J. Chem. Eng. Data **2006,** *51,* 2041−2044

Isochoric *PVTx* Measurements for the $N_2O + R125$ Binary System

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Isochoric *PVTx* measurements are reported for nitrous oxide (N_2O, R744A) + pentafluoroethane (CHF_2CF_3, R125) for both the two-phase and the superheated vapor regions at temperatures ranging from (217 to 363) K and pressures from (160 to 1853) kPa along six isochores. The data obtained in the two-phase region were used to derive vapor−liquid equilibrium (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. The dew points were then used to derive VLE parameters from CSD EOS. Results from the superheated region were compared with those predicted from the virial EOS and from the CSD EOS.

Introduction

In the search for fluids potentially suitable for low-temperature refrigeration applications (i.e., cascade cycles), we have turned our attention to systems consisting of R744A and R125. The cascade cycle is a very interesting application for the food industry, where evaporating temperatures between −30 °C and −40 °C are needed. Where lower temperatures are needed, carbon dioxide (R744) is no longer a feasible solution due to its triple-point temperature (216.58 K), which prevents its use in vapor compression cycles intended for use at lower temperatures. One of the chemicals potentially suitable for use in low-temperature refrigeration applications is R744A, whose critical parameters and saturated pressures are very similar to those of carbon dioxide (R744). The main advantage of R744A over R744 lies in its very low melting temperature (182.34 K), whereas its global warming potential (GWP, which is 310) is low but not low enough to be considered environmentally friendly.

R125, a hydrofluorocarbon, is an important refrigerant used as a constituent in some binary or ternary mixtures. Its thermophysical properties have been extensively studied during the past decade. Nevertheless, published data on *PVTx* properties of systems containing R744 or R744A as one of the components and a fluorocarbon as the second component are rare. Thus, the combination of R744A and R125 provides important data for future applications. In addition, to our knowledge no experimental results have been published in the open literature on the *PVTx* properties of this specific binary system. The study presented in this paper aims to partially fill this gap.

Isochoric measurements were consequently taken, covering temperatures from (217 to 363) K, to make up for the lack of vapor−liquid equilibrium (VLE) and *PVTx* data. VLE parameters were derived from data in the two-phase region, applying the Carnahan−Starling−De Santis equation of state (CSD EOS),[1] while data obtained from the superheated region were compared with the predictions obtained with the virial EOS and the CSD EOS.

Experimental Section

Chemicals. Nitrous oxide and pentafluoroethane were supplied by Sol SpA. Their purity was checked by gas chromatography, using a thermal conductivity detector, and found to be 99.99 % and 99.96 %, respectively, basing all estimations on an area response.

Apparatus. The setup has already been described elsewhere,[2] so it is only briefly outlined here. The main changes made to the original apparatus[3,4] concerned the twin thermostatic baths (7) filled with different silicone oils (Baysilone M10 and Baysilone M100, Bayer). After charging with the sample mixture, the setup 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 two silicone oils have different kinematic viscosity values (10^{-5} and 10^{-4} $m^2 \cdot s^{-1}$ at room temperature, respectively). The one with lower kinematic viscosity but of higher volatility and lower thermal stability was applied only for the low-temperature range, while that with a greater viscosity was applied only at the higher temperatures. The thermostatic baths were easy to move thanks to the new system configuration. The spherical cells and pressure transducer are immersed in one of the two thermostatic baths (7). An auxiliary thermostat (14) was used to reach below-ambient temperatures. The cell volume was estimated (as explained elsewhere[4]) 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.[3,4] 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, model 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.

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10.1021/je060140+ CCC: $33.50

Table 1. Measurements at Bulk Compositions z_1 and Masses m_1 and m_2 for the R744A (1) + R125 (2) System over the Temperature Range, ΔT, and Pressure Range, ΔP, with Resultant Dew Temperatures, T_d, and Dew Pressures, P_d

	ΔT	ΔP	N	m_1	m_2	T_d	P_d
z_1	K	kPa	mol	g	g	K	kPa
0.082	228−363	160−1853	0.1973	0.789	21.745	293.9	1327
0.147	238−363	250−1125	0.1116	0.721	11.428	273.8	779
0.280	217−363	161−1323	0.1323	1.633	11.428	274.6	915
0.475	218−363	223−1056	0.1028	2.148	6.479	259.2	699
0.649	218−363	310−1361	0.1331	3.800	5.608	258.2	893
0.793	218−363	403−1728	0.1696	5.916	4.225	255.8	1118

Table 2. Experimental Molar Volumes V as a Function of Pressure P and Temperature T at Composition z_1 within the VLE Boundary for the R744A (1) + R125 (2) System

T	P	V	T	P	V
K	kPa	$dm^3 \cdot mol^{-1}$	K	kPa	$dm^3 \cdot mol^{-1}$
	$z_1 = 0.082$		258.02	588	2.065
228.06	160	1.383	263.07	676	2.065
233.02	194	1.383	268.13	775	2.065
237.90	234	1.383	273.13	882	2.066
242.94	282	1.384		$z_1 = 0.475$	
247.92	336	1.384	218.52	223	2.653
252.94	399	1.384	223.13	259	2.654
257.98	471	1.385	228.10	302	2.654
263.03	552	1.385	233.08	349	2.655
268.11	646	1.385	238.04	401	2.655
273.10	749	1.386	242.99	460	2.656
278.03	864	1.386	247.97	528	2.656
283.01	993	1.386	253.15	602	2.657
288.00	1137	1.387	258.03	679	2.658
	$z_1 = 0.147$			$z_1 = 0.649$	
238.09	250	2.446	218.27	310	2.049
243.08	298	2.446	223.12	363	2.050
248.09	354	2.447	228.10	422	2.050
253.08	416	2.447	233.07	485	2.051
258.10	488	2.448	238.02	554	2.051
263.12	569	2.448	243.00	631	2.052
268.16	663	2.449	247.99	711	2.052
273.11	734	2.449	253.01	797	2.052
	$z_1 = 0.280$			$z_1 = 0.793$	
217.76	161	2.061	218.27	403	1.608
223.13	196	2.061	223.13	473	1.608
228.10	233	2.062	228.11	556	1.608
233.07	276	2.062	233.08	644	1.609
238.03	324	2.063	238.03	736	1.609
242.99	379	2.063	243.02	835	1.609
247.97	440	2.064	248.00	942	1.610
252.99	509	2.064	253.03	1049	1.610

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. Then 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 15 min. Next, the mixture was allowed to stabilize for about 20 min before the data recording.

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. On the basis of 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 number of data belonging to each region is also included in Table 1. 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.

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 R744A (1) + R125 (2) System

T	P	V	T	P	V
K	kPa	$dm^3 \cdot mol^{-1}$	K	kPa	$dm^3 \cdot mol^{-1}$
	$z_1 = 0.082$		317.99	1120	2.070
293.08	1298	1.387	322.99	1144	2.070
298.07	1360	1.387	328.11	1167	2.071
303.05	1401	1.387	333.10	1190	2.071
308.04	1440	1.388	338.09	1212	2.072
313.03	1480	1.388	343.08	1235	2.072
318.02	1518	1.388	348.07	1257	2.073
323.00	1557	1.389	353.05	1279	2.073
328.11	1595	1.389	358.03	1301	2.074
333.10	1632	1.389	363.02	1323	2.074
338.09	1670	1.390		$z_1 = 0.475$	
343.08	1707	1.390	263.07	703	2.658
348.06	1744	1.390	268.12	727	2.659
353.05	1780	1.391	273.11	752	2.659
358.03	1818	1.391	278.02	769	2.660
363.02	1853	1.391	283.00	787	2.661
	$z_1 = 0.147$		288.00	804	2.661
278.03	793	2.450	293.08	821	2.662
283.02	818	2.450	298.07	839	2.662
288.01	835	2.451	303.05	856	2.663
293.09	856	2.451	308.04	873	2.663
298.07	876	2.452	313.02	890	2.664
303.05	896	2.452	318.01	907	2.665
308.04	915	2.453	322.99	924	2.665
313.02	935	2.454	328.11	941	2.666
318.01	954	2.454	333.10	958	2.666
323.00	973	2.455	338.09	974	2.667
327.99	993	2.455	343.08	991	2.668
333.10	1012	2.456	348.07	1007	2.668
338.09	1031	2.456	353.03	1023	2.669
343.08	1050	2.457	358.02	1040	2.669
348.07	1069	2.457	363.01	1056	2.670
353.04	1088	2.458		$z_1 = 0.649$	
358.02	1106	2.458	258.04	876	2.053
363.02	1125	2.459	263.08	907	2.053
	$z_1 = 0.280$		268.13	936	2.054
278.02	919	2.066	273.12	965	2.054
283.01	955	2.067	278.05	987	2.055
288.00	979	2.067	283.01	1010	2.055
293.08	1004	2.068	287.98	1032	2.056
298.07	1028	2.068	293.08	1056	2.056
303.06	1051	2.069	298.07	1079	2.057
308.04	1075	2.069	303.06	1101	2.057
313.02	1098	2.070	308.04	1123	2.057
313.03	1145	2.058	283.01	1278	1.612
318.01	1167	2.058	287.99	1307	1.613
322.99	1188	2.059	293.08	1337	1.613
328.11	1211	2.059	298.07	1365	1.613
333.11	1232	2.060	303.04	1394	1.614
338.09	1254	2.060	308.02	1422	1.614
343.08	1275	2.061	313.01	1450	1.614
348.06	1297	2.061	317.99	1478	1.615
353.04	1318	2.062	322.98	1506	1.615
358.03	1340	2.062	328.10	1535	1.615
363.02	1361	2.062	333.09	1563	1.616
	$z_1 = 0.793$		338.08	1590	1.616
258.05	1118	1.610	343.07	1618	1.616
263.11	1160	1.611	348.05	1646	1.617
268.14	1190	1.611	353.04	1673	1.617
273.13	1220	1.612	358.01	1700	1.618
278.05	1250	1.612	363.01	1728	1.618

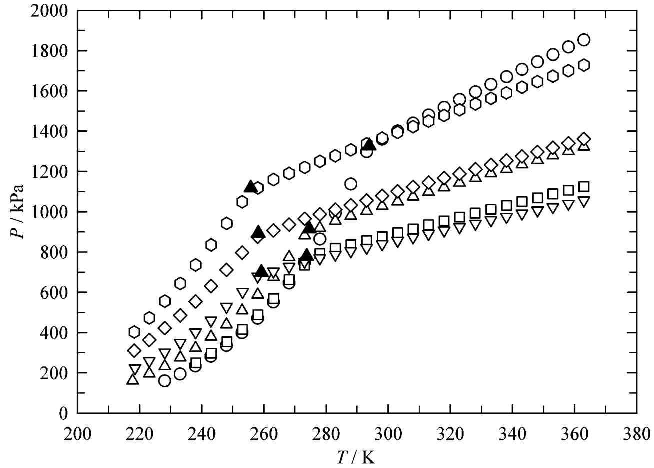

Figure 1. Experimental $P-T$ data and calculated dew points (▲). ○, $z_1 = 0.0816$; ▽, $z_1 = 0.4748$; □, $z_1 = 0.1469$; ◇, $z_1 = 0.6489$; △, $z_1 = 0.2804$; ⬡, $z_1 = 0.7925$.

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 ± 0.3 K and ± 2 kPa, respectively. An 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.[5] This EOS was chosen among two-parameter EOSs because its parameters are fitted to pressures and molar volumes along saturation. For this reason. it is able to accurately represent saturation pressures, volumetric properties along saturation, and vapor phase at superheated region.

One method involves deriving the VLE parameters by means of the "dew point" method with the CSD EOS. 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 both phases, which were calculated from the CSD EOS. 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

$$Q = \sum_i \left(\frac{\mathrm{d}P}{P}\right)^2$$

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 amounted to around ± 1 % for all series except for series 1 where higher deviations (up to 4 %) were evident. This might be caused by incidental greater (but systematic) uncertainty in temperature.

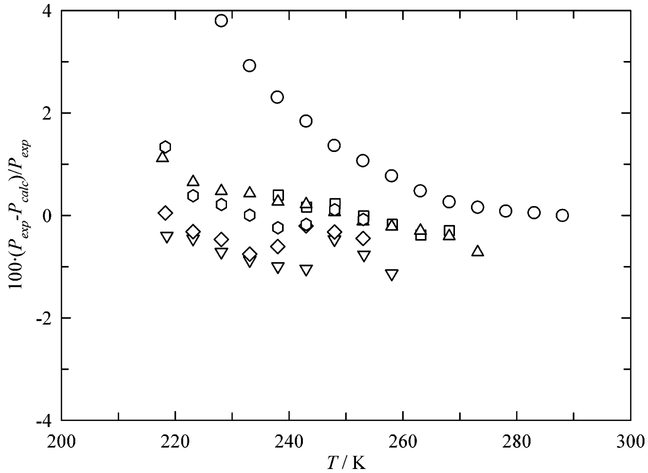

Figure 2. Pressure deviations between experimental values and those calculated with the K_{12} coefficients for the N_2O (1) + R125 (2) system. Symbols denoted as in Figure 1.

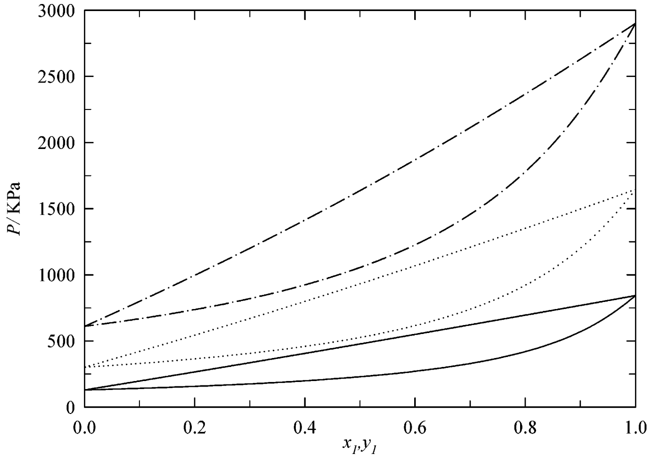

Figure 3. VLE representation from the CSD EOS for the N_2O (1) + R125 (2) system at three temperatures: $T = 233.15$ K (solid lines), $T = 253.15$ K (dotted lines), and $T = 273.15$ K (dash-dotted lines).

The average of the obtained binary interaction parameters values is $K_{12} = -0.027$ with a statistical uncertainty of ± 0.007. Using the averaged K_{12} value from our measurements in the two-phase region data, we calculated the VLE at three different temperatures ($T = 233.15$ K, $T = 253.15$ K, and $T = 273.15$ K). The results are given in Figure 3. The R744A + R125 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, we compared our experimental *PVTx* findings with data calculated using the virial EOS in the Leiden form. A temperature dependence of the third-degree polynomial was found for the second and third virial coefficients. Then the pressure values were calculated from the virial EOS in the Leiden form, using the isochoric experimental temperatures and molar volumes. The second and third virial coefficients for the two pure fluids (B_{ii}, B_{jj}, C_{iii}, and C_{jjj}) were drawn from our previous Burnett experiments for R744A[6] and for R125.[7] The following expressions were adopted for the cross virial coefficients (B_{ij}, C_{iij}, and C_{ijj}) because the binary system revealed an almost ideal behavior of VLE at lower temperatures:

$$B_{ij} = (B_{ii} + B_{jj})/2 \tag{2}$$

$$C_{iij} = (2C_{iii} + C_{jjj})/3 \tag{3}$$

$$C_{ijj} = (C_{iii} + 2C_{jjj})/3 \tag{4}$$

The results are given in Figure 4, showing the relative pressure deviations in the superheated region. The first point

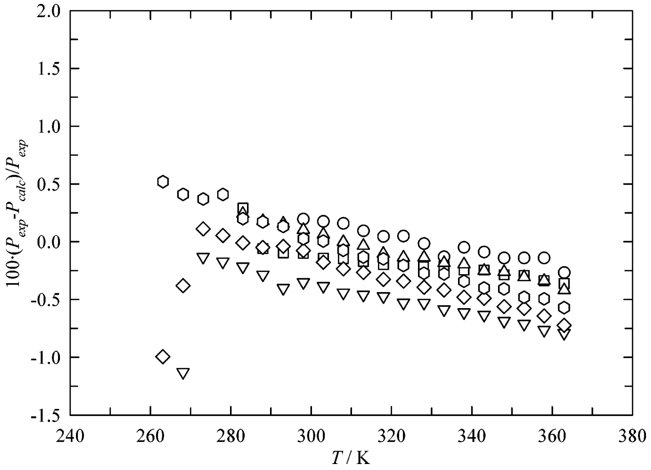

Figure 4. Relative pressure deviations for the N_2O (1) + R125 (2) system between experimental values from isochoric and data calculated with the virial EOS. Symbols denoted as in Figure 1.

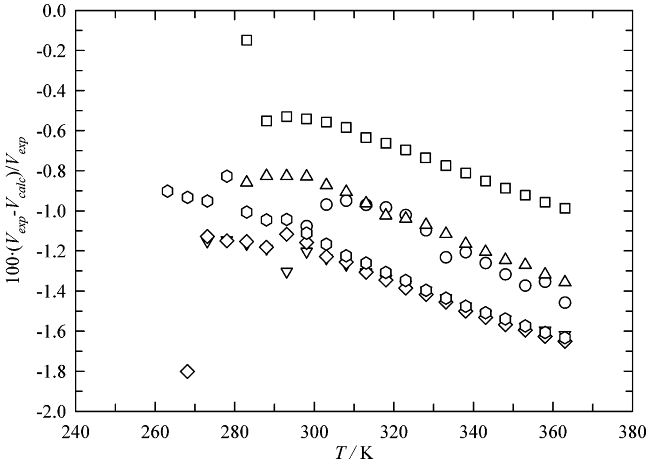

Figure 5. Relative molar volume deviations for the N_2O (1) + R125 (2) system between experimental values from isochoric and data calculated with the CSD EOS. Symbols denoted as in Figure 1.

measured after the change of phase produced always much higher deviations and was not considered in the elaboration. The deviations for all series were within ± 1 %. It is worth nothing that the higher deviation that appeared in the two-phase region for series 1 was not evident in the superheated vapor region, confirming the validity of the measurements. 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 saturation were extrapolated out of range. Also, the K_{12} value, tuned to the low-temperature two-phase data, was assumed to be temperature-independent. Deviations between experiments and CSD EOS are presented in Figure 5. Overall deviations in pressures from the CSD EOS prediction showed an AAD = 1.3 %. Deviations in Figure 5 showed a systematic shift of about −1 % if compared with Figure 4, being the deviations scattered between 0 and −2 %, again not considering the first point measured after the change of phase. Again, the higher deviation that appeared in the two-phase region for series 1 was not evident in the superheated vapor region. Both these models, which are based on different theoretical approaches, showed a similar trend of deviations in terms of temperature.

Conclusions

An isochoric apparatus has been used to obtain *PVTx* measurements on N_2O + R125. The binary interaction parameters were derived from experimental data in the two-phase region, applying the flash method and the CSD EOS. The dew point parameters were found by interpolating the $P-T$ isochoric sequences. The calculated binary interaction parameters were used to derive the VLE, which revealed an almost ideal behavior in terms of Raoult's law. The *PVTx* data were predicted by the virial EOS and the CSD EOS, using its coefficients for the system constituents derived from independent measurements. In general, the *PVTx* are slightly better represented by the virial EOS.

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Received for review March 28, 2006. Accepted July 23, 2006. This work was supported by MIUR, the Ministry of Education, University and Research.

JE060140+