

Critical Properties of Carbon Dioxide + Methanol, + Ethanol, + 1-Propanol, and + 1-Butanol

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Critical properties for carbon dioxide + methanol, + ethanol, + 1-propanol, and + 1-butanol were measured using a variable-volume view cell apparatus. Binary mixtures with carbon dioxide mole fractions of 0.976 to 0.637 have been investigated up to 430 K and 175 bar. The dew point and bubble point of the mixtures were measured, particularly in the vicinity of the critical point, in narrow increments in the P - T projection, and the critical point was estimated using two adjacent dew and bubble points. The experimental results were compared with the literature values.

Introduction

Phase equilibria and critical properties of binary mixtures have been measured using a variety of equipment and experimental techniques. Most of the studies have employed a high-pressure view cell, the phase boundary being determined by visual observation. The dew point and bubble point of the mixtures were determined by observing two different phase separation patterns. Normally, there is a sharp distinction between the two separation patterns in the region away from the mixtures' critical points. In the vicinity of the critical point, however, the small difference in density between the vapor and liquid phases prevents clear distinction between the two phases, and hence it becomes difficult to distinguish a dew point from a bubble point. Therefore, researchers have usually not studied the phase boundary in the region of the critical point, where the branches of dew and bubble points intersect.

Mixtures' critical points have been measured by the visual observation technique using constant- or variable-volume view cell equipments. In this study, we have focused on measurement of the phase boundary, particularly in the vicinity of the mixtures' critical points, using a variable-volume view cell apparatus. The equipment allowed us to determine the phase boundary for a particular mixture under isothermal conditions while maintaining a constant overall composition. The critical point is located between the two adjacent dew and bubble points in the P - T projection, the accuracy of the estimated critical point depending on how precisely the two dew and bubble points can be measured in the critical region. Therefore, the measurements were repeated by narrowing the experimental conditions toward the critical point until the intersection point of the dew and bubble point branches could be estimated. This methodology was used to measure the critical points of carbon dioxide + methanol, + ethanol, + 1-propanol, and + 1-butanol mixtures, and the results were compared with literature values.

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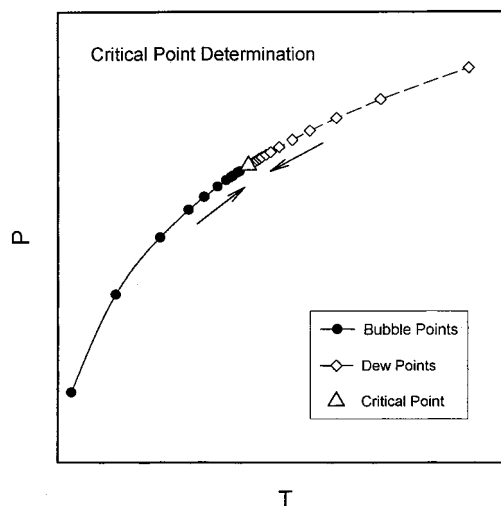


Figure 1. Illustration of the critical point determination by narrowing down the measurement of bubble and dew points in the vicinity of the critical point in a P - T projection.

Experimental Methods

Materials. Methanol, ethanol, 1-propanol, and 1-butanol with minimum purities of 99.5% were purchased from Aldrich Chemical Co. and used without further purification. Carbon dioxide with a purity of 99.9% was used in this study.

Apparatus and Procedure. The variable-volume view cell primarily consisted of a cylinder type view cell, equipped with a window and a movable piston (stainless steel 316, 1.89 cm i.d., 6.35 cm o.d., 12.06 cm length, maximum volume 26.71 cm³), a pressure generator (HIP 81-5.75-10), a borescope camera (Olympus F100-024-000-55) with a video monitor, and a graduated volumetric cylinder (1500 cm³). The view cell apparatus used in this study has a similar schematic to that in already published literature.¹ The pressure in the cell was measured using a pressure transducer with an accuracy of ± 0.35 bar, and the temperature was controlled within ± 0.1 K.

A detailed description of the experimental procedure is given in previous publications.^{1,2} A known mass of alcohol

Table 1. Dew Point (DP), Bubble Point (BP), and Critical Point (CP) Data for Carbon Dioxide (A) + Alcohol (B) Mixtures

x_A	T/K	P/bar	phase transit. pattern	x_A	T/K	P/bar	phase transit. pattern	x_A	T/K	P/bar	phase transit. pattern	x_A	T/K	P/bar	phase transit. pattern
CO ₂ (A) + Methanol (B)															
0.976	298.15	60.81	BP	0.809	303.15	65.19	BP	0.751	313.15	79.94	BP	0.654	343.15	125.95	BP
	303.15	68.29	BP		313.15	81.38	BP		323.15	93.72	BP		353.15	138.72	BP
	307.26	73.52	CP		323.15	95.51	BP		333.15	112.39	BP		360.65	145.33	CP
	308.15	74.82	DP		328.21	103.92	CP		340.65	124.04	CP		363.15	148.23	DP
	313.15	79.52	DP		333.15	112.67	DP		343.15	127.90	DP	0.589	383.15	160.98	BP
0.971	298.15	64.71	BP		343.15	126.94	DP		353.15	140.17	DP		388.15	163.25	BP
	303.15	70.08	BP	0.775	303.15	66.43	BP	0.721	323.15	95.24	BP		388.65	163.66	CP
	308.12	76.63	CP		313.15	80.70	BP		333.15	112.19	BP		389.15	164.22	DP
	313.15	82.49	DP		333.15	112.95	BP		342.94	127.07	CP		391.15	164.63	DP
	323.15	93.31	DP		335.19	115.56	CP		353.15	138.37	DP	0.492	418.15	164.42	BP
0.894	298.15	58.71	BP		343.15	125.97	DP		363.15	147.61	DP		421.15	164.22	BP
	303.15	65.40	BP		353.15	136.51	DP	0.696	343.15	127.83	BP		422.32	164.15	CP
	313.15	80.56	BP						353.15	140.44	BP		423.15	164.08	DP
	315.67	84.49	CP						355.65	141.68	CP				
	323.15	96.27	DP						363.15	145.47	DP				
	333.15	111.36	DP						368.15	149.88	DP				
CO ₂ (A) + Ethanol (B)															
0.956	298.15	61.81	BP	0.863	313.15	78.42	BP	0.697	363.15	137.34	BP	0.597	393.15	148.16	BP
	303.15	67.46	BP		323.15	93.38	BP		373.15	144.03	BP		409.15	151.74	BP
	310.58	77.73	CP		328.36	100.89	CP		376.15	146.78	BP		410.32	151.67	CP
	313.15	81.18	DP		333.15	107.64	DP		377.17	146.30	CP		411.15	151.61	DP
	323.15	93.10	DP		343.15	119.49	DP		378.16	145.89	DP		413.15	151.47	DP
0.938	303.15	66.78	BP	0.769	323.15	92.55	BP	0.646	390.15	150.99	BP				
	313.15	79.46	BP		333.15	106.88	BP		392.15	151.19	BP				
	318.24	86.35	CP		343.15	119.84	BP		393.08	151.54	CP				
	323.15	93.17	DP		350.62	128.04	CP		395.15	151.74	DP				
	333.15	104.95	DP		353.15	130.59	DP								
					363.15	138.31	DP								
CO ₂ (A) + 1-Propanol (B)															
0.967	298.15	62.71	BP	0.919	303.15	67.60	BP	0.857	313.15	81.32	BP	0.734	383.15	154.57	BP
	303.15	68.84	BP		313.15	81.18	BP		323.15	96.20	BP		388.15	156.64	BP
	313.15	83.38	BP		323.15	96.20	BP		333.15	111.71	BP		390.38	157.60	CP
	314.28	84.42	CP		324.28	97.85	CP		335.24	114.60	CP		391.15	157.81	DP
	323.15	94.68	DP		333.15	110.60	DP		343.15	124.87	DP	0.718	373.15	148.71	BP
	333.15	107.85	DP		343.15	123.14	DP		353.15	135.27	DP		393.15	158.91	BP
	343.15	115.56	DP	0.879	313.15	81.32	BP	0.811	343.15	123.08	BP		398.16	160.01	CP
0.944	303.15	67.74	BP		323.15	96.48	BP		353.15	135.82	BP		399.15	160.29	DP
	313.15	82.35	BP		329.06	105.30	CP		358.36	139.89	CP	0.637	393.15	153.33	BP
	319.26	91.10	CP		333.15	111.57	DP		363.15	144.03	DP		413.15	159.05	BP
	323.15	96.34	DP		343.15	124.25	DP		373.15	150.85	DP		423.15	158.91	BP
	333.15	108.88	DP										424.26	158.84	CP
													425.15	158.70	DP
CO ₂ (A) + 1-Butanol (B)															
0.967	303.15	70.63	BP	0.894	313.15	82.69	BP	0.799	363.15	150.92	BP	0.714	383.15	160.77	BP
	310.15	79.80	BP		323.15	98.27	BP		373.15	159.53	BP		403.15	170.56	BP
	312.15	83.45	BP		324.24	100.06	CP		378.15	162.49	BP		423.15	174.07	BP
	315.26	87.10	CP		325.15	101.78	DP		380.15	164.15	BP		427.24	173.73	CP
	316.15	89.31	DP		333.15	115.01	DP		381.98	165.45	CP		428.15	173.50	DP
	323.15	98.41	DP	0.849	323.15	98.54	BP		384.15	166.63	DP				
0.951	313.15	82.69	BP		333.15	114.67	BP								
	316.15	87.59	BP		336.15	120.39	BP								
	317.15	89.59	BP		337.34	121.84	CP								
	317.64	90.62	CP		338.15	123.21	DP								
	318.15	91.51	DP		343.15	129.55	DP								
	323.15	98.47	DP												

was charged into the cell. Liquid carbon dioxide was then loaded to the cell, typically up to 55.0 bar. The cell was heated to the desired temperature, and the cell contents were pressurized by the movable piston to form a single phase. The system was agitated using a magnetic stirrer to maintain thermal equilibrium of the cell contents. After the system pressure and temperature became stable, the system pressure was slowly decreased by moving the piston backward using the pressure generator. The pressure at which the cell contents became cloudy was recorded as a phase transition pressure. Two different phase transition patterns were clearly observed. At the dew point, the falling of dew generated a down flow pattern upon the phase

transition and a corresponding increase in the liquid level inside the cell. At the bubble point, ascending bubbles generated an up flow pattern and a corresponding decrease in the liquid level. After the experiment was finished, the amount of carbon dioxide loaded was measured by degassing the carbon dioxide through the graduated volumetric cylinder. The graduated cylinder was initially filled with water, and the volume of carbon dioxide vented was measured by reading the displacement of the water level.

For a particular mixture, the dew and bubble point pressures were determined at various temperatures, typically at every 10 K increase, and the two adjacent dew and bubble points were selected. The temperature was then

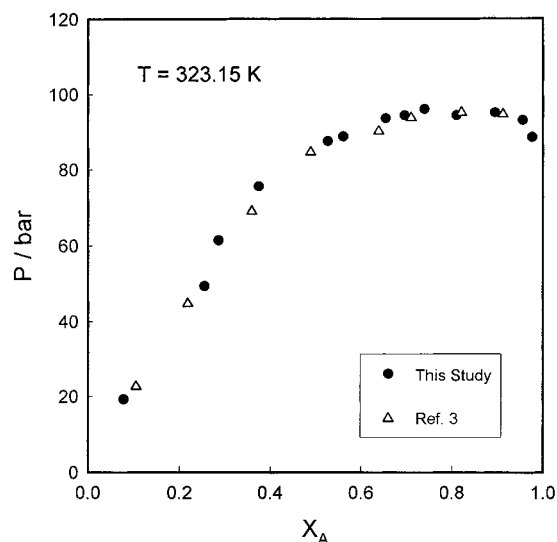


Figure 2. Pressure–concentration (mole fraction of carbon dioxide) diagram for carbon dioxide + methanol mixtures at 323.15 K. Experimental data of this study are compared with the literature data.³

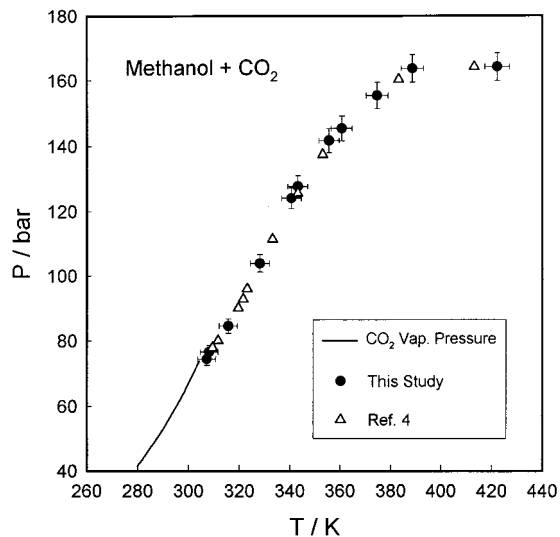


Figure 3. Critical point loci for carbon dioxide + methanol binary mixtures. Experimental data of this study are compared with the literature data.⁴

changed in 1.0 K intervals between the two dew and bubble points, and the measurement was repeated. Again, the two adjacent dew and bubble points were located and measurement was continued in 0.2 K increments between the two points. This tracing procedure was continued until the dew point and the bubble point differed by less than the accuracy of this equipment. Finally, the critical temperature and pressure were determined by averaging the two temperatures and pressures of the two most adjacent dew and bubble points, respectively. Figure 1 illustrates the procedure for the critical point determination by measuring the bubble and dew points in very small increments in the vicinity of the critical point.

Results

Table 1 shows the selected experimental data for the dew point and bubble point in the vicinity of the critical point and includes the calculated critical points for the carbon dioxide + methanol, + ethanol, + 1-propanol, and + 1-butanol binary mixtures. Mixtures with a carbon dioxide

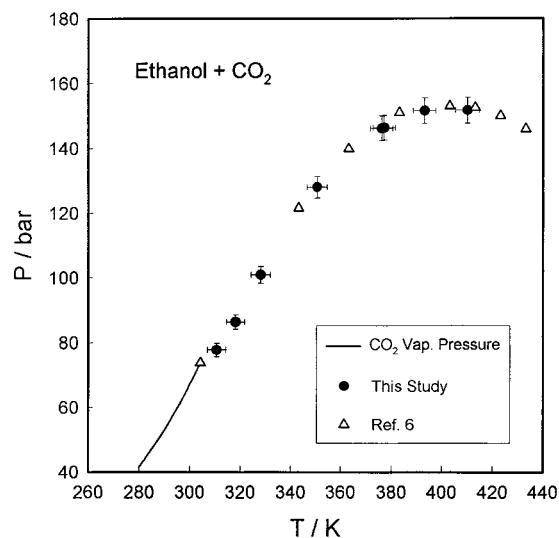


Figure 4. Critical point loci for carbon dioxide + ethanol binary mixtures. Experimental data of this study are compared with the literature data.⁶

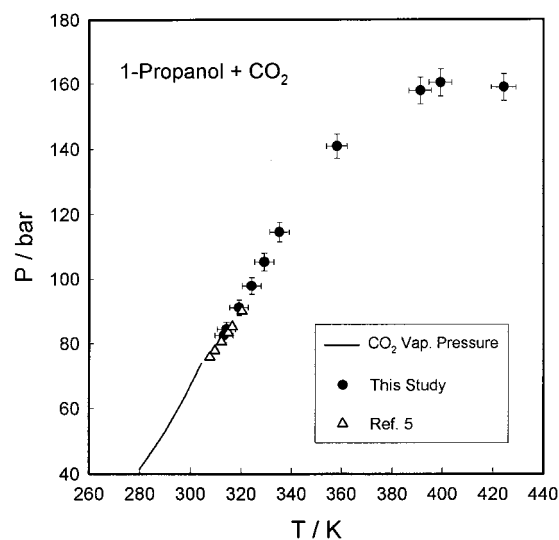


Figure 5. Critical point loci for carbon dioxide + 1-propanol binary mixtures. Experimental data of this study are compared with the literature data.⁵

mole fraction, x_A , from 0.976 to 0.637 were studied. The estimated maximum uncertainties of the critical temperature and the critical pressure data were 1.15 and 2.61%, respectively. Figure 2 shows the typical pressure–concentration diagram of the carbon dioxide + methanol binary mixtures at 323.15 K. The experimental data of this work were in accordance with data from the literature.³ Figures 2–6 show the critical point loci of the carbon dioxide + methanol, + ethanol, + 1-propanol, and + 1-butanol binary mixtures, respectively. The evaluated critical point data of this study were compared with experimental data from the literature. The literature data were obtained using different techniques by various investigators, including static optical cell techniques,⁴ a constant-volume sight gauge apparatus,⁵ and a peak-shape method using chromatographic equipment.⁶

This study focused on the measurement of the phase separation boundary near the mixtures' critical points. The visual observation indicated that the types of phase separation patterns (dew and bubble points) became more indistinct as the critical point was approached. However, in the temperature, pressure, and concentration ranges of

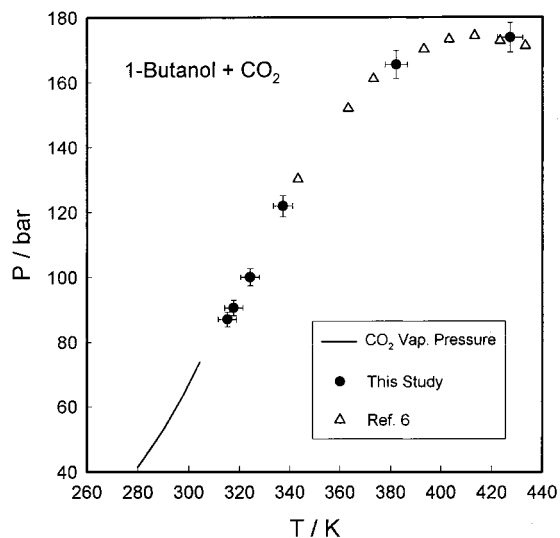


Figure 6. Critical point loci for carbon dioxide + 1-butanol binary mixtures. Experimental data of this study are compared with the literature data.⁶

the investigated mixtures, we were able to distinguish the two different phase separation patterns within the accuracy of this equipment. The results show that the data measured using the variable-volume view cell method of this study

agree well with the data obtained using various techniques, and verify that our method provides a reliable methodology for critical point determination.

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