308	0.307
$s \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.01	0.01	0.01	0.009	0.009	0.01	0.01	0.01	0.01	0.01
Propan-2-ol (1) + Linalool (2)										
			T/K = 283.15					T/K = 298.15		
$A_1 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−1.349	−1.340	−1.238	−1.223	−1.151	−1.273	−1.236	−1.205	−1.173	−1.137
$A_2 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−0.891	−0.879	−0.930	−0.899	−0.767	−0.827	−0.789	−0.741	−0.672	−0.683
$A_3 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	–	–	–	–	–	–	–	–	–	–
$s \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.02
			T/K = 313.15					T/K = 328.15		
$A_1 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−1.165	−1.113	−1.068	−1.070	−1.041	−1.049	−1.025	−0.953	−0.948	−0.920
$A_2 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−0.545	−0.549	−0.484	−0.420	−0.444	−0.343	−0.324	−0.338	−0.263	−0.276
$A_3 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	−0.264	−0.289	−0.236	−0.213	–	−0.301	–	−0.200	–	–
$s \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01

[a]

$$s = \sqrt{\sum_{i=1}^{N} (V^{\text{E}}_{\text{m}i,\text{exp}} - V^{\text{E}}_{\text{m}i,\text{calc}})^2/(N - P)}$$

where N = number of experimental points and P = number of adjustable parameters.

the other side, the minimal changes of α_P with x_1 observed for the propan-1-ol + linalool system are a logical consequence of the similar values of α_P for the pure compounds. In general, taking the x-axis as a reference, the convex shape established for κ_T and α_P versus x_1 could be explained as the result of a decrease in the free volume of the molecules within the mixtures.

Excess molar volumes as a function of the alcohol molar fraction, x_1, were determined at each P, T from densities of the two pure liquids, ρ_1 and ρ_2, and from that of their mixtures, ρ, according to the relation:

$$V^{\text{E}}_{\text{m}}(P, T) = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (6)$$

where M_1 and M_2 are the molar masses of alkanol and linalool, respectively. Table S3 of Supporting Information reports the calculated values of excess molar volumes. The estimated uncertainty on V_{m}^{E} is $\pm 5 \cdot 10^{-8}$ $\text{m}^3 \cdot \text{mol}^{-1}$. This excess quantity was fitted to the Redlich−Kister equation:

$$V^{\text{E}}_{\text{m}}(P, T)/\text{m}^3 \cdot \text{mol}^{-1} = x_1 x_2 (A_1 + A_2(2x_1 - 1) + A_3(2x_1 - 1)^2) \qquad (7)$$

where x_1 and x_2 are the molar fractions of alkanol and linalool, respectively, and A_i are the fitting parameters. The values of the A_i parameters and the standard deviations are shown in Table 3.

The variation of the excess molar volume and the fitted surface versus the composition of alkanol and pressure is also shown at (283.15 and 328.15) K in Figure 3. For all of the mixtures in the whole T, P range, this magnitude is negative (minimum $x_1 \approx 0.60$). Such relatively high negative values of excess volumes surely are the consequence of strong, oriented interactions such as hydrogen bonds due to alcohol groups. As a result these mixtures are better packed than the pure compounds. As Figure 3 shows, $|V_{\text{m}}^{\text{E}}|$ increases with the associating capacity of the alkanol, and the diagrams also

Table 4. Pure Component Properties Used for the Application of the Equations of State

	M_{w}	T_{c}	P_{c}	T_{b}	
compound	$\text{g} \cdot \text{mol}^{-1}$	K	MPa	K	ω
ethanol[a]	46.096	513.90	6.148	351.4	0.644[b]
propan-1-ol[a]	60.096	537.32	5.182	370.3	0.618[b]
propan-2-ol[a]	60.096	508.30	4.7616	355.4	0.665[b]
linalool	154.249	634.65[c]	2.582[c]	471.2[d]	0.761[b]

[a] Ref 32. [b] Calculated using Lee−Kesler method, ref 30. [c] Calculated using Joback's method, ref 29. [d] Ref 1.

Table 5. Pure Component Parameters Used for the Application of the Studied Equations of State

SAFT	m	$v^{oo}/L \cdot mol^{-1}$	$u^o/k/K$	κ	$\epsilon/k/K$
ethanol[4]	2.457	0.0120	213.48	0.02920	2759
propan-1-ol[4]	3.240	0.0120	225.68	0.01968	2619
propan-2-ol[4]	3.249	0.0120	202.94	0.02095	2670
linalool	5.453	0.0176	247.83	0.02310	2026

PC-SAFT	m_i	$\sigma_i/Å$	$\epsilon_i/k/K$	$\kappa^{A_iB_i}$	$\epsilon^{A_iB_i}/k/K$
ethanol[8]	2.3827	3.1771	198.24	0.032384	2653.3
propan-1-ol[8]	2.9997	3.2522	233.40	0.015268	2276.8
propan-2-ol[8]	3.0929	3.2085	208.42	0.024675	2253.9
linalool	4.1979	3.9193	271.74	0.001912	2187.3

Table 6. Absolute Average Percentage Deviation, AAD[a], for the Correlation of Saturation Properties and Prediction of Compressed Liquid Density

compound	EOS	AAD P^{sat}	AAD ρ^{sat}	$\Delta T_c/K$	$\Delta P_c/MPa$	AAD ρ^{comp}
linalool	PR	25.84	5.75			3.80
	SAFT	5.69	1.80	57.65	0.248	2.23
	PC-SAFT	4.70	0.25	44.05	0.391	0.26

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

illustrate differences with the temperature for the three binary systems. The excess volume of the system (linalool + propan-1-ol) appears as practically temperature-independent, and the systems containing ethanol and propan-2-ol show an opposite behavior. Apart from molecular packing considerations, this thermal inversion could be well explained on the basis of an opposite change with temperature of the overall interactions for the mixtures (ethanol + linalool), (propan-1-ol + linalool), and (propan-2-ol + linalool).

Equations of State (EOS's). Three EOS's were tested in this work to predict the $P\rho T$ behavior of the fluid mixtures. One of them is a cubic equation put forward by PR,[3] and the other two are based on the theory of perturbations: the SAFT (Huang and Radosz's version)[4−6] and PC-SAFT.[7,8]

The needed properties of the pure components are gathered in Table 4. Critical properties of linalool were calculated according to Joback's method,[29] and the acentric factor was estimated using the Lee−Kesler method.[30] The EOS parameters for linalool were evaluated from the correlation of vapor-pressure properties,[31] and liquid densities were extrapolated by eq 1. Table 5 shows the parameters obtained for linalool together with those of the alkanols found in the literature. The absolute average percentage deviation values (AAD) of saturation properties of pure linalool are shown in Table 6.

To determine the $P\rho T$ behavior of linalool + alkanol mixtures, the van der Waals one-fluid mixing rules were used, and classical quadratic combining rules for the cross-terms were selected in all cases. PR, SAFT, and PC-SAFT were tested as predictive models, so all of the binary interaction parameters were considered equal to zero.

The obtained results with the three equations of state are listed in Tables S4, S5, and S6 of Supporting Information. The best results for the predictions of experimental compressed densities of the binary mixtures under study were achieved with PC-SAFT, Figure 4. The ADD obtained for PC-SAFT for (ethanol + linalool), (propan-1-ol + linalool), and (propan-2-ol + linalool) were (0.44, 0.76, and 0.45) %, respectively. For the same three binary systems, the results achieved for PR and SAFT were (2.88, 1.82, and 2.19) % and (2.88, 2.50, and 2.11) %. Despite the similar ADD for PR and for SAFT equation, SAFT describes more adequately the behavior of the density with the mole composition of the mixture.

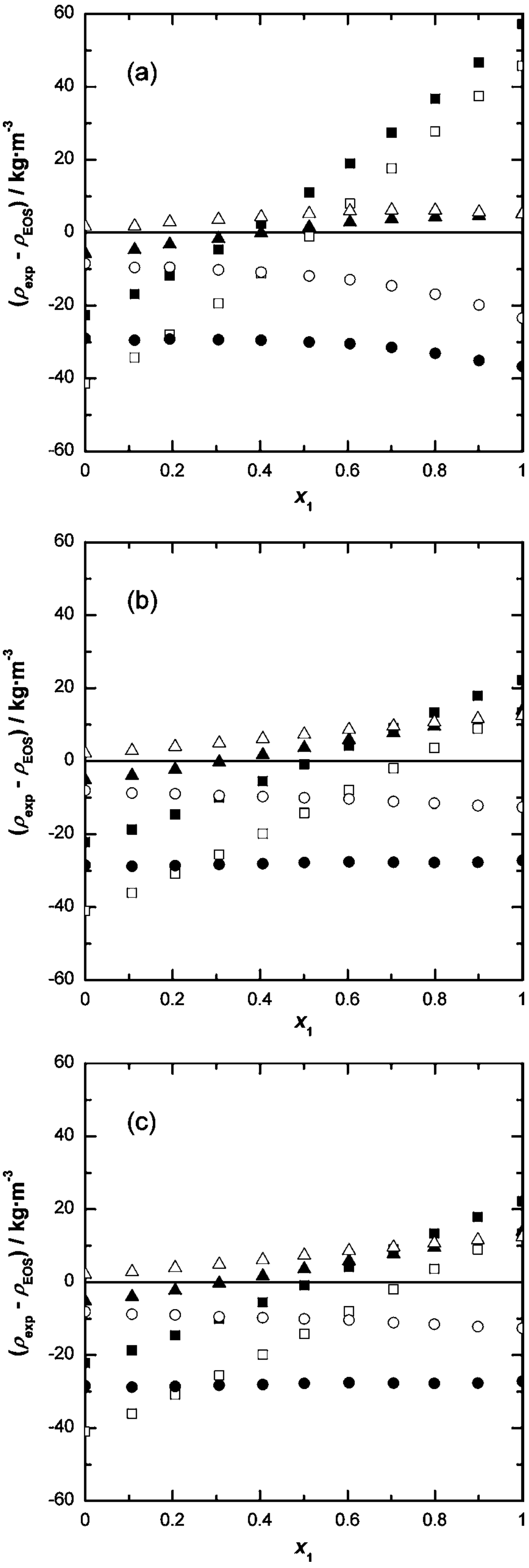

Figure 4. Residuals of density predictions of three EOS's, $k_{ij} = 0$, for the mixtures (a) ethanol (1) + linalool (2); (b) propan-1-ol (1) + linalool (2); and (c) propan-2-ol (1) + linalool (2) at 283.15 K and 20 MPa (filled symbols) and at 328.15 K and 0.1 MPa (open symbols): □, PR; ○, SAFT; △, PC-SAFT.

Conclusion

The density of nine compositions of three binary systems, (ethanol + linalool), (propan-1-ol + linalool), and (propan-2-

ol + linalool), has been measured in the range (283.15 to 328.15) K and up to 20 MPa with an overall uncertainty of ± $0.5 \cdot \text{kg} \cdot \text{m}^{-3}$. Isothermal compressibilities, isobaric thermal expansivities, and excess molar volumes, as well as their dependencies on temperature, pressure, and composition, have been obtained. A negative behavior of the excess molar volume versus composition has been found; moreover, depending on the binary system, this magnitude exhibits an opposite trend with temperature probably due to the different hydrogen-bond capacity of the different alkanols. PR, SAFT, and PC-SAFT have been tested to predict the $P\rho T$ equilibrium of the binary systems under study. The best results of the compressed densities of the mixtures are obtained using PC-SAFT with an overall ADD of 0.55 %. PC-SAFT appears as an invaluable tool to predict the $P\rho T$ behavior of the mixtures linalool + alkanols from only the vapor−liquid equilibrium and the saturated density of the pure components.

Supporting Information Available:

Calculated values of the isothermal compressibilities, the isobaric thermal expansions, and the excess molar volumes for the alkanol + linalool mixtures. $P\rho T$ predictions of PR, SAFT, and PC-SAFT equations of state. This material is available free of charge via the Internet at http://pubs.acs.org.

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