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Simultaneous Determination of Phase Equilibria Compositions and Phase Molar Densities of Hydrocarbon + CO_2 Systems

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This paper presents new phase equilibria compositions and density data for (1) a quaternary mixture of propane + pentane + octane + CO_2 at temperatures from 310 K to 394 K and pressures from 3 MPa to 6.374 MPa. Additionally, liquid densities for a ternary mixture of propane + pentane + octane at four temperatures and gas CO_2 densities are included for comparison with literature values. A single mixture load can be used to measure simultaneously phase equilibria compositions and densities at various pressures and temperatures. This can be accomplished using a uniquely designed pressure/volume/temperature-vapor/liquid /liquid equilibrium apparatus (*PVT*-VLLE) connected to a uniquely designed system for infinitesimal sampling to a gas cromatograph (GC) at high pressures and temperatures. Carbon dioxide density compares well with the published data of Vargaftik and the predicted densities by DDMIX. Saturated liquid hydrocarbon densities are within 0.5% of the densities predicted by the modified Rackett equation. For liquid mixtures containing CO_2, the deviations from the Rackett equation are within ±1%. Therefore we conclude that this methodology is suitable for determining volumetric and phase equilibria properties of multiphase systems with sufficient accuracy for most engineering applications.

Introduction

Carbon dioxide−hydrocarbon systems frequently occur in the petroleum industry either in CO_2 flooding for enhanced oil recovery or in downstream separation processes. Phase equilibria in these systems are complex and may involve three or more equilibrium phases (Reid and Robinson, 1981). In CO_2 flooding processes, CO_2 is injected through an injector well to displace oil within the reservoir to a producer well. In this process, mass transfer mechanisms cause multiphase separations including a vapor phase, a hydrocarbon-rich liquid phase, and occasionally a CO_2−rich liquid phase.

Numerous papers have investigated the phase behavior of CO_2/hydrocarbon systems. Among these are Orr and Silva (1983), Leu and Robinson (1987), Cheng *et al.* (1989), Weng and Lee (1992), and Barrufet *et al.* (1995, 1996a). Because the equipment needed to measure high-pressure, high-temperature phase equilibria is complex, experimental data are expensive and scarce.

Materials

The *PVT*-VLLE system was charged with the propane + pentane + octane + carbon dioxide mixture prepared gravimetrically using a Mettler PM No. 600 Delta range electronic balance (accuracy ±0.01 g). All hydrocarbons used were from Aldrich Chemical Co. with 99+% purity. The water content was less than 0.0005% and the evaporation residue less than 0.0003%. The CO_2 used was +99.99% purity.

PVT−VLLE Apparatus and Sampling System

A mercury-free Ruska *PVT* Model 2370 is connected to a Hewlett Packard 5880 gas chromatograph (GC) using a specially designed sampling system capable of measuring the compositions of all equilibrium phases on-line at pressures up to 27 MPa and temperatures up to 500 K. Digitally-operated valves are used for injection of very small fluid volumes (0.1−0.5 μL); each of these valves is connected to a switching valve for back-flushing to eliminate column contamination and to separate columns for various phase composition analyses. Since the volumes used for analysis represent less than 10^{-5}% of the sample volume, the mass withdrawn for analysis is negligible as well and does not disturb the equilibrium of the system. Thus, systematic errors are minimized. Figure 1 sketches the connection between the GC and the *PVT* system. The volume of the two *PVT* cells can be changed separately by computer-controlled stepping motors, and sample mobility within the system can be achieved at constant temperature and pressure. This allows the measurement of phase volumes by positioning the interface at a specific location in the sapphire, see-through window located at the top of cell. This setup has been explained in greater detail in our previous publications (Rahman and Barrufet, 1995; Barrufet *et al.*, 1996b).

Measured volumes depend upon the dimensions of the cylinders, piston position, temperature, pressure, reference points, and magnet volume. The internal volumes for both cells and interconnecting tubing have been calibrated, including pressure and temperature correction coefficients (Ruska M2370, 1990). These volumes are entered into a computer code and accurate phase volumes can be measured by placing the phase boundary at a reference point in the sapphire window. The sample mixing in both cells is accomplished by stirring a magnetic coupling.

This system has been calibrated and validated by reproducing experimental three-phase equilibrium pressures and compositions for hexane + water systems (Tsnonopolous and Wilson, 1983), and for octane + water systems (Heidman *et al.*, 1985; Rahman and Barrufet, 1995; Rahman, 1996; Barrufet *et al.*, 1996b).

Measurement of Phase Compositions

During this portion of the experiment, the valve at the top of the piston cell is opened. The oven is heated to the desired temperature and the fluids are allowed to expand and vaporize until equilibrium is achieved. The liquid phase is at the bottom of the pump cell and the rest of the

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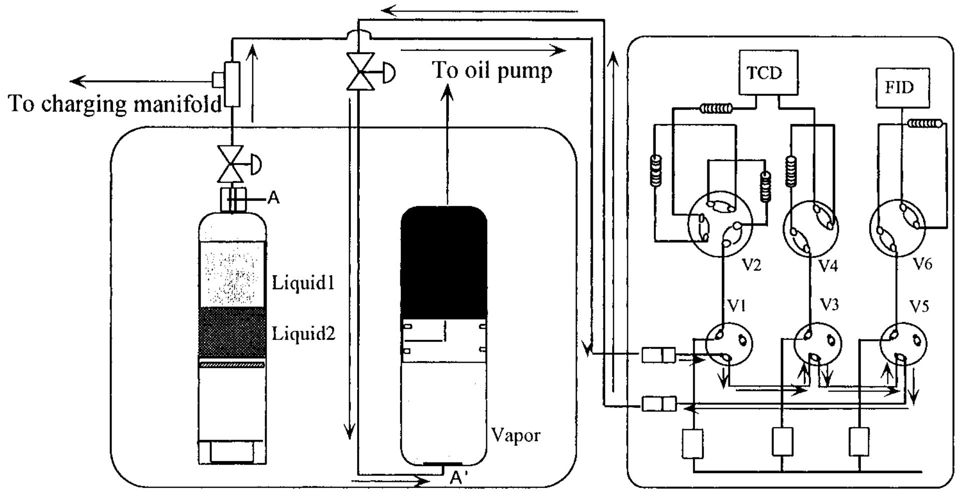

Figure 1. Schematics of the *PVT*–VLLE integrated experimental setup.

volume is occupied by the vapor phase. The fluid within the sampling loop is vapor and is analyzed for composition. After the vapor phase analysis, the piston of the pump cell is moved upward and the float piston cell is moved up simultaneously by removing hydraulic oil. Both pistons are moved with identical volumetric speed so that the overall volume of the system is constant and equilibrium is maintained. The process of fluid movement continues until the liquid phase reaches the sampling loop and can be sampled for compositional analysis. For this procedure to be successful, one must optimize the total amount of mixture charged in the cell to ensure that the volumes of the equilibrium phases are larger than the dead volume of the blind tubes (35 cm^3) and small enough to cover a wide range of pressures and temperatures. This blind volume is indicated between points A and A′ in Figure 1. This blind volume was obtained from previous calibrations (Rahman, 1996), and it is kept at the same temperature and pressure of main the *PVT* cell.

The variable volume cell and sampling features of our experimental setup make this methodology 4–7 times faster than the current methods for phase equilibria and density determinations.

The temperatures in these experiments are considered accurate to ±0.2 K, whereas the pressures are accurate to ±0.005 MPa. This uncertainty was obtained from earlier tests by comparing three-phase equilibrium pressures of binary systems of water + *n*-alkanes from the literature (Rahman, 1996). The compositions reported are the average of three measurements and the reproducibility of these is better than 0.03%. The estimated maximum uncertainty on the equilibrium ratios (*K* values) calculated from these compositions is ±1%. The chromatographic techniques used were the ASTM (1989) simulation distillation (SIMDIS) procedures.

Evaluation of Phase Fractions and Densities

The material balance equations relating overall (or feed) compositions with phase compositions and molar phase fractions (i.e. vapor and liquid) are

$$z_i = x_i f_l + y_i f_v \qquad i = 1, n \tag{1}$$

$$f_l + f_v = 1 \tag{2}$$

where z_i, x_i, and y_i, are the experimentally measured feed, hydrocarbon liquid, and vapor molar phase compositions respectively, n is the number of components and f_l and f_v are the liquid and vapor phase fractions, respectively.

Table 1. Gas CO$_2$ Measured Densities

T/K	P/MPa	ρ/g·cm^{-3}
299.78	0.614	0.0111
299.78	0.683	0.0125
299.78	0.772	0.0144
299.78	0.91	0.0169
299.78	1.11	0.0208
299.78	1.407	0.0267
299.78	1.931	0.0379
299.78	3.034	0.0639
299.78	3.483	0.0758
299.78	4.007	0.0928
299.78	4.746	0.1178
299.78	5.062	0.1311
373.11	1.887	0.0279
373.11	2.483	0.0368
373.11	2.96	0.0446
373.11	3.587	0.0559
373.11	4.634	0.0727
373.11	6.221	0.1048
419.78	1.924	0.0251
419.78	2.207	0.0286
419.78	2.566	0.0334
419.78	3.034	0.0401
419.78	3.766	0.0501
419.78	4.89	0.0661
419.78	6.89	0.0972
419.78	7.727	0.1098

Table 2. Comparison of Measured and Predicted Liquid Densities from the Rackett Equation for a Ternary Mixture of Propane (x_1 = 0.5404) + Pentane (x_2 = 0.2032) + Octane (x_3 = 0.2564)

T/K	P/MPa	ρ_m/g·cm^{-3}	ρ_r/g·cm^{-3}	$100x(\rho_m - \rho_r)/\rho_m$
297.00	2.046	0.599	0.600	−0.282
322.00	2.219	0.578	0.575	0.532
352.56	2.429	0.542	0.540	0.404
394.22	2.716	0.489	0.485	0.817

Placing eq 2 into eq 1, a four-component mixture exhibiting two-phase equilibria provides four different equations that could be used to determine the phase fractions. Due to experimental errors, these will likely provide different values for the phase fractions even with carefully prepared experiments. If the experiments were error free, one could select any equation to solve for the phase fraction. We used a least squares procedure and a self-correcting algorithm to provide consistent phase fractions.

Phase densities are evaluated from the measured phase volumes, overall mass charged into the system, and the

Table 3. Phase Equilibrium Compositions for the Carbon Dioxide (1) + Propane (2) + Pentane (3) + Octane (4) System (Mixture Overall Composition: $z_1 = 0.3108$, $z_2 = 0.4139$, $z_3 = 0.1804$

T/K	P/MPa	f_l	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
310.93	3.08	0.8443	0.2419	0.4396	0.2070	0.1115	0.6846	0.2751	0.0361	0.0043
310.93	3.25	0.8739	0.2563	0.4343	0.2015	0.1079	0.6883	0.2732	0.0341	0.0044
310.93	3.42	0.9140	0.2730	0.4287	0.1948	0.1035	0.7125	0.2554	0.0295	0.0026
324.82	3.58	0.8144	0.2330	0.4400	0.2126	0.1144	0.6525	0.2994	0.0392	0.0089
324.82	3.78	0.8619	0.2549	0.4336	0.2028	0.1087	0.6601	0.2910	0.0405	0.0084
324.82	4.00	0.9096	0.2750	0.4266	0.1946	0.1037	0.6710	0.2852	0.0388	0.0050
338.71	4.16	0.7855	0.2250	0.4399	0.2157	0.1194	0.6252	0.3193	0.0506	0.0049
338.71	4.44	0.8274	0.2445	0.4353	0.2070	0.1132	0.6288	0.3114	0.0532	0.0066
338.71	4.73	0.8951	0.2721	0.4264	0.1964	0.1051	0.6411	0.3046	0.0477	0.0066
352.59	4.78	0.7648	0.2380	0.4282	0.2148	0.1190	0.5477	0.3676	0.0686	0.0162
352.59	5.06	0.8307	0.2570	0.4279	0.2050	0.1100	0.5749	0.3453	0.0598	0.0200
352.59	5.45	0.8779	0.2721	0.4275	0.1957	0.1047	0.5892	0.3166	0.0706	0.0236
366.48	5.31	0.7191	0.2259	0.4275	0.2212	0.1254	0.5281	0.3794	0.0761	0.0165
380.37	5.82	0.6799	0.2301	0.4204	0.2203	0.1293	0.4823	0.4003	0.0958	0.0216
394.26	6.37	0.6426	0.2278	0.4170	0.2221	0.1331	0.4602	0.4084	0.1054	0.0260

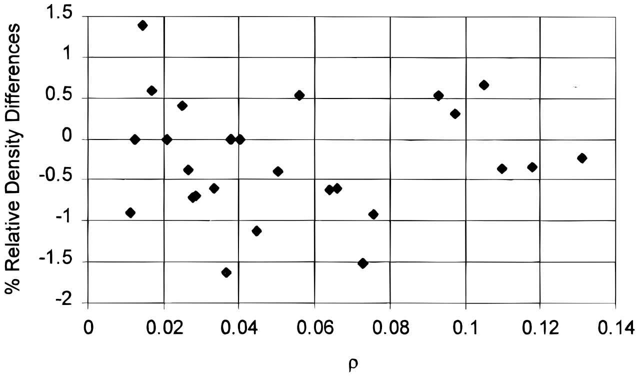

Figure 2. Carbon dioxide percent relative density differences from DDMIX (Ely, 1989).

phase fractions obtained from material balance as follows.

$$\rho_v/\text{g·cm}^{-3} = \frac{f_v n_t/\text{mol}\sum_{i=1}^{n} y_i M_{wi}/\text{g·mol}^{-1}}{V_v/\text{cm}^3} \qquad (3)$$

Densities of pure CO_2 were measured from the mass charged into the system and the volumetric measurements. Table 1 reports the measured densities for CO_2 in this work. Figure 2 shows a percent relative difference plot of these densities from the values estimated by DDMIX (Ely, 1989). It can be observed that all were within ±0.8% in the average. If Vargaftik (1975) values are used as a comparison, these deviations are about ±0.5%.

To further test the procedure, we measured liquid densities for a ternary hydrocarbon mixture slightly above its bubble-point pressures. Saturated hydrocarbon liquid densities are well predicted from the modified Rackett equation (Spencer and Adler 1978), so we compared our measurements with those predicted from this equation. Table 2 shows the composition used for this mixture, the liquid densities measured and predicted from the Rackett equation, and the percent deviation from this equation, which were all within ±0.5%.

Preliminary calibrations of this system with propane indicated that measured liquid densities were within ±0.5% of those obtained by Thomas and Harrison (1982). Additionally, DDMIX (Ely, 1989) was used to verify these densities. We did not use DDMIX in this work because our mixtures contained octane, and the highest hydrocarbon component number in DDMIX data base is heptane.

Phase equilibrium compositions measured for the quaternary system are listed in Table 3. The estimated uncertainty in the measurements is considered better than 1% in compositions, and Table 4 shows the densities calculated for this system from material balance and volumetric measurements, as indicated in eq 3. Since liquid and gas compositions are measured simultaneously, equilibrium ratios can be calculated as the ratio of vapor and liquid mole fractions of component.

Table 4. Experimental Vapor and Liquid Densities for a Carbon Dioxide (1) + Propane (2) + Pentane (3) + Octane (4) System (Liquid and Vapor Compositions from Table 3; Predicted Liquid Density (ρ_{lp}) from the Rackett Equation)

T/K	P/MPa	ρ_v/g·cm^{-3}	ρ_l/g·cm^{-3}	ρ_{lp}/g·cm^{-3}	100x·($\rho_l - \rho_{lp}$)/ρ_l
310.93	3.080	0.0683	0.6147	0.6102	0.7385
310.93	3.252	0.0786	0.6137	0.6124	0.2163
310.93	3.418	0.0912	0.6219	0.6149	1.1218
324.82	3.576	0.0823	0.5947	0.5901	0.7885
324.82	3.783	0.0874	0.6031	0.5927	1.7277
324.82	4.003	0.0989	0.6116	0.5953	2.6600
338.71	4.162	0.0956	0.5747	0.5698	0.8502
338.71	4.437	0.1086	0.5879	0.5713	2.8276
338.71	4.734	0.1219	0.5879	0.5737	2.4179
352.59	4.782	0.1088	0.5515	0.5509	0.0945
352.59	5.058	0.1130	0.5695	0.5503	3.3582
352.59	5.450	0.1525	0.5675	0.5501	3.0530
366.48	5.306	0.1313	0.5205	0.5283	−1.4961
380.37	5.822	0.1527	0.4925	0.5051	−2.5517
394.26	6.374	0.1742	0.4622	0.4780	−3.4198

Conclusions

We measured simultaneously volumetric and phase equilibria data using a uniquely designed apparatus. We provide new phase equilibria compositions and phase density data for (1) a quaternary mixture of CO_2 + propane + pentane + octane, (2) liquid densities for a mixture of propane + pentane + octane, and (3) gas CO_2 densities as calibration data. These and previous calibration tests compare well with literature values. Because of the online infinitesimal and variable volume cell features, more and faster measurements can be made, using a single charge, than using conventional *PVT*-VLLE measurements. The data obtained are considered of enough accuracy for most engineering applications.

Literature Cited

ASTM Technical Publication No. 577; American Society for Testing Materials: Philadelphia, 1989.

Barrufet, M. A.; Wirawan, J. F. S.; Iglesias-Silva, G. An Efficient Procedure to Measure Bubble-Point Pressures for Hydrocarbon + CO_2 Mixtures. *J. Chem. Eng. Data* **1995**, *40*, 1072−1076.

Barrufet, M. A.; El-Sayed Salem, S. K.; Tantawy, M.; Iglesias-Silva, G. Liquid Viscosities of Carbon Dioxide + Hydrocarbons from 310 K to 403K. *J. Chem. Eng. Data* **1996a**, *41*, 436−439.

Barrufet, M. A.; Liu, K.; Rahman, S.; Wu, C. Simultaneous Vapor-Liquid-Liquid Equilibria and Phase Molar Densities of a Quaternary System of Propane + Pentane + Water. *J. Chem. Eng. Data*, **1996b,** *41*, 918−922.

Cheng, H.; de Fernandez, M. E. P.; Zollweg, J. A.; Streett, W. B. Vapor-Liquid-Liquid Equilibrium in the System Carbon Dioxide + n-Pentane from 252 to 458K at Pressures to 10 MPa. *J. Chem. Eng. Data* **1989**, *34*, 319−323.

Ely, J. F. NBS Standard Reference Database 14 DDMIX - Mixture Property Program; Thermophysics Division, National Institute of Standards and Technology: Boulder, CO, 80303, 1989.

Heidman, J. L.; Tsonopolous, C.; Brady, C. J.; Wilson, G. M. High-temperature Mutual Solubilities of Hydrocarbons and Water. Part II: Ethylbenzene, Ethylcyclohexane, and n-Octane. *AIChE J.* **1985**, *31*, 376−384.

Leu, A. D.; Robinson. D. B. Equilibrium Phase Properties of Selected Carbon Dioxide Binary Systems: n-Pentane-Carbon Dioxide and Isopentane-Carbon Dioxide. *J. Chem. Eng. Data* **1987**, *32*, 447−450.

Orr, F. M., Jr.; Silva, M. K. Equilibrium Phase Compositions for CO_2-Hydrocarbon Mixtures: Measurement by a Continuous Multiple Contact Experiment. *SPEJ* **1983**, *23*, 272−280.

Rahman, S. Simultaneous Phase Behavior and Compositional Analysis of CO_2 and Hydrocarbon Mixtures. A New Technique. Ph.D. Dissertation, Department of Petroleum Engineering, Texas A&M University, College Station, TX, 1996.

Rahman, S.; Barrufet, M. A. A New Technique for Simultaneous Measurement of PVT and Phase Equilibria Properties of Fluids at High Temperatures and Pressures. *J. Petrol. Sci. Eng.* **1995**, *14*, 15−23.

Reid, T. B.; Robinson, H. J. Lick Creek Meakin Sand Unit Immiscible CO_2/Waterflood Project. *J. Petrol. Technol.* **1981**, September, 1723−1729.

Ruska. PVT System Model 2370 Users manual; Ruska: Houston, TX, September 1990.

Spencer, C. V.; Adler, S. B. A. A Critical Review of Equations for Predicting Saturate Liquid Density. *J. Chem. Eng. Data* **1978**, *23*, 82−89.

Thomas, R. H. P.; Harrison, R. H. Pressure Volume Temperature Relations of Propane. *J. Chem. Eng. Data* **1982**, *27,* 1−11.

Tsonopolous, C.; Wilson, G. M. High-temperature Mutual Solubilities of Hydrocarbons and Water. Part I: Benzene, Cyclohexane and n-Hexane. *AIChE J.* **1983**, *29*, 990−999.

Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed.; Hemisphere Publishing Corp.: Washington, London, 1975.

Weng, W. L.; Lee, M. J. Vapor-Liquid Equilibrium of the Octane/Carbon Dioxide, Octane/Ethane, and Octane/Ethylene Systems. *J. Chem. Eng. Data* **1992**, *37*, 213−215.

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