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Equilibrium Phase Properties of Selected Carbon Dioxide Binary Systems: *n*-Pentane-Carbon Dioxide and Isopentane-Carbon Dioxide

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Vapor and liquid equilibrium phase compositions were determined for the *n*-pentane-carbon dioxide system at 135, 160, and 190 °C and for the isopentane-carbon dioxide system at 135, 160, and 180 °C. Measurements were made at pressures from the vapor pressure of the pentanes to the critical region at each temperature. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The critical temperatures and corresponding critical pressures were measured or determined graphically and the critical loci were constructed for both binary systems.

Introduction

For predicting the phase behavior and other thermodynamic properties of multicomponent systems of industrial interest, reliable interaction parameters are required for each of the possible binary pairs which can be formed from the components in the mixture. As a continuation of a program to provide data on binary systems of interest to the petroleum and natural gas industry, the behavior of the *n*-pentane- and isopentane-carbon dioxide systems was studied at temperatures up to the critical region of carbon dioxide in both binary systems. The *n*-pentane-carbon dioxide system has been studied earlier by Besserer and Robinson (1) in the temperature range from about 4 to 104 °C, and by Poettmann and Katz (2) in a range from 27 to 138 °C. The isopentane-carbon dioxide system was studied by Besserer and Robinson (3) at temperatures from 4 to 104 °C.

It is desirable to have vapor-liquid equilibrium data available over as wide a temperature range as possible for evaluating binary interaction parameters. Accordingly, it was decided to extend the range covered by the earlier work for the *n*-pentane-carbon dioxide system from 130 to 190 °C and for the isopentane-carbon dioxide system from 130 to 180 °C.

The transparent variable-volume vapor-liquid equilibrium cell used for this work made it possible to observe and determine the behavior of each system in the neighborhood of the critical point. As a result of these observations, it was possible to construct the critical loci for both systems.

Experimental Section

The experiments were carried out in a variable-volume vapor-liquid equilibrium cell consisting of a transparent sapphire cylinder mounted between two steel headers. This has been described in detail by Robinson et al. (4). The body of the cell

was 2.54 cm inside diameter with a length of 15.2 cm. The cell had an internal capacity of about 45 cm³. The main cell and all the necessary auxiliary lead lines and valves were mounted inside a controlled temperature bath. The techniques were basically the same as those described previously by Huang et al. (5).

Equilibrium was attained by mechanically rocking the entire assembly. The gas phase was sampled first by continuously drawing off a vapor stream through the sample valve under isobaric isothermal conditions. The withdrawn vapor was mixed with a stream of heated helium and circulated through the chromatographic switching valve. Samples were taken for analysis through the switching valve at periodic intervals. After the remainder of the vapor phase plus a small interface portion of the liquid was removed, the liquid phase was then sampled and analyzed by using a similar procedure.

The critical region was approached isothermally by adjusting pressure and/or composition by adding more material. After the equilibration process had been completed, the critical pressure corresponding to a given experimental temperature was determined by performing isothermal compression and expansion on either side of the critical point to observe both the phase boundary and the color changes taking place within the system. The critical composition was determined by taking a sample as described above, but the isobaric sampling pressure was kept at least 0.14 MPa higher than the observed critical pressure.

Temperatures were measured with iron-constantan thermocouples which had been calibrated against a platinum resistance thermometer. Each temperature was read out on a digital voltmeter. Temperatures are believed known to within ±0.1 °C or better. Pressures were measured by a strain gauge pressure transducer calibrated with a precision dead-weight gauge. The pressures are believed known to within ±0.15% of full scale.

The phase compositions were determined with a Hewlett-Packard (HP) Model 5750B gas chromatograph coupled with an HP-3353 data acquisition system. A thermal conductivity detector on isothermal mode was used for both binary systems. The column used was a 2.44 m by 3.18 mm diameter stainless steel tube packed with Porapak-QS. It was maintained at 160 °C for the *n*-pentane-carbon dioxide system and at 150 °C for the isopentane-carbon dioxide system. The response factors for conversion from area fraction to mole fraction relation to carbon dioxide were 2.0790 and 1.9169 for *n*-pentane and isopentane, respectively. These factors were obtained by calibration made for each component using a gravimetric me-

Table I. Equilibrium Phase Properties of the *n*-Pentane-Carbon Dioxide System

press./MPa	composition ^a		equilibrium constant	
	x	y	K_{CO_2}	K_{nC_5}
<i>T</i> = 135.0 °C				
1.200	0.	0.		1.00
1.400	0.0108	0.1135	11.3	0.888
1.779	0.0323	0.2683	8.30	0.756
2.413	0.0699	0.4388	6.28	0.603
3.282	0.1281	0.5643	4.41	0.500
4.912	0.1832	0.6250	3.41	0.459
5.564	0.2695	0.6810	2.53	0.437
7.288	0.3880	0.6908	1.78	0.505
8.074	0.4501	0.6852	1.52	0.574
8.791	0.5371	0.6656	1.24	0.722
8.998	0.6214	0.6214	1.00	1.00
<i>T</i> = 165.0 °C				
2.048	0.	0.		1.00
2.206	0.0089	0.0519	5.8	0.96
2.820	0.0428	0.1930	4.51	0.843
3.840	0.1049	0.3546	3.38	0.721
4.875	0.1681	0.4235	2.52	0.693
5.909	0.2367	0.4671	1.97	0.698
6.778	0.3123	0.4579	1.47	0.788
6.915	0.3431	0.4409	1.28	0.851
7.046	0.3984	0.3984	1.00	1.00
<i>T</i> = 190.0 °C				
2.992	0.	0.		1.00
3.137	0.0081	0.0241	3.0	0.98
3.496	0.0289	0.0746	2.58	0.953
3.868	0.0540	0.1209	2.24	0.929
4.178	0.0768	0.1478	1.92	0.923
4.502	0.1018	0.1607	1.58	0.934
4.551	0.1062	0.1619	1.52	0.938
4.640	0.1150	0.1590	1.38	0.950
4.695	0.1424	0.1424	1.00	1.00

^a Mole fraction carbon dioxide.

thod to prepare the standard solution for gas chromatographic analysis. At least six samples of each phase were taken for analysis so that the reported compositions are the result of averaging at least four out of six determinations. The precision of the analysis was generally better than 2% relative standard deviation.

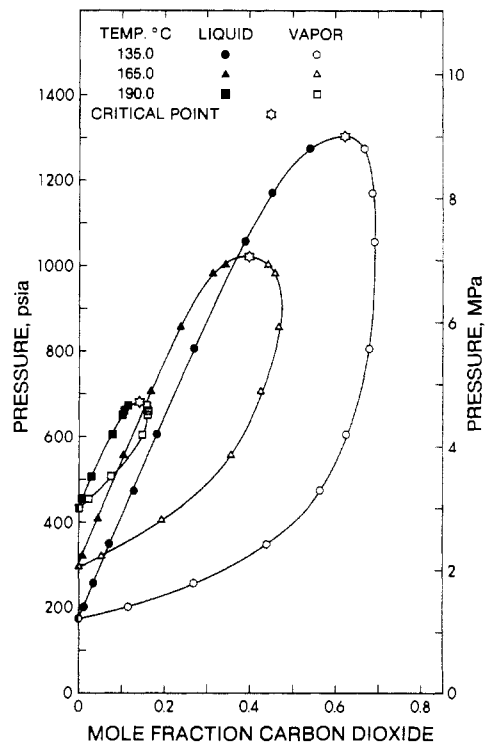
In determining the physical properties in the critical region, the given experimental temperature was considered as the critical temperature. The corresponding critical pressure was determined by averaging the two values obtained from isothermal compression and expansion observations. The associated composition was determined as above.

Materials

The high performance liquid chromatography grade *n*-pentane of 99.4 mol % was obtained from the Fisher Scientific Co. The Gold Label, spectrophotometric grade isopentane (2-methylbutane) of 99+ mol % was obtained from the Aldrich Chemicals Co. Industrial grade carbon dioxide containing 99.9+ mol % purity was obtained from Linde. Gas chromatograms were run on these compounds but no detectable impurities were found. Thus, these materials were used without further purification. The pentanes were degassed in the equilibrium cell before the addition of carbon dioxide.

Results

The experimentally measured equilibrium liquid and vapor compositions for the *n*-pentane-carbon dioxide system are presented in Table I. The vapor- and liquid-phase envelopes

**Figure 1.** Pressure-equilibrium phase composition diagram for the *n*-pentane-carbon dioxide binary system.**Table II. Equilibrium Phase Properties of the Isopentane-Carbon Dioxide System**

press./MPa	composition ^a		equilibrium constant	
	x	y	K_{CO_2}	K_{iC_5}
<i>T</i> = 135.0 °C				
1.482	0.	0.		1.00
1.613	0.0091	0.0774	8.5	0.93
1.951	0.0286	0.2077	7.25	0.815
2.503	0.0624	0.3448	5.50	0.699
3.234	0.1073	0.4595	4.28	0.605
4.226	0.1734	0.5511	3.18	0.543
5.268	0.2425	0.5998	2.47	0.528
5.923	0.2910	0.6223	2.14	0.533
6.660	0.3448	0.6265	1.82	0.570
7.267	0.3929	0.6238	1.59	0.620
7.715	0.4312	0.6141	1.42	0.678
8.150	0.4817	0.5771	1.20	0.816
8.294	0.5284	0.5284	1.00	1.00
<i>T</i> = 165.0 °C				
2.413	0.	0.		1.00
2.599	0.0129	0.0548	4.26	0.958
3.165	0.0455	0.1609	3.54	0.879
3.813	0.0843	0.2474	2.94	0.822
4.819	0.1566	0.3307	2.11	0.794
5.619	0.2244	0.3468	1.55	0.842
5.964	0.2647	0.3335	1.26	0.906
6.054	0.2982	0.2982	1.00	1.00
<i>T</i> = 180.0 °C				
3.013	0.	0.		1.00
3.172	0.0105	0.0311	2.96	0.979
3.523	0.0313	0.0786	2.51	0.951
3.854	0.0532	0.1117	2.10	0.938
4.144	0.0755	0.1398	1.85	0.931
4.344	0.0927	0.1468	1.58	0.940
4.495	0.1109	0.1484	1.34	0.958
4.578	0.1325	0.1325	1.00	1.00

^a Mole fraction carbon dioxide.

for this system are shown graphically in Figure 1 for three isotherms at 135, 165, and 190 °C. The calculated equilibrium ratios for each component in the binary system at each of the

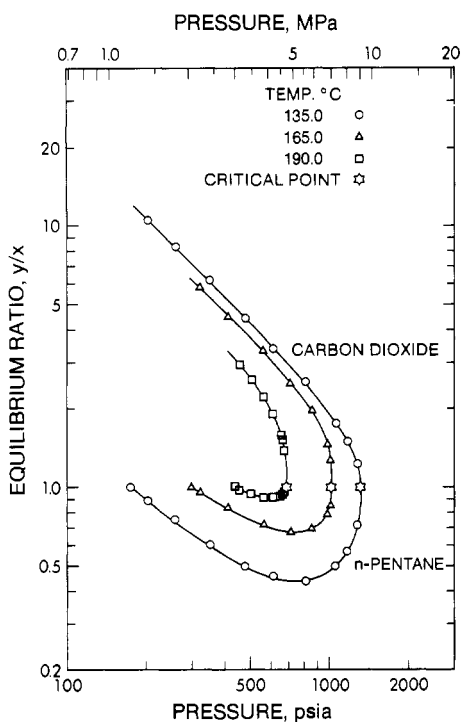


Figure 2. Equilibrium ratios for *n*-pentane and carbon dioxide in the *n*-pentane-carbon dioxide binary system.

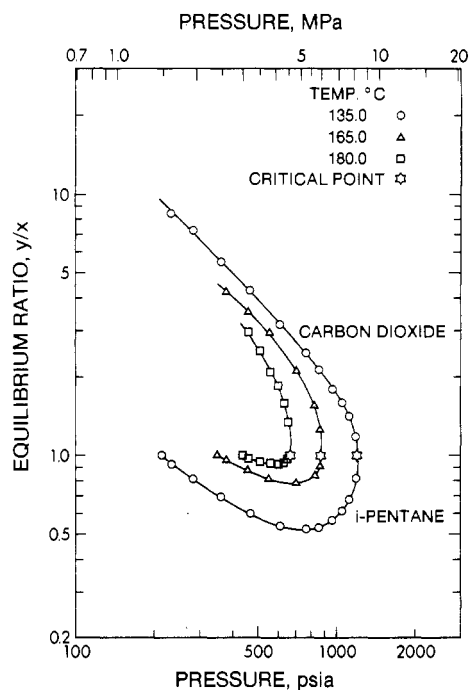


Figure 4. Equilibrium ratios for isopentane and carbon dioxide in the isopentane-carbon dioxide binary system.

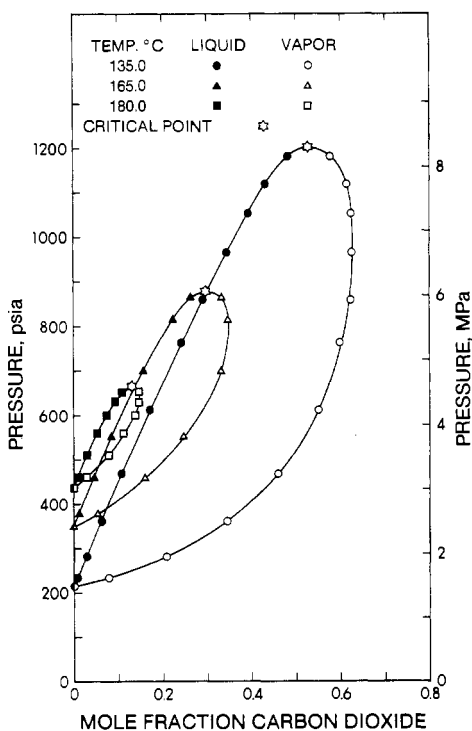


Figure 3. Pressure-equilibrium phase composition diagram for the isopentane-carbon dioxide binary system.

three temperatures are also given in Table I and are shown in Figure 2.

The equilibrium phase composition for the isopentane-carbon dioxide system are given in Table II and are shown in Figure 3 for each of the three isotherms at 135, 165, and 180 °C. The calculated equilibrium ratios for each component in this binary system at each of the three isotherms are also given in Table II and are shown in Figure 4.

The observed critical temperatures and corresponding pressures for these two binary systems are presented in Table III. Based on the convergence pressure concept, whereby the

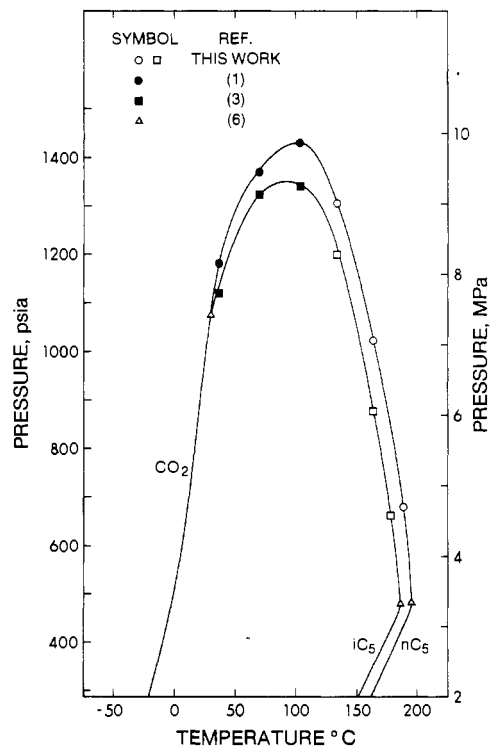


Figure 5. Critical loci for the *n*-pentane- and isopentane-carbon dioxide binary systems.

Table III. Critical Temperatures and Corresponding Critical Pressures on the Critical Locus of the Binary Systems

system	temp./°C	press./MPa
<i>i</i> C ₅ -CO ₂	135.0	8.288
	165.0	6.054
	180.0	4.578
<i>n</i> C ₅ -CO ₂	135.0	8.998
	165.0	7.046
	190.0	4.688

equilibrium ratios for each component in a binary system converge to unity at the critical pressure of the mixture that has any specified temperature as its critical temperature, it is possible to estimate the critical pressure from a graphical representation of equilibrium ratios as a function of pressure at fixed temperatures. This method was used to estimate the critical pressures at 37.8, 71.1, and 104.4 °C from the data of Besserer and Robinson (1, 3).

The critical loci for the binary systems studied in this work were constructed by using the values given in Table III and are presented graphically in Figure 5. This shows the six binary critical points and the vapor pressure curves and critical point for each of the pure components.

Discussion

The completion of this study has filled the temperature gap that existed in the binary vapor-liquid equilibrium data for the *n*-pentane- and isopentane-carbon dioxide binary systems. The additional information will be useful for evaluating any possible temperature dependence of the binary interaction parameters for these systems. This may assist in improving the reliability of vapor-liquid equilibrium and fluid property predictions based on equations of state or other correlations requiring these parameters for multicomponent calculations.

Additional work is in progress on vapor-liquid equilibrium measurements in mixtures of neopentane with carbon dioxide.

This will complete the vapor-liquid equilibrium data required for carbon dioxide with all the pentanes.

Glossary

K	equilibrium ratio, y/x
K_{CO_2}	equilibrium ratio for carbon dioxide
K_{nC_5}	equilibrium ratio for <i>n</i> -pentane
K_{iC_5}	equilibrium ratio for isopentane
P	pressure, MPa
T	temperature, °C
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Registry No. *n*-C₅, 109-66-0; *i*-C₅, 78-78-4; CO₂, 124-38-9.

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Measurement of γ^∞ Using GLC. 2. Results for the Stationary Phases *N*-Formylmorpholine and *N*-Methylpyrrolidone

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Gas-liquid chromatography (GLC) has been used to determine activity coefficients at infinite dilution for a variety of classes of substances; the stationary phases employed were *N*-formylmorpholine (NFM) and *N*-methylpyrrolidone (NMP). These two substances are used technically as solvents in extractive distillation, particularly for the separation of alkanes from aromatics or alkanes from alkenes. In order to prevent the columns with these substances from "bleeding out" during the measurements, the apparatus was modified in such a way that the carrier gas is saturated with the liquid stationary phase before entering the column.

Introduction

The measurement of activity coefficients at infinite dilution is an alternative to the conventional static and dynamic methods for the determination of vapor-liquid equilibria. The basic idea of the γ^∞ measurements is to use the information on the activity coefficients at infinite dilution to predict the behavior of the activity coefficients and the vapor-liquid equilibrium across the whole concentration range with the help of a suitable thermo-

Table I. Vapor Pressures of NFM and NMP as a Function of Temperature

	Antoine constants		
	A	B	C
NFM	7.28945	2075.15	228.119
NMP	8.2789	2570.30	273.15
T , °C	P_{NFM} , mmHg		P_{NMP} , mmHg
25	0.12		0.46
50	0.67		2.11
75	2.78		7.87
100	9.23		24.59
125	25.87		66.57

dynamic model. The obtained data were also stored in the Dortmund Data Bank (1) and, together with VLE (2) and h^E data (3), used for the further development of group contribution methods (4). The GLC method, together with the theoretical background to γ^∞ measurements carried out using gas chromatography, is described in detail by Weidlich and Gmehling (5); the stationary phases used there are octacosane, 1-docosanol, 10-nonadecanone, and 1-eicosene. The aim of the present work was to modify the apparatus in such a way that it is also possible to carry out measurements using stationary phases which have relatively high vapor pressures at the temperatures used.

The phases chosen were *N*-methylpyrrolidone (NMP) and *N*-formylmorpholine (NFM). Both are used technically as sol-

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