Phase-Equilibria Behavior of the Binary Systems Carbon Dioxide–n-Butylbenzene and Carbon Dioxide–trans-Decalin

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Pressure, liquid-phase composition, and liquid-phase molar volume data are presented for the binary vapor–liquid systems CO_2–*trans*-decalin at 0, 25, 50, and 75 °C and CO_2–*n*-butylbenzene at 0 and 20 °C. Also, pressure, liquid-phase compositions, and molar volumes of the two coexisting liquid phases as a function of temperature are presented for the same binary systems along their L_1–L_2–V loci. The termination points of these loci are located and characterized.

The authors have been engaged in studying the phase equilibria behavior of CO_2–hydrocarbon systems, with a view to providing data which would be useful for the design of economically attractive separation processes using CO_2 as a selective solvent. To date, the phase equilibria behavior of binary and ternary CO_2–hydrocarbon mixtures along liquid–vapor, solid–liquid–vapor, and liquid–liquid–vapor surfaces has been studied by Huie et al. (*3*), CO_2–*n*-decane–*n*-eicosane; Kulkarni et al. (*5*), CO_2–*n*-decane–2-methylnaphthalene; Zarah et al. (*8*), CO_2–*n*-butylbenzene–*n*-eicosane; and Yang et al. (*7*), CO_2–*n*-butylbenzene–2-methylnaphthalene. These studies focused on systems high in the concentration of the heavier hydrocarbon species, including the binary limit where the only hydrocarbon present was the heavier one.

In an effort to broaden insight into the behavior of the aforementioned systems, study has been undertaken of the phase behavior of CO_2 with the lighter hydrocarbons, which study generally demands cryogenic experimental conditions. Kulkarni et al. (*4*) examined the phase behavior of CO_2–*n*-decane along three-phase loci, including the L_1–L_2–V curve, in order to provide information related to the behavior of CO_2 with normal alkanes.

In the same spirit as ref 4, we have investigated the phase behavior of the binary systems CO_2–*n*-butylbenzene and CO_2–*trans*-decalin along their L_1–L_2–V loci, and along representative L–V isotherms as well. These studies provide a comparison of CO_2–hydrocarbon system behavior, where the hydrocarbon is aromatic or naphthenic, with the behavior of the earlier studied CO_2–*n*-decane system. In addition, the insight into the behavior of the system CO_2–*n*-butylbenzene further elucidates the nature of the systems studied in ref 7 and 8. The study of the system CO_2–*trans*-decalin is complementary to studies presently underway by the authors on the ternary systems CO_2–*trans*-decalin–*n*-eicosane and CO_2–*trans*-decalin–2-methylnaphthalene. With the exception of Francis' (*2*) qualitative study, very little data exist for CO_2–hydrocarbon systems where the hydrocarbon is both nonparaffinic and well defined.

Experimental Section

A detailed description of the experimental equipment and procedure is given elsewhere (*3, 6*). Briefly, for the L–V isotherms, a known amount of the desired hydrocarbon was placed in a 10-mL glass equilibrium cell. During the experimental runs, measured amounts of pure CO_2 gas were added to the thermostated equilibrium cell from a high-pressure bomb, through the use of a positive displacement mercury pump. By a mass bal-

ance, the moles of CO_2 added to the liquid phase were then determined.

In the case of the L_1–L_2–V runs, the moles of CO_2 in an individual liquid phase were determined by making a run in which the other liquid phase was present in a trace amount. Thus, two runs were required to obtain the properties of both L_1 and L_2. Procedures for determining the termination points of the L_1–L_2–V loci (*Q*, UCST, and *K* points) are rather routine and are discussed elsewhere (*3, 6*).

Temperature was controlled with a Pt-resistance thermometer to an estimated accuracy of ±0.02 °C for the L–V isotherms and measured to an estimated accuracy of ±0.10 °C for the L_1–L_2–V data. Pressure was measured with Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge, to an estimated accuracy of ±0.07 atm. The viewable glass cell was marked, carefully calibrated, and judged to give volumetric readings to an accuracy of ±0.02 cm^3.

Materials

The CO_2 (mol wt = 44.01) used in this study was obtained from the Matheson Co. as "Coleman Grade" material with a stated minimum purity of 99.99%. Oxygen, nitrogen, carbon monoxide, and hydrogen were the major impurities.

The CO_2 was prepared for use by flashing it from the cylinder at room temperature to the 3000-cm^3 storage reservoir maintained at 0 °C. In doing this, the resulting liquefaction of the CO_2 makes it free from impurities, the impurities remaining in the vapor space. Subsequent venting of the vapor phase in the reservoir then removes these impurities.

The Kuenen criterion of purity (the difference between the bubble point and the dew-point pressure divided by the critical pressure) was less than 0.01. The properties vapor pressure, sublimation pressure, and critical and triple point were within 0.3 atm and 0.1 °C of the literature values (*1*).

Table I. Smoothed Values of Liquid Phase Composition and Liquid Molar Volume as a Function of Pressure for the Binary Vapor–Liquid System CO_2–n-Butylbenzene

Pressure, atm	Comp (mole fraction CO_2)	Molar volume, mL/g-mol
$T = 20$ °C, $\bar{V}_{CO_2} = 46.7$, $\bar{V}_{nBB} = 156.6$		
10	0.106	145.4
15	0.163	138.8
20	0.223	132.0
25	0.287	124.9
30	0.357	117.3
35	0.433	109.1
40	0.516	99.5
45	0.619	87.9
50	0.778	72.0
$T = 0$ °C, $\bar{V}_{CO_2} = 44.5$, $\bar{V}_{nBB} = 154.8$		
10	0.160	136.2
15	0.252	125.9
20	0.356	114.8
25	0.474	101.7
30	0.671	80.0

Table II. Smoothed Values of Liquid Phase Composition and Liquid Molar Volume as a Function of Pressure for the Binary Vapor–Liquid System CO_2-*trans*-decalin

Pressure, atm	Comp (mole fraction CO_2)	Molar volume, mL/g-mol
$T = 75\ °C,\ \bar{V}_{CO_2} = 52.5,\ \bar{V}_{td} = 167.9$		
10	0.049	162.1
15	0.074	159.3
20	0.099	156.4
25	0.124	153.6
30	0.148	150.8
35	0.172	148.0
40	0.196	145.2
45	0.220	142.5
50	0.244	139.8
55	0.268	137.0
60	0.291	134.2
65	0.314	131.5
70	0.337	128.8
$T = 50\ °C,\ \bar{V}_{CO_2} = 50.8,\ \bar{V}_{td} = 162.3$		
10	0.059	156.0
15	0.089	152.6
20	0.120	149.2
25	0.149	145.8
30	0.179	142.4
35	0.209	139.0
40	0.240	135.6
45	0.271	132.1
50	0.302	128.6
55	0.334	125.2
60	0.368	121.4
65	0.401	117.5
70	0.439	113.0
$T = 25\ °C,\ \bar{V}_{CO_2} = 49.0,\ \bar{V}_{td} = 159.7$		
10	0.075	151.6
15	0.114	147.1
20	0.154	142.5
25	0.195	137.7
30	0.237	132.8
35	0.281	127.9
40	0.330	122.7
45	0.383	117.0
50	0.445	110.5
55	0.524	101.8
60.2 (formation of L_2 phase; see Table IV)		
$T = 0\ °C,\ \bar{V}_{CO_2} = 43.9,\ \bar{V}_{td} = 155.5$		
10	0.113	143.1
15	0.176	135.8
20	0.242	128.0
25	0.320	119.4
30	0.425	107.7
33.4 (formation of L_2 phase; see Table IV)		

The *n*-butylbenzene (mol wt = 134.21) used in this study was supplied by the Aldrich Chemical Co. and was certified to be better than 99% pure. The *trans*-decalin (mol wt = 138.25) was supplied by the Columbia Organic Chemicals Co. and was also certified to be better than 99% pure. Refractive indices of both hydrocarbons were in agreement with the literature, and both hydrocarbons were used without further purification.

Results

Table I presents smoothed liquid-phase composition and liquid molar volume data as a function of pressure for the 20 and 0 °C isotherms for the vapor–liquid system CO_2-*n*-butylbenzene. Reference 8 presents isotherms at 37, 50, 75, and 100 °C for the same binary system. It was assumed that negligible hydrocarbon was present in the vapor phase in all experiments per-

Table III. Smoothed Three-Phase Vapor–Liquid 1–Liquid 2 Behavior in the Carbon Dioxide–*n*-Butylbenzene System

Temp, °C	Pressure, atm	Mole fraction CO_2		Molar volume, mL/g-mol	
		L_1	L_2	L_1	L_2
-41.17[a]	9.41	0.819	0.819	57.4	57.4
-42.0	9.04	0.761	0.884	51.0	64.7
-44.0	8.40	0.704	0.915	47.7	70.4
-46.0	7.78	0.671	0.932	45.9	74.3
-48.0	7.20	0.644	0.942	44.6	77.4
-50.0	6.65	0.622	0.950	43.6	79.9
-52.0	6.11	0.602	0.955	42.6	81.9
-54.0	5.61	0.581	0.960	41.8	83.5
-56.0	5.17	0.554	0.964	41.0	86.2
-57.11[b]	4.98	0.533	0.965	40.4	88.1

[a] UCST. [b] Quadruple point (L_1–L_2V–S_2).

Table IV. Smoothed Three-Phase Vapor–Liquid 1–Liquid 2 Behavior in the Carbon Dioxide–*trans*-Decalin System

Temp, °C	Pressure, atm	Mole fraction CO_2		Molar volume, mL/g-mol	
		L_1	L_2	L_1	L_2
43.30[a]	87.67	0.706		82.0	
40	81.7	0.706	0.958	82.0	65.7
35	73.8	0.704	0.945	81.7	62.4
30	66.3	0.700	0.937	81.8	60.3
25	60.2	0.690	0.933	82.2	59.0
20	53.5	0.672	0.933	83.0	57.3
15	47.9	0.649	0.935	84.2	55.8
10	42.5	0.625	0.939	86.4	54.3
5	37.7	0.599	0.945	89.2	52.8
0	33.4	0.572	0.949	92.0	50.8
-5	29.4	0.544	0.955	94.8	49.1
-10	25.7	0.517	0.961	97.8	47.6
-15	22.3	0.496	0.967	100.5	46.2
-20	19.2	0.452	0.971	103.2	44.8
-25	16.5	0.418	0.976	105.7	43.6
-30	14.0	0.402	0.979	108.1	42.5
-35	11.8	0.351	0.980	110.0	41.5
-38.7[b]	10.4	0.342	0.981	111.5	40.5

[a] Type-K singular point. [b] Quadruple point (L_1–L_2–V–S_1).

formed. An estimate of the *maximum* vapor mole fraction of hydrocarbon is 0.003. Generally, it is at least an order of magnitude smaller.

Table II presents smoothed liquid-phase composition and liquid molar volume data as a function of pressure for the isotherms 75, 50, 25, and 0 °C for the vapor–liquid system CO_2-*trans*-decalin. The partial molar volumes given at the beginning of Tables I and II are those computed from the v–x_{CO_2} data that follows. Since v is virtually linear in x_{CO_2} for the range of x_{CO_2} studied in each isotherm, the partial molar volumes are given as single values for each isotherm. Again, the hydrocarbon present in the vapor phase is negligible.

Table III presents smoothed pressure, temperature, composition, and molar volume data for the CO_2-*n*-butylbenzene L_1-L_2-V locus. This locus extends for a range of 15.94 °C and is terminated by a Q point and a UCST point.

Table IV presents smoothed pressure, temperature, composition, and molar volume data for the CO_2-*trans*-decalin L_1-L_2-V locus. In contrast to the CO_2-butylbenzene locus and the previously studied CO_2-*n*-decane locus (5), this locus extends from the Q point at -38.7 °C over a very wide range of temperature to a K point at 43.3 °C.

In the CO_2-*trans*-decalin L_1-L_2-V system a phase inversion between L_1 and L_2 occurs at about 9.8 °C. At that point the mass density of both phases is 0.916 g/mL. Below the inversion

temperature, the CO_2-rich phase L_2, which forms second upon pressurization of the initial L–V system with CO_2, appears below the L_1 phase in the cell. Above the inversion temperature, the L_2 phase forms above the L_1 phase. In the CO_2–butylbenzene system, the L_2 phase is denser than the L_1 phase. Phase inversions have been previously observed by the authors in L_1–L_2–V systems, specifically for the ternary system CO_2–*n*-butylbenzene–n-eicosane (*8*), as the CO_2-free mole fraction of *n*-butylbenzene in *n*-eicosane in L_1 reached 0.79.

The melting point of *n*-butylbenzene is low enough that the solid crystals at the *Q* point in Table III are CO_2 (labeled S_2). The solid crystals at the *Q* point in Table IV are *trans*-decalin (labeled S_1).

The standard deviations of the raw data from the smoothed values of composition and molar volume in Tables I and II are ±0.004 and ±0.7 mL/g-mol, respectively, while, for the L_1–L_2–V systems in Tables III and IV, for pressure, compositions, and molar volumes, they are ±0.15 atm, ±0.004, and ±0.6 mL/g-mol, respectively. In the case of Tables I and II, the "flatness" of the data with respect to pressure at high pressures, for temperatures below the critical temperature of CO_2, increases the standard deviations significantly, to about twice the value encountered in the higher temperature experiments.

Glossary

K	*K* point (critical point of L_2 and V in a L_1–L_2–V system)
L_1	CO_2-lean liquid phase
L_2	CO_2-rich liquid phase
Q	quadruple point (coexistence of the four phases L_1–L_2–V–S)
S_1	solid *trans*-decalin
S_2	solid CO_2
UCST	upper critical solution temperature of L_1 and L_2
V	vapor phase (assumed to be pure CO_2)
$\underline{v}$	liquid-phase molar volume, mL/g-mol
$\overline{V}_i$	partial molar volume of species i (mL/g-mol
x_i	mole fraction of species i

Subscripts

nBB	*n*-butylbenzene
td	*trans*-decalin

Literature Cited

(1) Din, F., "Thermodynamic Functions of Gases", Butterworths, London, 1956, pp 102–134.
(2) Francis, A. W., *J. Phys. Chem.*, **58**, 1099 (1954).
(3) Huie, N. C., Luks, K. D., Kohn, J. P., *J. Chem. Eng. Data*, **18**, 311 (1973).
(4) Kulkarni, A. A., Zarah, B. Y., Luks, K. D., Kohn, J. P., *J. Chem. Eng. Data*, **19**, 349 (1974).
(5) Kulkarni, A. A., Luks, K. D., Kohn, J. P., *J. Chem. Eng. Data*, **19**, 349 (1974).
(6) McCaffrey, D. S., Kohn, J. P., *Chem. Eng. Prog., Symp. Ser.*, **64** (88), 22 (1968).
(7) Yang, H., Luks, K. D., Kohn, J. P., *J. Chem. Eng. Data*, **21**, 330 (1976).
(8) Zarah, B. Y., Luks, K. D., Kohn, J. P., *Chem. Eng. Prog., Symp. Ser.*, **140** (70), 91 (1974).

Activity Measurements on Liquid Thallium–Indium Alloys

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The activity of thallium in liquid In–Tl alloys in the temperature range 790–1040 K has been determined by means of vapor pressure methods. The measurements were carried out by use of a multiple rotating Knudsen source coupled with a mass spectrometer and the torsion effusion technique. The values so obtained indicate that small positive deviations from ideality exist at low temperatures.

Activity values of the elements for In–Tl alloys are not well known. The only data available concerning the liquid system are those reported by Kundys and Terpilowski (*6*) and obtained from emf measurements carried out in the temperature range 653–793 K. Apparently, no other direct determinations of the thallium activity are reported in literature. Therefore, we thought it useful to carry out some measurements of this parameter by using a multiple rotating Knudsen cell coupled with a mass spectrometer and the torsion effusion method.

Experimental Section

Samples of In–Tl alloys of eight compositions varying from 17 to 80 atom % of thallium were prepared employing spectrographic pure elements and their composition and homogenities were then checked by chemical and polarographic analysis (*8*).

The vaporization of the alloy samples was carried out by using both the mass spectrometric and the torsion effusion techniques.

Mass Spectrometry. In the mass spectrometric measurements a Bendix Time of Flight (Model 3015) mass spectrometer coupled with a multiple-rotating Knudsen cell was used. Details of the method and of the experimental procedure are reported in a previous work (*1*). The Knudsen cell has been machined from a cylindrical block of pirophyllite in which three housings have been drilled and its heating was accomplished by radiation from a tungsten filament. The temperatures were measured by using a calibrated iron–constantan thermocouple placed in the center of the block.

The In–Tl alloys were studied in five sets of vaporization experiments carried out in the temperature range 783–878 K and employing sufficient amounts of samples in order to warrant the constancy of their composition during the vaporization.

At the highest temperature, Tl^+ was the only ion species observed in the mass spectrum and, therefore, the variation of its intensity with the temperature was measured over the temperature range explored. The log I^+T vs. $1/T$ points were then treated by the least-squares method, and the relative constants of the ion intensity–temperature equations so derived are reported in Table I. The measured ion intensity values have been corrected for the calibration factors, γ_1, which account for the