

Phase Equilibrium Behavior of the Carbon Dioxide + Benzophenone Binary System

David E. Tarantino, James P. Kohn,* and Joan F. Brennecke

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Pressure, liquid-phase composition, and liquid-phase molar volumes are presented for the binary vapor-liquid system CO₂ + benzophenone at 25, 35, and 50 °C. Also, pressure, liquid-phase compositions, and liquid-phase molar volumes on the S₁-L₁-V curve and L₁-L₂-V curve are presented. The termination points of these loci are located and characterized.

Introduction

Phase equilibrium behavior of various binary CO₂ + hydrocarbon mixtures has been studied by many researchers, providing data which are useful in the design of economically attractive separation processes using carbon dioxide as a solvent. The study of phase equilibrium behavior of carbon dioxide and aromatic hydrocarbons along liquid-vapor and liquid-liquid-vapor lines has been conducted by Ohgaki and Katayama (7), CO₂ + benzene; Ng and Robinson (4) and Sebastian et al. (10), CO₂ + toluene; Ng and Robinson (5), CO₂ + *m*-xylene; Occhiogrosso et al. (6), CO₂ + isopropylbenzene; Suppes and McHugh (11), CO₂ + styrene; and Tan et al. (12), CO₂ + ethylbenzene and CO₂ + styrene.

The present investigation of the phase equilibrium behavior of the CO₂ + benzophenone binary system will complement the aforementioned studies and help elucidate the nature of the phase equilibria of CO₂ + aromatic hydrocarbon systems in general. In addition, the phase equilibrium behavior of the CO₂ + benzophenone system is of particular interest because this system is used in other experiments in our laboratory. Specifically, benzophenone is used as a reactant to study the solvent effect on reactions in supercritical carbon dioxide by Roberts et al. (8).

Experimental Section

A detailed description of the apparatus and the procedure is given elsewhere (2). Briefly, for the liquid-vapor (L₁-V) isotherms, a known amount of liquid benzophenone (1) was placed in a calibrated 10-mL glass equilibrium cell. During the experimental runs, measured amounts of pure CO₂ (2) gas were added to the thermostated equilibrium cell from a high-pressure bomb, through the use of a positive displacement mercury pump. Using a mass balance, the number of moles of CO₂ gas added to the liquid phase was determined. In all cases, the vapor phase was assumed to be pure CO₂.

In the case of the S₁-L₁-V runs, measured amounts of liquid benzophenone were added to the glass equilibrium cell. By cooling the cell to slightly below 46.0 °C, crystals of benzophenone were formed. The crystals were carefully maintained by further cooling as carbon dioxide was added to the cell. At the equilibrium pressure, an identifiable small number of crystals were present in the liquid phase of the cell. Lowering the temperature of the cell a few tenths of a Celsius degree would result in a significant increase in the number of crystals. The S₁-L₁-V temperatures reported are those when only a few small crystals were in stable thermal equilibrium. At this point, the pressure was recorded also,

and from these data, the composition of the liquid phase and its molar volume could be determined.

For the S₁-L₁-V experimental runs, if carbon dioxide was added in large amounts when no benzophenone crystals were in the cell, no crystals of benzophenone were ever generated over the temperature range between 46 °C and the lowest temperature reached, which was -20.9 °C. There are reported to be four different solid phases for benzophenone over a temperature range of +48.1 to -51.0 °C (3); however, due to the extraordinarily large subcooling effects encountered in this study, none were formed unless solid crystals were introduced at the beginning of the run. This is the most dramatic example of subcooling ever encountered by this laboratory.

In the case of the L₁-L₂-V runs, the number of moles of CO₂ in a specific liquid phase was determined from individual runs in which either a small amount or a large quantity of benzophenone was initially injected into the cell. If a large quantity of benzophenone was used, the liquid volume would dilate as carbon dioxide was added to the cell, and eventually a trace amount of carbon dioxide-rich liquid (the L₂ phase) would appear on top of the benzophenone-rich liquid (L₁) phase. At this point, all three phases (L₁, L₂, and V) were present, and only 1 degree of thermodynamic freedom existed. If the temperature was lowered, the L₂ phase would increase in volume. If the temperature was raised, the amount of the L₂ phase would decrease. At relatively high temperatures, the L₂ phase could only be maintained by adding carbon dioxide to the cell.

To secure information on the L₂ phase, only a small quantity of benzophenone was added initially to the empty equilibrium cell. Upon addition of carbon dioxide to the cell, the volume of the benzophenone-rich liquid phase (L₁) would increase until the carbon dioxide-rich liquid phase (L₂) was formed. At this point, the addition of carbon dioxide was continued until a large volume of the L₂ phase existed in the cell, and the volume of the L₁ phase was consequently reduced to a small, but finite, amount. By using the data from several runs at different initial benzophenone loadings, the compositions and molar volumes of both the L₁ and L₂ phases could be calculated. This procedure was used over the relatively narrow temperature range from the quadruple point to the type-K singular point.

Temperatures were taken using a platinum resistance thermometer which was accurate to within ±0.03 °C. Pressures were measured using Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge to an estimated accuracy of ±0.07 bar. The viewable glass equilibrium cell was marked, carefully calibrated, and judged to give volumetric readings to an accuracy of ±0.02 cm³.

* To whom correspondence should be addressed.

Table 1. Smoothed Values of Liquid-Phase Composition and Liquid Molar Volume V as a Function of Pressure for the Binary Vapor-Liquid System Benzophenone (1) + CO₂ (2)

P/bar	x_2	$V/(\text{cm}^3 \text{mol}^{-1})$	P/bar	x_2	$V/(\text{cm}^3 \text{mol}^{-1})$
$t = 25\text{ }^\circ\text{C}$					
0.0	0.000	163.6 ^a	58.5	0.522	100.3 ^b
45.0	0.410	114.2 ^a	60.0	0.534	98.8
50.0	0.451	109.1 ^a	63.8	0.572	93.8
$t = 35\text{ }^\circ\text{C}$					
0.0	0.000	165.0 ^a	40.0	0.326	124.6
24.0	0.207	139.4 ^a	50.0	0.392	116.5
30.0	0.253	133.7 ^a	60.0	0.456	108.5
36.4	0.280	130.3 ^b	70.0	0.516	101.1
$t = 50\text{ }^\circ\text{C}$					
0.0	0.000	167.3	40.0	0.246	136.8
10.0	0.078	157.6	50.0	0.316	128.2
20.0	0.147	149.1	60.0	0.366	122.0
30.0	0.204	142.0	70.0	0.414	116.0

^a Subcooled liquid phase. ^b Equilibrium freezing point.

Table 2. Smoothed Values of Pressure, Temperature, Liquid-Phase Compositions, and Molar Volume of the Solid 1-Liquid 1-Vapor Locus for the Binary System Benzophenone (1) + CO₂ (2)

$t/^\circ\text{C}$	P/bar	x_2	$V/(\text{cm}^3 \text{mol}^{-1})$
48.1	1.0	0.000	167.1
46.0	6.5	0.057	161.0
44.0	11.8	0.096	155.5
42.0	17.5	0.136	150.2
40.0	23.5	0.181	144.8
38.0	29.0	0.225	139.7
36.0	33.9	0.268	134.3
34.0	39.0	0.310	129.0
32.0	44.4	0.347	123.6
30.0	48.0	0.383	118.3
28.0	52.2	0.421	113.0
26.0	57.0	0.462	107.7
23.9	62.3	0.572	93.6 ^a

^a Quadruple point.

Table 3. Smoothed Values of Pressure, Temperature, Compositions, and Liquid Molar Volume V of the Liquid 1-Liquid 2-Vapor Locus for the Binary System Benzophenone (1) + CO₂ (2)

$t/^\circ\text{C}$	P/bar	x_2		$V/(\text{cm}^3 \text{mol}^{-1})$	
		L_1	L_2	V_1	V_2
23.9	62.30 ^a	0.572	0.996	93.6	52.0
25.0	63.80	0.572	0.995	93.6	52.9
26.0	65.30	0.571	0.995	93.6	54.0
27.0	66.70	0.571	0.994	93.7	55.1
28.0	68.20	0.571	0.994	93.7	56.5
29.0	69.80	0.571	0.993	93.7	58.0
30.0	71.40	0.571	0.993	93.7	59.8
31.0	73.00	0.570	0.992	93.8	62.0
32.0	74.70	0.570	0.992	93.8	72.0
32.8	76.08 ^b	0.570	0.990	93.8	81.7

^a Quadruple point. ^b Type-K singular point.

Materials. The CO₂ used in this study was obtained from Mittler Supply, Inc., and was Linde "bone dry grade" material with a minimum purity of 99.8%. Oxygen, nitrogen, and methane were the major impurities.

The CO₂ was prepared for use by distilling it from a cylinder of CO₂ at room temperature into a 3000 cm³ storage cylinder maintained at 0 °C. Approximately 20% of the gas phase was slowly vented from the storage cylinder to lower the amount of noncondensable components.

Dew-bubble point isotherms at 25 °C were determined on the carbon dioxide which was used in all of the experiments. The dew point pressure of the gas was 0.59 bar lower than the

Table 4. Raw Data for Benzophenone (1) + CO₂ (2)

run	P/bar	$t/^\circ\text{C}$	liquid		comment
			x_2	$V/(\text{cm}^3 \text{mol}^{-1})$	
1	4.71	47.18	0.0614	153.3	S ₁ -L-V
	14.37	42.95	0.1194	148.5	S ₁ -L-V
	29.40	38.09	0.2272	137.7	S ₁ -L-V
	38.37	33.97	0.3070	134.3	S ₁ -L-V
	43.47	31.93	0.3500	124.8	S ₁ -L-V
2	7.35	45.78	0.0612	159.3	S ₁ -L-V
	18.51	41.42	0.1395	150.4	S ₁ -L-V
	24.92	39.78	0.1867	142.5	S ₁ -L-V
	10.37	44.39	0.0905	152.6	S ₁ -L-V
3	38.64	33.91	0.3120	127.1	S ₁ -L-V
	38.95	35.00	0.3100	127.2	L ₁ -V
	47.40	35.00	0.3670	120.5	L ₁ -V
	59.33	35.00	0.4400	111.2	L ₁ -V
	50.22	25.08	0.4390	110.6	L ₁ -V
4	14.79	50.00	0.1055	154.1	L ₁ -V
	28.58	50.00	0.1929	143.8	L ₁ -V
	36.09	50.00	0.2380	137.9	L ₁ -V
	44.50	50.00	0.2860	132.0	L ₁ -V
	53.33	50.00	0.3340	126.0	L ₁ -V
	60.78	50.00	0.3700	121.7	L ₁ -V
	67.74	50.00	0.4030	117.3	L ₁ -V
	18.51	50.00	0.1393	149.9	L ₁ -V
	28.65	50.00	0.2035	141.9	L ₁ -V
	24.23	35.00	0.2116	140.6	L ₁ -V
5	32.85	35.00	0.2760	131.2	L ₁ -V
	39.61	35.00	0.3240	125.1	L ₁ -V
	46.36	35.00	0.3710	119.4	L ₁ -V
	53.26	35.00	0.4140	113.9	L ₁ -V
	12.65	50.00	0.1044	154.3	L ₁ -V
	26.03	50.00	0.1825	146.5	L ₁ -V
	23.13	35.00	0.1988	140.7	L ₁ -V
	30.09	35.00	0.2520	134.4	L ₁ -V
	36.04	35.00	0.3150	125.1	L ₁ -V
	44.64	35.00	0.3570	120.9	L ₁ -V
6	51.71	35.00	0.4030	115.2	L ₁ -V
	59.26	35.00	0.4520	108.8	L ₁ -V
	65.95	35.00	0.4930	103.4	L ₁ -V
	56.64	25.00	0.5090	101.3	L ₁ -V
	65.12	25.00	0.5750	93.4	L ₁ -V
	65.53	25.00	0.5820	93.2	L ₁ -L ₂ -V, L ₁
	19.82	41.13	0.1527	147.6	S ₁ -L-V
	36.72	35.00	0.2840	130.4	S ₁ -L-V
	44.58	31.80	0.3470	122.1	S ₁ -L-V
	52.92	27.69	0.4270	112.7	S ₁ -L-V
7	59.47	25.00	0.4900	104.7	S ₁ -L-V
	65.67	22.65	0.5740	93.7	S ₁ -L-V
	60.51	22.66	0.9938	50.3	L ₁ ^a -L ₂ -V, L ₂
	72.29	30.57	0.9923	61.0	L ₁ -L ₂ -V, L ₂
	76.02	32.67	0.9978	81.7	type-K, V
	68.51	28.06	0.9949	55.7	L ₁ -L ₂ -V, L ₂
	62.09	23.75	0.9931	52.5	L ₁ ^a -L ₂ -V, L ₂
	54.92	18.42	0.9919	49.4	L ₁ ^a -L ₂ -V, L ₂
	27.00	-9.36	0.9875	41.5	L ₁ ^a -L ₂ -V, L ₂
	19.21	-20.90	0.9863	39.6	L ₁ ^a -L ₂ -V, L ₂
8	15.89	50.00	0.1161	151.7	L ₁ -V
	29.13	50.00	0.1973	141.4	L ₁ -V
	40.85	50.00	0.2650	133.2	L ₁ -V
	34.30	35.00	0.2750	130.3	L ₁ -V
	43.61	35.00	0.3430	122.5	L ₁ -V
	53.12	35.00	0.4090	114.0	L ₁ -V
	45.54	25.00	0.4140	112.5	L ₁ -V
	52.85	25.00	0.4750	105.5	L ₁ -V
	51.81	24.00	0.4780	104.8	L ₁ -V
	62.36	24.00	0.5720	93.5	L ₁ -L ₂ -V, L ₁
9	59.74	22.13	0.5730	93.2	L ₁ ^a -L ₂ -V, L ₁
	63.81	25.00	0.5710	93.7	L ₁ -L ₂ -V, L ₁
	66.64	27.00	0.5730	93.7	L ₁ -L ₂ -V, L ₁
	71.40	30.00	0.5710	93.5	L ₁ -L ₂ -V, L ₁
	72.91	31.00	0.5690	93.5	L ₁ -L ₂ -V, L ₁
	76.08	32.81	0.5700	93.8	type-K, V

^a Subcooled liquid phase.

literature value (I), and the dew point gas molar volume was within 0.3% of the literature value (I). The bubble point pressure of the experimental CO₂ was 0.15 bar higher than

the literature value (I), and the bubble point molar volume was within 1.8% of the literature value (I).

The benzophenone used in this study was obtained from Fisher Scientific Co. as "certified grade benzophenone". The melting point of this benzophenone was 48.2 °C, and it was used without further purification.

Results

Table 1 presents smoothed composition, pressure, temperature, and molar volume data in the vapor-liquid two-phase region at temperatures of 25, 35, and 50 °C. The data were smoothed graphically, and the standard deviations of the raw data from the smoothed mole fraction x and molar volumes V in Table 1 are ± 0.0068 in x and ± 0.8 cm³ mol⁻¹ in V at 25 °C, ± 0.0047 in x and ± 0.6 cm³ mol⁻¹ in V at 35 °C, and ± 0.0036 in x and ± 0.6 cm³ mol⁻¹ in V at 50 °C. Values of composition and molar volume are reported for subcooled liquids at 25 and 35 °C under conditions in which the liquid phase is metastable, as discussed above. These conditions are indicated by an italic a in Tables 1 and 4. The italic b indicates the highest pressure under which solid benzophenone could be present. Dew point computations were not accurate enough to give the vapor-phase compositions because the benzophenone mole fraction x_1 was below about 0.001, thus justifying the assumption that the vapor phase is essentially pure CO₂.

Table 2 presents the solid-liquid-vapor three-phase data for the CO₂ + benzophenone system. The standard deviations of the raw data from the smoothed liquid-phase mole fraction x and molar volumes V in Table 2 are ± 0.009 in x and ± 1.0 cm³ mol⁻¹ in V . Additionally, the standard deviation of the raw data from the smoothed freezing point temperatures is ± 0.4 K.

Table 3 presents the liquid-liquid-vapor three-phase data for the system. The standard deviations of the liquid-phase compositions and molar volumes of the raw data from the smoothed data in Table 3 are ± 0.002 in x and ± 0.25 cm³ mol⁻¹ in V for the L₁ phase and ± 0.71 cm³ mol⁻¹ in V for the L₂ phase. The indicated quadruple point was observed a number of times, but only when approached from lower pressures along the S₁-L₁-V locus. Solid benzophenone could not be nucleated by approaching the quadruple point along the L₁-L₂-V locus, even with cooling to -20.9 °C, due to the subcooling problem mentioned previously.

Figure 1 shows the phase equilibria in the immediate region of the quadruple point at pressures above 57 bar. The pressure difference between the vapor pressure curve of pure carbon dioxide and the L₁-L₂-V line is slightly less than 1.0 bar at the quadruple point and increases to approximately 1.5 bar at the critical temperature of pure carbon dioxide.

All of the two- and three-phase equilibrium data were fit with two models: regular solution theory (RST) plus a Flory-Huggins term and the Scatchard modification of regular solution theory. The data of Angus et al. (I) were used for the pure CO₂ fugacities. RST plus Flory-Huggins fits the data with a single value of the interchange parameter of 7.728 kJ mol⁻¹, and the standard deviation which corresponds to this value of the interchange parameter is $\pm 0.66\%$. The Scatchard activity coefficient model alone is less satisfactory. The fitted value of the interchange parameter is 4.966 kJ mol⁻¹ with a standard deviation of $\pm 3.3\%$. Moreover, the magnitude of this parameter increased 10.2% as the pressure was increased from 10 to 66 bar. Details of the model calculations can be found in Rodrigues et al. (9).

The data along the L₁-V, S₁-L₁-V, and L₁-L₂-V lines were predicted with good accuracy with the Flory-Huggins model using the interchange energy parameter above. The best results of the Flory-Huggins model were achieved on the liquid-vapor two-phase data where the computed fugacities

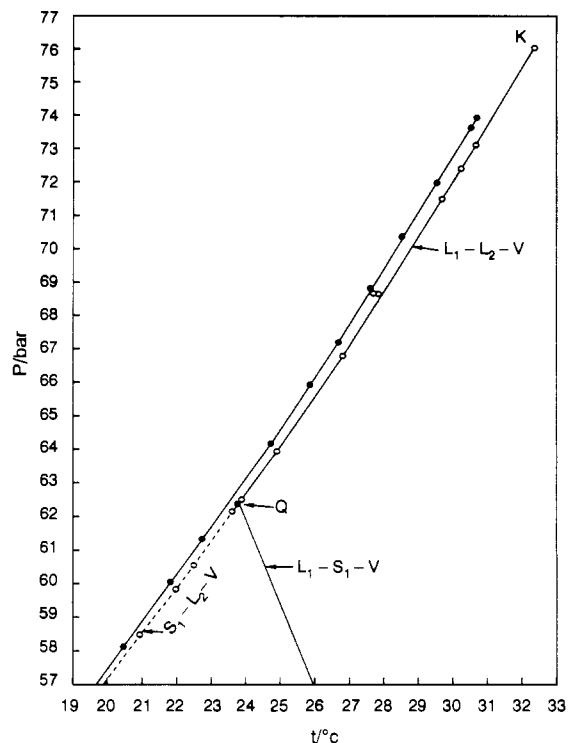


Figure 1. Pressure-temperature profile in the immediate region of the quadruple point: ●, pure CO₂; ---, subcooled L₁ phase.

of the gas-phase carbon dioxide had standard deviations from the smoothed data of only ± 0.3 bar.

Nomenclature

L₁ = CO₂-lean liquid phase

L₂ = CO₂-rich liquid phase

P = pressure, bar

Q = quadruple point (coexistence of the four phases V-L₁-L₂-S)

S = solid benzophenone

t = temperature, °C

type-K point = L₂ = V in the presence of the noncritical L₁ phase

V = vapor phase

V = molar volume, cm³ mol⁻¹

X = composition

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