

# Densities of Carbon Dioxide + 2-Propanol at 313.15 K and Pressures to 9.8 MPa

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Densities for carbon dioxide + 2-propanol are measured at 313.15 K and pressures up to 9.8 MPa using a density meter. Densities and pressures along the saturation line were indirectly determined by a synthetic method.

## Introduction

Volumetric properties and vapor–liquid equilibria (VLE) at high pressure are required in the practical use, such as in the design and operation of supercritical fluid extraction.

Radosz (1986) and Yao et al. (1988) previously measured VLE for carbon dioxide + 2-propanol by a circulation apparatus. The compositions of vapor and liquid phases were analyzed by gas chromatography. Suzuki et al. (1991) previously measured the solubility of 2-propanol in supercritical carbon dioxide using a flow-type apparatus. The differences among these measurements are significant. Radosz (1986), Yao et al. (1988), and Suzuki et al. (1991) did not report *PVT* results.

In the present study, densities as a function of pressure for carbon dioxide + 2-propanol are measured at 313.15 K. The saturated pressures are further evaluated, almost similar to Kodama et al. (1996).

## Experimental Section

The experimental apparatus is schematically shown in Figure 1. The apparatus is the same as that described previously (Kato et al., 1991). The maximum temperature and pressure of the apparatus are 400 K and 20 MPa, respectively. The main parts of the apparatus are a variable volume cell A, piston P, Ruska air dead weight gauge N, Ruska oil dead weight gauge O, hand pump syringe S, Anton Paar DMA 512 density meters D, circulation pumps C, gas reservoir F, and Ruska pressure transducers T. The apparatus is in a constant temperature liquid bath controlled within  $\pm 0.01$  K. The volume of the lower space in the cell is variable from 229 cm<sup>3</sup> to 296 cm<sup>3</sup> by the motion of the piston with a sensitivity of  $\pm 0.01$  cm<sup>3</sup>. The accuracy of the total volume is about  $\pm 1$  cm<sup>3</sup>.

At the start of the experiment, carbon dioxide is charged into the cell after it is evacuated. The pressure difference between the upper and lower spaces is kept close to zero. The temperature and pressure are measured. The volume is determined by the motion of the piston. The amount of carbon dioxide is evaluated from the volume and density. 2-Propanol is charged in to the cell with the hand pump syringe S. The amount is determined with a sensitivity of  $\pm 0.01$  cm<sup>3</sup>. As the volume of cell A is changed, volumetric properties can be measured at fixed composition. From the break point for the pressure vs cell volume, the saturated pressure can be determined, as typically shown in Figure 2.

The saturated vapor points are determined as described previously (Kodama et al., 1996). The equilibrium vapor compositions near the critical region are close to unity in mole fraction of carbon dioxide. The saturated vapor composition can be determined from the single-phase density of known composition, the saturated vapor density of mixture at VLE separation, and the density of carbon dioxide at the same temperature and pressure. Figures 3 and 4 show the experimental principle. Assuming a linear relation on the molar volume vs mole fraction curve, the saturated vapor composition can be evaluated as follows

$$y_1 = \frac{\bar{v}_2^\infty - (M_2/\rho)}{\bar{v}_2^\infty - (M_2/\rho) - v_1^0 + (M_1/\rho)} \quad (1)$$

where

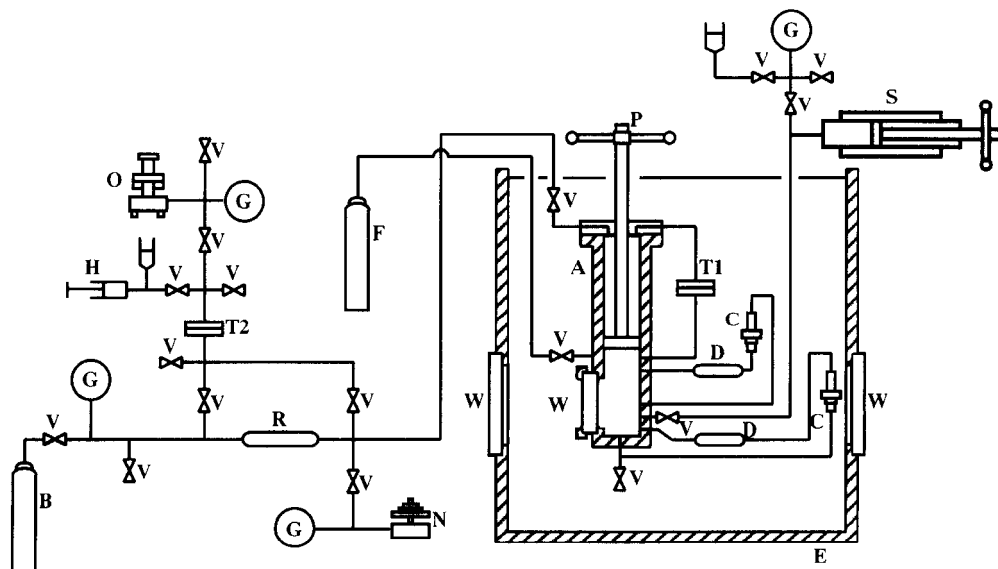
$$v_1^0 = \frac{M_1}{\rho_1^0}, \quad \bar{v}_2^\infty = \frac{v^G - y_1^G v_1^0}{y_2^G} \quad (2)$$

$$v^G = \frac{y_1^G M_1 + y_2^G M_2}{\rho^G} \quad (3)$$

in which,  $M$ ,  $v$ ,  $\bar{v}$ ,  $y$ , and  $\rho$  denote molecular weight, molar volume, partial molar volume, vapor mole fraction, and density, respectively. The superscripts, 0,  $\infty$ , and G, represent pure component, infinite value, and given composition, respectively. The subscripts 1 and 2 denote carbon dioxide and 2-propanol, respectively.

In the experiments, carbon dioxide is first charged into the cell A. The pressure, volume, and density of feed gas are measured. The amount of carbon dioxide is evaluated from the volume and density. A small amount of 2-propanol is next charged into the cell. The fluid in the cell is circulated with the circulation pump C until the single phase is achieved. The volume of the cell A is changed, the pressure is kept constant. After attainment of the homogeneous fluid, the density, total volume, pressure, and temperature are measured. The amount of mixture is evaluated from the total volume and density. From the difference between the amounts of carbon dioxide and mixture, the amount of 2-propanol is evaluated. The composition can be evaluated from the amounts of each component.

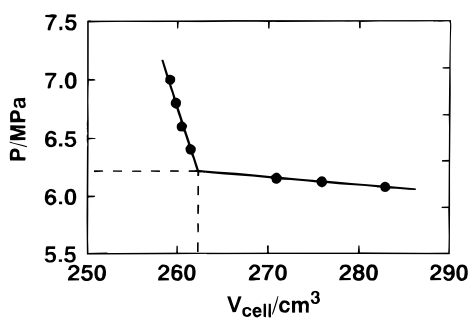
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**Figure 1.** Schematic diagram of experimental apparatus: (A) variable volume cell; (B) nitrogen reservoir; (C) circulation pump; (D) density meter; (E) constant temperature liquid bath; (F) gas reservoir; (G) pressure gauge; (H) hand pump; (N) air dead weight gauge; (O) oil dead weight gauge; (P) piston; (R) reservoir; (S) hand syringe pump; (T) pressure transducer; (V) valve; (W) visual glass window.

**Table 1.** Experimental Density, Mole Fraction  $x$ , and Pressure  $P$  for Carbon Dioxide (1) + 2-Propanol (2) at 313.15 K

$x_1$	$P/\text{MPa}$											
	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	9.5	9.8	
						$\rho/(\text{kg}\cdot\text{m}^{-3})$						
0.000	768.7	769.6	770.6	771.6	772.5	773.5	774.4	775.3	776.2	776.7	776.9	
0.100		777.4	778.5	779.6	780.8	781.9	783.0	784.0	785.1	785.6	785.9	
0.200				786.9	788.2	789.6	790.9	792.2	793.4	794.0	794.4	
0.300					794.4	796.1	797.7	799.3	800.8	801.6	802.0	
0.400						800.5	802.6	804.6	806.6	807.5	808.1	
0.500							805.2	807.8	810.4	811.7	812.4	
0.600							803.5	807.4	811.0	812.7	813.8	
0.700								800.3	805.9	808.5	810.0	
0.800									778.1	788.2	792.7	
0.900									721.6	746.0	755.4	
0.950										691.9	710.3	
0.970										650.4	678.9	
0.985										586.9	636.5	
0.990										560.7	621.4	
1.000	17.6	37.0	58.8	83.6	112.9	149.0	197.9	277.5	484.9	579.8	612.0	

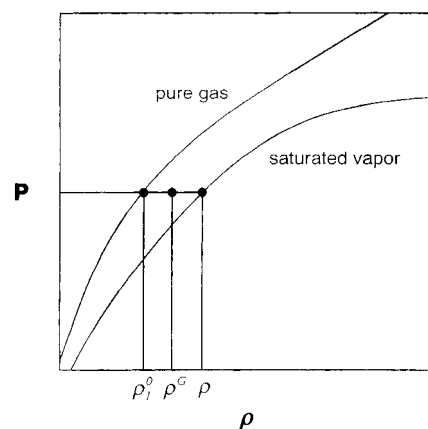


**Figure 2.** Typical example of experimental results by synthetic method, 0.500  $\text{CO}_2$  mole fraction: (●) experimental.

The saturated vapor density of mixture at VLE separation is separately measured by the experimental apparatus shown in Figure 1, changing the feed and/or cell volume. The VLE separation can be observed through the glass window W.

The accuracies of density, temperature, pressure, and mass fraction, respectively, are  $\pm 0.1 \text{ kg/m}^3$ ,  $\pm 0.01 \text{ K}$ ,  $\pm 1 \text{ kPa}$ , and  $\pm 0.0003$ .

Carbon dioxide was supplied by Nihon Sanso Co. Ltd. with the guarantee of 99.9 mol % purity. 2-Propanol was the special grade reagent of Wako Pure Chemicals Co. Ltd.

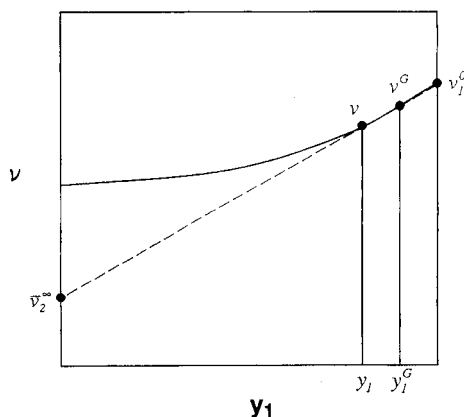


**Figure 3.** Density measurements at constant temperature and pressure: ( $\rho_i^0$ ) density of pure gas; ( $\rho^G$ ) density of given composition; ( $\rho$ ) saturated vapor density.

The purity of 2-propanol is 99.9% in gas chromatograph peak areas.

## Results

Table 1 gives the experimental density in the single phase for carbon dioxide + 2-propanol at 313.15 K. Table



**Figure 4.** Molar volume linear approximation: ( $v$ ) molar volume; ( $y_1$ ) mole fraction of pure gas; ( $v^G$ ) molar volume of given composition  $y_1^G$ ; ( $v_1^0$ ) molar volume of pure gas.

**Table 2. Saturation Pressure  $P$ , Liquid Mole Fraction  $x$ , Vapor Mole Fraction  $y$ , Liquid Density  $\rho_L$ , and Vapor Density  $\rho_V$  for Carbon Dioxide (1) + 2-Propanol (2) at 313.15 K**

$P/\text{MPa}$	$x_1$	$y_1$	$\rho_L/(\text{kg}\cdot\text{m}^{-3})$	$\rho_V/(\text{kg}\cdot\text{m}^{-3})$
1.836	0.100 <sup>a</sup>		777.0 <sup>a</sup>	
2.000				38.0 <sup>b</sup>
2.996				61.2 <sup>b</sup>
3.275	0.200 <sup>a</sup>		785.7 <sup>a</sup>	
4.000				85.7 <sup>b</sup>
4.461	0.300 <sup>a</sup>		793.4 <sup>a</sup>	
5.000				116.9 <sup>b</sup>
5.472	0.400 <sup>a</sup>		799.2 <sup>a</sup>	
6.000		0.9920 <sup>c</sup>	802.9 <sup>a</sup>	155.0 <sup>b</sup>
6.207	0.500 <sup>a</sup>		802.9 <sup>a</sup>	
6.500				179.8 <sup>b</sup>
6.684	0.600 <sup>a</sup>		802.2 <sup>a</sup>	
7.000		0.9880 <sup>c</sup>		211.8 <sup>b</sup>
7.082	0.700 <sup>a</sup>		794.4 <sup>a</sup>	
7.472	0.800 <sup>a</sup>		772.3 <sup>a</sup>	
7.500		0.9844 <sup>c</sup>		257.2 <sup>b</sup>
7.751	0.900 <sup>a</sup>		712.7 <sup>a</sup>	
7.800				301.1 <sup>b</sup>
8.000		0.9744 <sup>c</sup>		354.7 <sup>b</sup>
8.019	0.950 <sup>a</sup>		621.1 <sup>a</sup>	
8.092				423.1 <sup>b</sup>
8.103				433.0 <sup>b</sup>
8.137	0.970 <sup>a</sup>		509.7 <sup>a</sup>	

<sup>a</sup> Synthetic method. <sup>b</sup> VLE separation. <sup>c</sup> Molar volume linear approximation.

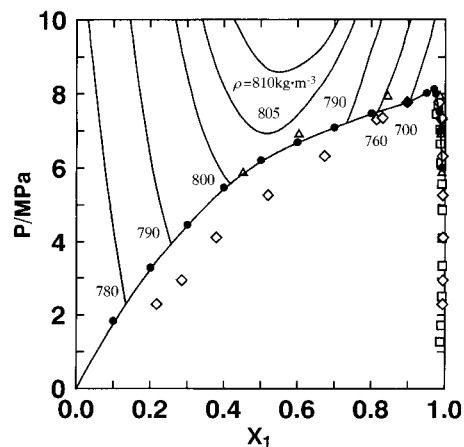
2 gives the experimental saturated densities and pressures. Figure 5 shows the VLE relations and the density curves. Figure 6 gives the saturation densities.

## Conclusions

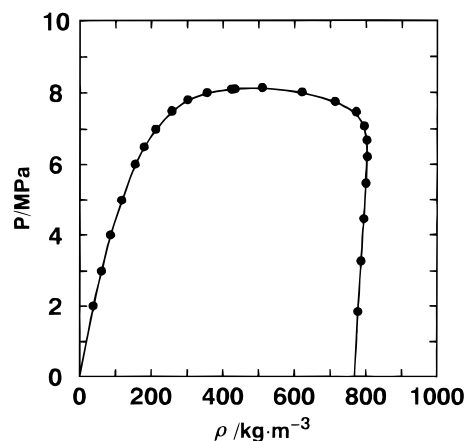
Densities both in the liquid phase and along the saturation line were measured for carbon dioxide + 2-propanol at 313.15 K. Along the saturation  $P$ - $x$ - $y$  curve, the results agreed fairly well with those reported by Radosz (1986) and Suzuki et al. (1991) but significantly deviated from those of Yao et al. (1988).

## Acknowledgment

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**Figure 5.** VLE and density curves for carbon dioxide (1) + 2-propanol (2) at 313.15 K: (—●—) this work; ( $\Delta$ ) Radosz (1986); ( $\diamond$ ) Yao et al. (1988); ( $\square$ ) Suzuki et al. (1991).



**Figure 6.** Saturated density behaviors for carbon dioxide (1) + 2-propanol (2) at 313.15 K: (—●—) this work.

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