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Vapor–Liquid Equilibrium in the System Carbon Dioxide + Cyclopentane from 275 to 493 K at Pressures to 12.2 MPa

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Isothermal vapor–liquid equilibrium data have been measured for the carbon dioxide + cyclopentane system at 15 temperatures from 276.64 to 493.11 K and at pressures to 12.2 MPa. The mixture critical line has been located and is shown to be continuous in p–T–x space between the critical points of the pure components. The results are compared with the only other set of measurements on this system in the literature, which were made at temperatures below 333 K. The data sets are also correlated by using two cubic equations of state, the Soave–Redlich–Kwong and Peng–Robinson equations. Both equations provide phase compositions in good agreement with experiment except near the critical points of mixtures. Binary interaction parameters for the system are reported for both equations of state over the entire temperature range.

Introduction

This study is a continuation of a research program to provide vapor–liquid equilibrium (VLE) data on binary systems of interest to the petroleum and natural gas industry. VLE data for CO_2 + n-pentane (*1*), CO_2 + n-butane (*2*), and CO_2 + 2,2-dimethylpropane (*3*) have been reported previously. There is a recent report of VLE data for the binary system CO_2 + cyclopentane at three temperatures by Eckert and Sandler (*4*). Their work did not include measurement of mixture critical points, and it covers only a small portion of the temperature range of vapor–liquid equilibrium for this system. This paper presents VLE data at temperatures to within 20 K of the critical temperature of cyclopentane and at pressures to the critical line of the mixture.

Experimental Section

The apparatus and the procedure used in this study are essentially the same as those used by Shah et al. (*3*) and the studies mentioned in that paper. It is a vapor recirculation system designed for the measurement of liquid- and vapor-phase compositions as a function of pressure at fixed temperature. The details of the method have been given in earlier papers (*5*–*7*).

Two sets of apparatus were used in this study, depending on the temperature. A high-temperature apparatus was used for temperatures greater than 320 K. One change was made in the apparatus for this study. The glass-windowed equilibrium cell was replaced by a stainless steel cell fitted with eight small windows of synthetic sapphire. This cell was used earlier by Pozo and Streett (*5*) to study the dimethyl ether + water system. More details about the cell are available there. The low-temperature apparatus used for the isotherms below 320 K was the same as that described by Shah et al. (*3*).

Temperature was measured on IPTS-68 using a platinum resistance thermometer and Mueller bridge with an accuracy of 0.02 K. Pressures were measured with an uncertainty of 0.007 MPa or 0.5% (whichever is greater) by using a digital pressure gauge (Autoclave Engineers, Inc., Model DPS-0021) calibrated in this laboratory against a Ruska DDR-6000 direct-reading quartz spiral gauge that was in turn calibrated against a Ruska dead-weight gauge.

The phase compositions were determined by withdrawing samples through capillary lines and analyzing them with a Hewlett-Packard Model 5840A gas chromatograph equipped with a thermal conductivity detector. A stainless steel column (0.312-cm o.d., 50.8-cm length) packed with 100/120 mesh Porapak Q was used for separation of CO_2 and cyclopentane. The gas chromatograph was calibrated by using mixtures of known composition that were prepared gravimetrically. The phase compositions reported here are estimated to be accurate within 0.3 mol % near the middle of the mole fraction range and better near the extremes. In the immediate vicinity of the critical line, the uncertainty may be as large as 0.5 mol %.

The CO_2 used in this work was supplied by Air Products and Chemicals Inc. and had a purity of 99.99 mol %. The cyclopentane was supplied by Phillips Petroleum Co. with a minimum purity of 99 mol %. These chemicals were used without further purification.

Results

Vapor and liquid compositions have been measured at 15 temperatures from 276.64 to 493.11 K and pressures to 12.2 MPa. The experimental results are presented in Table I, and the isotherms are plotted on a pressure–composition (p–x) diagram in Figure 1. The system exhibits large positive deviations from Raoult's law at low pressures. The pressure–temperature (p–T) extent of the region covered by this study, together with a few isopleths, is shown in Figure 2. AB and CD are the vapor pressure curves for CO_2 and cyclopentane, respectively, with critical points B and D. BED is the mixture critical line. Data for the critical line are listed in Table II. The critical pressure and composition for each isotherm were located by performing an extrapolation using the equilibrium values at the four or five highest pressures in an algorithm that uses the assumption that the variation of composition with pressure about the critical value is cubic. Phase compositions were measured at pressures within ~0.3 MPa of the critical

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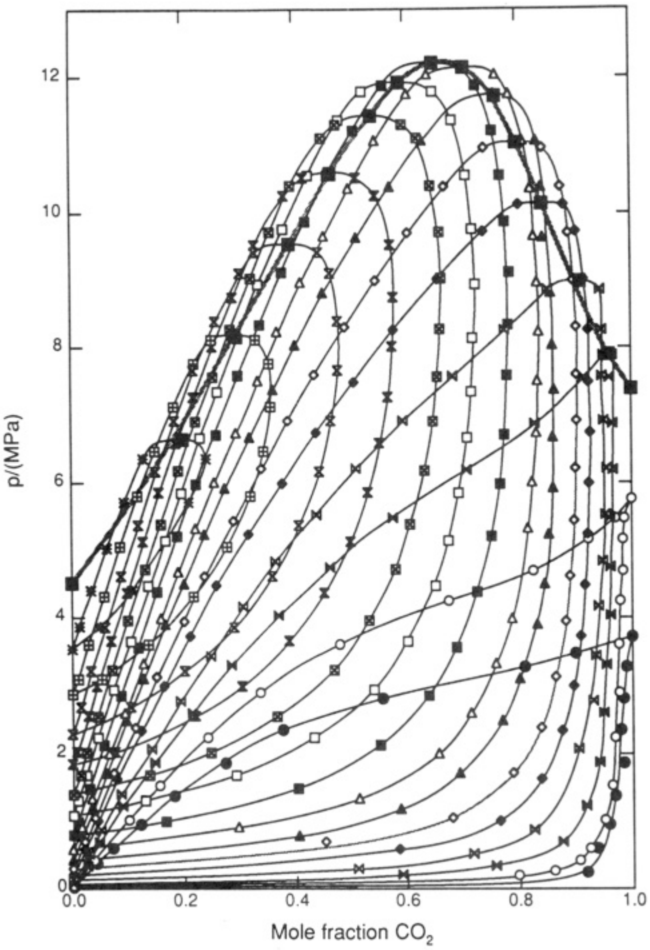

Figure 1. Experimental isotherms for the carbon dioxide + cyclopentane system. Symbols denote isotherms as follows: ●, 276.64 K; ○, 293.14 K; ⧓, 313.08 K; ⋈, 328.23 K; ◆, 344.70 K; ◇, 358.06 K; ▲, 375.15 K; △, 388.11 K; ■ (smaller), 403.07 K; □, 419.15 K; ⊠, 433.21 K; ⧗, 448.81 K; ⧖, 463.23 K; ⊞, 478.17 K; ✱, 493.11 K. Critical points are denoted by ■ (larger) and the critical line is shown as a wide shaded curve.

pressure on most isotherms. For those isotherms where no measurements were made close to the critical pressure, the extrapolated values are somewhat more uncertain. In Figure 3, K values are plotted as a function of pressure ($K_i \equiv y_i/x_i$, where y_i is the mole fraction of component i in the vapor phase and x_i is the mole fraction of component i in the liquid phase) for four representative isotherms. K values for CO$_2$, the more volatile component, are always greater than unity, and the K values for cyclopentane are less than unity. Below the critical temperature of CO$_2$, an isotherm in the K-value diagram is composed of two separate branches, one for each component, but above that temperature, the branches converge at a critical point where $K = 1$ and the curve has a vertical tangent. Smooth K-value plots indicate internal consistency of the VLE data, as they tend to exaggerate scatter in the results. At low pressures, which correspond to dilute solutions of CO$_2$ in cyclopentane, the isotherms should asymptotically approach unit negative slope in logarithmic coordinates because the solute (CO$_2$) should obey Henry's law and the solvent (cyclopentane) should obey Raoult's law.

Comparison with Published Data

There were no published data for this system when this study was started. Since then, Eckert and Sandler (*4*) have published data for three isotherms not far from the critical temperature of CO$_2$. They did not measure the critical pressures for the isotherms but have reported estimations made by using a cubic equation of state. The results presented here are in good agreement with those estimates. Since their measurements were made at different temperatures from ours, comparison of isotherms on a $p-x$ diagram is not very useful. Instead, we have cross-plotted both sets of data as isobars on a $T-x$ diagram in Figure 4. Because measurements were not made at low temperatures, part of the 1-MPa isobar is not shown. The data agree well at the higher temperature, but at lower temperatures their phase compositions tend to be richer in CO$_2$.

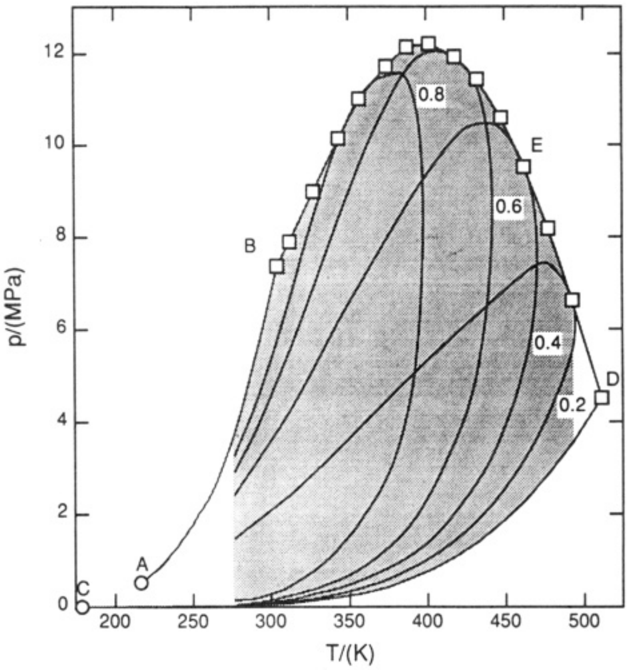

Figure 2. Pressure-temperature diagram for carbon dioxide + cyclopentane. The shaded area is the $p-T$ region covered in this work. AB and CD are the vapor pressure curves of carbon dioxide and cyclopentane, respectively, and BED is the mixture critical line. Critical points are denoted by □ and triple points by ○. Four isopleths are also shown. Each is labeled with its mole fraction of CO$_2$ to the right of the vapor branch.

Equation of State Calculations

The experimental data have been compared with the predictions of two equations of state, the Soave-Redlich-Kwong (SRK) equation (*8*) and the Peng-Robinson (PR) equation (*9*):

SRK equation

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

PR equation

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{2}$$

The parameters a and b are concentration-dependent. The mixing rules for binary mixtures are

SRK

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \tag{3}$$

$$b = b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2 \tag{4}$$

PR

$$a = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \tag{5}$$

$$b = b_{11}x_1 + b_{22}x_2 \tag{6}$$

where

$$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2} \tag{7}$$

$$b_{12} = (1 - j_{12})(b_{11} + b_{22})/2 \tag{8}$$

Table I. Equilibrium Phase Properties of the Carbon Dioxide (1) + Cyclopentane (2) System: Pressure p, Temperature T, Liquid Mole Fraction x_1, and Vapor Mole Fraction y_1

p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1
T = 276.64 K			T = 293.14 K			T = 313.08 K			T = 328.23 K		
0.0166	0.000	0.000	0.0346	0.000	0.000	0.0740	0.000	0.000	0.1228	0.000	0.000
0.234		0.918	0.200		0.796	0.200		0.590	0.290		0.512
0.386	0.043		0.276		0.860	0.331	0.026	0.758	0.503	0.029	0.718
0.607	0.070	0.936	0.421	0.036	0.905	0.683	0.047	0.876	0.855	0.051	0.827
0.958	0.121	0.957	0.607		0.924	1.207	0.090	0.918	1.393	0.088	
1.372	0.182	0.968	1.014	0.099	0.949	1.855	0.148	0.942	2.062	0.142	0.906
1.862	0.274	0.983	1.531	0.156	0.964	2.579	0.216	0.951	2.765	0.196	0.931
2.337	0.377	0.978	2.227	0.243	0.967	3.296	0.288	0.956	3.434	0.250	0.936
2.813	0.556	0.983	2.896	0.338	0.975	4.020	0.372	0.962	4.151	0.308	0.943
3.261	0.810	0.990	3.592	0.479	0.977	4.723	0.464	0.962	4.819	0.367	0.950
3.482	0.901		4.240	0.675	0.978	5.454	0.579	0.964	5.516	0.441	0.955
3.723	1.000	1.000	4.688	0.826	0.985	6.178	0.710	0.967	6.185	0.513	0.957
			5.143	0.924	0.984	6.860	0.832	0.967	6.888	0.597	0.953
			5.461	0.970	0.987	7.536	0.917	0.963	7.550	0.687	0.950
			5.757	1.000	1.000	7.881	0.952	0.969	8.239	0.778	0.950
									8.853	0.856	0.948
T = 344.70 K			T = 358.06 K			T = 375.15 K			T = 388.11 K		
0.1993	0.000	0.000	0.2877	0.000	0.000	0.4119	0.000	0.000	0.5845	0.000	0.000
0.572	0.021	0.585	0.676	0.020	0.454	0.772	0.017	0.405	0.910	0.016	0.299
0.993	0.046	0.765	1.043	0.040	0.682	1.176	0.036	0.589	1.318	0.034	0.515
1.613	0.079	0.839	1.696	0.075	0.789	1.696	0.060	0.695	1.998	0.065	0.657
2.330	0.124	0.877	2.368	0.113	0.838	2.471	0.098	0.770	2.595	0.094	0.715
2.985	0.165	0.897	3.110	0.154	0.866	3.103	0.129	0.803	3.316	0.128	0.761
3.716	0.213	0.910	3.927	0.202	0.883	3.885	0.170	0.833	3.975	0.160	0.788
4.462	0.262	0.918	4.593	0.241	0.893	4.496	0.202	0.846	4.661	0.193	
5.217	0.319	0.924	5.423	0.294	0.901	5.224	0.241	0.855	5.316	0.223	0.818
5.965	0.380	0.927	6.192	0.343	0.903	5.904	0.277	0.863	6.000	0.259	0.827
6.727	0.440	0.928	6.892	0.391	0.905	6.645	0.323	0.863	6.727	0.298	0.833
7.483	0.508	0.927	7.586	0.439	0.905	7.373	0.365	0.865	7.503	0.339	0.837
8.245	0.580	0.925	8.286	0.493	0.904	8.032	0.403	0.862	8.231	0.373	0.838
8.993	0.660	0.919	8.986	0.548	0.899	8.801	0.454	0.859	8.952	0.415	0.837
9.707	0.742	0.906	9.686	0.608	0.893	9.618	0.514	0.848	9.645	0.456	0.832
10.112	0.805	0.884	10.380	0.673	0.879	10.366	0.575	0.844	10.345	0.500	0.825
			10.942	0.743	0.848	11.052	0.633	0.837	11.045	0.548	0.813
									11.732	0.608	0.789
									12.027	0.643	0.765
T = 403.07 K			T = 419.15 K			T = 433.21 K			T = 448.81 K		
0.7935	0.000	0.000	1.0870	0.000	0.000	1.3930	0.000	0.000	1.8250	0.000	0.000
1.002	0.009	0.167	1.297	0.009	0.129	1.682	0.012	0.137	2.018	0.009	0.076
1.483	0.028	0.403	1.682	0.024	0.294	2.011	0.024	0.247	2.547	0.028	0.222
2.128	0.055	0.552	2.224	0.045	0.433	2.540	0.045	0.368	2.979	0.045	0.305
2.849	0.086	0.638	2.931	0.074	0.540	3.226	0.072	0.470	3.638	0.071	0.391
3.563	0.118	0.690	3.638	0.105	0.602	3.961	0.101	0.534	4.352	0.099	0.455
4.373	0.154	0.725	4.469	0.138	0.652	4.702	0.132	0.580	5.101	0.130	0.502
5.197	0.190	0.751	5.135	0.168	0.675	5.382	0.160	0.608	5.842	0.159	0.532
5.959	0.225	0.767	5.842	0.198	0.695	6.165	0.193	0.632	6.556	0.190	0.555
6.707	0.260	0.776	6.652	0.233	0.711	6.892	0.224	0.648	7.256	0.221	0.570
7.579	0.302	0.782	7.338	0.264	0.717	7.558	0.255	0.657	8.004	0.255	0.579
8.334	0.340	0.783	8.128	0.301	0.721	8.272	0.288	0.663	8.732	0.292	0.581
9.110	0.380	0.786	8.924	0.337	0.725	9.020	0.324	0.664	9.501	0.333	0.575
9.865	0.421	0.779	9.741	0.382	0.720	9.714	0.358	0.661	10.235	0.384	0.549
10.544	0.463	0.771	10.544	0.427	0.711	10.400	0.397	0.646	10.510	0.419	0.514
11.217	0.508	0.756	11.361	0.483	0.685	11.100	0.451	0.622			
11.876	0.562	0.729	11.780	0.526	0.652	11.293	0.477	0.597			
T = 463.23 K			T = 478.17 K			T = 493.11 K					
2.2871	0.000	0.000	2.8682	0.000	0.000	3.5330	0.000	0.000			
2.684	0.015	0.105	3.103	0.010	0.054	3.879	0.014	0.049			
3.206	0.035	0.203	3.611	0.029	0.137	4.393	0.035	0.107			
3.858	0.060	0.294	4.318	0.057	0.220	5.018	0.063				
4.559	0.090	0.361	5.046	0.088	0.279	5.698	0.096	0.211			
5.348	0.121	0.410	5.801	0.120	0.322	6.336	0.130	0.242			
6.144	0.154	0.445	6.453	0.150	0.346						
6.899	0.186	0.467	7.119	0.184	0.360						
7.647	0.222	0.479	7.757	0.221	0.357						
8.382	0.260	0.481	8.121	0.254	0.333						
9.082	0.305	0.467									
9.398	0.333	0.446									

For both equations, the temperature dependence of the constant a is given by an expression based on the Pitzer acentric factor (*8*, *9*). The parameters b_{11} and b_{22} are evaluated from critical data for the pure components.

The binary interaction parameter k_{12} is adjusted for each isotherm individually to produce the best fit by the equations of state to the experimental data. No attempt was made to optimize the fit by adjusting the binary parameter j_{12}, which was taken to be zero for this work. The values of k_{12} so calculated are presented in Table III along with the root mean square

Table II. Critical Line of the Carbon Dioxide (1) + Cyclopentane (2) System: Critical Temperature T, Critical Pressure p, Critical Mole Fraction x_1

T/K	p/MPa	x_1	T/K	p/MPa	x_1
304.19	7.382	1.000	419.15	11.91	0.591
313.08	7.88	0.959	433.21	11.42	0.540
328.23	8.97	0.911	448.81	10.58	0.468
344.70	10.13	0.845	463.23	9.52	0.392
358.06	11.03	0.799	478.17	8.19	0.295
375.15	11.73	0.763	493.11	6.64	0.202
388.11	12.14	0.707	511.75	4.513	0.000
403.07	12.20	0.652			

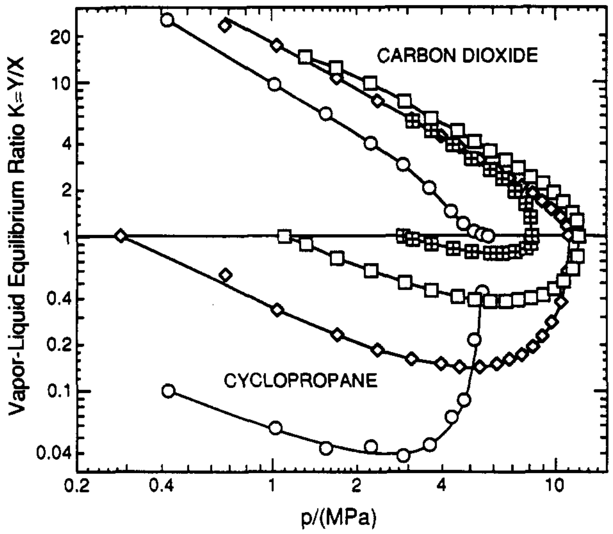

Figure 3. Equilibrium ratios for carbon dioxide + cyclopentane at four temperatures. The symbols denote isotherms as follows: ○, 293.14 K; ◇, 358.06 K; □, 419.15 K; ⊞, 478.17 K.

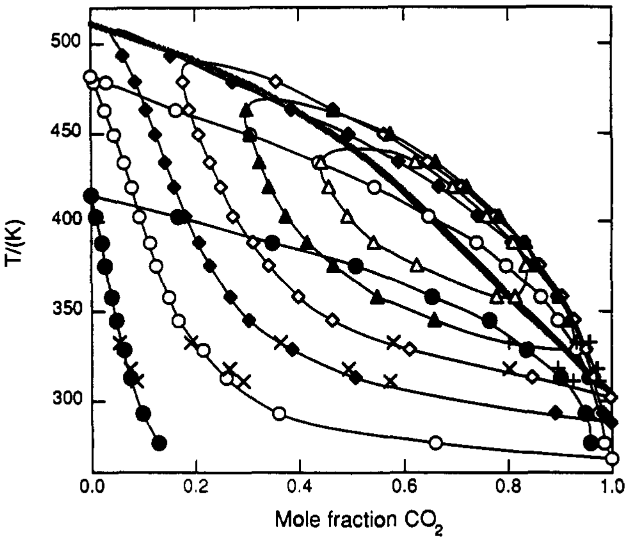

Figure 4. Temperature–mole fraction diagram for carbon dioxide + cyclopentane. The symbols denote isobars as follows: ●, 1 MPa; ○, 3 MPa; ◆, 5 MPa; ◇, 7 MPa; ▲, 9 MPa; △, 11 MPa. Liquid-phase data interpolated along isotherms of ref 4 are denoted by × and vapor data by +.

Table III. Root Mean Square Deviations between Calculated and Experimental Liquid, rms(x), and Vapor, rms(y), Mole Fractions Using the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) Equations of State (EOS) with Adjusted Interaction Parameters k_{12} for the System Carbon Dioxide + Cyclopentane

T/K	EOS	k_{12}	rms(x)	rms(y)
276.64	PR	0.133	0.0168	0.0180
	SRK	0.134	0.0179	0.0192
293.14	PR	0.127	0.0181	0.0122
	SRK	0.129	0.0202	0.0143
313.08	PR	0.123	0.0148	0.0138
	SRK	0.125	0.0151	0.0162
328.23	PR	0.119	0.0121	0.0194
	SRK	0.125	0.0118	0.0210
344.70	PR	0.116	0.0211	0.0194
	SRK	0.124	0.0197	0.0209
358.06	PR	0.118	0.0159	0.0291
	SRK	0.124	0.0155	0.0304
375.15	PR	0.116	0.0162	0.0140
	SRK	0.128	0.0153	0.0173
388.11	PR	0.120	0.0121	0.0154
	SRK	0.129	0.0123	0.0195
403.70	PR	0.130	0.0100	0.0188
	SRK	0.143	0.0101	0.0238
419.15	PR	0.133	0.0095	0.0212
	SRK	0.144	0.0110	0.0280
433.21	PR	0.138	0.0096	0.0204
	SRK	0.152	0.0113	0.0287
448.81	PR	0.141	0.0104	0.0214
	SRK	0.139	0.0170	0.0297
463.23	PR	0.162	0.0083	0.0202
	SRK	0.197	0.0083	0.0285
478.17	PR	0.178	0.0080	0.0195
	SRK	0.181	0.0124	0.0268
493.11	PR	0.232	0.0010	0.0075
	SRK	0.266	0.0011	0.0039

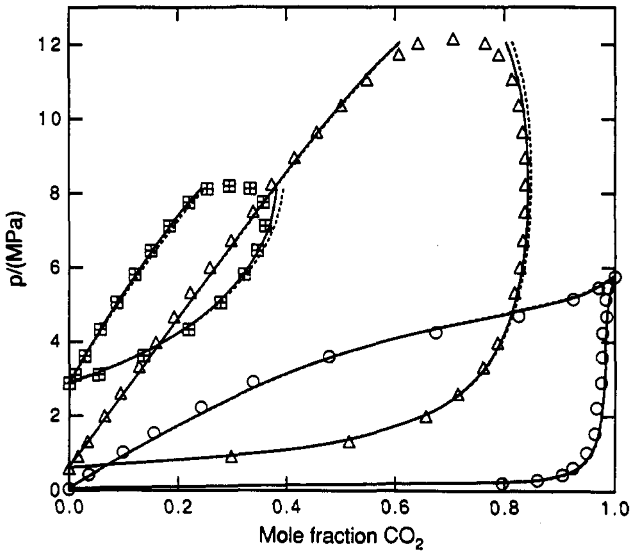

Figure 5. Comparison of three isotherms with equation of state calculations. Symbols denote isothermal data as follows: ○, 293.14 K; △, 388.11 K; ⊞, 478.17 K. The predictions of the Soave–Redlich–Kwong equation are shown by dashed lines and the Peng–Robinson equation by solid lines.

deviations of the vapor, rms(y), and liquid, rms(x), compositions. We observe that the k_{12}'s for the PR equation show a minimum near 350 K, whereas Eckert and Sandler (*4*) see a sharp increase over their temperature range (310–333 K). Three typical isotherms are plotted in Figure 5. The fit of both equations of state to the data are comparable, especially at low temperatures. At higher temperatures, the fit for the SRK equation is marginally worse than for the PR equation. One can see in Figure 5 that, for the isotherms above the critical temperature of CO_2, the cubic equations give a critical pressure that is greater than the experimental values. Both equations predict vapor-phase composition values greater than the experimental values, especially at the higher temperatures. The predicted vapor compositions are relatively insensitive to k_{12}. The deviations between the fits to cubic equations and experimental data are in the opposite direction for this system from the deviations seen for CO_2 + 2,2-dimethylpropane (*3*).

List of Symbols

a, b	coefficients in cubic equation of state
a_{ij}, b_{ij}	coefficients in quadratic mixing rules for equation of state
j_{ij}	interaction parameter describing deviations from the linear combining rule for covolumes in the SRK equation
k_{ij}	interaction parameter describing deviations from the geometric mean combining rule for the unlike pair attraction parameter in cubic equations
K_i	$\equiv y_i/x_i$
p	pressure
R	molar gas constant
rms(x, y)	root mean square deviation between calculated and experimental mole fractions on one isotherm
T	absolute temperature
V	molar volume
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i

Registry No. CO_2, 124-38-9; cyclopentane, 287-92-3.

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High-Pressure Vapor–Liquid Equilibrium of Some Binary Mixtures of Cyclopentane, Argon, Nitrogen, *n*-Butane, and Neopentane

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Accurate high-pressure vapor–liquid equilibrium and phase density data for binary systems of cyclopentane with carbon dioxide, nitrogen, and argon and of argon also with neopentane and *n*-butane are reported, each at two isotherms. These data are correlated with the Peng–Robinson equation of state using one- and two-parameter versions of the van der Waals one-fluid mixing rules with both generalized and fluid-specific equation of state parameters.

Introduction

This study is the continuation of a research program on the measurement of vapor–liquid equilibrium data for mixtures consisting of hydrocarbons and inorganic gases. A set of mixtures has been chosen for this purpose based on their relative interaction energies (as reflected in the values of the critical temperatures T_c) and on molecular size (based on values of critical molar volumes V_c). The mixtures consist of the inorganic gases Ar, N_2, and CO_2 with the hydrocarbons *n*-butane, cyclopentane, and neopentane. The experimental data we obtain consist of pressure P, temperature T, liquid x_i, and vapor y_i, equilibrium mole fractions, and phase densities ρ, along two isotherms. Further we use these data to test the correlative ability of a simple cubic equation of state with various mixing rules. In this work we use the $P-T-x-y$ data to determine the optimal value of the binary equation of state interaction parameters, and then we predict the phase densities, which are compared with our measured values. This is an additional test of the accuracy of the equation of state and its mixing rules. Also, we compare the results of using both the generalized equation of state parameters and temperature-dependent parameters determined specifically for each fluid.

Equipment and Experiment

The apparatus used for the experiments was described by Shibata (*1*) and Shibata and Sandler (*2*). It consists of a visual equilibrium cell, recirculation pumps (vapor and liquid), and vibrating-tube density meters. The circulating vapor is bubbled into the bottom of the cell, and the liquid is sprayed from the top, which ensures good vapor–liquid contact in the equilibrium cell; both phases are also circulated through the density meters. The entire system is enclosed in a constant-temperature air oven. System temperatures are monitored by five thermocouples located in the cell with an accuracy of ±0.05 K. The pressure is measured with a dead weight tester coupled to a null differential pressure indicator with an accuracy of ±0.14 bar at the high pressures measured here. Small separate samples of the equilibrated gas and liquid mixtures are drawn into evacuated and preheated gas bombs that contain motor-driven mixers. The samples are analyzed with a gas chromatograph. The chromatograph, other ancillary equipment, and the calibration procedures used have all been described previously (*2*). The sampling procedures used usually lead to area fractions in the three sample injections with a standard deviation of 0.003 in mole fraction.

Results and Discussion

The experimental data obtained in this work are reported in Table I. These data have been correlated with the Peng–Robinson equation of state (*3*)

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \qquad (1)$$

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