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Isochoric *PVTx* measurements for carbon dioxide + 1,1-difluoroethane binary system

Giovanni Di Nicola, Fabio Polonara, Giulio Santori

Dipartimento di Energetica, Università Politecnica delle Marche, Via Brecce Bianche, 60100, Ancona, Italy

Roman Stryjek

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

Abstract

PVTx measurements for carbon dioxide (CO_2, R744) + 1,1-difluoroethane (CH_3CHF_2, R152a) for both the two-phase and the superheated vapor regions are presented. The measurements were taken with a constant volume apparatus at temperatures ranging from (223 to 343) K and pressures from (60 to 3890) kPa along 8 isochores. The data obtained in the two-phase region were used to derive VLE parameters using a flash method with the Carnahan-Starling-De Santis equation of state (CSD EOS). The dew point was also found for each isochore from the intersection of the *P*-*T* sequences. Results from the superheated region were compared both with the predicted from the CSD EOS. The complete set of data was also compared with the REFPROP 7.0 prediction.

Introduction

Low-temperature refrigeration applications, i.e. cascade cycles operating with two different working fluids,[1] are a very interesting field for the food industry. The validity of the cascade cycle has recently been extended to temperatures between 243 K and 233 K by using carbon dioxide as the low-stage refrigerant. Due to its triple-point temperature of 216.58 K, carbon dioxide is no longer a feasible solution for vapor compression cycles intended for use at lower temperatures. An obvious solution to overcome this drawback could be a blend containing carbon dioxide. For this reason, recently, our attention turned to systems composed of hydrofluorocarbons (HFCs) in mixtures with CO_2.

In previous studies, the *P,V,T,x* properties of the CO_2+R41, CO_2+R116, CO_2+R125, CO_2+R32, CO_2+R23 systems were measured by an isochoric method,[2-4] Burnett method[5-9] and solid-liquid equilibrium apparatus.[10-11] In this paper, the *PVTx* properties of the CO_2+R152a binary system are studied with a constant volume apparatus.

R152a is an important hydrofluorocarbon used as refrigerant, blowing agent, aerosol propellant and cleaning agent. The combination of CO_2 and R152a provides important information for future applications. To our knowledge no experimental results have been published in the open literature on the *PVTx* properties of this specific binary system. Isochoric measurements were consequently taken, covering temperatures from (223 to 343) K, to make up for the lack of VLE and *PVTx* data. VLE parameters were derived from data in the two-phase region, applying the CSD EOS.[12] Data obtained from the superheated region were also compared with the predictions obtained with the CSD EOS.

Experimental section

Chemicals. Carbon dioxide and 1,1-difluoroethane were supplied by Sol SpA and Union Carbide, respectively. Their purity was checked by gas chromatography, using a thermal conductivity detector, and found to be 99.99 % and 99.94 %, respectively, basing all estimations on an area response.

Apparatus. The set-up has already been described elsewhere,[13] so it is only briefly outlined here. The main changes made to the original apparatus[13,14] concerned the twin thermostatic baths filled with different silicone oils (Baysilone M10 and Baysilone M100, Bayer). After charging with the sample mixture, the set-up could be operated over two temperature ranges, approximately from (210 to 290) K and from (290 to 360) K, depending on which bath was used.

The thermostatic baths were easy to move thanks to the new system configuration. The spherical cells and pressure transducer were immersed in one of the two thermostatic baths. An auxiliary thermostat was used to reach below-ambient temperatures. The cell volume was estimated (as explained elsewhere[13]) to be (273.5 ±0.3) cm^3 at room temperature.

The pressure and temperature data acquisition systems were identical to those of the previous apparatus.[13,14] A PID device was used to control the temperature, which was measured using a calibrated resistance thermometer; the total uncertainty of the temperature measurements was ±0.02 K. The uncertainty in the pressure measurements stems from the uncertainty of the transducer and null indicator system, and the pressure gauges. The uncertainty of the digital pressure indicator (Ruska, mod. 7000) is ±0.003 % of its full scale (6000 kPa). Temperature fluctuations due to bath instability can also affect the total uncertainty in the pressure measurement, which was nonetheless found to be less than ±1 kPa.

Experimental procedure. Mixtures were prepared using the gravimetric method. First of all, the pure samples were charged in different bottles, degassed to remove non-condensable gases and air, and then weighed with an analytical balance (uncertainty ±0.3 mg). After evacuating the cell, the bottles were then emptied into the cell immersed in the bath. The mixtures were charged in vapour phase. The bottles were weighed again and the mass of the charge was calculated from the difference between the two masses. The dispersion of the mass inside the duct was estimated to be between 0.01 and 0.06 g, depending on the charging temperature, pressure and molar mass of the fluid, and finally subtracted from the total mass of the sample. The uncertainty in mixture preparation was estimated to be constantly lower than 0.001 in mole fraction.

After reaching the experimental temperature, the mixing pump was activated for about fifteen minutes and, next, the mixture was allowed to stabilize for about twenty minutes before the data recording. After having charged each mixture composition, the temperature was increased step by step.

Results and discussion

The temperature and pressure ranges are shown in Table 1, along with the mixture's composition and the number of moles charged.

Based on the analysis of the slope of each *T,P* sequence, the experimental points were each attributed either to the superheated or to the two-phase region. Table 2 shows the experimental data within the VLE boundary, while Table 3 contains the *PVTx* data. The data for the two-phase region were fitted using the Antoine equation, while those relating to the superheated region were fitted by a second-degree polynomial, taking temperature as the independent variable. Then the solution of the two equations representing the system's behavior in the two-phase and superheated regions was used to find the dew point temperature and pressure algebraically for each isochore. The uncertainty of temperature and pressure of the dew points arising from the error distribution of the data correlated with the Antoine and polynomial equations were estimated to be of the order of ±0.4 K and ±2 kPa, respectively. The example of the dew point estimation method based on the slope discontinuity is reported in Figure 1. The solutions are given in Table 1.

VLE derivation. The method used to derive VLE data from the isochoric measurements using the CSD EOS was described elsewhere.[15] This EOS was chosen amongst two-parameters EOSs, because its parameters are fitted to pressures and molar volumes along the saturation curve. For this reason it is able to accurately represent saturation pressures, volumetric properties along saturation and the vapor phase at superheated region.

The method involves deriving the VLE parameters for each data point in the two-phase region using the "flash method" with the CSD EOS. For this method to be applied to isochoric data, we also need the volumetric properties of the two phase region. The volumetric properties could be taken either from the EOS involved (assuming that it holds true for the representation over the entire range of the parameters) or from independent sources. Here, it was assumed that the CSD EOS holds true with the necessary accuracy over the entire range of the parameters.

T, z_i and n (number of moles charged) were kept constant during the correlation having the isochoric cell volume from the gravimetric calibration, the objective function:

$$Q = \sum_i \left(\frac{dP}{P} \right)^2 \qquad (1)$$

was minimized tuning the K_{12} value. The correlation gives also the parameters of VLE (pressure, and composition of both phases) at the bubble and dew point (not reported in tables) which were considered, obviously, as dependent variables. Figure 2 shows the scatter diagram of the relative pressure deviations which are almost temperature-independent. The pressure deviations were found to be within ±2 % for all series except few points. The same trend of results was obtained comparing the experimental data together with the REFPROP 7.0 prediction, as shown in Figure 3. The obtained binary interaction parameters are reported in Table 1 together with the ones obtained by the dew point intersection method.[15] The average of the values are $K_{12} = -0.020$ and $K_{12dew} = -0.051$, both with a statistical uncertainty of ±0.005. Using the averaged K_{12} value from our measurements obtained with the flash method in the two-phase region data, we calculated the VLE at three different temperatures (T=223.15 K, T=248.15 K and T=273.15 K). The results are given in Figure 4. The CO_2+R152a system reveals almost ideal behavior in terms of Raoult's law.

PVTx. Since there are no published data on the superheated vapor region for the binary systems considered, density at superheated region were also compared with the CSD EOS prediction. In this case, the coefficients of the CSD EOS fitted to data along the saturation line were extrapolated out of the range where they were fitted and, also, the K_{12} value, tuned to the low temperature two-phase data, was assumed to be temperature independent. The AAD (V) = 1.74 % was obtained, while slightly better results were achieved comparing the experimental findings with the REFPROP 7.0 prediction,[16] obtaining an AAD (V) = 1.02 %.

Conclusions

An isochoric apparatus has been used to obtain *PVTx* measurements on CO_2 + R152a. The binary interaction parameters were derived from experimental data in the two-phase region, applying the flash method and the Carnahan-Starling-De Santis equation of state. The dew point parameters were found by interpolating the *P-T* isochoric sequences. The calculated binary interaction parameter were used to derive the VLE, which revealed an almost ideal behavior in terms of Raoult's law. The *PVTx* data were compared by the CSD EOS and by REFPROP 7.0 prediction.

Acknowledgement

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Figure captions

Figure 1. Experimental *P*-*T* data and calculated dew points (▲): ○, z_1=0.117; □, z_1=0.250; △, z_1=0.389; ▽, z_1=0.503; ◇, z_1=0.631; ●, z_1=0.658; ■, z_1=0.731; ▼, z_1=0.873.

Figure 2. Pressure deviations between experimental values and those calculated with the K_{12} coefficients for the CO_2 (1) + R152a (2) system. Symbols denoted as in Figure 1.

Figure 3. Pressure deviations between experimental values and those calculated with the REFPROP 7.0 for the CO_2 (1) + R152a (2) system. Symbols denoted as in Figure 1.

Figure 4. VLE representation from the CSD EOS for the CO_2 (1) + R152a (2) system at three temperatures: ---, T = 223.15 K; ···, T = 248.15 K; ——, T = 273.15 K.

Table 1. Measurements at bulk compositions z_1 and masses m_1 and m_2 for the CO_2 (1) + R152a (2) system over the temperature range ΔT, and pressure range ΔP, with resultant dew temperatures, T_d, dew pressures, P_d, and binary interaction parameters K_{12} and K_{12dew}.

z_1	ΔT / K	ΔP / kPa	N / mol	m_1 / g	m_2 / g	T_d / K	P_d / kPa	K_{12}	K_{12dew}
0.117	223-343	60-689	0.0721	0.371	4.206	293.4	565	-0.023	-0.097
0.250	223-343	99-700	0.0728	0.802	3.615	288.4	566	-0.023	0.001
0.389	223-343	157-850	0.0889	1.519	3.587	289.5	690	-0.028	-0.121
0.503	223-343	232-1136	0.1193	2.642	3.923	291.8	926	-0.022	-0.057
0.631	223-343	332-1545	0.1668	4.066	4.629	290.9	1279	-0.027	-0.036
0.658	223-343	356-1580	0.1678	4.864	3.794	291.8	1281	-0.016	-0.047
0.731	223-343	428-1936	0.2072	6.661	3.686	291.1	1560	-0.011	-0.030
0.873	223-343	578-3890	0.4599	17.661	3.868	291.4	2996	-0.008	-0.018
							Avg.	-0.020	-0.051

Table 2. Experimental molar volumes V as a function of pressure P and temperature T at overall composition z_1 in the two phase region for the CO_2 (1) + R152a (2) system

T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$	T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$
z_1=0.117			z_1=0.389		
223.09	60	3.783	223.11	157	3.071
228.04	72	3.784	228.06	179	3.071
232.98	85	3.785	233.00	203	3.072
237.92	101	3.786	237.93	228	3.073
242.88	120	3.786	242.89	256	3.073
247.89	143	3.787	247.90	286	3.074
252.93	169	3.788	252.94	320	3.075
257.97	199	3.789	257.98	358	3.075
263.03	234	3.790	263.05	400	3.076
268.10	275	3.791	268.11	447	3.077
272.96	320	3.791	273.10	499	3.077
277.98	373	3.792	278.03	557	3.078
283.00	433	3.793	283.01	622	3.079
287.97	500	3.794	287.99	663	3.079
z_1=0.250			z_1=0.503		
223.11	99	3.739	223.12	232	2.284
228.05	114	3.740	228.06	265	2.285
232.99	132	3.741	233.00	299	2.285
237.92	151	3.742	237.94	334	2.286
242.87	173	3.743	242.90	372	2.286
247.89	199	3.744	247.93	412	2.287
252.93	228	3.744	252.96	455	2.287
257.98	261	3.745	258.00	501	2.288
263.04	299	3.746	263.05	551	2.288
268.11	342	3.747	268.12	606	2.289
273.10	390	3.748	273.11	665	2.289
278.02	445	3.748	278.03	729	2.290
283.00	506	3.749	283.01	800	2.290
288.00	563	3.750	288.00	879	2.291

Table 2. (continued)

T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$	T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$
z_1=0.631			z_1=0.731		
223.13	332	1.636	223.11	428	1.317
228.07	382	1.636	228.05	499	1.317
233.03	433	1.637	232.99	574	1.317
237.96	486	1.637	237.92	650	1.318
242.91	540	1.637	242.88	727	1.318
247.92	597	1.638	247.89	806	1.318
253.01	661	1.638	252.93	887	1.318
258.03	721	1.638	257.98	968	1.319
263.07	785	1.639	263.05	1050	1.319
268.11	854	1.639	268.12	1135	1.319
273.11	927	1.639	273.11	1222	1.320
277.94	1001	1.640	278.03	1312	1.320
282.98	1085	1.640	283.01	1408	1.320
287.96	1174	1.641	287.99	1509	1.320
z_1=0.658			z_1=0.873		
223.10	356	1.624	223.11	578	0.593
228.04	411	1.625	228.05	695	0.593
232.98	467	1.625	233.00	829	0.593
237.92	524	1.625	237.94	976	0.594
242.88	583	1.626	242.90	1137	0.594
247.89	643	1.626	247.93	1311	0.594
252.93	705	1.627	252.95	1493	0.594
257.97	769	1.627	258.00	1689	0.594
263.04	836	1.627	263.06	1883	0.594
268.12	907	1.628	268.11	2077	0.594
273.11	982	1.628	273.10	2266	0.594
278.02	1060	1.628	277.98	2451	0.595
283.02	1144	1.629	283.01	2637	0.595
288.00	1234	1.629	287.97	2818	0.595

Table 3. Experimental molar volumes V as a function of pressure P and temperature T at composition z_1 in the superheated vapor region for the CO_2 (1) + R152a (2) system

T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$	T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$
z_1=0.117			z_1=0.503		
292.99	562	3.795	293.09	930	2.291
298.08	576	3.796	298.07	952	2.292
303.06	589	3.796	303.05	973	2.292
308.03	602	3.797	308.04	994	2.293
313.02	615	3.798	313.03	1015	2.293
318.01	627	3.799	318.01	1035	2.294
323.00	640	3.800	323.00	1056	2.294
327.98	652	3.801	327.98	1076	2.295
332.97	664	3.801	332.97	1096	2.295
337.96	677	3.802	337.95	1116	2.296
342.95	689	3.803	342.94	1136	2.296
z_1=0.250			z_1=0.631		
293.09	577	3.751	293.10	1257	1.641
298.07	590	3.752	298.09	1287	1.641
303.05	602	3.753	303.07	1317	1.642
308.04	615	3.753	308.05	1346	1.642
313.03	627	3.754	313.04	1375	1.642
318.02	640	3.755	318.03	1404	1.643
323.00	652	3.756	323.01	1433	1.643
327.99	664	3.757	328.00	1461	1.643
332.98	676	3.758	332.98	1489	1.644
337.96	688	3.758	337.97	1517	1.644
342.95	700	3.759	342.96	1545	1.645
z_1=0.389			z_1=0.658		
293.09	699	3.080	293.09	1290	1.629
298.07	715	3.081	298.08	1320	1.630
303.06	731	3.081	303.06	1350	1.630
308.04	746	3.082	308.04	1380	1.630
313.03	761	3.083	313.03	1409	1.631
318.01	776	3.084	318.01	1438	1.631
323.00	791	3.084	323.00	1467	1.632
327.99	806	3.085	327.99	1496	1.632
332.97	820	3.086	332.97	1524	1.632
337.95	835	3.086	337.96	1553	1.633
342.94	850	3.087	342.94	1580	1.633

Table 3. (continued)

T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$	T / K	P / kPa	V / $dm^3 \cdot mol^{-1}$
z_1=0.731			z_1=0.873		
293.09	1572	1.321	293.08	3005	0.595
298.07	1610	1.321	298.07	3114	0.595
303.06	1648	1.321	303.04	3203	0.595
308.05	1685	1.322	308.03	3292	0.595
313.03	1722	1.322	313.02	3380	0.595
318.02	1758	1.322	318.00	3467	0.596
323.00	1794	1.322	323.00	3554	0.596
327.98	1830	1.323	327.97	3638	0.596
332.97	1866	1.323	332.96	3723	0.596
337.96	1901	1.323	337.94	3807	0.596
342.94	1936	1.324	342.93	3890	0.596

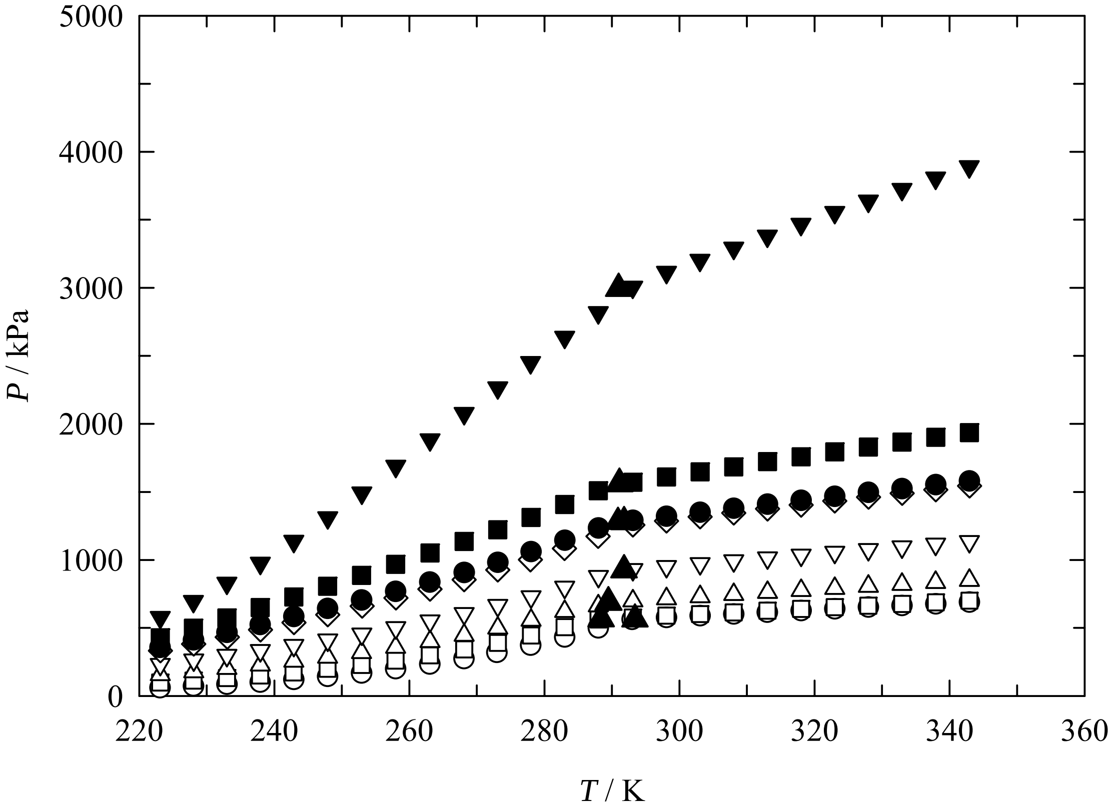

Figure 1. Experimental *P*-*T* data and calculated dew points (▲): ○, z_1=0.117; □, z_1=0.250; △, z_1=0.389; ▽, z_1=0.503; ◇, z_1=0.631; ●, z_1=0.658; ■, z_1=0.731; ▼, z_1=0.873.

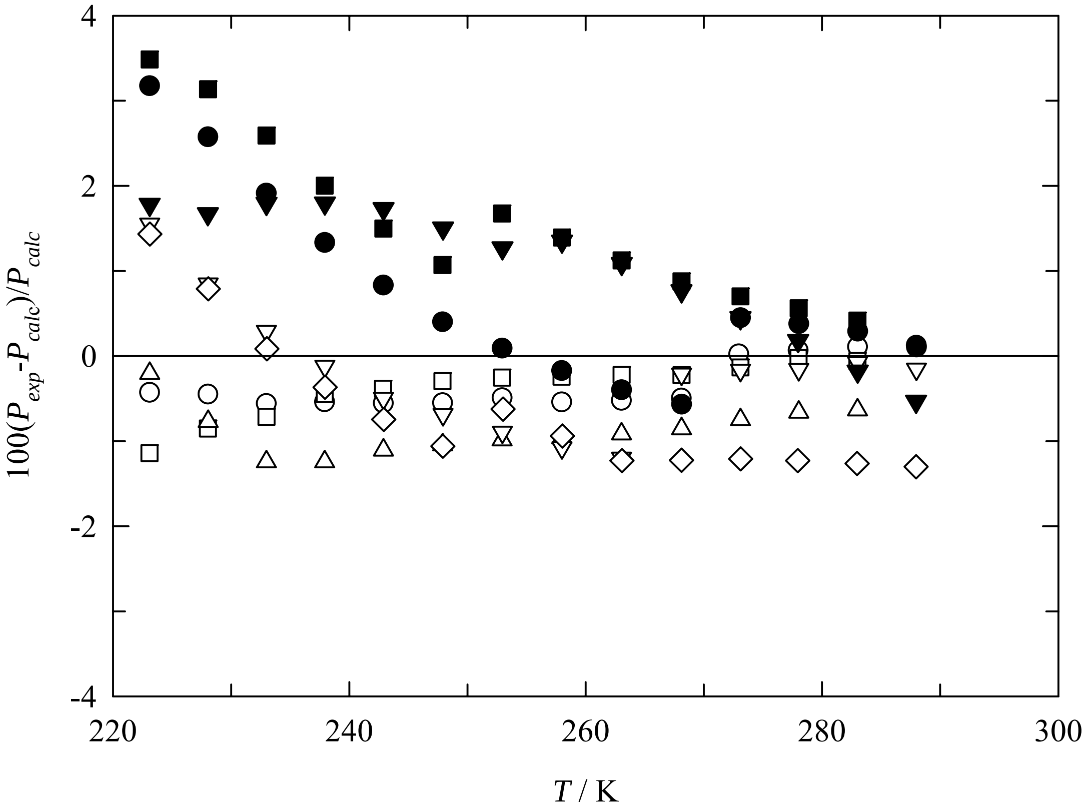

Figure 2. Pressure deviations between experimental values and those calculated with the K_{12} coefficients for the CO_2 (1) + R152a (2) system. Symbols denoted as in Figure 1.

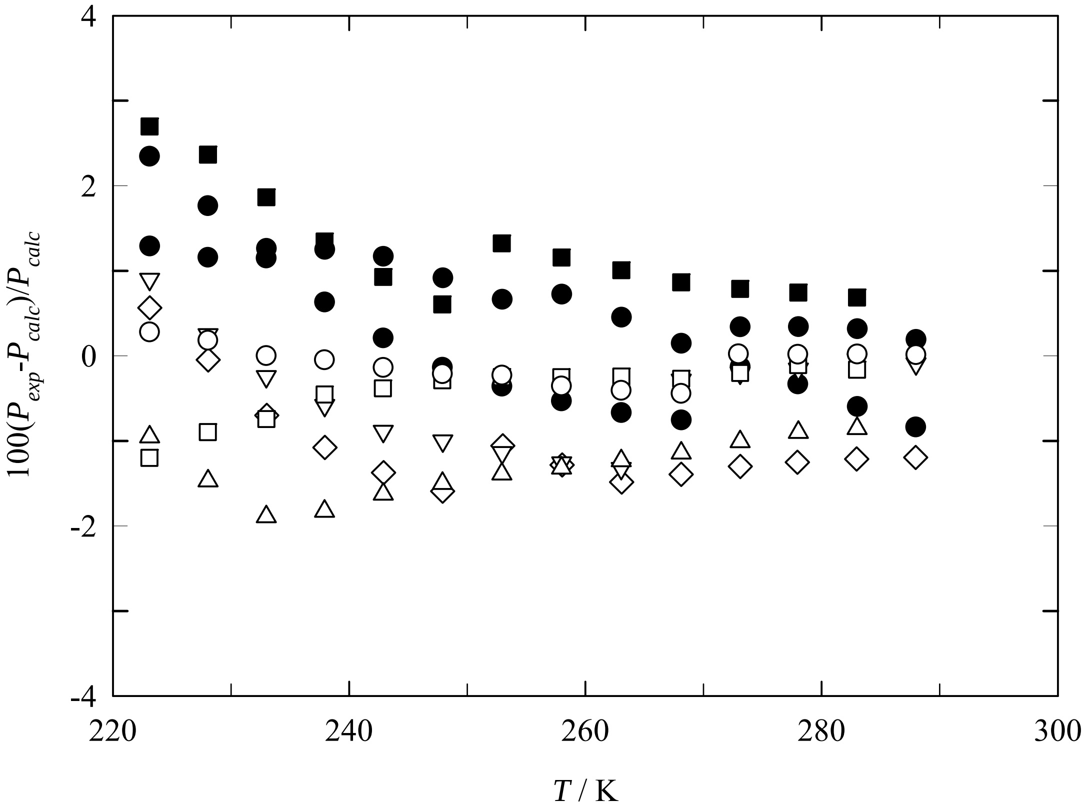

Figure 3. Pressure deviations between experimental values and those calculated with the REFPROP 7.0 for the CO_2 (1) + R152a (2) system. Symbols denoted as in Figure 1.

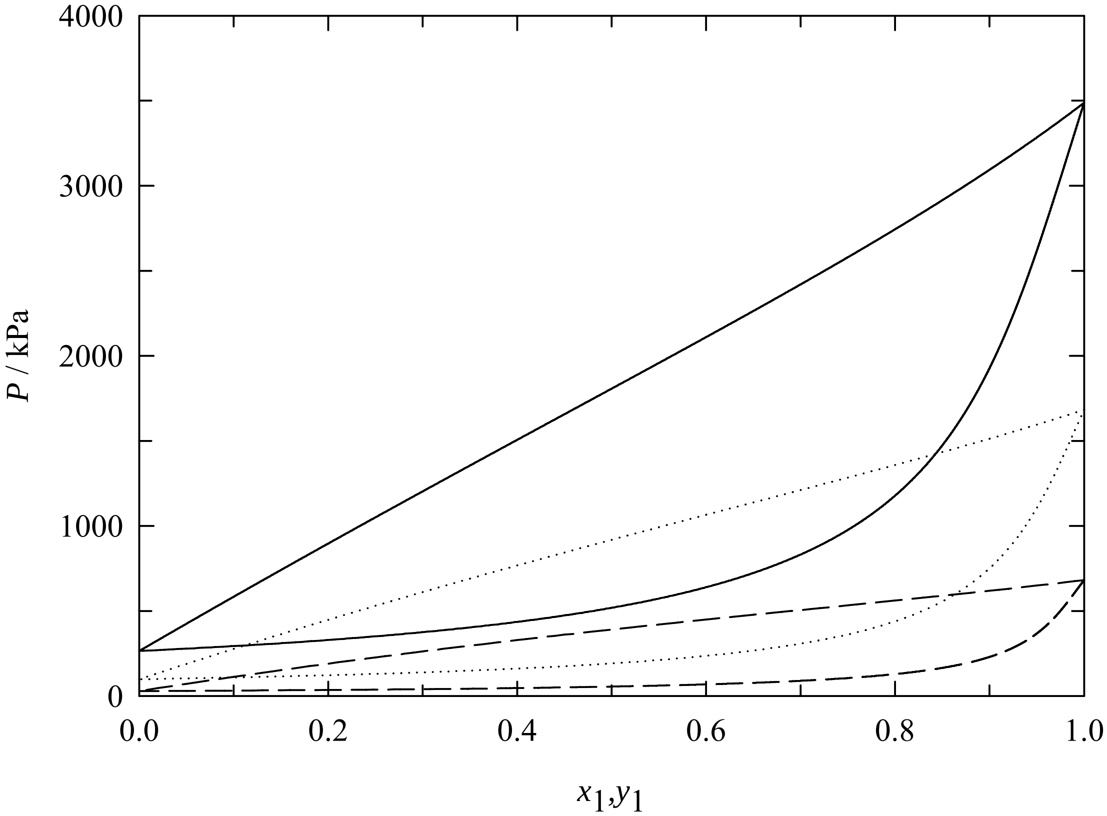

Figure 4. VLE representation from the CSD EOS for the CO_2 (1) + R152a (2) system at three temperatures: ---, T = 223.15 K; ···, T = 248.15 K; ——, T = 273.15 K.