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Two-Phase and Vapor Phase *PvTx* Properties of the Difluoromethane + *cis*-1,3,3,3-Tetrafluoroprop-1-ene Binary System

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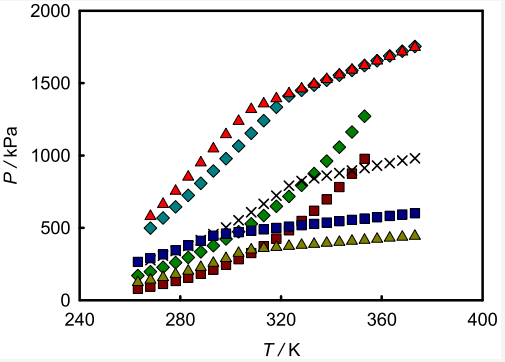
ABSTRACT: This paper provides 84 two-phase and 66 vapor phase *PvTx* measurements for binary blends comprising difluoromethane (R32) and *cis*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(*Z*)). The data are for seven isochores (0.013352, 0.016365, 0.023746, 0.026769, 0.035001, 0.070089, 0.071713) $m^3 \cdot kg^{-1}$ for the temperature range from (263 to 373) K for seven R32 mole fractions (0.0871, 0.2980, 0.3620, 0.5232, 0.7128, 0.8015, 0.8973). The flash method coupled with the Peng−Robinson equation of state and a two-parameter cubic equation of state proposed by Stryjek was used to derive the vapor−liquid equilibrium of the R32 (1) + R1234ze(Z) (2) binary pair from the two-phase measurements. The measured properties in the superheated vapor region were correlated through the aforementioned equations of state and a truncated virial equation of state. The *PvTx* data display good agreement with both the values calculated from the equations of state and from REFPROP 10.0 predictions.



INTRODUCTION

Many hydrofluorocarbon (HFC) refrigerants are potent greenhouse gases with increasingly stringent restrictions being placed on their productions and uses.[1,2] As a result, the heating, ventilating, air conditioning, and refrigeration (HVAC&R) industry is increasingly being forced to actively seek low global warming potential (GWP) alternatives to more conventional HFC working fluids.

McLinden et al.[3,4] recently conducted exhaustive searches and analyses of a publicly available database containing more than 60 million chemical substances for possible applications as low GWP working fluids in HVAC&R applications. They showed that only a small number of single-component working fluids possess the right combination of environmental (e.g., low GWP and essentially no ozone depletion potential), safety (e.g., flammability and toxicity), and performance (e.g., energy efficiency and appropriate volumetric cooling (or heating) capacity) characteristics for many HVAC&R applications. All is not lost, however, as one way to overcome this limited pool of single-component options is to blend them in order to optimize the desired characteristics of the blended working fluid for the application of interest.

The authors have previously reported vapor phase *PvTx* data for 12 binary blends of low GWP refrigerants: (1) nitrogen + *trans*-1,3,3,3-tetrafluoroprop-1-ene,[5] (2) methane + *trans*-1,3,3,3-tetrafluoroprop-1-ene,[5] (3) propane + 2,3,3,3-tetrafluoroprop-1-ene,[6] (4) propane + *cis*-1,2,3,3,3-pentafluoroprop-1-ene,[6] (5) isobutane + 2,3,3,3-tetrafluoroprop-1-ene,[7] (6) isobutane + *trans*-1,3,3,3-tetrafluoroprop-1-ene,[7] (7) isobutane + *cis*-1,3,3,3-tetrafluoroprop-1-ene,[8] (8) isobutane + *trans*-1-chloro-3,3,3-trifluoroprop-1-ene,[8] (9) isobutane + *cis*-1,2,3,3,3-pentafluoroprop-1-ene,[9] (10) isobutane + 3,3,3-trifluoropropene,[9] (11) difluoromethane + 2,2,2,3-tetrafluoroprop-1-ene,[10] and (12) difluoromethane + *trans*-1,3,3,3-tetrafluoroprop-1-ene.[11]

The present paper expands the authors' work by presenting 150 *PvTx* measurements for binary blends consisting of difluoromethane (R32) and *cis*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(Z)) both in the two-phase and superheated vapor regions using an isochoric test cell. The measured data are correlated with several equations of state, as well as are compared with REFPROP 10.0[12] predictions. The combination of the experimental data and the accompanying fitting models presented herein expand the publicly available thermodynamic property database of low-GWP refrigerant blends.

EXPERIMENTAL SECTION

Materials. Table 1 provides details for the samples of difluoromethane (R32, CH_2F_2, CASRN 75-10-5) and *cis*-1,3,3,3-tetrafluoroprop-1ene (R1234ze(Z), $CF_3CH{=}CHF$, CASRN 29118-25-0). The measured samples were subjected to several cycles of freezing, evacuation, thawing, and ultrasonic stirring to remove any remaining noncondensable

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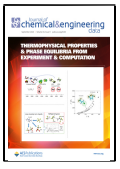

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Table 1. Descriptions of R32 and R1234ze(Z) Samples

chemical name	CASRN	source	initial mole fraction purity	purification method	final mole fraction purity	analysis method
R32[a]	75-10-5	Ausimont SpA	0.9957	several cycles of freezing, evacuation, melting, and ultrasonic agitation	0.9998	GC
R1234ze(Z)[b]	29118-25-0	Central Glass Ltd.	>0.99[c]	several cycles of freezing, evacuation, melting, and ultrasonic agitation	0.9970	GC

[a]Difluoromethane. [b]*cis*-1,3,3,3-Tetrafluoroprop-1-ene. [c]Value reported in the manufacturer's data sheet.

Table 2. Bulk Mole Fractions z, Average Specific Volumes v, Temperature Ranges ΔT, Pressure Ranges ΔP, Numbers of Charged Moles n, and Amounts of Charged Masses m for Binary Blends of R32 (1) and R1234ze(Z) (2)

series	z_1	v/m^3·kg^{-1}	ΔT/K	ΔP/kPa	n/mol	m_1/g	m_2/g
1	0.0871	0.013352	263.15−353.15	79.5−976.6	0.1887	0.855	19.649
2	0.2980	0.016365	263.15−353.15	170.4−1270.8	0.1751	2.714	14.016
3	0.3620	0.071713	263.15−373.15	123.8−443.2	0.0417	0.785	3.034
4	0.5232	0.035001	268.15−373.15	276.8−981.0	0.0959	2.610	5.214
5	0.7128	0.070089	263.15−373.15	264.9−600.6	0.0560	2.075	1.833
6	0.8015	0.023746	268.15−373.15	498.2−1752.9	0.1793	7.477	4.059
7	0.8973	0.026769	268.15−373.15	579.9−1747.3	0.1753	8.181	2.052

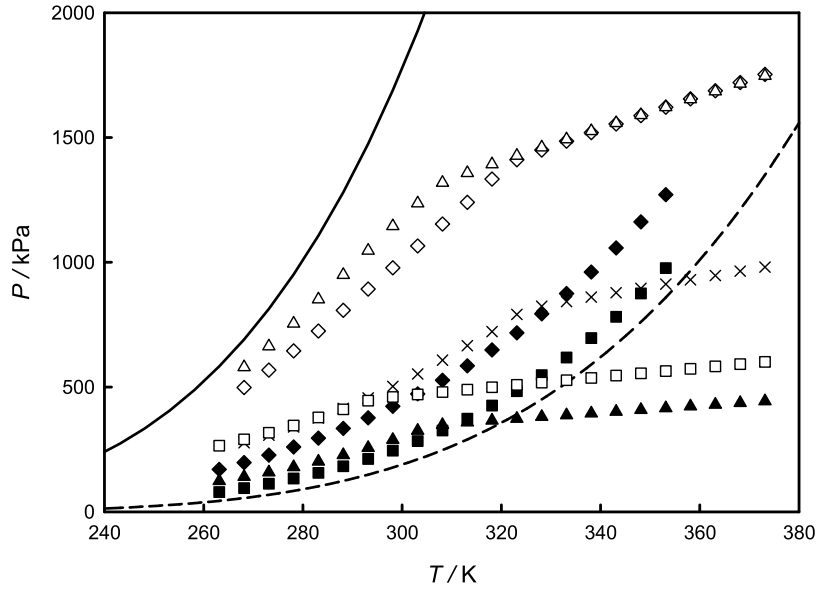

Figure 1. Pressure P, temperature T, bulk mole fraction z, and specific volume v data (Table 3 and Table SI in the Supporting Information) for R32 (1) + R1234ze(Z) (2) binary blends measured both in the two-phase and superheated vapor regions: ■, z_1 = 0.0871 and v = 0.013352 m^3·kg^{-1}; ◆, z_1 = 0.2980 and v = 0.016365 m^3·kg^{-1}; ▲, z_1 = 0.3620 and v = 0.071713 m^3·kg^{-1}; ×, z_1 = 0.5232 and v = 0.035001 m^3·kg^{-1}; □, z_1 = 0.7128 and v = 0.070089 m^3·kg^{-1}; ◇, z_1 = 0.8015 and v = 0.023746 m^3·kg^{-1};△, z_1 = 0.8973 and v = 0.026769 m^3·kg^{-1}. The behaviors of the vapor pressure for R32 (solid line) and R1234ze(Z) (dashed line) calculated by REFPROP 10.0 are also shown.

gases. A gas chromatograph (GC) with a thermal conductivity detector was used to verify the R32 purity. The mole fraction purities measured with the GC and reported in Table 1 are the GC peak area percentages.

Experimental Apparatus and Procedure. The experimental apparatus consists of an isochoric sphere and two separate thermostatic baths capable of operating in a lower temperature range of (210 to 298) K and in a higher temperature range of (303 to 390) K. Only a summary description of the experimental setup and test procedures are provided below since more detailed descriptions are provided elsewhere.[7,8,13,14]

A gravimetric method was used to prepare the binary blends. To begin, the desired mass of the lower pressure refrigerant (refrigerant 1) was discharged into an evacuated container (container 1), of known tare weight, and weighed using an analytical balance possessing an uncertainty of ±0.3 mg. Next container 1 and a second evacuated container (container 2), of known tare weight, were both connected to the isochoric cell. The isochoric cell and all tubing were evacuated prior to connection. Next the desired mass of refrigerant 1 was discharged into the isochoric cell. After charging and isolating the isochoric cell, any refrigerant remaining in the connection tubing was recovered into container 2, after which the masses of both containers 1 and 2 were measured. The mass of refrigerant 1 charged into the isochoric cell was determined to be the difference in the combined masses of containers 1 and 2 before and after charging of refrigerant 1 into the isochoric cell. The procedure was then repeated for the higher pressure refrigerant (refrigerant 2). The expanded uncertainty of the mass of the binary blend (refrigerant 1 + refrigerant 2) charged

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Table 3. Experimental Values of Temperature T, Pressure P, Specific Volume v, and Bulk Mole Fraction z in the Superheated Vapor Region for R32 (1) + R1234ze(Z) (2) Binary Blends[a]

T/K	P/kPa	v/m^3·kg^{-1}	T/K	P/kPa	v/m^3·kg^{-1}
	z_1 = 0.3620(16)			z_1 = 0.8015(3)	
308.15[b]	348.4[b]	0.071682(79)[b]	323.15[b]	1411.0[b]	0.023749(26)[b]
313.15[b]	358.7[b]	0.071697(79)[b]	328.15	1450.1	0.023754(26)
318.15[b]	366.4[b]	0.071713(79)[b]	333.15	1485.3	0.023759(26)
323.15[b]	373.6[b]	0.071729(79)[b]	338.15	1519.9	0.023765(26)
328.15	380.7	0.071744(79)	343.15	1554.1	0.023770(26)
333.15	387.8	0.071760(79)	348.15	1587.9	0.023775(26)
338.15	394.8	0.071776(79)	353.15	1621.4	0.023780(26)
343.15	401.7	0.071792(79)	358.15	1654.6	0.023785(26)
348.15	408.8	0.071807(79)	363.15	1687.8	0.023791(26)
353.15	415.9	0.071823(79)	368.15	1720.5	0.023796(26)
358.15	422.9	0.071839(79)	373.15	1752.9	0.023801(26)
363.15	429.8	0.071854(79)			
368.15	436.5	0.071870(79)			
373.15	443.2	0.071886(79)			
	z_1 = 0.5232(5)			z_1 = 0.8973(6)	
323.15[b]	791.3[b]	0.035005(38)[b]	308.15[b]	1318.8[b]	0.026755(29)[b]
328.15	823.9	0.035012(38)	313.15[b]	1358.1[b]	0.026761(29)[b]
333.15	842.5	0.035020(38)	318.15[b]	1393.0[b]	0.026766(29)[b]
338.15	860.4	0.035028(38)	323.15	1427.2	0.026772(29)
343.15	878.1	0.035035(38)	328.15	1460.5	0.026778(29)
348.15	895.6	0.035043(38)	333.15	1493.5	0.026784(29)
353.15	912.6	0.035051(38)	338.15	1526.1	0.026790(29)
358.15	930.1	0.035058(38)	343.15	1558.4	0.026796(29)
363.15	947.2	0.035066(38)	348.15	1590.4	0.026802(29)
368.15	964.3	0.035074(38)	353.15	1622.2	0.026807(29)
373.15	981.0	0.035081(38)	358.15	1653.8	0.026813(29)
			363.15	1685.1	0.026819(29)
			368.15	1716.3	0.026825(29)
			373.15	1747.3	0.026831(29)
	z_1 = 0.7128(9)				
298.15[b]	460.5[b]	0.070027(77)[b]			
303.15	470.5	0.070043(77)			
308.15	480.3	0.070058(77)			
313.15	489.8	0.070074(77)			
318.15	499.3	0.070089(77)			
323.15	508.8	0.070104(77)			
328.15	518.2	0.070120(77)			
333.15	527.5	0.070135(77)			
338.15	536.8	0.070150(77)			
343.15	546.0	0.070166(77)			
348.15	555.2	0.070181(77)			
353.15	564.4	0.070196(77)			
358.15	573.5	0.070212(77)			
363.15	582.6	0.070227(77)			
368.15	591.7	0.070243(77)			
373.15	600.6	0.070258(77)			

[a]Expanded uncertainties are $U(T)$ = 0.03 K and $U(P)$ = 1 kPa. $U(v)$ and $U(z_1)$ at the 95% confidence level are provided between parentheses (the uncertainty values refer to the corresponding last digits of the experimental values). [b]Not included in the regression analysis.

into the isochoric cell with a coverage factor of 2 (95% confidence level) was determined to be 1.2 mg.

The temperatures of the thermostatic baths were measured using a Hart Scientific 5680 platinum resistance (25 ohm) thermometer. The refrigerant pressure in the isochoric cell was measured using a Ruska 7000 pressure transducer. The volume (V_{iso}) of the isochoric cell at 298 K was determined to be 273.3 cm^3. As described elsewhere,[13] a correction for the thermal expansion of the isochoric cell was included. The expanded uncertainties for the temperature, pressure, and volume with coverage factors of 2 (95% confidence level) were determined to be 0.03 K, 1 kPa, and 0.3 cm^3, respectively. The expanded uncertainty of the pressure measurements included effects from changes in the thermostatic bath temperatures.

The uncertainties for the specific volumes and the mole fractions of the studied blends were estimated as reported elsewhere.[7,8] The uncertainty of the specific volume is a function of the uncertainties of the volume estimation and

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Table 4. Absolute Average Relative Deviations of the Pressure (AARD (*P*)) Calculated by the "Flash Method" Coupled with the Select EoSs Using (a) Average $\overline{k}_{12}$ Regressed from All the Two-Phase Measurements of the R32 (1) + R1234ze(Z) (2) Binary Blend and (b) k_{12} Adjusted for Each Isochore

		PR EoS			Stryjek EoS			REFPROP 10.0
series	z_1	AARD (*P*)[a]/%	k_{12}	AARD (*P*)[b]/%	AARD (*P*)[c]/%	k_{12}	AARD (*P*)[b]/%	AARD (*P*)/%
1	0.0871	0.48	0.00297	0.46	0.45	0.00012	0.41	7.66
2	0.2980	1.55	0.01258	0.34	1.65	0.00920	0.19	9.29
3	0.3620	0.79	−0.00637	0.25	0.86	−0.01045	0.33	6.46
4	0.5232	1.47	0.01366	0.56	1.55	0.01043	0.57	6.61
5	0.7128	0.58	−0.00272	0.33	0.61	−0.00577	0.38	6.08
6	0.8015	1.13	−0.00590	0.30	1.10	−0.00882	0.41	6.22
7	0.8973	1.19	−0.00849	0.35	1.18	−0.01140	0.37	4.29
avg		1.05		0.38	1.09		0.37	7.12

[a]Calculated using $\overline{k}_{12}$ = 0.00281. [b]Calculated using k_{12} fitted for each series. [c]Calculated using $\overline{k}_{12}$ = −0.00037.

mass measurements. On the basis of the propagation of uncertainty, the uncertainty of the mole fraction depends on the mass of the charged sample, the calculated specific volume, and the mole fraction itself. The expanded uncertainties in the specific volumes with coverage factors of 2 (95% confidence level) for the various blends are provided in Table SI in the Supporting Information and in Table 3. The expanded uncertainties with coverage factors of 2 (95% confidence level) for the various R32 mole fractions (z_1) of binary blends of R32 (1) + R1234ze(Z) (2) are also provided in Table SI in the Supporting Information and in Table 3.

The measurement procedure consisted of allowing the thermostatic bath temperature to stabilize at the desired test temperature, after which a circulating pump within the isochoric cell mixed the refrigerant sample for 15 min. The refrigerant sample was then allowed to stabilize for an hour, after which the sample pressure was measured. The procedure was then repeated for all of the desired temperature levels.

RESULTS AND DISCUSSION

In this section, the *PvTx* data for R32 (1) + R1234ze(Z) (2) binary system measured with the isochoric apparatus are reported. Moreover, the results obtained by comparing the experimental data with the values calculated using different models are presented.

Experimental Data. *PvTx* measurements for seven R32 (1) and R1234ze(Z) (2) blends were taken along isochores of (0.013352, 0.016365, 0.023746, 0.026769, 0.035001, 0.070089, 0.071713) $m^3 \cdot kg^{-1}$ for R32 mole fractions of (0.0871, 0.2980, 0.3620, 0.5232, 0.7128, 0.8015, 0.8973) over a temperature range from (263 to 373) K. Table 2 provides the measured temperature and pressure ranges for the seven blends, and in addition, the compositions, the average specific volumes, and the number of moles and masses charged into the isochoric cell, all for the same seven blends. Figure 1 shows *P*−*T* behaviors for the seven isochores both in the two-phase and superheated vapor regions together with the behaviors of the vapor pressure for R32 and R1234ze(Z) calculated by REFPROP 10.0.[12] The demarcation points marking the boundaries between the two-phase and superheated vapor regions were determined from the changes in the slopes of the respective *P*−*T* curves. The measured *P*−*T* values for the two-phase region are reported in Table SI in the Supporting Information. Table 3 provides the measured *P*−*T* values for the superheated vapor region.

Vapor−Liquid Equilibrium Assessment. The vapor−liquid equilibrium (VLE) properties of R32 (1) + R1234ze(Z) (2) binary blends were determined from the two-phase *PvTx* measurements by implementing the "flash method" and (1) the Peng -Robinson Equation of State (PR EoS)[15] coupled with the van der Waals one-fluid mixing rules[16] with a binary interaction parameter (k_{12}) and (2) a two-parameter cubic EoS proposed by Stryjek[17,18] coupled with the van der Waals one-fluid mixing rules[16] with a k_{12}. The latter EoS was chosen since it generally shows somewhat better VLE behavior for blends containing low-GWP refrigerants when compared with other, more conventional two-parameter cubic EoSs.[19,20]

As described elsewhere,[10,21] the "flash method" yields the values of *P* and of the mole fractions of the liquid phase (x_i) and of the vapor phase (y_i) for each isochoric point subject to isofugacity conditions and through the minimization of the difference between the calculated isochoric sphere volume and the experimental isochoric sphere volume estimated from the gravimetric calibration. While *T*, z_i, and *n* are fixed at their experimental values for calculation purposes, the k_{12} values were determined by minimizing the following objective function:

$$Q = \sum_{i=1}^{N} \left(\frac{P_{\mathrm{exp,i}} - P_{\mathrm{calc,i}}}{P_{\mathrm{exp,i}}} \right)^2 \quad (1)$$

where *N* is the number of experimental data. The volume condition of the "flash" method requires the calculated (from the EoS) volumetric properties of the liquid and vapor phases.

Table 4 provides the absolute average relative deviations of the pressure (AARD (*P*)) provided by the "flash method" coupled with the PR[15] and the cubic EoS of Styjek[17,18] using (a) average $\overline{k}_{12}$ regressed from all the two-phase measurements of the R32 (1) + R1234ze(Z) (2) binary blend and (b) k_{12} adjusted for each isochore. The AARD (*P*) was calculated from

$$\mathrm{AARD}(P)/\% = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{P_{\mathrm{exp,i}} - P_{\mathrm{calc,i}}}{P_{\mathrm{exp,i}}} \right| \quad (2)$$

Table 4 provides the $\overline{k}_{12}$ values and the k_{12} values for each refrigerant blend. Table 5 provides pressures and compositions of liquid and vapor phases derived from the "flash method" with the select EoSs using the k_{12} values determined for each isochore. Figure 2 shows the relative deviations between the measured pressures and the values calculated with each EoS with the k_{12} values having been determined for each refrigerant blend. The resulting deviations are generally within ±1% for nearly all of the experimental points.

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Table 5. Pressures P_{calc}, Mole Fractions of the Liquid Phase $x_{1,calc}$, and Mole Fractions of the Vapor Phase $y_{1,calc}$ Estimated through the "Flash Method" Coupled with the Select EoSs Using k_{12} Adjusted for Each Bulk Mole Fraction z_1 of the R32 (1) + R1234ze(Z) (2) Binary Blend (Table 4) for the Experimental Temperatures T

	PR EoS			Stryjek EoS		
T/K	P_{calc}/kPa	$x_{1,calc}$	$y_{1,calc}$	P_{calc}/kPa	$x_{1,calc}$	$y_{1,calc}$
			z_1 = 0.0871			
263.15	78.5	0.0668	0.4737	78.5	0.0674	0.4694
268.15	93.9	0.0646	0.4467	94.0	0.0653	0.4429
273.15	111.7	0.0624	0.4201	111.8	0.0631	0.4169
278.15	132.0	0.0602	0.3941	132.1	0.0610	0.3915
283.15	155.2	0.0580	0.3688	155.4	0.0588	0.3669
288.15	181.5	0.0558	0.3444	181.7	0.0567	0.3430
293.15	211.3	0.0537	0.3210	211.5	0.0546	0.3200
298.15	244.9	0.0517	0.2986	245.2	0.0525	0.2981
303.15	282.7	0.0497	0.2773	282.9	0.0505	0.2772
308.15	324.9	0.0477	0.2572	325.2	0.0486	0.2574
313.15	372.1	0.0459	0.2382	372.4	0.0468	0.2387
318.15	424.7	0.0441	0.2204	424.9	0.0450	0.2211
323.15	483.1	0.0425	0.2038	483.2	0.0433	0.2046
328.15	547.6	0.0409	0.1882	547.7	0.0417	0.1892
333.15	618.9	0.0394	0.1737	618.9	0.0402	0.1748
338.15	697.4	0.0380	0.1603	697.3	0.0388	0.1614
343.15	783.6	0.0367	0.1478	783.3	0.0374	0.1490
348.15	878.1	0.0354	0.1362	877.6	0.0362	0.1374
353.15	981.3	0.0342	0.1255	980.6	0.0350	0.1267
			z_1 = 0.2980			
263.15	172.5	0.2296	0.7936	171.4	0.2317	0.7912
268.15	199.5	0.2216	0.7732	198.5	0.2239	0.7710
273.15	229.2	0.2135	0.7513	228.2	0.2159	0.7495
278.15	261.7	0.2054	0.7282	260.7	0.2079	0.7267
283.15	297.1	0.1972	0.7038	296.2	0.1999	0.7027
288.15	335.6	0.1892	0.6784	334.9	0.1919	0.6776
293.15	377.4	0.1813	0.6520	376.9	0.1841	0.6516
298.15	422.9	0.1736	0.6249	422.5	0.1765	0.6248
303.15	472.3	0.1662	0.5972	472.1	0.1691	0.5976
308.15	526.0	0.1591	0.5692	526.0	0.1620	0.5700
313.15	584.4	0.1523	0.5411	584.5	0.1552	0.5422
318.15	647.7	0.1459	0.5131	648.1	0.1487	0.5145
323.15	716.6	0.1398	0.4854	717.1	0.1426	0.4871
328.15	791.4	0.1341	0.4581	792.0	0.1368	0.4601
333.15	872.6	0.1287	0.4315	873.4	0.1314	0.4337
338.15	960.8	0.1237	0.4056	961.6	0.1262	0.4079
343.15	1056.4	0.1190	0.3805	1057.3	0.1215	0.3830
348.15	1159.9	0.1146	0.3563	1160.9	0.1170	0.3589
353.15	1272.0	0.1105	0.3331	1273.0	0.1129	0.3358
			z_1 = 0.3620			
263.15	123.0	0.1627	0.6931	122.7	0.1659	0.6909
268.15	139.6	0.1494	0.6552	139.4	0.1525	0.6534
273.15	158.1	0.1371	0.6161	157.9	0.1401	0.6146
278.15	178.7	0.1259	0.5763	178.6	0.1288	0.5752
283.15	201.8	0.1157	0.5366	201.8	0.1185	0.5359
288.15	227.7	0.1065	0.4975	227.8	0.1092	0.4971
293.15	256.9	0.0982	0.4594	257.0	0.1007	0.4595
298.15	289.6	0.0908	0.4229	289.7	0.0931	0.4232
303.15	326.3	0.0841	0.3883	326.4	0.0863	0.3888
			z_1 = 0.5232			
268.15	274.1	0.3357	0.8539	273.2	0.3392	0.8532
273.15	307.3	0.3161	0.8330	306.6	0.3197	0.8325
278.15	342.3	0.2969	0.8099	341.7	0.3007	0.8097
283.15	379.3	0.2785	0.7847	378.8	0.2824	0.7847
288.15	418.4	0.2610	0.7577	418.1	0.2650	0.7579
293.15	460.1	0.2446	0.7289	460.0	0.2485	0.7294
298.15	504.8	0.2293	0.6988	504.9	0.2331	0.6996
303.15	552.8	0.2151	0.6676	553.1	0.2188	0.6687
308.15	604.7	0.2020	0.6357	605.1	0.2056	0.6370
313.15	660.9	0.1900	0.6034	661.5	0.1935	0.6049
318.15	721.9	0.1790	0.5711	722.6	0.1823	0.5728
			z_1 = 0.7128			
263.15	262.2	0.4261	0.8954	261.8	0.4300	0.8954
268.15	289.6	0.3924	0.8740	289.3	0.3967	0.8740
273.15	317.7	0.3605	0.8496	317.5	0.3650	0.8498
278.15	347.0	0.3309	0.8225	347.0	0.3354	0.8228
283.15	378.0	0.3037	0.7928	378.1	0.3083	0.7934
288.15	411.1	0.2791	0.7610	411.4	0.2835	0.7618
293.15	446.9	0.2569	0.7276	447.2	0.2611	0.7285
			z_1 = 0.8015			
268.15	492.4	0.7126	0.9625	491.7	0.7142	0.9628
273.15	565.7	0.6958	0.9564	564.9	0.6978	0.9568
278.15	643.3	0.6767	0.9490	642.3	0.6792	0.9495
283.15	724.2	0.6555	0.9402	723.3	0.6586	0.9408
288.15	807.6	0.6324	0.9297	806.9	0.6360	0.9305
293.15	892.7	0.6078	0.9174	892.3	0.6120	0.9184
298.15	979.1	0.5823	0.9032	979.2	0.5869	0.9044
303.15	1066.8	0.5563	0.8870	1067.4	0.5614	0.8885
308.15	1155.8	0.5304	0.8689	1157.1	0.5358	0.8706
313.15	1246.7	0.5051	0.8489	1248.7	0.5108	0.8509
318.15	1340.1	0.4807	0.8271	1342.7	0.4865	0.8294
			z_1 = 0.8973			
268.15	573.8	0.8335	0.9812	573.6	0.8344	0.9815
273.15	662.6	0.8183	0.9775	662.3	0.8196	0.9778
278.15	756.7	0.7997	0.9726	756.2	0.8014	0.9731
283.15	854.0	0.7773	0.9663	853.5	0.7796	0.9669
288.15	952.4	0.7512	0.9583	952.2	0.7541	0.9591
293.15	1050.2	0.7216	0.9482	1050.4	0.7253	0.9492
298.15	1146.2	0.6896	0.9359	1147.1	0.6940	0.9372
303.15	1240.4	0.6563	0.9213	1242.1	0.6613	0.9228

The measured pressures were also compared with values predicted by REFPROP 10.0,[12] which is based on an EoS explicit in reduced Helmholtz energy.[22] Table 4 and Figure 2 provide the deviations between the measured pressures and the values predicted by REFPROP 10.0. Figure 2 clearly shows that REFPROP 10.0 systematically overestimates (deviations from a few percent to well more than −20%) the pressure. The poor agreement likely occurs because the binary interaction parameters contained in REFPROP 10.0 are estimated and not based on experimental data since the publicly available literature experimental data are absent for the binary pair reported herein. Notwithstanding this fact, comparisons between the experimental data reported herein and REFPROP 10.0 are included because of the widespread use of REFPROP 10.0 in the air conditioning and refrigeration communities. Thus, the large discrepancies should not be taken as an indication of a limitation in REFPROP 10.0 predictions, but rather the predictions are included for completeness and because readers familiar with REFPROP 10.0 would expect such a comparison to be made.

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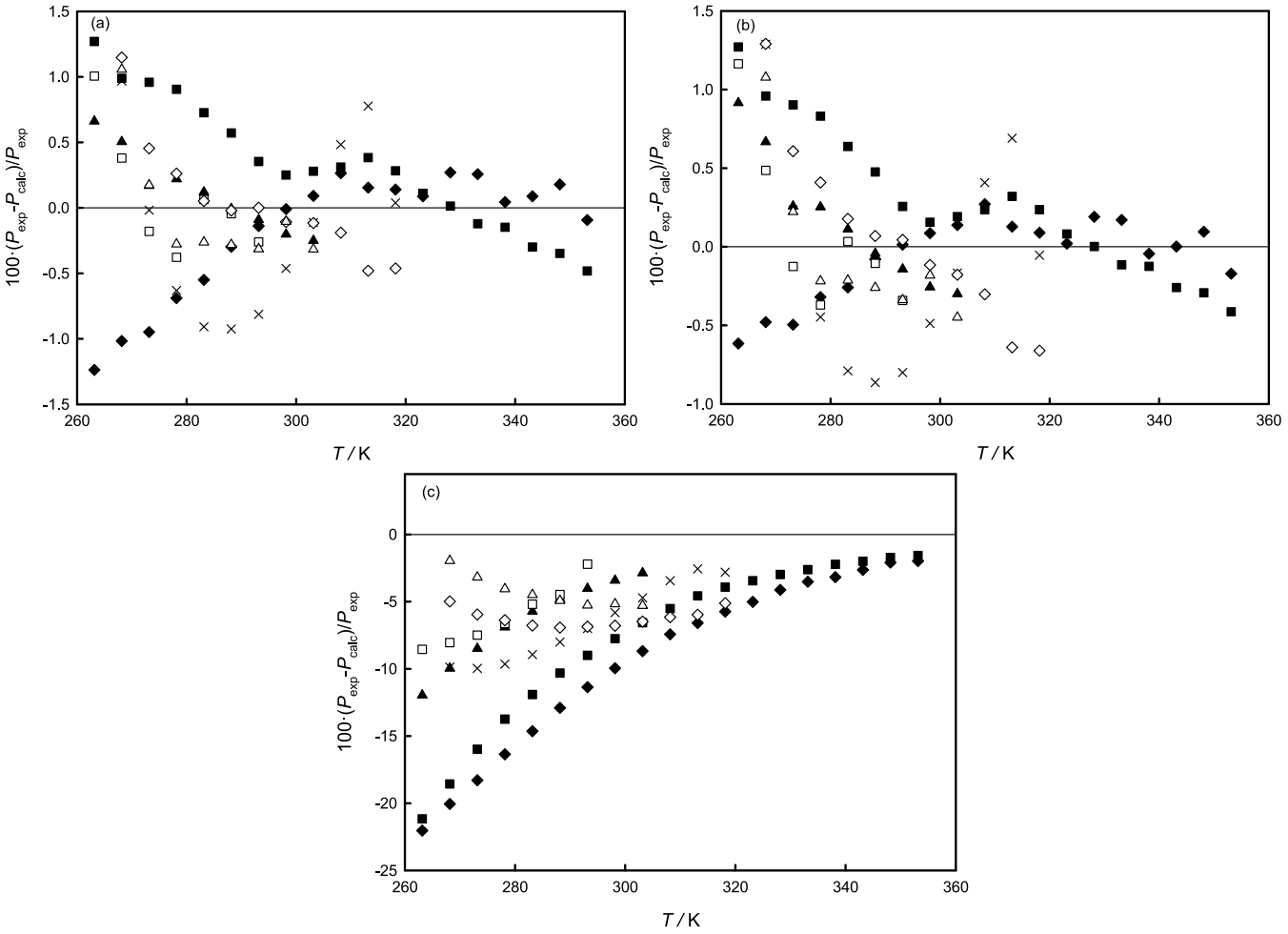

Figure 2. Deviations between the measured pressures of the binary blends of R32 (1) + R1234ze(Z) (2) listed in Table SI in the Supporting Information (P_{exp}) and calculated values (P_{calc}) obtained from (a) the "flash method" coupled with the Peng−Robinson EoS using k_{12} fitted for each isochore, (b) the "flash method" coupled with a cubic EoS proposed by Styjek using k_{12} fitted for each isochore, and (c) REFPROP 10.0: ■, z_1 = 0.0871 and v = 0.013352 $m^3 \cdot kg^{-1}$; ◆, z_1 = 0.2980 and v = 0.016365 $m^3 \cdot kg^{-1}$; ▲, z_1 = 0.3620 and v = 0.071713 $m^3 \cdot kg^{-1}$; ×, z_1 = 0.5232 and v = 0.035001 $m^3 \cdot kg^{-1}$; □, z_1 = 0.7128 and v = 0.070089 $m^3 \cdot kg^{-1}$; ◇, z_1 = 0.8015 and v = 0.023746 $m^3 \cdot kg^{-1}$; △, z_1 = 0.8973 and v = 0.026769 $m^3 \cdot kg^{-1}$.

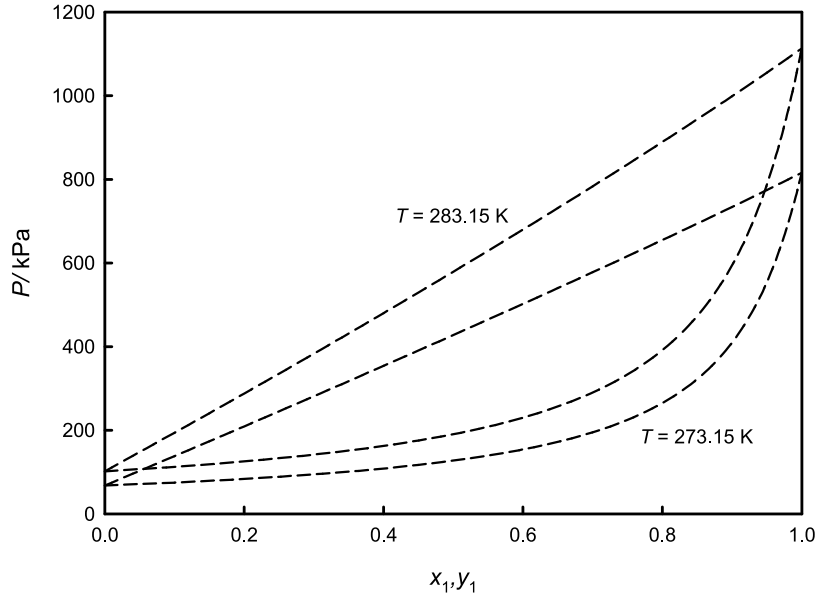

Figure 3. VLE representation for the R32 (1) + R1234ze(Z) (2) blends using the Peng−Robinson EoS with $\overline{k}_{12}$ = 0.00281 for T = 273.15 K and T = 283.15 K.

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Table 6. Coefficients for B_{blend} [eq 3] and for C_{blend} [eq 4] for R32 (1) + R1234ze(Z) (2) Binary Blends

B_1	B_2	B_3	B_4	B_5
−1.7750	−923.8710	−98.6313	100.3795	−8.3694
C_1	C_2	C_3	C_4	C_5
3.6723	1371.0771	104.5247	−70.4911	−29.8528

Figure 3 illustrates the VLE behaviors of the R32 (1) + R1234ze(Z) (2) binary blends calculated at temperatures of 273.15 and 283.15 K using the PR EoS with an average k_{12} determined by the "flash method". The resulting value is $\bar{k}_{1212}$ = 0.00281. Since no experimental data are available in the open literature for blends of R32 + R1234ze(Z), it is not possible to compare the calculated values of Figure 3 with publicly available and experimentally determined VLE properties. It is to be noted that Figure 3 clearly demonstrates ideal behavior per Raoult's law.

Correlation of Vapor-Phase *PvTx* Properties. The measured vapor-phase *PvTx* data for the R32 (1) + R1234ze(Z) (2) binary blends were correlated with (1) the PR EoS[15] coupled with the van der Waals one-fluid mixing rules,[16] (2) a cubic EoS proposed by Stryjek[17,18] coupled with the van der Waals one-fluid mixing rules,[16] and (3) a truncated (second order) virial EoS. The measured data were also compared with REFPROP 10.0[12] calculations. The measured vapor-phase data that were located too close to the two-phase region (denoted in Table 3 with a "b") were excluded during the development of the correlations mentioned above since these data exhibited much higher pressure deviations than data located further from the two-phase region.

Minimizing the AARD (P) yielded a k_{12} value of −0.11090 for the PR EoS[15] coupled with the van der Waals one-fluid mixing rules[16] and a k_{12} value of −0.20463 for the cubic EoS proposed by Stryjek[17,18] coupled with the van der Waals one-fluid mixing rules.[16] These k_{12} values yielded AARD (P) of 0.49% and 0.53% for the PR EoS[15] and the Stryjek cubic EoS,[17,18] respectively.

As provided in our previous publications,[7−9] the second virial coefficient (B_{blend}) and the third virial coefficient (C_{blend}) employed in the truncated (second order) virial EoS can be fitted to the following functional forms:

$$B_{blend} = B_1 \ln(T/K) + \frac{B_2}{T} + B_3 x_1^2 + B_4 x_1 + B_5 \quad (3)$$

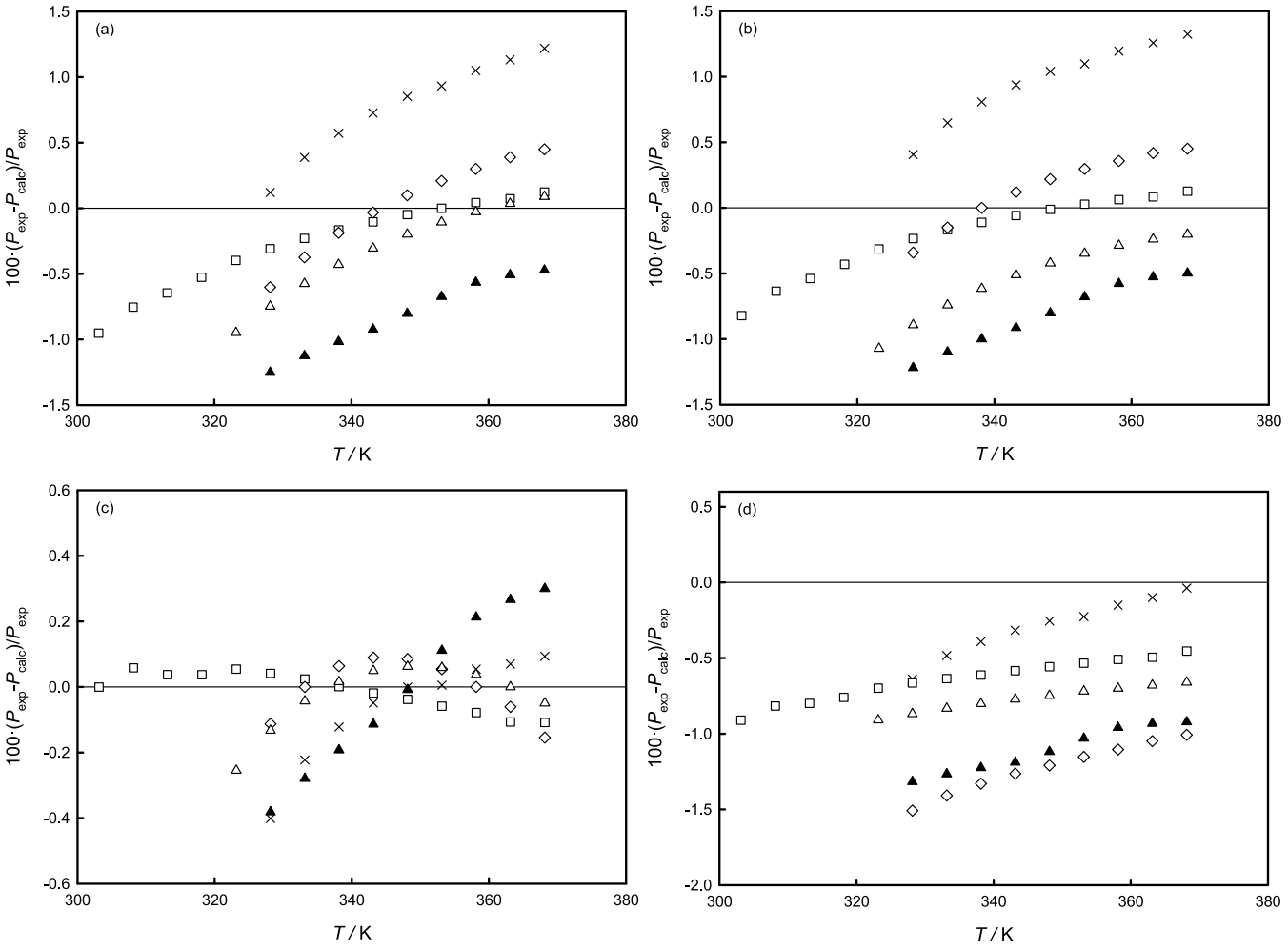

Figure 4. Deviations between the measured pressures of the binary blends of R32 (1) + R1234ze(Z) (2) listed in Table 3 (P_{exp}) and calculated values (P_{calc}) determined from (a) the Peng−Robinson EoS, (b) a cubic EoS proposed by Styjek, (c) the truncated virial EoS, and (d) REFPROP 10.0: ▲, z_1 = 0.3620 and v = 0.071713 $m^3 \cdot kg^{-1}$; ×, z_1 = 0.5232 and v = 0.035001 $m^3 \cdot kg^{-1}$; □, z_1 = 0.7128 and v = 0.070089 $m^3 \cdot kg^{-1}$; ◇, z_1 = 0.8015 and v = 0.023746 $m^3 \cdot kg^{-1}$; △, z_1 = 0.8973 and v = 0.026769 $m^3 \cdot kg^{-1}$.

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$$C_{blend} = C_1 \ln(T/K) + \frac{C_2}{T} + C_3 x_1^2 + C_4 x_1 + C_5 \quad (4)$$

Table 6 reports the coefficients of eqs 3 and 4, which were determined by minimizing the AARD (*P*) of the vapor phase *PvTx* data set. The resulting AARD (*P*) between the vapor-phase *PvTx* data of the R32 (1) + R1234ze(Z) (2) binary blends and the values calculated using the truncated (second order) virial EoS is 0.10%.

Finally, the measured *PvTx* data were also compared with REFPROP 10.0[12] calculations, yielding an AARD (*P*) = 0.77%.

Figure 4 shows the relative deviations between measured pressure values in the superheated vapor region and (1) the values estimated by the fitting models described above and (2) by REFPROP 10.0.[12] Each of the three fitting models show good agreement with one another and result in small values of AARD (*P*) = 0.77%. It is to be noted, however, that REFPROP 10.0[12] systematically overestimates the pressure predictions.

CONCLUSIONS

The present paper presents 150 *PvTx* measurements for binary blends consisting of difluoromethane (R32) and *cis*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(Z)) both in the two-phase and superheated vapor regions using an isochoric test cell. The superheated vapor data were correlated with the Peng–Robinson (PR) equation of state (EoS), the cubic EoS of Styjek, a truncated (second order) virial EoS, and REFPROP 10.0. The absolute average relative deviation of the pressure (AARD (*P*)) for the PR EoS, Styjek EoS, virial EoS, and REFROP 10.0 were 0.49%, 0.53%, 0.10%, and 0.77%, respectively, indicating good agreement with the measured values. The "flash method" coupled with (1) the PR EoS and the van der Waals one-fluid mixing rules and (2) the Styjek EoS and the van der Waals one-fluid mixing rules were used to derive the VLE data from the two-phase measurements. The AARD (*P*) values for these two methods were 0.38% and 0.37%, respectively. In addition, the VLE data were compared with REFPROP 10.0 predications, which yielded an unacceptably large AARD (*P*) of 7.12%. This disagreement is not unanticipated since the binary interaction parameters contained in REFPROP 10.0 are estimated and not based on experimental data.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.0c00334.

Values of the *PvTx* measurements in the two-phase region (PDF)

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Notes

The authors declare no competing financial interest.

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