



## (Vapor + liquid) equilibrium data for (carbon dioxide + 1,1-difluoroethane) system at temperatures from (258 to 343) K and pressures up to about 8 MPa

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### ABSTRACT

Accurate thermo-physical data are of utmost interest for the development of new efficient refrigeration systems. Carbon dioxide (R744) and 1,1-difluoroethane (R152a) are addressed here. Isothermal (vapor + liquid) equilibrium data are reported herein for (R744 + R152a) binary system in the (258–343) K temperature range and in the (0.14 to 7.65) MPa pressure range. A reliable “static-analytic” method taking advantage of two online ROLSI™ micro capillary samplers is used for all thermodynamic measurements. The data are correlated using our in-house *ThermoSoft* thermodynamic model using the Peng–Robinson equation of state, the Mathias–Copeman alpha function, the Wong–Sandler mixing rules, and the NRTL model.

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## 1. Introduction

In the wake of the global response for the protection of environment and sustainable development, the refrigeration industry is forced to find new fluids as refrigerants. The Montreal Protocol (1987) is one of the landmarks towards the replacement of ozone-destroying refrigerants like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) with ozone friendly and non-green house fluids. CFCs were prohibited in 1996 in signatory countries of the Montreal Protocol. The deadline for HCFCs which have low ozone depletion potential is 2030.

1,1-Difluoroethane, C<sub>2</sub>H<sub>4</sub>F<sub>2</sub>, R152a, CAS no: 75-37-6 is composed of carbon, hydrogen, and fluorine. At standard temperature and pressure, it is a colorless gas. It is classified as a halogenated aliphatic. It is used for refrigeration and as an aerosol propellant. It is most commonly found in electronic cleaning products, and many consumer aerosol products that must meet stringent VOC (volatile organic compounds) requirements.

On the other hand, carbon dioxide, CO<sub>2</sub>, R744, CAS no: 124-38-9, is a major component of the carbon cycle. Its balance however is

critical for normal functioning of various species and the planet. It is currently at a globally averaged concentration of approximately 383 ppm by volume in the Earth's atmosphere [1], although this varies both by location and time. Carbon dioxide is an important greenhouse gas because it transmits visible light but absorbs strongly in the infrared. Increasing trends in the quantities of carbon dioxide is because of its generation in the process of combustion, industries, and transportation. Inorganic carbon dioxide is output by volcanoes and other geothermal processes such as hot springs.

For the development of new refrigeration mixtures with minimal environmental impact (ozone depletion and global warming), it is necessary to rely on reliable thermodynamic properties about a maximum of refrigerating fluid mixtures. This has been the utmost motivation of the research carried out on refrigerants in our group [2–8] and is still current. Our main objective is to provide consistent thermodynamic data and efficient thermodynamic models useful for scientific community and industry. In this work, we present 134 VLE data points for the (R744 + R152a) binary system at various temperatures in the (258–343) K temperature range. Half of isotherms correspond to temperatures below critical temperature of R744 and half above. The data are correlated using our in-house *ThermoSoft* thermodynamic model using the Peng–Robinson equation of state, the Mathias–Copeman alpha function, the Wong–Sandler mixing rules, and the NRTL model for the  $g^E$  term [2,3].

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## Nomenclature

### List of symbols

<i>a</i>	parameter of the PR equation of state (energy parameter [ $\text{J} \cdot \text{m}^3 \cdot \text{mol}^{-2}$ ])
<i>b</i>	parameter of the PR equation of state (molar co volume parameter [ $\text{m}^3 \cdot \text{mol}^{-1}$ ])
<i>c</i>	Mathias–Copeman coefficient
<i>C</i>	numerical constant equal to $-0.62323$
<i>F</i>	objective function
<i>g</i>	molar Gibbs free energy [ $\text{J} \cdot \text{mol}^{-1}$ ]
<i>k<sub>ij</sub></i>	binary interaction parameter
<i>N</i>	number of experimental points
<i>P</i>	pressure [MPa]
<i>R</i>	gas constant [ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ]
<i>T</i>	temperature [K]
<i>x</i>	liquid mole fraction
<i>y</i>	vapor mole fraction

### Greek letters

$\alpha$	alpha function (equations (1) and (2))
$\alpha_{ij}$	non-randomness NRTL model parameter (equation (6))

$\tau_{ij}$	NRTL model binary interaction parameter (equation (6)), [ $\text{J} \cdot \text{mol}^{-1}$ ]
$\omega$	acentric factor
$\Delta U$	deviation ( $U_{\text{exp}} - U_{\text{cal}}$ )
$\infty$	infinite pressure reference state

### Superscript

<i>E</i>	excess property
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### Subscripts

<i>C</i>	critical property
<i>cal</i>	calculated property
<i>exp</i>	experimental property
<i>ij</i>	molecular species
<i>1</i>	R744 ( $\text{CO}_2$ )
<i>2</i>	R152a

## 2. Experimental section

### 2.1. Chemicals

The R152a was purchased from ARKEMA (France) with 99 vol% certified purity and R744 from Air Liquide (France) with 99.995 vol% certified purity. Both chemicals were used as delivered.

### 2.2. Apparatus

The apparatus used in this work is based on a “static-analytic” method with liquid and vapor phase sampling. This apparatus is similar to that described by Laugier and Richon [9] and used in various studies [2,3].

The equilibrium cell is immersed inside a temperature regulated liquid bath. Temperatures are measured by means of two platinum resistance thermometer probes (Pt100) inserted inside walls of the equilibrium cell. These Pt100 probes are calibrated against a 25  $\Omega$  reference probe (TINSLEY Precision Instrument) certified by the Laboratoire National d'Essais (Paris) following the International Temperature Scale 1990 protocol.

Pressures are measured using a pressure transducer (Druck, type PTX611, range: (0 to 20) MPa). This sensor is calibrated against a dead weight pressure balance (52025 model from Desgranges & Huot).

Temperature and pressure data acquisition are performed with a computer linked to an HP unit (HP34970A). The resulting uncertainties in this work are  $\pm 0.02$  K and  $\pm 0.0004$  MPa.

The analytical work was carried out using a gas chromatograph (Perichrom, France) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system.

The analytical column is Porapak Q model, 80/100 Mesh (1/8 in. silcosteel tube, 4 m length, from Resteck France). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe in the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of analyses, resulting uncertainties on vapor and liquid mole numbers are estimated to be less than  $\pm 2.0\%$ .

### 2.3. Experimental procedure

At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell is first loaded with R152a as

a liquid (about  $5 \text{ cm}^3$ ). Equilibrium temperature is assumed to be reached when the two Pt100 probes (one located at top of equilibrium cell, the other in the bottom) give equivalent temperature values within the experimental uncertainty for at least 10 min. The vapor pressure of R152a (the heavier component) is first recorded at equilibrium temperature. Then R744 (the lighter component) is introduced step by step, leading to successive equilibrium mixtures of increasing overall R744 content. After each new R744 introduction, equilibrium is assumed when the total pressure remains unchanged within  $\pm 1.0$  kPa during a period of 10 min under efficient stirring. For each equilibrium condition, at least five samples of both vapor and liquid phases are withdrawn using the ROL-SI™ pneumatic samplers [10] and analyzed in order to check for measurements repeatability. Each isothermal two-phase envelope contains at least eight Pxy data points (for both liquid and vapor phases).

## 3. Correlations

The critical temperatures ( $T_c$ ) and critical pressures ( $P_c$ ) for each of the two pure components are provided in table 1. Our experimental VLE data are correlated by means of our homemade software TEP-ThermoSoft. We have used the PR EoS [11] with the Mathias–Copeman alpha function (equations (1) and (2)) [12] for accurate representation of the pure component vapor pressures.

$$\alpha(T) = \left[ 1 + c_1 \left( 1 - \sqrt{\frac{T}{T_c}} \right) + c_2 \left( 1 - \sqrt{\frac{T}{T_c}} \right)^2 + c_3 \left( 1 - \sqrt{\frac{T}{T_c}} \right)^3 \right]^2 \quad (1)$$

If  $T > T_c$ ,

$$\alpha(T) = \left[ 1 + c_1 \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (2)$$

**TABLE 1**  
Critical parameters (DDB [22])

Compound	$T_c/\text{K}$	$P_c/\text{MPa}$	$\omega$
R744	304.20	7.377	0.225
R152a	386.35	4.499	0.226

The Wong–Sandler (WS) mixing rules are chosen here [13],

$$b = \frac{\sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij}}{1 - \left( \frac{\sum_i x_i b_i}{RT} + \frac{g^E(T, P = \infty, x_i)}{CRT} \right)}, \quad (3)$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij}, \quad (4)$$

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[ \left( b - \frac{a}{RT} \right)_i + \left( b - \frac{a}{RT} \right)_j \right] (1 - k_{ij}), \quad (5)$$

$k_{ij}$  is an adjustable binary interaction parameter.

The excess Gibbs free energy model chosen is the NRTL [14] local composition model.

$$\frac{g^E(T, P, x_i)}{RT} = \sum_i x_i \sum_j \frac{x_j \exp(-\alpha_{ji} \frac{\tau_{ji}}{RT})}{\sum_k x_k \exp(-\alpha_{ki} \frac{\tau_{ki}}{RT})} \tau_{ji}, \quad (6)$$

where  $\tau_{ii} = 0$  and  $\alpha_{ii} = 0$ .

$\alpha_{ji}$ ,  $\tau_{ji}$  and  $\tau_{ij}$  are adjustable parameters. It is recommended [14] to use  $\alpha_{ji} = \alpha_{ij} = 0.3$  for systems similar to this one.

$\tau_{ji}$  and  $\tau_{ij}$  are adjusted directly onto VLE data through a modified Simplex algorithm [15] using the following objective function:

$$F = \frac{100}{N} \left[ \sum_1^N \left( \frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}} \right)^2 + \sum_1^N \left( \frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}} \right)^2 \right], \quad (7)$$

where  $N$  is the number of data points,  $x_{\text{exp}}$  and  $x_{\text{cal}}$  are, respectively, the measured and calculated liquid phase mole fractions,  $y_{\text{exp}}$  and  $y_{\text{cal}}$  are, respectively, the measured and calculated vapor phase mole fractions.

## 4. Results and discussion

### 4.1. Vapor pressure data

R152a vapor pressures were measured at 20 temperatures from (253 to 348) K and used to adjust Mathias–Copeman parameters (see table 2). Experimental and calculated vapor pressures values are reported in table 3. The absolute relative deviation observed is less than 0.10% for R152a. Concerning the R744, the Mathias–Copeman parameters are taken from reference [16] (see table 2).

### 4.2. (Vapor + liquid) equilibrium data for (R744 + R152a)

The experimental and calculated VLE data are reported in table 4 and plotted in figure 1. The adjusted parameters corresponding to the WS mixing rules involving the NRTL model, associated to the PR EoS, are given in table 5, and plotted in figures 2 and 3.

We have chosen to fit binary interaction parameter for each temperature because measurements were done for  $T < T_{C\text{CO}_2}$  and  $T > T_{C\text{CO}_2}$ . There is a discontinuity of binary interaction parameters at  $T = T_{C\text{CO}_2}$  [4,8].

The deviations, MRDUs, and BIASUs, applied on liquid and vapor phase mole fractions, are defined by

$$\text{MRDU} = (100/N) \sum | (U_{\text{cal}} - U_{\text{exp}}) / U_{\text{exp}} |, \quad (8)$$

$$\text{BIASU} = (100/N) \sum ((U_{\text{exp}} - U_{\text{cal}}) / U_{\text{exp}}), \quad (9)$$

where  $N$  is the number of data points, and  $U = x_1$  or  $y_1$ .

**TABLE 2**  
Mathias–Copeman coefficients used

Coefficients	R152a	R744 [16]
$c_1$	0.82549	0.704606
$c_2$	-0.74729	-0.314862
$c_3$	3.44620	1.89083

**TABLE 3**  
Experimental and calculated vapor pressures for R152a

T/K	$P_{\text{exp}}/\text{MPa}$	$P_{\text{cal}}/\text{MPa}$	$\Delta P/\text{MPa}$
253.6 <sub>8</sub>	0.115 <sub>2</sub>	0.1153	-0.0001
258.4 <sub>4</sub>	0.142 <sub>2</sub>	0.1422	0.0000
263.3 <sub>9</sub>	0.174 <sub>9</sub>	0.1750	-0.0001
268.3 <sub>2</sub>	0.213 <sub>7</sub>	0.2131	0.0006
273.2 <sub>3</sub>	0.256 <sub>8</sub>	0.2569	-0.0001
278.1 <sub>9</sub>	0.308 <sub>1</sub>	0.3077	0.0004
283.3 <sub>1</sub>	0.368 <sub>5</sub>	0.3676	0.0008
288.2 <sub>7</sub>	0.432 <sub>9</sub>	0.4335	-0.0006
293.2 <sub>3</sub>	0.506 <sub>8</sub>	0.5078	-0.0010
298.1 <sub>7</sub>	0.590 <sub>3</sub>	0.5907	-0.0004
303.3 <sub>7</sub>	0.687 <sub>6</sub>	0.6884	-0.0009
308.3 <sub>1</sub>	0.791 <sub>0</sub>	0.7918	-0.0008
313.1 <sub>9</sub>	0.904 <sub>5</sub>	0.9049	-0.0003
318.2 <sub>5</sub>	1.034 <sub>8</sub>	1.0342	0.0006
323.2 <sub>6</sub>	1.175 <sub>4</sub>	1.1754	0.0000
328.1 <sub>2</sub>	1.326 <sub>8</sub>	1.3255	0.0013
333.3 <sub>1</sub>	1.502 <sub>3</sub>	1.5012	0.0011
338.1 <sub>9</sub>	1.683 <sub>5</sub>	1.6818	0.0017
343.1 <sub>0</sub>	1.879 <sub>6</sub>	1.8795	0.0001
348.2 <sub>6</sub>	2.104 <sub>6</sub>	2.1058	-0.0012

These indicators, which give information about the agreement between model and experimental results, are presented in table 6. We have also found a discontinuity of binary interaction parameters around the critical temperature of  $\text{CO}_2$ .

### 4.3. Comparison with literature data

We have found VLE data of (R744 + R152a) binary system, using probably other measurement techniques, in the Dortmund database (reference [17]) initial source being a thesis dissertation. The study has been achieved at (318.20, 333.00, and 347.70) K. Parameters of our model have been adjusted on the data of reference [17]. From table 6 we note that MRD (defined in equation (8)) and BIAS (defined in equation (9)) are very high. Moreover, the model based on our parameters does not well represent the data of reference [17] particularly around the critical point region. We have no information about the experimental techniques used in reference [17]. Data from reference [17] were never published elsewhere in good journals, maybe because they were not considered as sufficiently reliable as observed herein.

### 4.4. Critical line computation

The method proposed by Heidemann and Khalil [18] for these purposes is a direct method allowing calculation of critical points of multicomponent mixtures. Heidemann and Khalil started with Gibbs' condition [19] for thermodynamic stability as critical point is a limit of stability. Heidemann and Khalil [19] have correlated Helmholtz energy instead of Gibbs free energy.

They developed an algorithm to calculate the critical point with a van der Waals type EoS, combined with the classical mixing rules. In 1998, Stockfleth and Dohrn [20] improved this method by generalizing the previous algorithm to a generalized equation of state. This last method is chosen in this work to calculate the critical line using the PR EoS with WS mixing rules involving the NRTL model. The temperature dependent binary parameters are those obtained by fitting VLE data in the R744 supercritical domain. Figure 5 gives the calculated shape of the critical locus line (type I according to van Konynenburg and Scott classification [21]). Determination of accurate mixture critical point value would need direct measurement at the concerned temperature.

Another method was chosen to estimate critical points. It is based on our experimental relative volatility ( $\alpha_{12}$ ) values.

TABLE 4

(Vapor + liquid) equilibrium pressures and phase compositions for {R744 (1) + R152a (2)},  $\Delta x$  and  $\Delta y$  are deviations in liquid and vapor mole fractions

$P_{exp}/\text{MPa}$	$x_{1,exp}$	$x_{1,cal}$	$y_{1,exp}$	$y_{1,cal}$	Deviations	
					$\Delta x$	$\Delta y$
$T = 258.4_4/\text{K}$						
0.144 <sub>0</sub>	0.0000	0.0000	0.0000	0.0000		
0.392 <sub>6</sub>	0.1241	0.1309	0.6264	0.6622	-0.0068	-0.0358
0.588 <sub>7</sub>	0.2249	0.2272	0.7794	0.7888	-0.0023	-0.0094
0.860 <sub>5</sub>	0.3586	0.3553	0.8658	0.8699	0.0033	-0.0041
1.102 <sub>2</sub>	0.4748	0.4671	0.9105	0.9095	0.0077	0.0011
1.336 <sub>3</sub>	0.5860	0.5752	0.9378	0.9352	0.0108	0.0026
1.506 <sub>8</sub>	0.6603	0.6540	0.9516	0.9498	0.0063	0.0018
1.780 <sub>6</sub>	0.7793	0.7793	0.9690	0.9690	0.0000	0.0000
1.964 <sub>6</sub>	0.8586	0.8604	0.9800	0.9803	-0.0018	-0.0002
2.294 <sub>0</sub>	1.0000	1.0000	1.0000	1.0000		
$T = 278.2_5/\text{K}$						
0.311 <sub>7</sub>	0.0000	0.0000	0.0000	0.0000		
0.762 <sub>8</sub>	0.1424	0.1449	0.6021	0.6166	-0.0025	-0.0145
1.081 <sub>8</sub>	0.2416	0.2424	0.7411	0.7434	-0.0008	-0.0022
1.443 <sub>4</sub>	0.3541	0.3495	0.8209	0.8208	0.0046	0.0001
1.815 <sub>8</sub>	0.4641	0.4568	0.8724	0.8699	0.0073	0.0025
2.416 <sub>9</sub>	0.6298	0.6243	0.9217	0.9201	0.0055	0.0016
2.776 <sub>6</sub>	0.7241	0.7206	0.9423	0.9419	0.0035	0.0004
3.300 <sub>2</sub>	0.8516	0.8526	0.9682	0.9684	-0.0010	-0.0002
3.619 <sub>3</sub>	0.9245	0.9256	0.9829	0.9832	-0.0011	-0.0003
3.977 <sub>0</sub>	1.0000	1.0000	1.0000	1.0000		
$T = 298.8_4/\text{K}$						
0.604 <sub>4</sub>	0.0000	0.0000	0.0000	0.0000		
0.856 <sub>6</sub>	0.0539	0.0540	0.2811	0.2972	-0.0001	-0.0161
1.200 <sub>6</sub>	0.1285	0.1281	0.5036	0.5055	0.0004	-0.0018
1.565 <sub>7</sub>	0.2044	0.2060	0.6306	0.6296	-0.0016	0.0010
2.224 <sub>1</sub>	0.3370	0.3404	0.7570	0.7541	-0.0034	0.0029
2.912 <sub>1</sub>	0.4707	0.4708	0.8291	0.8271	-0.0001	0.0020
3.470 <sub>3</sub>	0.5736	0.5696	0.8673	0.8669	0.0040	0.0004
4.218 <sub>3</sub>	0.6928	0.6940	0.9063	0.9063	-0.0012	0.0000
4.809 <sub>8</sub>	0.7863	0.7860	0.9313	0.9313	0.0003	0.0000
5.269 <sub>1</sub>	0.8537	0.8526	0.9490	0.9490	0.0011	0.0000
5.932 <sub>2</sub>	0.9354	0.9377	0.9741	0.9743	-0.0023	-0.0002
6.502 <sub>6</sub>	1.0000	1.0000	1.0000	1.0000		
$T = 308.3_7/\text{K}$						
0.812 <sub>5</sub>	0.0000	0.0000	0.0000	0.0000		
1.191 <sub>6</sub>	0.0722	0.0715	0.3157	0.3306	0.0007	-0.0149
1.573 <sub>8</sub>	0.1420	0.1417	0.4930	0.4969	0.0003	-0.0039
1.986 <sub>3</sub>	0.2148	0.2166	0.6097	0.6079	-0.0018	0.0019
2.447 <sub>4</sub>	0.2950	0.2972	0.6937	0.6897	-0.0022	0.0040
3.203 <sub>9</sub>	0.4194	0.4207	0.7783	0.7756	-0.0013	0.0027
3.849 <sub>6</sub>	0.5197	0.5185	0.8239	0.8239	0.0012	0.0000
4.517 <sub>8</sub>	0.6201	0.6138	0.8621	0.8609	0.0063	0.0012
5.240 <sub>6</sub>	0.7176	0.7112	0.8922	0.8921	0.0064	0.0001
5.937 <sub>7</sub>	0.7994	0.7996	0.9179	0.9174	-0.0002	0.0005
6.583 <sub>6</sub>	0.8755	0.8748	0.9387	0.9391	0.0007	-0.0004
6.982 <sub>0</sub>	0.9152	0.9165	0.9507	0.9525	-0.0013	-0.0018
7.200 <sub>5</sub>	0.9355	0.9376	0.9594	0.9600	-0.0021	-0.0006
$T = 323.3_0/\text{K}$						
1.185 <sub>5</sub>	0.0000	0.0000	0.0000	0.0000		
1.686 <sub>8</sub>	0.0743	0.0739	0.2788	0.2893	0.0004	-0.0105
2.208 <sub>3</sub>	0.1497	0.1503	0.4515	0.4542	-0.0006	-0.0027
2.554 <sub>5</sub>	0.1999	0.2004	0.5295	0.5285	-0.0005	0.0010
3.222 <sub>0</sub>	0.2908	0.2939	0.6352	0.6293	-0.0031	0.0059
3.750 <sub>0</sub>	0.3615	0.3643	0.6909	0.6850	-0.0028	0.0059
4.435 <sub>0</sub>	0.4516	0.4508	0.7417	0.7386	0.0008	0.0031
5.133 <sub>7</sub>	0.5398	0.5342	0.7808	0.7794	0.0056	0.0014
6.022 <sub>1</sub>	0.6320	0.6342	0.8206	0.8183	-0.0022	0.0023
6.933 <sub>5</sub>	0.7319	0.7316	0.8482	0.8480	0.0003	0.0002
7.361 <sub>4</sub>	0.7760	0.7764	0.8546	0.8586	-0.0004	-0.0040
7.648 <sub>2</sub>	0.8088	0.8068	0.8522	0.8638	0.0020	-0.0116
$T = 343.2_0/\text{K}$						
1.891 <sub>7</sub>	0.0000	0.0000	0.0000	0.0000		
2.604 <sub>8</sub>	0.0826	0.0836	0.2400	0.2493	-0.0010	-0.0093
3.313 <sub>8</sub>	0.1628	0.1633	0.3915	0.3947	-0.0005	-0.0032
3.936 <sub>5</sub>	0.2310	0.2312	0.4847	0.4811	-0.0002	0.0036
4.695 <sub>8</sub>	0.3117	0.3117	0.5657	0.5560	0.0000	0.0097
5.220 <sub>2</sub>	0.3651	0.3660	0.6012	0.5948	-0.0009	0.0064
6.029 <sub>8</sub>	0.4491	0.4484	0.6467	0.6401	0.0007	0.0066

TABLE 4 (continued)

$P_{exp}/\text{MPa}$	$x_{1,exp}$	$x_{1,cal}$	$y_{1,exp}$	$y_{1,cal}$	Deviations	
					$\Delta x$	$\Delta y$
6.545 <sub>9</sub>	0.5001	0.5006	0.6640	0.6615	-0.0005	0.0025
7.166 <sub>3</sub>	0.5650	0.5650	0.6794	0.6794	0.0000	0.0000
7.411 <sub>7</sub>	0.5941	0.5921	0.6710	0.6833	0.0020	-0.0123

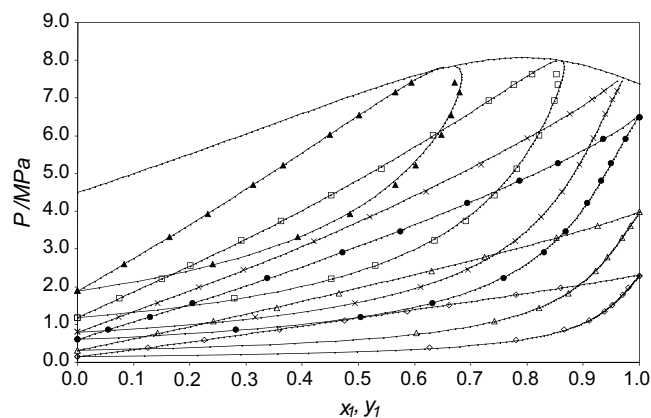


FIGURE 1. VLE of {R744 (1) + R152a (2)} system at different temperatures:  $\diamond$ , 258.4 K;  $\triangle$ , 278.2 K;  $\bullet$ , 298.8 K;  $\times$ , 308.4 K;  $\square$ , 323.3 K;  $\blacktriangle$ , 343.2 K. ---, Predicted mixture critical line. —, Solid lines: phase envelopes calculated with PR EoS, Wong-Sandler mixing rules and NRTL activity coefficient model with parameters from table 5.

TABLE 5

Values of the binary parameters at each temperature

Data	$T/\text{K}$	$\tau_{12}/(\text{J} \cdot \text{mol}^{-1})$	$\tau_{21}/(\text{J} \cdot \text{mol}^{-1})$	$k_{12}$
This work	258.44	4898	-2003	0.121
	278.25	2448	-1463	0.216
	298.84	-2211	3343	0.249
	308.37	-2682	4214	0.264
	323.30	-2525	3946	0.262
	343.20	627	-152	0.273
[17]	318.20	4099	-2791	0.243
	333.00	1696	-1407	0.195
	347.70	886	-929	0.224

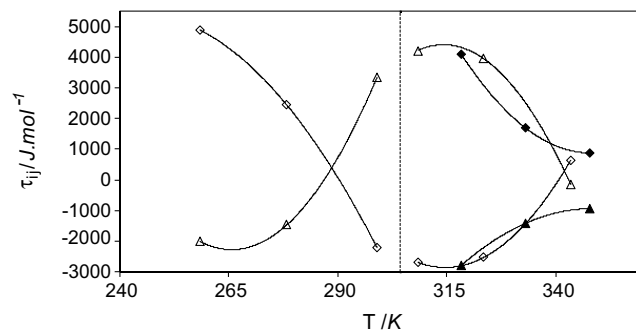
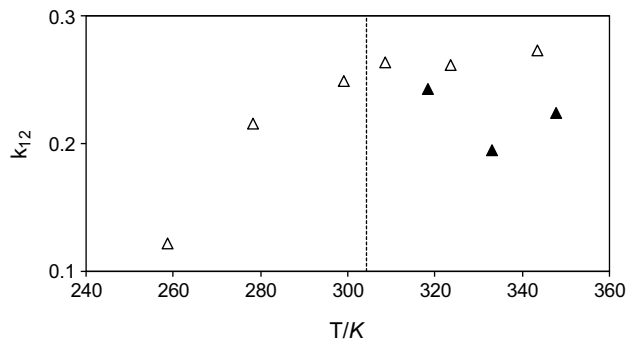
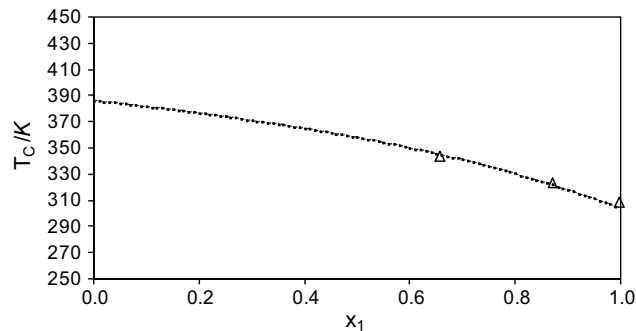


FIGURE 2.  $\tau_{12}$  ( $\diamond$ ) and  $\tau_{21}$  ( $\triangle$ ) binary parameters as a function of temperature. Black symbols: parameters determined from [17]. Solid line: tendency curve. Vertical dotted line represents the R744 critical temperature.

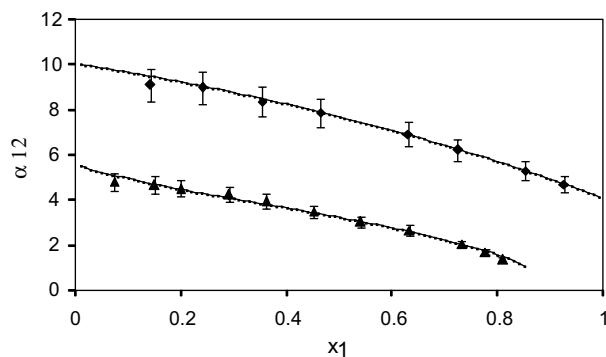
Calculated critical points from this method appear in figure 6, along with critical line calculated with Heidemann and Khalil method. Good agreement is observed.



**FIGURE 3.**  $k_{12}$  binary parameter as a function of temperature. Black symbols: parameters determined from [17]. Vertical dotted line represents the R744 critical temperature.



**FIGURE 6.** Plot of critical temperature as a function of  $\text{CO}_2$  mole fraction, calculated through relative volatility model. Dotted: calculated value using Heidemann and Khalil method.



**FIGURE 4.** Relative volatility as a function of  $\text{CO}_2$  mole fraction at (278.25 and 323.30) K. Error band is 8%.

## 5. Conclusion

In this paper, VLE data are presented at six temperatures for the (R744 + R152a) system. They were obtained using a “static-analytic” method. The experimental results are given with following uncertainties:  $\pm 0.015$  K,  $\pm 0.0004$  MPa, and  $\pm 2.0\%$  for vapor and liquid mole numbers.

The data are well correlated using our in-house (ThermoSoft) thermodynamic model based on the Peng–Robinson equation of state, the Mathias–Copeman alpha function, the Wong–Sandler mixing rules, and the NRTL model. Critical conditions have also been reported for the system under study. Mixture critical point line is calculated using our model. This system can be classified as a diagram of type I according to van Konynenburg and Scott classification [21]. The relative volatility plotted against mole fraction is presented in figure 4. The corresponding uncertainties are estimated to be below 8%.

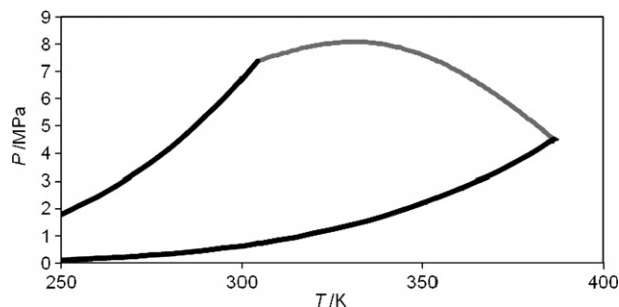
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**TABLE 6**

Relative deviation MRDU and BIASU obtained in fitting experimental VLE data with PR EoS, Mathias–Copeman alpha function and WS mixing rules involving NRTL model

Data	T/K	Bias x/%	MRD x/%	Bias y/%	MRD y/%
This work	258.44	−1.24	1.51	−0.86	1.00
	278.25	0.24	0.82	−0.28	0.41
	298.84	−0.12	0.36	−0.53	0.69
	308.37	0.09	0.47	−0.36	0.58
	323.30	−0.08	0.45	0.30	0.82
	343.20	−0.17	0.28	−0.18	1.07
[17]	318.20	1.17	2.95	−0.91	1.18
	333.00	0.47	2.48	−0.29	1.06
	347.70	−0.31	1.24	−0.20	1.39



**FIGURE 5.** PT diagram of the (R744 + R152a) binary system. Bold black solid line: R744 and R152a pure component vapor pressures. Grey line: mixture critical point locus.