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Equilibrium-Phase Properties of *i*-Butane-Carbon Dioxide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the *i*-butane–carbon dioxide system at 100°, 160°, 220°, and 250°F from the vapor pressure of *i*-butane to pressures in the critical region. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index data by use of the Lorentz-Lorenz molar refractivity relationship.

Current methods for predicting the phase behavior and other thermodynamic properties of multicomponent systems of industrial interest usually require interaction parameters for each of the possible binary pairs which can be formed from the components in the mixture. As part of a general program to provide data of this type for systems of interest to the petroleum and natural gas industry, we studied the behavior of the *i*-butane–carbon dioxide binary because measurements on this system had not previously been reported in the literature.

The study included an experimental determination of the compositions and the refractive indices of the coexisting equilibrium phases at temperatures of 100°, 160°, 220°, and 250°F and at pressures from the vapor pressure of *i*-butane to the critical region of the system. The refractive index measurements were used to calculate the phase densities by use of the Lorentz-Lorenz molar average refractivity.

The mixtures of *i*-butane and carbon dioxide were confined between two pistons in a glass-windowed stainless-steel cell which has been described in detail by Besserer and Robinson (*1*). The hydraulic fluid preheating coils were not long enough for operations at temperatures above 200°F. Consequently, this fluid was initially passed through a coil immersed in a 200°F bath before entering the preheat coils in the shroud. The large temperature difference between the oil in the pump and the oil in the cell caused a small change in the working volume of the cell when the pistons were being moved simultaneously up or down. This situation was remedied by connecting a 10-cc displacement pump to one of the oil lines.

The temperature was measured with an iron-constantan thermocouple sheathed in 316 stainless steel with its reference junction in an ice bath and its measuring junction in the cell contents. The thermocouple was calibrated at the triple point and steam point of water. The cell temperature was controlled to within ±0.1°F of the set operating temperature.

The pressure was measured with a 0–1500-psi pressure transducer calibrated at atmospheric pressure and the vapor pressure of carbon dioxide at 20°C. The maximum combined nonlinearity and hysteresis of the transducer was ±3 psi. The pressure in the cell was easily maintained constant to 0.2 psi by manual adjustments.

The refractive indices of the phases were determined by measuring the minimum deviation angle of a beam of monochromatic light at a wavelength of 6328 Å which was passed through a prism of the fluid as described in the earlier paper (*1*).

Analytical

Samples of the equilibrium liquid and vapor phases were expanded to a pressure of 0.2 atm through micrometering valves into an evacuated line connected to the gas chromatograph gas sampling valve. The pressure in the line was measured with a differential pressure transducer. Two samples of each phase were taken, and triplicate chromatographs were run on each sample. The average size of each sample corresponded to about 0.2% depletion of the average load. For each point the six analyses (three from each of the two samples) were generally repeatable to within ±0.2 mol %, and the accuracy is judged to be within ±0.3 mol %.

The gas chromatograph was a Hewlett-Packard Model 700 equipped with a thermal conductivity cell detector. The detector was maintained at 200°C with a filament current of 150 mA. Helium was passed through the column at a rate of 25 cc/min. The column was ⅛ in. in diameter and 6-ft long and was packed with 10% UC-W98 oil on 80–100-mesh silica. The oven temperature was 20°C.

The chromatograph was calibrated with pure components, and the response was linear with sample size for the 1-cc sample loop at pressures up to 0.3 atm. To convert from area fraction to mole fraction, the area of the carbon dioxide peak was multiplied by 1.665, and the area of the *i*-butane peak by 1.000.

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Materials

The *i*-butane was instrument grade obtained from the Matheson Co., and the carbon dioxide was obtained from Canadian Liquid Air. Both materials had a purity which was better than 99.9 mol %.

Results

The experimentally determined phase compositions and refractive indices, the molar volumes of each phase calculated from the refractive index and composition data, and the equilibrium ratios for each component are presented in Table I.

The isothermal pressure-composition diagram at each of the four experimental temperatures is shown graphically in Figure 1. The refractive indices of the coexisting equilibrium phases, the calculated molar volumes of the vapor and liquid phases, and the calculated equilibrium ratios for each of the components at each temperature are presented in Figures 2, 3, and 4, respectively.

The equilibrium-phase densities were calculated from the experimental-phase compositions and refractive indices by use of the Lorentz-Lorenz molar refractivity relationship:

$$R_{\mathrm{LL}} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \tag{1}$$

Theoretically, the refractivity of a mixture is not strictly an additive property except for ideal gases (*2*); however, it was assumed additive for all mixtures studied. This assumption can be clearly justified by the near additivity in a large number of mixtures and by the manner in which atomic and radical refractivities can be summed to give molecular refractivities (*4*). A value of 6.65 cc/g mol at a wavelength of 6328 Å was used for the molar refractivity of carbon dioxide. This was obtained from the work of Stoll (*5*) and was assumed to be essentially constant over the range of temperature and pressure considered.

The effect of temperature and pressure on the refractivity of pure *i*-butane was obtained from

$$R_{\mathrm{LL}} = R_{\mathrm{LL}}{}^0 - 6.9(10^{-5})P \tag{2}$$

where $R_{\mathrm{LL}}{}^0$ is obtained from Table II.

Table I. Experimental Equilibrium-Phase Properties for *i*-Butane–Carbon Dioxide System

Press, psia	Composition[a]		Refractive index[b]		Molar vol[c]		Equilibrium constant	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Carbon dioxide	*i*-Butane
				100°F				
73	0.000	0.000	1.3063	1.00696	1.750	...	...	1.000
105	0.0251	0.2657	1.30420	1.00795	1.716	51.17	10.586	0.7532
179	0.0881	0.5668	1.30038	1.01040	1.660	29.38	6.434	0.4751
309	0.2056	0.7297	1.28606	1.01517	1.588	16.55	3.549	0.3403
401	0.2891	0.7872	1.27653	1.01929	1.531	12.02	2.723	0.2993
514	0.3991	0.8267	1.26249	1.02469	1.458	8.858	2.071	0.2884
632	0.5195	0.8480	1.24473	1.03133	1.382	6.758	1.632	0.3163
733	0.6205	0.8690	1.22691	1.03813	1.327	5.374	1.400	0.3452
811	0.7073	0.8822	1.21096	1.04444	1.277	4.515	1.247	0.4025
902	0.7828	0.8959	1.19010	1.05405	1.271	3.634	1.144	0.4793
971	0.8324	0.9058	1.17053	1.06474	1.310	2.988	1.088	0.5621
1018	0.8694	0.9125	1.15554	1.07501	1.349	2.554	1.050	0.6700
1042	0.8845	0.9154	1.14372	1.08533	1.419	2.238	1.035	0.7325
				160.0°F				
P	x	y	n_L	n_V	V_L	V_V	$K_{\mathrm{CO_2}}$	$K_{i\text{-}\mathrm{C_4}}$
170	0.000	0.000	1.2774	1.01581	1.930	...	...	1.000
314	0.0946	0.4154	1.26685	1.02165	1.849	16.55	4.391	0.6457
414	0.1573	0.5481	1.25900	1.02598	1.814	12.07	3.484	0.5363
530	0.2320	0.6166	1.24895	1.03168	1.775	9.170	2.658	0.4992
673	0.3227	0.6706	1.23420	1.04012	1.741	6.794	2.078	0.4863
787	0.3930	0.7006	1.22230	1.04862	1.717	5.404	1.783	0.4932
908	0.4814	0.7177	1.20202	1.06155	1.726	4.184	1.491	0.5444
956	0.5191	0.7209	1.19130	1.06833	1.748	3.757	1.389	0.5804
				220.0°F				
327	0.000	0.000	1.2368	1.03495	2.220	...	...	1.000
525	0.1242	0.3288	1.23276	1.04537	2.061	8.600	2.647	0.7664
583	0.1490	0.3638	1.22061	1.04013	2.127	9.414	2.442	0.7476
663	0.1960	0.4054	1.21307	1.05766	2.120	6.251	2.068	0.7396
749	0.2390	0.4160	1.20236	1.06696	2.150	5.402	1.741	0.7674
830	0.2833	0.4149	1.18891	1.08035	2.213	4.517	1.465	0.8164
899	0.3419	0.4369	1.16501	1.10169	2.395	3.509	1.278	0.8556
				250.0°F				
438	0.000	0.000	1.2110	1.05715	2.520	...	...	1.000
524	0.0597	0.1464	1.19677	1.06502	2.536	6.998	2.45	0.908
579	0.0856	0.1865	1.19361	1.06814	2.528	6.478	2.18	0.890
659	0.1308	0.2345	1.18092	1.08533	2.608	4.996	1.79	0.881
701	0.1601	0.2361	1.16034	1.09833	2.865	4.338	1.47	0.910

[a] Mole fraction carbon dioxide. [b] Relative to vacuum at 6328 Å. [c] Ft^3/lb mol calculated from refractive index and composition data.

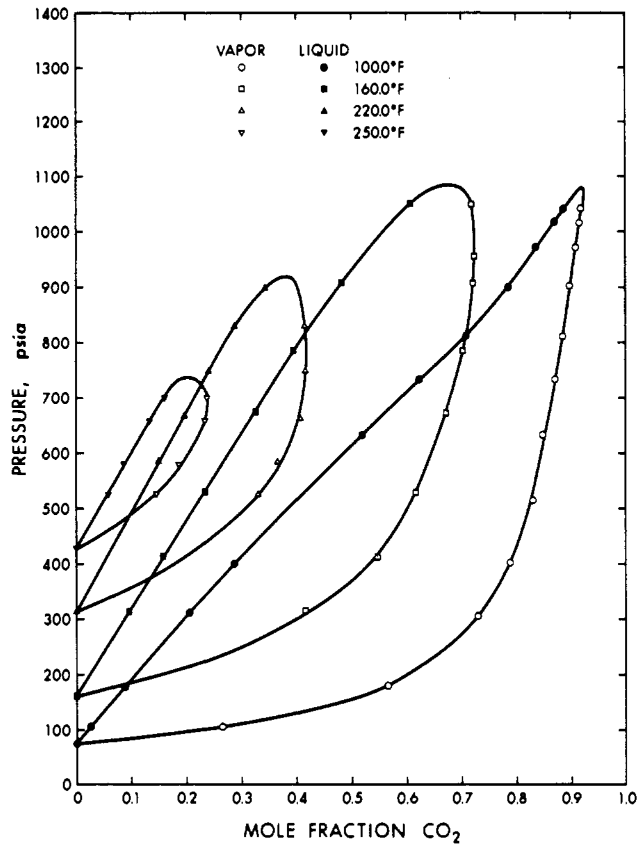

Figure 1. Pressure-equilibrium phase composition diagram for *i*-butane-carbon dioxide system

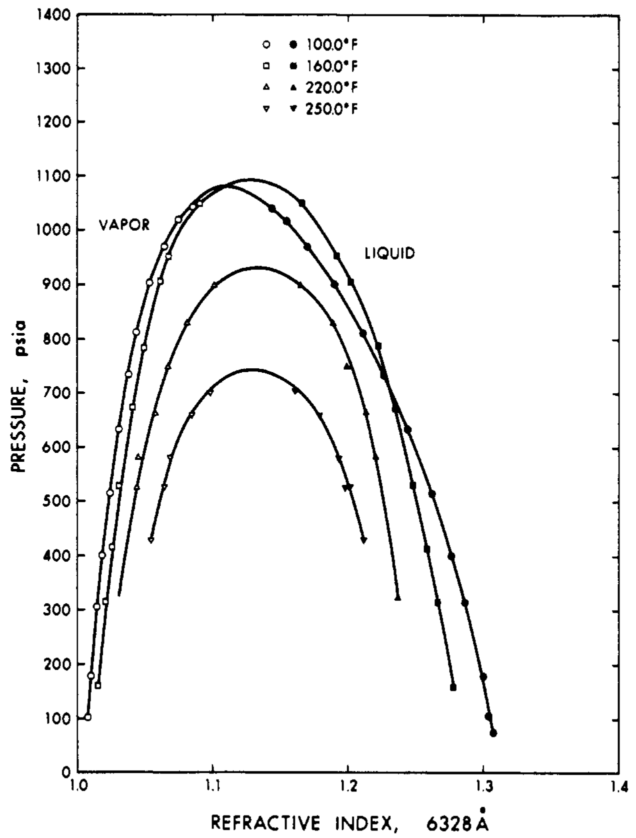

Figure 2. Pressure-equilibrium phase refractive index diagram for *i*-butane-carbon dioxide system

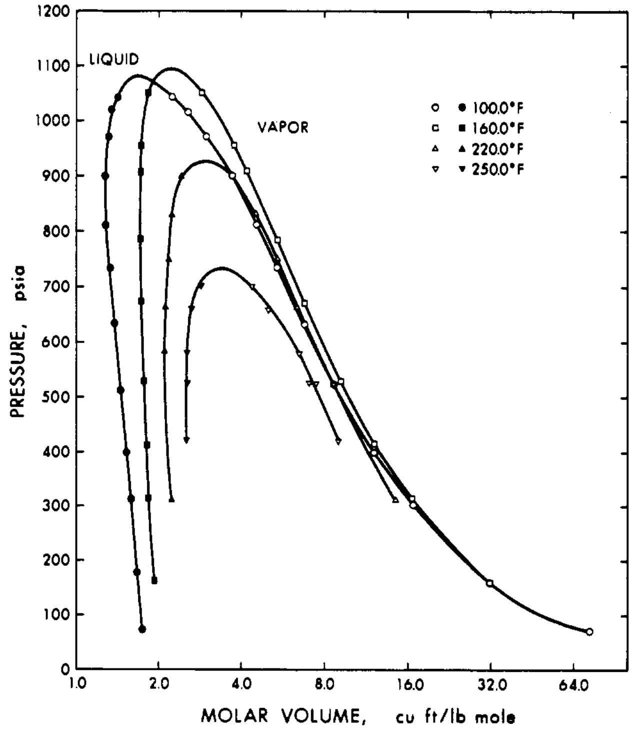

Figure 3. Pressure-equilibrium phase molar volume diagram for *i*-butane-carbon dioxide system

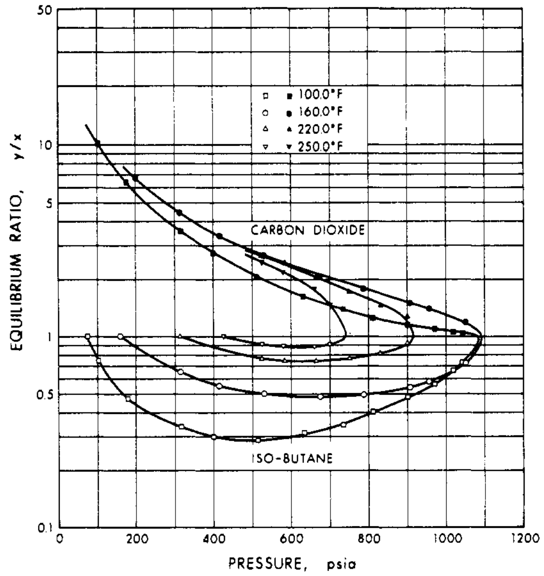

Figure 4. Equilibrium ratios for *i*-butane and carbon dioxide in *i*-butane-carbon dioxide binary system

Table II. Zero-Pressure Refractivity of *i*-Butane

Temp, °F	R_{LL}^0, cc/g mol
100	20.64
160	20.72
220	20.78
250	20.82

These values were calculated by using the measured refractive indices of pure *i*-butane together with the volumetric data reported by Sage and Lacey (*3*).

Discussion

No comparison is made between the experimental results obtained in this work and those of other workers, because no previous investigation of this binary system is reported in the literature.

Although the refractive indices of the phases can be measured with high accuracy, there are some limitations to the accuracy of the calculated densities. These limitations are caused by the slight variation of the Lorentz-Lorenz molar refractivity with density for both pure components and mixtures and also by the existence of minor nonadditive terms. In general, these limitations seldom cause inaccuracies greater than 1 or 2% in the calculated density. When results of higher precision are required, the nature and magnitude of the variation of the refractivity with density and composition must be determined by some independent density measurements.

Nomenclature

K_{CO_2} = equilibrium ratio for carbon dioxide
$K_{i\text{-}C_4}$ = equilibrium ratio for *i*-butane
M = molecular weight
n = refractive index
n_L = refractive index of liquid
n_V = refractive index of vapor
P = pressure, psia
R_{LL} = Lorentz-Lorenz molar refractivity, cc/g mol
R_{LL}^0 = zero-pressure Lorentz-Lorenz refractivity
V_L = molar volume of liquid
V_V = molar volume of vapor
x = mole fraction of a component in the liquid phase
y = mole fraction of a component in the vapor stage
ρ = density

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Equilibrium-Phase Properties of *i*-Butane–Ethane System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the *i*-butane–ethane system at 100.6°, 160.4°, 219.7°, and 249.6°F from the vapor pressure of *i*-butane to pressures in the critical region for the system. An analysis of data reported earlier on this system at temperatures of 32°, −4°, −40°, −76°, and −94°F indicates the possibility of significant errors, particularly in the vapor-phase data at the lower three temperatures.

Ethane and *i*-butane are present in essentially all multicomponent mixtures of interest to the petroleum and natural gas processing industry. The only previous work reported in the literature on the phase behavior of this binary system is that of Skripa et al. (*4*) who reported five isotherms in the region from 0° to −70°C. This work includes higher temperatures in the region from 100° to 250°F. This study is a continuation of the program referred to in an earlier paper (*2*) and includes experimental measurements of the phase compositions and refractive indices of the coexisting phases.

Experimental

The equipment described earlier by Besserer and Robinson (*1, 2*) was used without further modification for the present study. Experiments were carried out at each of four temperatures which were nominally 100°, 160°, 220°, and 250°F. At each temperature, measurements were made at a series of pressures between the vapor pressure of *i*-butane and the critical pressure for the system.

The *i*-butane was instrument grade purchased from the Matheson Co. The ethane was research grade supplied by the Phillips Petroleum Co. In both cases, analysis showed the materials to be greater than 99.9 mol % pure.

The analytical procedures were the same as those reported earlier (*2*). The column was ⅛-in. diameter stainless-steel, 6-ft long filled with Poropak Q. The oven temperature was 100°C. The thermal conductivity cell detector was maintained at 200°C with a filament current of 150 mA at a helium flow rate of 25 cc/min. The chromatograph was calibrated by use of pure components, and area fractions were converted to mole fractions by multiplying the area of the ethane peak by 1.5110 and the area of the *i*-butane peak by 1.000.

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