

High-Pressure Vapor-Liquid Equilibria for CO₂/*n*-Decane, CO₂/Tetralin, and CO₂/*n*-Decane/Tetralin at 71.1 and 104.4 °C

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Vapor-liquid equilibria are reported for CO₂/*n*-decane, CO₂/tetralin, and CO₂/*n*-decane/tetralin; all systems were measured at 71.1 and 104.4 °C for pressures to near-critical. For CO₂/*n*-decane, both isotherms from this work are in good agreement with those by Reamer and Sage. For CO₂/tetralin at 71.1 °C and for CO₂/*n*-decane/tetralin at 71.1 °C and 119.3 bar, there exists a slight systematic deviation between data from this work and those by Inomata et al. At all other conditions, data presented here are new measurements not previously reported. At all conditions studied, CO₂ is more soluble in *n*-decane than in tetralin, contrary to expectations.

Introduction

Carbon dioxide (CO₂)/hydrocarbon systems are of interest in enhanced-oil-recovery applications where CO₂ is used as a miscible flooding agent to displace oil from a reservoir. Vapor-liquid equilibria (VLE) for such systems are required for simulation of petroleum reservoirs and for design of separation processes. While equilibrium data for binary CO₂/hydrocarbon mixtures are plentiful, equilibrium data for ternary CO₂/hydrocarbon mixtures are scarce, especially for ternary systems containing heavy hydrocarbons (C₁₀⁺) and/or hydrocarbons other than paraffins.

We report here experimental VLE data for the ternary system CO₂/*n*-decane/tetralin and for the binary systems CO₂/*n*-decane and CO₂/tetralin at 71.1 and 104.4 °C for pressures to near-critical. For CO₂/*n*-decane, several authors have reported VLE data at temperatures similar to those in this work (see, for example, ref 1-3). This binary system serves as a test for our apparatus and procedure; we compare our data with those reported by Reamer and Sage (1).

For CO₂/tetralin, Sebastian et al. (4) measured VLE data at elevated temperatures (>188 °C); Inomata et al. (5) recently extended the VLE measurements to lower temperatures. We compare our CO₂/tetralin data at 71.1 °C to those reported by Inomata et al. (5) at 72.8 °C; the 104.4 °C isotherm presents measurements not previously reported.

For CO₂/*n*-decane/tetralin, Inomata et al. (6) recently measured VLE data at 70.2 and 247 °C; we compare our ternary measurements at 71.1 °C and 119.3 bar with their data at 70.2 °C and 118.1 bar (the condition nearest to that in this work). All other data reported here for CO₂/*n*-decane/tetralin are for conditions not previously studied.

Experimental Section

Apparatus. Vapor-liquid-equilibrium data were obtained with a static equilibrium apparatus with vapor recirculation. Details

of the apparatus are given elsewhere (7); only a brief description is given here. The apparatus consists of two main sections: one for achieving phase equilibrium and one for analyzing fluid samples. Figure 1 presents a schematic diagram of the phase-equilibrium section. The principal components include a windowed equilibrium cell (EC), a high-pressure recirculation pump (RP), a temperature-control and -measurement system, and a pressure-generation and -measurement system. The volume of the equilibrium cell is approximately 100 cm³. Vapor-liquid equilibria are achieved by recirculating the vapor phase through the liquid phase.

The equilibrium cell is connected to two sampling ports: one for the vapor phase and one for the liquid phase. Each sampling port contains a specially designed sampling valve (β), here called a microcell (MC). Figure 2 shows a cross-sectional view of the microcell; each microcell has a sample cavity of approximately 30 μ L. During sampling, a microcell collects an equilibrium-phase sample at conditions of the equilibrium cell; the microcell is then taken from the apparatus to the sample-analysis system for composition analysis.

The entire equilibrium system is enclosed in a constant-temperature air bath. Temperatures are measured at several locations in the air bath and directly inside the equilibrium cell with type-T copper-constantan thermocouples; the estimated accuracy of the thermocouples is within ± 0.2 °C. The maximum difference between the temperature inside the equilibrium cell and that outside is approximately 0.6 °C.

The pressure of the system is measured with bourdon-tube pressure gauges (PG) that are calibrated against a dead-weight gauge; the estimated accuracy of the pressure gauges is within $\pm 0.1\%$ of the full-scale reading. High pressure in the system is attained by pumping the gaseous component (carbon dioxide) into the equilibrium cell with a manual compressor (C). Fine adjustments in pressure are achieved by a hand-operated pressure generator (HG), consisting of a piston-and-cylinder assembly.

The second main section of the experimental apparatus is the sample-analysis system, shown in Figure 3. This system consists primarily of a temperature-controlled microcell oven and a gas chromatograph. The microcell oven contains a microcell housing, a flash vessel (FV), a recirculation system, and a gas chromatograph sampling valve (SV) connected to a sample loop (SL). A microcell containing a fluid sample is inserted into the microcell housing from which the high-pressure sample is vaporized into the flash vessel. The flash vessel is a variable-volume bellows assembly that also acts as a pump to recirculate the flashed sample through the sampling valve so that the fluid inside the sample loop is homogeneous. The sample is injected into the gas chromatograph by purging carrier gas (helium) through the sample loop.

The gas chromatograph (Shimadzu GC-9A) uses thermal conductivity detectors; its response is measured by an electronic integrator. Both binary and ternary mixtures are separated on a $1/8$ -in. \times 4-ft stainless-steel column, packed with 10% OV-101 on 80/100-mesh Chromosorb W-HP.

Materials. Carbon dioxide is supplied by Matheson Gas (Coleman Instrument Grade, 99.99% purity). Tetralin

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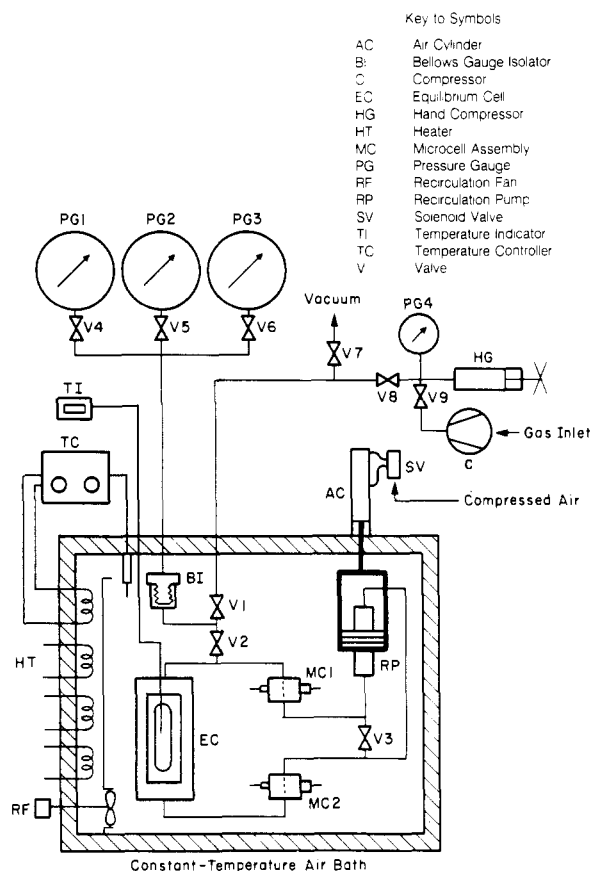


Figure 1. Schematic diagram of phase-equilibrium apparatus.

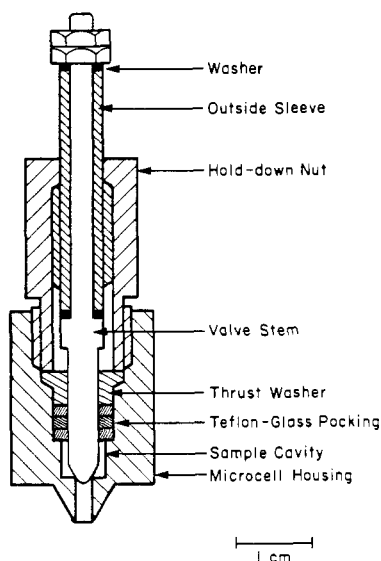


Figure 2. Cross-sectional view of microcell.

(1,2,3,4-tetrahydronaphthalene, 99%) and *n*-decane (Gold Label, 99+%) are both supplied by Aldrich Chemical Co. All materials are used without further purification.

Procedure. The experiment begins by charging the equilibrium cell with a mixture of liquid hydrocarbons of known composition. The liquid is degassed in the cell; to prevent leakage of air into the system, enough CO₂ is added to provide a slight positive pressure. The cell is then heated slowly to the experimental temperature; slow heating is important to prevent sudden thermal stresses on cell glass windows. For ternary experiments, isothermal data are taken at different starting compositions of liquid hydrocarbons. To avoid thermal cycling of the apparatus, the starting composition is changed by adding

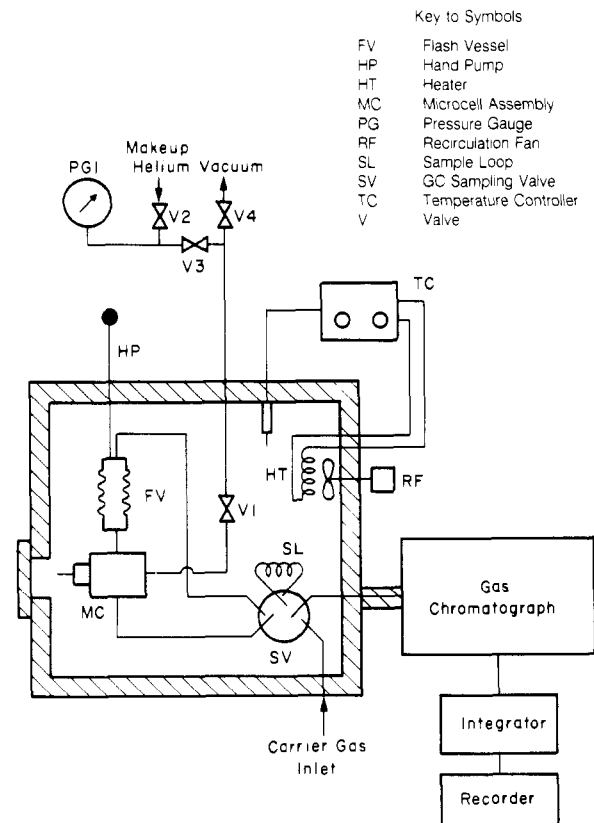


Figure 3. Schematic diagram of sample-analysis apparatus.

Table I. Vapor-Liquid Equilibria for CO₂/*n*-Decane

temp, °C	pressure, bar	mole fraction CO ₂	
		liquid	vapor
71.1	40.7	0.315	0.999
	81.3	0.581	0.996
	103.8	0.721	0.992
	119.3	0.841	0.982
104.4	49.9	0.310	0.994
	93.9	0.522	0.991
	131.9	0.695	0.983
	154.5	0.798	0.964

liquid hydrocarbons to the cell at the experimental temperature.

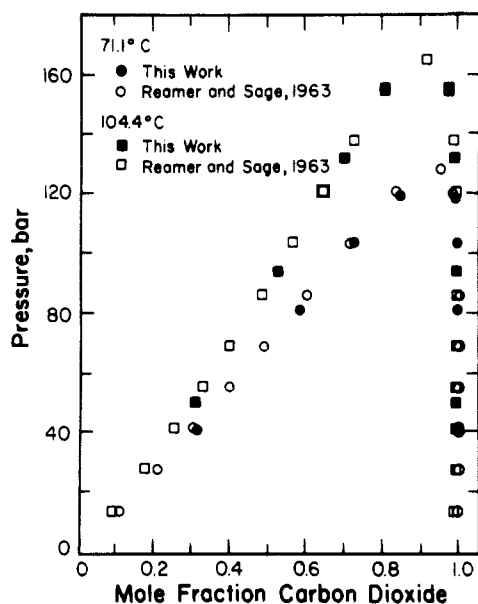
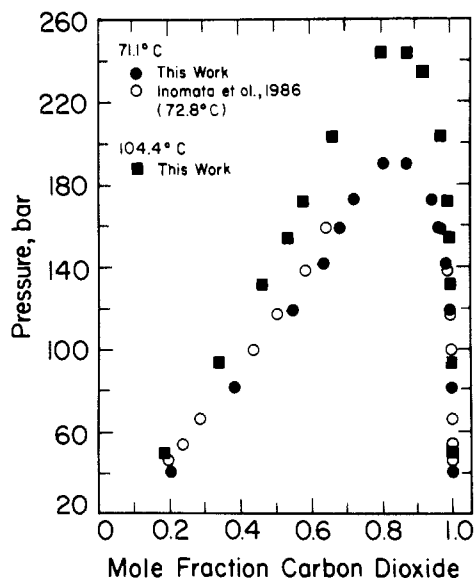
When the experimental temperature reaches steady state, the cell is pressurized with carbon dioxide. The vapor phase is recirculated through the liquid phase by the recirculation pump; equilibrium between the two phases is generally attained in approximately 1 h.

Prior to sampling, the microcells are evacuated and heated in the sampling port to near the equilibrium-cell temperature. During sampling, the recirculation pump is shut off and the pump bypass valve is opened to allow liquid to flow out of the cell into the liquid-sampling line connected to the liquid microcell. Vapor and liquid samples are taken simultaneously; there is no noticeable pressure drop in the equilibrium cell due to sampling. After sampling, the microcells containing the high-pressure samples are sequentially transported to the analysis section for composition analysis.

To determine the compositions of the fluid samples, an absolute calibration of gas chromatographic area vs moles injected is established for each component. Compared to relative calibration, absolute calibration is more tedious to perform and usually requires greater accuracy; however, for determining composition of ternary mixtures, absolute calibration eliminates the requirement for interpolation between relative calibration curves. Each sample is analyzed two or three times by repeatedly turning the gas-chromatograph sampling valve; reproducibility between analyses is better than $\pm 2\%$.

Table II. Vapor-Liquid Equilibria for CO₂/Tetralin

temp, °C	pressure, bar	mole fraction CO ₂	
		liquid	vapor
71.1	40.7	0.206	0.999
	81.3	0.382	0.998
	119.3	0.546	0.993
	141.9	0.635	0.981
	159.2	0.680	0.960
	172.9	0.720	0.937
104.4	190.6	0.801	0.868
	49.9	0.185	0.998
	93.9	0.337	0.997
	131.9	0.460	0.993
	154.5	0.531	0.989
	172.1	0.574	0.983
	185.5		0.974
	203.6	0.658	0.963
	234.4		0.910
	243.8	0.794	0.865

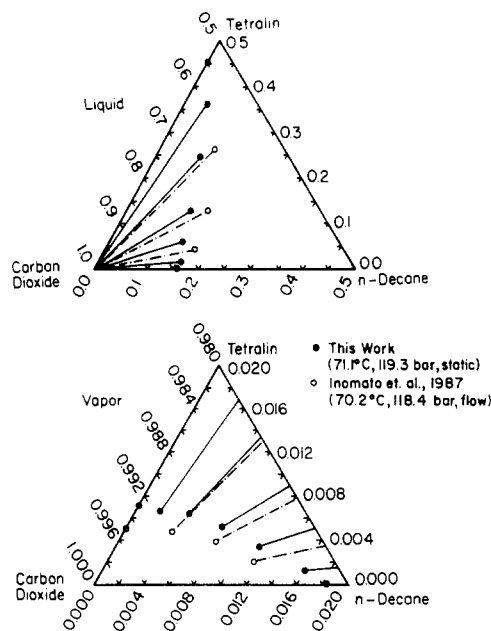
Figure 4. Vapor-liquid equilibria for CO₂/n-decane.Figure 5. Vapor-liquid equilibria for CO₂/tetralin.

Results and Discussion

Tables I-IV present experimental vapor-liquid-equilibrium data for CO₂/n-decane, CO₂/tetralin, and CO₂/n-decane/tet-

Table III. Vapor-Liquid Equilibria for CO₂ (1)/n-Decane (2)/Tetralin (3) at 71.1 °C

pressure, bar	mole fraction in liquid			mole fraction in vapor		
	1	2	3	1	2	3
40.7	0.206	0	0.794	0.999	0	0.001
	0.217	0.089	0.694			
	0.241	0.199	0.560			
	0.272	0.344	0.384			
	0.291	0.491	0.218			
	0.309	0.628	0.063			
81.3	0.315	0.685	0	0.999	0.001	0
	0.382	0	0.618	0.998	0	0.002
	0.407	0.063	0.530	0.9978	0.0005	0.0017
	0.448	0.151	0.401	0.9972	0.0012	0.0016
	0.511	0.239	0.250	0.9971	0.0018	0.0011
	0.548	0.312	0.140	0.9962	0.0029	0.0009
	0.586	0.376	0.038	0.9965	0.0033	0.0002
	0.581	0.419	0	0.996	0.004	0
	0.546	0	0.454	0.993	0	0.007
	0.592	0.045	0.363	0.991	0.002	0.007
119.3	0.668	0.086	0.246	0.989	0.004	0.007
	0.749	0.123	0.128	0.987	0.008	0.005
	0.802	0.137	0.061	0.985	0.011	0.004
	0.832	0.153	0.015	0.983	0.016	0.001
	0.841	0.159	0	0.982	0.018	0
	0.635	0	0.365	0.981	0	0.019
	0.683	0.030	0.287	0.975	0.004	0.021
	0.787	0.056	0.157	0.955	0.015	0.030
	0.680	0	0.320	0.960	0	0.040
	0.767	0.023	0.210	0.943	0.008	0.049
172.9	0.720	0	0.280	0.937	0	0.063
	0.795	0.020	0.185	0.885	0.013	0.102
190.6	0.801	0	0.199	0.868	0	0.132

Figure 6. Vapor-liquid equilibria for CO₂/n-decane/tetralin at 71.1 °C and 119.3 bar.

ralin. The estimated uncertainties are 0.2 °C for temperature; 0.2 and 0.5 bar, respectively, for pressures less than and greater than 150 bar; and ± 0.005 and ± 0.002 , respectively, for mole fractions in liquid and vapor.

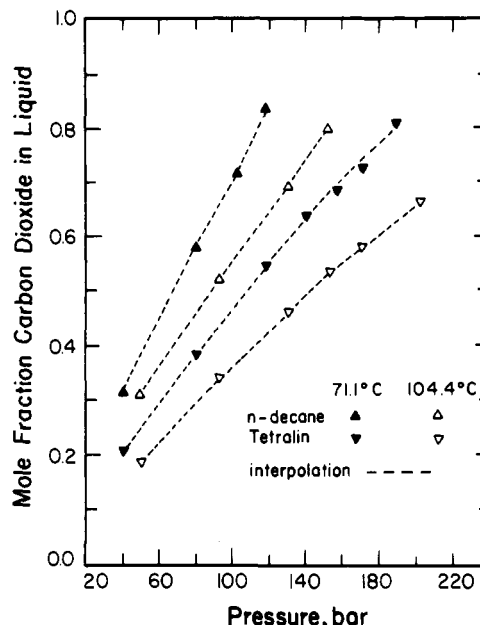
For binary systems, each VLE measurement is repeated at least once; reproducibility between measurements is within $\pm 4\%$ for liquid and $\pm 2\%$ for vapor. The larger deviations in liquid occur at higher pressures where gas entrainment in liquid samples is the most likely source of error. For the ternary system, VLE measurements depend on the composition of the initial hydrocarbon charge, which cannot be reproduced exactly due to degassing of the equilibrium cell at the beginning of each

Table IV. Vapor-Liquid Equilibria for CO₂ (1)/*n*-Decane (2)/Tetralin (3) at 104.4 °C

pressure, bar	mole fraction in liquid			mole fraction in vapor		
	1	2	3	1	2	3
49.9	0.185	0	0.815	0.998	0	0.002
	0.196	0.075	0.729	0.997	0.001	0.002
	0.220	0.210	0.570			
	0.251	0.352	0.397	0.996	0.003	0.001
	0.270	0.479	0.251	0.995	0.004	0.001
	0.302	0.637	0.061	0.9942	0.0055	0.0003
93.9	0.310	0.690	0	0.994	0.006	0
	0.337	0	0.663	0.997	0	0.003
	0.358	0.060	0.582			
	0.400	0.161	0.439			
	0.440	0.262	0.298	0.994	0.004	0.002
	0.484	0.339	0.177	0.992	0.006	0.002
131.9	0.520	0.438	0.042	0.991	0.008	0.001
	0.522	0.478	0	0.991	0.009	0
	0.460	0	0.540	0.993	0	0.007
	0.481	0.048	0.471	0.991	0.002	0.007
	0.548	0.120	0.332	0.989	0.005	0.006
	0.607	0.183	0.210	0.987	0.008	0.005
154.5	0.658	0.224	0.118	0.985	0.011	0.004
	0.692	0.281	0.027	0.983	0.016	0.001
	0.695	0.305	0	0.983	0.017	0
	0.531	0	0.469	0.989	0	0.011
	0.558	0.040	0.402	0.986	0.003	0.011
	0.626	0.098	0.276	0.982	0.007	0.011
172.1	0.687	0.144	0.169	0.978	0.013	0.009
	0.753	0.171	0.076	0.970	0.023	0.007
	0.798	0.202	0	0.964	0.036	0
	0.574	0	0.426	0.983	0	0.017
	0.618	0.034	0.348	0.980	0.003	0.017
	0.710	0.075	0.215	0.970	0.011	0.019
185.5	0.773	0.104	0.123	0.956	0.024	0.020
	0.832	0.117	0.051	0.934	0.048	0.018
	0			0.974	0	0.026
	0.655	0.030	0.315	0.970	0.005	0.025
	0.759	0.062	0.179	0.955	0.016	0.029
	0.828	0.078	0.094	0.924	0.038	0.038
203.6	0.658	0	0.342	0.963	0	0.037
	0.713	0.024	0.263	0.954	0.006	0.040
	0.834	0.043	0.123	0.894	0.030	0.076

experiment; therefore, each ternary datum represents a single measurement.

For CO₂/*n*-decane, Figure 4 shows that data from this work are in good agreement with those by Reamer and Sage (1); for liquid, agreement is within 1.5 mol % and for vapor, better than 0.5 mol %. For CO₂/tetralin and CO₂/*n*-decane/tetralin, Figures 5 and 6 compare data from this work with those by Inomata et al. (5, 6) at similar conditions; agreement is better than 0.2 mol % CO₂ for vapor and within 4.5 mol % CO₂ for liquid. Aside from the small differences in experimental temperature and pressure between the two sources, there seems to exist a slight systematic deviation in liquid-phase composition. From studying the three articles by Inomata et al. (3, 5, 6), the expected cause for the disagreement may be due to the difference in experimental uncertainties associated with different experimental techniques. Inomata et al. used a flow-type equilibrium apparatus; their samples are analyzed volumetrically for CO₂. In this work, a static equilibrium apparatus is used; samples are analyzed with a gas chromatograph. The uncertainties in composition in this work are closely related to the accuracy of the absolute calibration. Data from this work, as indicated in Figure 4, tend to have positive deviations in liquid-phase mole fraction CO₂ compared to those reported earlier, while data by Inomata et al. tend to have negative deviations

Figure 7. Solubility of carbon dioxide in *n*-decane and tetralin.

compared to those reported earlier (3, 5).

Figure 7 compares the solubility of CO₂ in the two hydrocarbon liquids. Contrary to expectation, CO₂ is more soluble in *n*-decane than in tetralin at both 71.1 and 104.4 °C. Tetralin, due to its aromatic nature, is expected to dissolve more CO₂ than does *n*-decane. The observed higher solubility in *n*-decane may be due to entropic effects since *n*-decane is much more flexible than tetralin.

Conclusions

Vapor-liquid equilibria have been measured for the binary systems CO₂/*n*-decane and CO₂/tetralin and for the ternary system CO₂/*n*-decane/tetralin at 71.1 and 104.4 °C for pressures to near-critical. At all conditions examined here, CO₂ is found to be more soluble in *n*-decane than in tetralin, possibly due to entropic effects.

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