Equilibrium Phase Properties of the *n*-Butane–Carbon Dioxide and Isobutane–Carbon Dioxide Binary Systems

Ah-Dong Leu and Donald B. Robinson*

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

Vapor and liquid equilibrium phase compositions were determined at 95, 120, and 145 °C for the *n*-butane–carbon dioxide system and at 110 and 125 °C for the isobutane–carbon dioxide system at pressures from the vapor pressure of the butanes to the critical pressure for the binary systems 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 and the critical loci were constructed for both binary systems.

Introduction

The behavior of carbon dioxide in mixtures of light hydro-carbons has been a subject of considerable interest for many years. Recently, data on these systems have become increasingly important because of the anticipated use of carbon dioxide in enhanced oil recovery operations.

Phase behavior in the *n*-butane–carbon dioxide system has been the subject of study by Hsu et al. (*1*), Olds et al. (*2*), Behrens and Sandler (*3*), and Poettmann and Katz (*4*). Data on the isobutane–carbon dioxide system have been reported by Besserer and Robinson (*5*). However, none of these earlier publications have reported studies at higher temperatures near the critical temperatures for the pure butanes.

The object of the work undertaken herein was to fill in these gaps in vapor–liquid equilibrium data for both binary systems and to complete the delineation of the binary critical locus for each system. This would then permit the evaluation of binary interaction parameters over the complete temperture range of possible interest.

Experimental Equipment and Methods

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 equipment and the method of operation have been described in detail by Huang et al. (*6*).

Prior to commencing an experimental run, the equipment was thoroughly cleaned and evacuated. The less volatile component was then introduced into the cell, followed by the second more volatile component. The contents of the cell were mixed by rocking the cell assembly about a horizontal axis. During this time the cell was simultaneously brought to the desired temperature and pressure. When equilibrium had been established, the rocking motion was stopped and the sampling process commenced.

The gas phase was sampled by continuously drawing off a small vapor stream through the sampling valve under isobaric isothermal conditions. The sample was mixed with a stream of helium and circulated through the chromatographic switching valve. Samples were taken for analysis at periodic intervals through the chromatographic valve until at least two successive

samples agreed within the expected experimental accuracy. After the vapor phase had been analyzed, the remainder of the vapor phase plus a small interface portion were removed from the cell. The liquid phase was then sampled and analyzed by using a similar procedure.

At the completion of each pressure point, a new set of conditions was established by adjusting pressure and/or adding more material. The equilibration and sampling sequence was then repeated.

The critical region was studied by using an iterative experimental procedure involving changes in temperature, pressure, and composition. When the cell contained a mixture which was judged to be at near-critical composition, a series of isothermal observations were made at different pressures in the vicinity of the bubble/dew point. Color changes were closely monitored. Depending on whether the mixture was determined to be bubble point or dew point, an increment of material was added to or removed from the cell and the observations repeated as above. In this way, the critical pressure, temperature, and composition were established. When the critical mixture had been obtained, a sample of the single-phase fluid above the critical pressure was withdrawn for analysis.

Experimental Accuracy

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 (HP-3455A), such that temperatures are believed known to within ±0.1 °C.

Pressures were measured by a strain gauge pressure transducer (Bell & Howell 4-356-003), calibrated with a precision dead weight gauge. Each pressure was read out on a digital voltmeter (HP-3455A). Pressures are believed known to within ±0.15% of full scale.

The phase compositions were determined with a Hewlett-Packard Model 5750B gas chromatograph coupled with a Hewlett-Packard Model 3353 data acquisition system. A thermal conductivity detector on isothermal mode was used. A calibration was made for each component by gravimetrically preparing a standard mixture. The relative response factor was obtained from the peak area ratio. The column used was a 2.44 m by 3.18 mm diameter stainless steel tube, packed with Porapak-QS maintained at 125 °C for *n*-butane–carbon dioxide and at 115 °C for isobutane–carbon dioxide. Helium gas at a flow rate of 25 cm³/min was used as carrier gas for both systems.

The response factor for conversion from area fraction to mole fraction was 1.7155 for *n*-butane and 1.6823 for isobutane compared to 1.0000 for carbon dioxide. At least eight samples of each phase were taken for analysis so that the reported compositions are the result of averaging at least six determinations. The precision of the analyses was generally better than 2% relative standard deviation.

Research grade *n*-butane of 99.9+ mol % purity and instrument grade 2-methylpropane (isobutane) of 99.5+ mol % were used for the experimental work. They were obtained from Matheson Gas Products, Canada, Inc. Chromatograms were
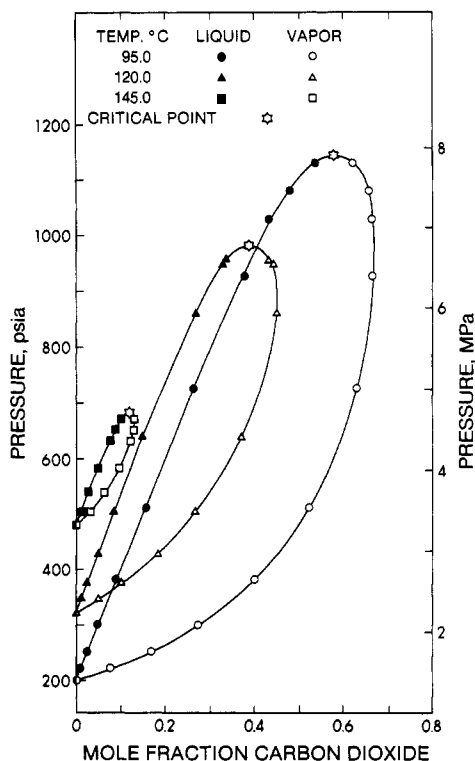
Figure 1. Pressure–equilibrium phase composition diagram for the *n*-butane–carbon dioxide binary system.
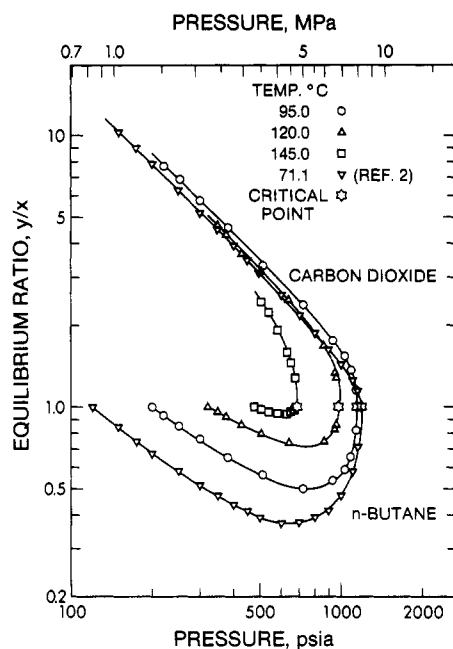

Figure 2. Equilibrium ratios for *n*-butane and carbon dioxide in the *n*-butane–carbon dioxide binary system.

run on these two compounds but no detectable impurities were found. They were degassed in the equilibrium cell before the introduction of carbon dioxide. Industrial grade carbon dioxide of 99.9+ mol % purity was obtained from the Linde Division of Union Carbide. All of these materials were used without further purification.

Results and Discussion

The experimental measurements of the equilibrium phase compositions for the *n*-butane–carbon dioxide system are given in Table I. The vapor- and liquid-phase envelopes for this

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

| press./MPa | composition[a] | | equilibrium constant | |
	x	y	K_{CO_2}	K_{nC_4}
	$T = 95.0\ °C$			
1.386	0.	0.		1.00
1.531	0.0099	0.0764	7.75	0.933
1.737	0.0243	0.1683	6.94	0.852
2.082	0.0478	0.2750	5.76	0.761
2.641	0.0878	0.4026	4.59	0.655
3.530	0.1568	0.5225	3.33	0.566
5.006	0.2631	0.6286	2.39	0.504
6.405	0.3782	0.6652	1.76	0.538
7.102	0.4320	0.6643	1.54	0.591
7.460	0.4811	0.6571	1.37	0.661
7.798	0.5394	0.6206	1.15	0.824
7.901	0.5783	0.5783	1.00	1.00
	$T = 120.0\ °C$			
2.206	0.	0.		1.00
2.392	0.0109	0.0506	4.64	0.960
2.592	0.0236	0.1016	4.31	0.920
2.951	0.0496	0.1828	3.68	0.860
3.482	0.0844	0.2661	3.15	0.802
4.399	0.1480	0.3686	2.49	0.741
5.936	0.2670	0.4495	1.68	0.751
6.536	0.3293	0.4422	1.34	0.832
6.584	0.3361	0.4304	1.28	0.858
6.771	0.3895	0.3895	1.00	1.00
	$T = 145.0\ °C$			
3.316	0.	0.		1.00
3.482	0.0131	0.0320	2.44	0.981
3.716	0.0282	0.0632	2.24	0.964
4.020	0.0494	0.0959	1.94	0.951
4.358	0.0756	0.1209	1.60	0.951
4.495	0.0858	0.1277	1.46	0.956
4.626	0.1030	0.1314	1.28	0.968
4.702	0.1206	0.1206	1.00	1.00

[a] Mole fraction carbon dioxide.

Table II. Equilibrium Phase Properties of the Isobutane–Carbon Dioxide System

| press./MPA | composition[a] | | equilibrium constant | |
	x	y	K_{CO_2}	K_{iC_4}
	$T = 110.0\ °C$			
2.456	0.	0.		1.00
2.599	0.0139	0.0504	3.64	0.963
2.820	0.0304	0.1027	3.38	0.926
3.165	0.0558	0.1698	3.04	0.879
3.723	0.0975	0.2551	2.62	0.825
4.620	0.1717	0.3445	2.01	0.791
5.323	0.2361	0.3814	1.62	0.810
5.633	0.2683	0.3832	1.43	0.843
5.916	0.3164	0.3700	1.17	0.922
5.998	0.3436	0.3436	1.00	1.00
	$T = 125.0\ °C$			
3.172	0.	0.		1.00
3.316	0.0145	0.0365	2.52	0.978
3.523	0.0305	0.0721	2.36	0.957
3.868	0.0555	0.1128	2.03	0.939
4.164	0.0782	0.1448	1.85	0.928
4.433	0.1041	0.1725	1.66	0.924
4.620	0.1264	0.1827	1.45	0.936
4.771	0.1441	0.1788	1.24	0.959
4.847	0.1623	0.1623	1.00	1.00

[a] Mole fraction carbon dioxide.

system are shown in Figure 1 for three isotherms at 95.0, 120.0, and 145.0 °C.

The calculated equilibrium ratios for each component in the binary system at each of the three temperatures are also given in Table I and are shown in Figure 2. The results obtained
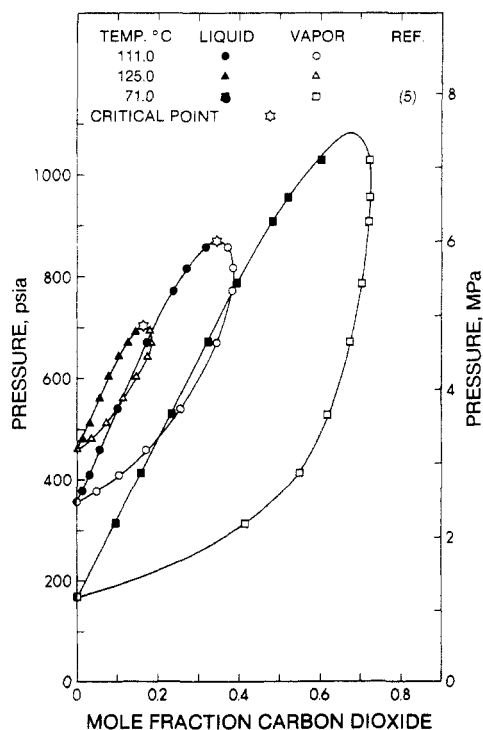
Figure 3. Pressure–equilibrium phase composition diagram in the isobutane–carbon dioxide binary system.

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

system	temp/°C	press./MPa
nC_4–CO_2	95.0	7.901
	120.0	6.771
	145.0	4.702
iC_4–CO_2	110.0	5.998
	125.0	4.847

from Olds et al. (*2*) for the binary system at 71.1 °C are included in Figure 2 for comparison.

The equilibrium phase compositions for the isobutane–carbon dioxide system are given in Table II and are shown in Figure 3 for both isotherms at 110.0 and 125.0 °C. The results of Besserer et al. (*5*) at 71.1 °C are included in Figure 3 for comparison. The calculated equilibrium ratios for each component in this binary system at each of the two temperatures are also given in Table II and are presented graphically in Figure 4. The results of Besserer at 104.4 °C are included for comparison as in Figure 3.

The measured critical temperatures and corresponding pressures for these two binary systems are presented in Table III. The vapor pressure curves for the pure components (*7*), the critical properties at the conditions investigated in this work, and the critical properties determined in earlier studies (*1–5*) for these systems are shown graphically in Figure 5. With the exception of one point on the *n*-butane–carbon dioxide critical locus, all of the results are in very good agreement.

This work has extended the temperature range over which data for these two binary systems exist. The information obtained will be useful for the evaluation of binary interaction parameters for the binary pairs.

Glossary

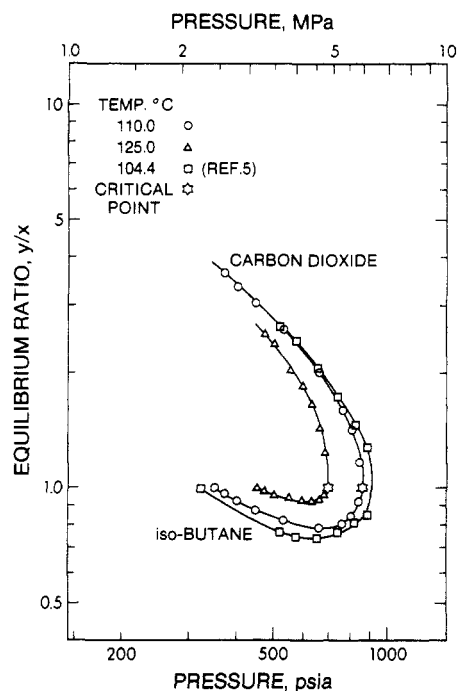|	
K	equilibrium ratio, y/x
K_{CO_2}	equilibrium ratio for carbon dioxide
K_{nC_4}	equilibrium ratio for *n*-butane
K_{iC_4}	equilibrium ratio for isobutane
P	pressure, MPa

Figure 4. Equilibrium ratios for isobutane and carbon dioxide in the isobutane–carbon dioxide binary system.
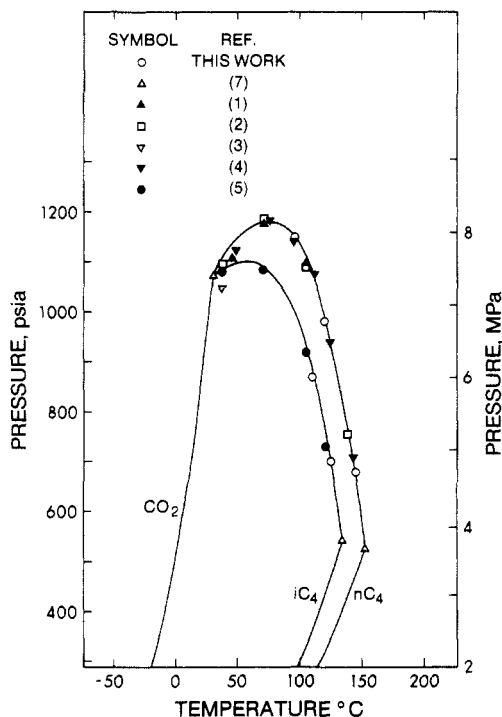

Figure 5. Critical loci for the *n*-butane– and isobutane–carbon dioxide binary systems.

T	temperature, °C
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Registry No. *n*-C_4, 106-97-8; *i*-C_4, 75-28-5; CO_2, 124-38-9.

Literature Cited

(1) Hsu, J. J.-C.; Nagarajan, N.; Robinson, R. L. *J. Chem. Eng. Data* **1985**, *30*, 485–491.
(2) Olds, R. H.; Reamer, H. H.; Sage, B. H.; Lacey, W. N. *Ind. Eng. Chem.* **1949**, *41*, 475–482.
(3) Behrens, P. K.; Sandler, S. I. *J. Chem. Eng. Data* **1983**, *28*, 52–56.

(4) Poettmann, F. H.; Katz, D. L. *Ind. Eng. Chem.* **1945**, *37*, 847–853.
(5) Besserer, G. J.; Robinson, D. B. *J. Chem. Eng. Data* **1973**, *18*, 298–301.
(6) Huang, S.-S.; Leu, A.-D.; Ng, H.-J.; Robinson, D. B. *Fluid Phase Equilib.* **1985**, *19*, 21–32.
(7) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

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

Ah-Dong Leu and Donald B. Robinson*

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

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 cm^3. 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-