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Experimental $P-T-\rho$ Measurements of Carbon Dioxide and 1,1-Difluoroethene Mixtures

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Pressure and temperature data were experimentally measured for binary supercritical mixtures of carbon dioxide and 1,1-difluoroethene. The temperature range for the experiments was from 310 K to 370 K. The pressure range was from 7.0 MPa to 31.0 MPa. It was determined that the Peng−Robinson equation of state can predict fluid behavior of supercritical carbon dioxide and 1,1-difluoroethene with a deviation of 2.5% ± 0.1%. A binary interaction parameter was obtained from a regression analysis over the temperature range of interest.

Introduction

The investigation of fluoro-polymerization in supercritical media is a growing field. The authors of this paper and others have been particularly interested in the polymerization of 1,1-difluoroethene in supercritical carbon dioxide.[1] However, the ability to understand, control, and characterize the polymerization reactions is dependent upon the ability to accurately predict the density of the binary supercritical mixture using an equation of state. After an extensive search of the literature, no experimental data was found for binary mixtures of carbon dioxide and 1,1-difluoroethene (HFC-1132a, vinylidene fluoride, VF2) at supercritical conditions. To verify $P-T-\rho$ relations predicted by the Peng−Robinson equation of state (PREOS) for binary mixtures of supercritical CO_2 and VF2, it was necessary to experimentally measure pressure, temperature, and density relations. Experiments were carried out using a stainless steel pressure vessel immersed in a constant-temperature bath. A binary interaction parameter was regressed for the PREOS from the experimental data to improve the density predictions when temperature, total pressure, and CO_2 partial pressure are known.

PREOS. The PREOS[2] is expressed in the following form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

where

$$b = 0.077\,80\frac{RT_c}{P_c} \tag{2}$$

$$a(T) = \alpha(T)0.457\,24\frac{R^2T_c^{\,2}}{P_c} \tag{3}$$

and

$$\alpha(T) = [1 + m(1 - T_r^{\,1/2})]^2 \tag{4}$$

$$m = 0.374\,64 + 1.542\,26\omega - 0.269\,92\omega^2 \tag{5}$$

The attractive interaction parameter for a mixture is expressed by

$$a = \sum_i\sum_j x_ix_ja_{ij} \tag{6}$$

where

$$a_{ij} = (1 - k_{ij})\sqrt{a_ia_j} \tag{7}$$

If $i \neq j$, then $a_{ij} = a_{ji}$, and if $i = j$, then the binary interaction parameter k_{ij} is 0. The covolume of the mixture is expressed by

$$b = \sum_i x_ib_i \tag{8}$$

Listed in Table 1 are the parameters used in the PREOS.[3]

Experimental Section

Chemicals. The carbon dioxide used was instrument grade from Praxair with a 99.99% purity, and the 1,1-difluoroethene was provided by Atofina with a 99.8% purity. Both compounds were used without further purification.

Apparatus and Procedure. The experimental apparatus was composed of a 300-mL stainless steel pressure vessel, equipped with a type K thermocouple, valve, and pressure transducer. The thermocouple extended 15 cm into the vessel at one end while the valve and pressure transducer teed into stainless steel tubing connected to the other end. Isometric experiments were carried out by charging the apparatus with known masses of CO_2 and VF2 and then submerging the apparatus in a temperature controlled water bath. The insulated bath temperature was controlled with a Julabo FP 50 circulator and agitation was provided using an impeller. Pressure and temperature data were collected from the aforementioned pressure transducer (Omega model PX215-3KGI, 0 MPa to 20.79 MPa), connected to a pressure indicator, Omega model DP25-E-A, and type K thermocouple connected to a temperature

Table 1. Pure Component Parameters

component	T_c/K	P_c/MPa	ω	MW/g·mol^{-1}
CO_2	304.19	7.382	0.228	44.010
VF2	302.80	4.458	0.139	64.035

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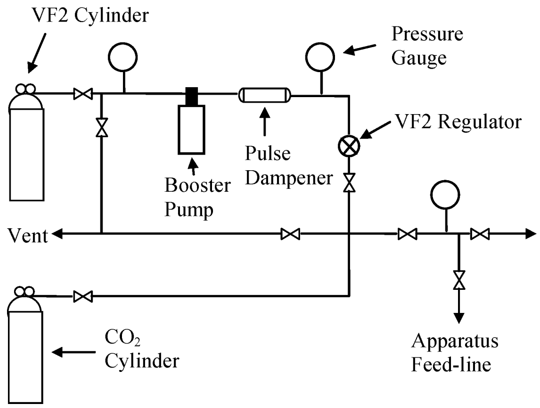

Figure 1. CO_2 and VF2 feed system flow diagram.

indictor, Cole-Parmer model 791JF. All valves used were regulated stem needle valves, Autoclave Engineers model 5W-6081. Mass was measured using a digital balance, Sartorius model PT6-OUR, with reading increments of 1 g. The uncertainty of the measured pressure was estimated to be ±0.05 MPa, and the uncertainty of the measured temperature was estimated to be ±0.6 K.

To charge the pressure vessel with CO_2 and VF2 for each constant-density experiment, the apparatus was connected at its valve to a separately constructed feed system, which is shown in Figure 1. The feed system is equipped so that CO_2 and VF2 can both be fed in a controlled manner and also so that pressure vessel and feed line purging can be done to prevent air contamination. Of note, while CO_2 was fed up to its room-temperature vapor pressure, a Haskel Gas Booster, AG-30C, was used to develop VF2 pressure for charging into the apparatus.

The pressure vessel, pressure transducer, valves, and fittings are rated to 69 MPa. 1,1-difluoroethene must be carefully handled because it is flammable and at room temperature and pressure is denser than air. A flammability detector, American Gas and Chemical model SB0-209-8, was used to monitor for fugitive VF2 emissions and ensure that a combustible vapor was not present.

The procedure for pressurizing the apparatus involved charging with CO_2 and then VF2 while measuring the mass of the apparatus between charges while disconnected from the feed system. The mass of the apparatus was first measured at ambient conditions and then connected to the feed system. Air was then removed from the apparatus by purging four times with CO_2 from 2.86 MPa to 0.27 MPa, after which the apparatus was charged to a predetermined pressure of CO_2. The apparatus was then disconnected and weighed. The CO_2-charged apparatus was then reconnected to the feed system and air was removed from the feed line by purging it four times with VF2 from 2.86 MPa to 0.27 MPa. The apparatus was charged with VF2 and then disconnected to measure the total mass of the apparatus. While charging with VF2, the VF2 line pressure was maintained above that of the vessel pressure to prevent back flow of CO_2 into the feed line.

Table 2. Numerical Values of the b_{ij} Coefficients for Equation 9

	b_{ij}						
i	$j = 0$	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$	$j = 6$
0	−0.725 854 44	−1.683 329 74	0.259 587 221	0.376 945 574	−0.670 755 37	−0.871 456 13	−0.149 156 93
1	0.447 869 183	1.260 506 91	5.969 570 49	15.464 5885	19.444 947 5	8.648 804 97	0
2	−0.172 012	−1.834 581 78	−4.614 876 77	−3.821 219 26	3.601 713 49	4.922 655 52	0
3	0.004 463 049	−1.763 005 41	−11.143 670 5	−27.821 544 6	−27.168 572	−6.421 778 72	0
4	0.255 491 571	2.374 142 46	7.509 251 41	6.611 333 18	−2.426 632 1	−2.579 440 32	0
5	0.059 466 73	1.169 746 83	7.437 064 1	15.064 673 1	9.574 968 45	0	0
6	−0.147 960 01	−1.692 330 71	−4.682 199 37	−3.135 174 48	0	0	0
7	0.0136 710 44	−0.100 492 33	−1.636 538 06	−1.870 829 88	0	0	0
8	0.039 228 458	0.441 503 812	0.886 741 97	0	0	0	0
9	−0.011 987 21	−0.084 605 19	0.046 456 437	0	0	0	0

Table 3. Experimental Pressure P for Mixtures of Carbon Dioxide (1) and 1,1-Difluoroethene (2) as a Function of Temperature T and Experimental Molar Density ρ

	mixture 1	mixture 2	mixture 3	mixture 4	mixture 5	mixture 6	mixture 7
ρ_1	8.94 mol·L^{-1}	8.09 mol·L^{-1}	7.24 mol·L^{-1}	6.01 mol·L^{-1}	5.16 mol·L^{-1}	5.08 mol·L^{-1}	2.39 mol·L^{-1}
ρ_2	2.01 mol·L^{-1}	3.92 mol·L^{-1}	6.14 mol·L^{-1}	4.93 mol·L^{-1}	6.30 mol·L^{-1}	5.72 mol·L^{-1}	6.73 mol·L^{-1}
ρ_{total}	10.95 mol·L^{-1}	12.01 mol·L^{-1}	13.38 mol·L^{-1}	10.94 mol·L^{-1}	11.46 mol·L^{-1}	10.90 mol·L^{-1}	9.12 mol·L^{-1}

mixture 1		mixture 2		mixture 3		mixture 4		mixture 5		mixture 6		mixture 7	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
310.9	8.75	311.5	9.36	312.0	12.06	310.9	8.51	311.5	9.07	314.8	9.18	311.5	7.02
315.7	9.69	319.8	11.36	317.0	13.62	312.6	8.84	315.9	10.14	317.6	9.77	316.5	7.88
321.5	10.82	322.6	12.02	318.2	13.97	327.0	11.96	320.9	11.37	321.5	10.64	322.0	8.81
325.9	11.68	327.3	13.27	319.8	14.58	328.4	12.20	325.4	12.50	327.0	11.87	325.4	9.40
331.5	12.79	328.2	13.41	324.8	16.31	328.4	12.23	331.5	14.01	332.0	12.93	325.4	9.36
336.5	13.79	330.7	14.03	326.5	16.77	334.0	13.43	335.4	15.04	339.8	14.61	333.2	10.68
342.6	14.93	332.0	14.34	328.2	17.34	342.9	15.37	340.9	16.44	340.9	14.88	335.9	11.17
347.6	15.81	336.5	15.49	329.5	17.67	356.5	18.26	345.4	17.43	347.6	16.32	338.2	11.51
352.6	16.82	341.5	16.63	330.4	17.94	365.9	20.20	347.0	17.86	351.5	16.95	338.7	11.63
355.9	17.45	346.5	17.88	331.5	18.37	367.0	20.50	352.6	19.15	356.5	18.21	342.3	12.24
		350.9	18.94	332.3	18.61			353.2	19.33	360.9	19.20	347.6	13.06
		356.2	20.23	333.2	18.90			356.5	20.19	361.5	19.22	351.5	13.71
				334.3	19.24			359.8	20.96				
				334.8	19.45								
				336.2	19.87								
				338.4	20.63								
				339.3	20.92								

After completion of charging, the apparatus was placed in the constant-temperature bath and a temperature set point would be entered into the Julabo circulator. The temperature in the pressure vessel was allowed to equilibrate over a minimum of 1 h at which point the temperature and pressure inside the vessel were recorded. The temperature of the water bath was then increased incrementally in 5 °C to 8 °C steps, each time allowing for stabilization and data recording. Thus, trials were performed until the pressure in the vessel reached 20.79 MPa or the water bath reached its maximum achievable temperature (370 K). The pressure vessel was then removed from the water bath, allowed to dry, and then re-weighed to ensure that no leaks occurred during the experiment. Finally, the vessel was depressurized.

The internal volume of the experimental apparatus, 296 mL ± 1 mL, was determined by charging it with a known mass of CO_2 and recording a range of temperature−pressure data. The density was then obtained from a regression analysis of the temperature and pressure data by using an analytical equation of state for carbon dioxide:[4]

$$P = RT\rho[1 + \omega \sum_{i=0}^{9} \sum_{j=0}^{J_i} b_{ij}(\tau - 1)^j(\omega - 1)^i] \tag{9}$$

$$\omega = \rho/d \tag{10}$$

$$\tau = f/T \tag{11}$$

where d = 0.010 63 mol·cm^{-3} and f = 304.2 K. Values for the b_{ij} coefficients[4] may be found in Table 2.

The experimental molar density, ρ, was determined by dividing the number of moles of a component in the system by the volume of the experimental apparatus. The uncertainty of the molar density was estimated to be ±0.05 mol·L^{-1}.

Results and Discussion

The pressure and temperature data obtained from the experiments are presented in Table 3, sorted by decreasing CO_2 density. A comparison between the predicted values of the pressure for the PREOS and the experimental data showed a root-mean-square error (RSME) of 0.38 MPa and an absolute mean percent error of 2.5%. Root-mean-square error is defined as

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=0}^{N}[P_{\mathrm{i}}^{\mathrm{calc}} - P_{\mathrm{i}}^{\mathrm{exp}}]^2} \tag{12}$$

The mean binary interaction parameter, k_{ij}, for the data set was determined to be −0.0204 with a standard error of 0.0010 and a standard deviation of 0.0091. The root-mean-square error between the experimental values and the calculated values using the binary interaction parameter was reduced to 0.12 MPa, and the absolute mean percent error was reduced to 0.7%. A representative sample of the predicted values and experimental data is shown in Figure 2. This figure demonstrates the slight over-prediction of the pressure by the PREOS and the increased accuracy obtained by utilizing a k_{ij} of −0.0204. An analysis of variance with a confidence interval of 95% shows that the regressed binary interaction parameter is dependent upon both temperature and composition. Indeed, Figure 3 does show that the absolute percent error appears to decrease with increasing temperature with both the uncorrected and corrected predicted pressures. However, correlation of temperature dependence was found to be unnecessary due to the already high accuracy obtained by the fixed value of k_{ij}. As could be expected, the largest errors were obtained at temperatures closer to the critical points of the fluids.

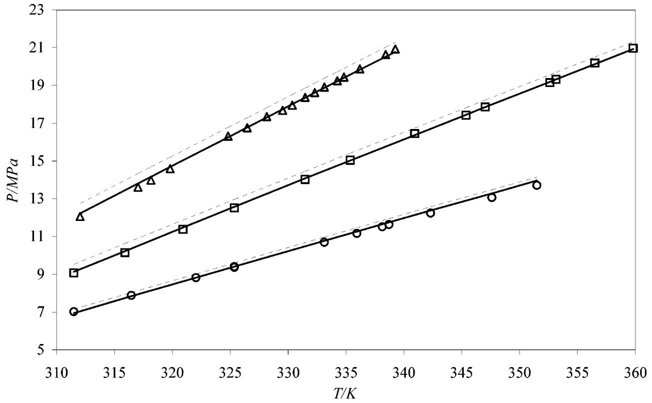

Figure 2. Experimental pressure, P, of mixtures of CO_2 and VF2: △, mixture 3; □, mixture 5; ○, mixture 7; dashed line, predicted pressure using PREOS with k_{ij} = 0; and solid line, predicted pressures using PREOS with k_{ij} = −0.0204.

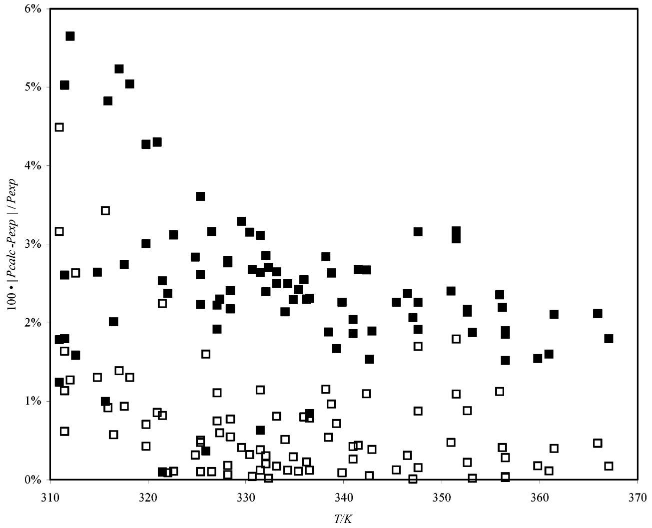

Figure 3. Absolute percentage deviation of pressure related to temperature: ■, PREOS with k_{ij} = 0; and □, PREOS with k_{ij} = −0.0204.

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