

# Volumetric Properties of Carbon Dioxide + Acetone at High Pressures

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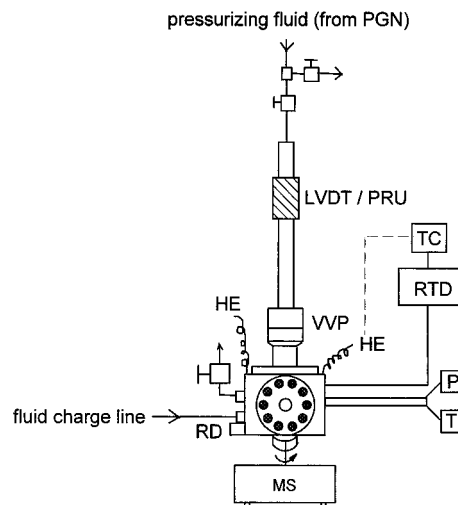
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The volumetric properties of carbon dioxide + acetone mixtures have been determined at 323, 348, 373, 398, and 423 K at pressures up to 70 MPa using a variable-volume view cell. Densities for pure components and mixtures containing 90, 80, 70, and 50% by mass carbon dioxide are reported as a function of pressure at each temperature. It is shown that this system undergoes a density crossover at high pressures with each composition, a phenomenon previously reported also for mixtures of carbon dioxide + pentane and carbon dioxide + toluene. In the composition range investigated, the excess volume of the mixtures becomes more positive with increasing pressure but more negative with increasing temperature.

## Introduction

The investigation of binary mixtures of carbon dioxide with organic solvents is of particular importance for the development of new supercritical fluid processing technologies. This is because supercritical carbon dioxide is recognized as a replacement fluid for environmentally objectionable organic solvents and can be used to reduce their use. From a scientific perspective, binary fluid mixtures introduce a useful parameter, i.e., the fluid composition, which can be used as an additional parameter to fine-tune the properties of processing fluids for a specific application. In our laboratory, we employ near-critical and supercritical fluid mixtures for polymer applications. Mixture composition along with pressure and temperature is used as a key parameter to bring about miscibility or phase separation or changes in viscosity, diffusivity, or reactivity (Kiran, 1994; Kiran and Balkan, 1994; Xiong and Kiran, 1995; Kiran, 1995; Kiran and Gökmenoglu, 1996; Kiran et al., 1996a,b).

Unlike high-pressure vapor–liquid equilibria and critical data, information on the volumetric properties of carbon dioxide + organic solvent mixtures at high pressures is rather limited. We have recently reported on the volumetric properties of carbon dioxide + pentane (Kiran et al., 1996a,b), carbon dioxide + sulfur hexafluoride (Gökmenoglu et al., 1996), and carbon dioxide + toluene (Pöhler and Kiran, 1996) over a wide range of compositions and temperatures at pressures up to 70 MPa. A very interesting study was also recently reported on the vapor–liquid equilibria and the volumetric expansion of the liquid phases in the binary mixtures of carbon dioxide with ethyl acetate, 1,4-dioxane, dimethylformamide, dimethyl sulfoxide, and ethanol, but at pressures up to about 10 MPa and temperatures below 313 K (Kordikowski et al., 1995). For carbon dioxide + acetone mixtures, critical data have been reported for mixtures with acetone content less than 7 mol % (Gurdial et al., 1993). Critical data have also been reported for the ternary mixtures carbon dioxide + acetone + water (Wendland, 1994). A recent publication reports on the vapor–liquid equilibria for carbon dioxide + acetone mixtures and provides data on the liquid- and vapor-phase densities in the temperature range from 291 to 313 K at pressures below 5 MPa (Day et al., 1966) and compares



**Figure 1.** Schematic diagram of the experimental system (LVDT/PRU = piston position readout unit; TC = temperature controller; RTD = resistance temperature detector; HE = heating elements; VVP = variable-volume part; RD = rupture disk; MS = magnetic stirrer).

the results with earlier publications by Tanaka and Kato (1995) and Katayama et al. (1975).

The present report is on the volumetric behavior of binary mixtures of carbon dioxide and acetone at pressures up to 70 MPa. Pressure–density data are reported for the mixtures containing 0, 50, 70, 80, 90, and 100 mass% carbon dioxide at 323, 348, 373, 398, and 423 K. The excess volumes for these mixtures and their variation with composition, temperature, and pressure are also reported.

## Experimental Section

**Apparatus.** A detailed description of the experimental system and procedures for determination of the densities is given in our previous publications (Kiran et al., 1995; Gökmenoglu et al., 1996). Figure 1 shows only the essential elements of the system. The main part is a variable-volume view cell. It is heated with four cartridge heaters. The pressure and temperature inside the cell are monitored with flush-mount Dynisco transducers. The pressure is measured with an accuracy of  $\pm 0.06$  MPa and read with a resolution of  $\pm 0.007$  MPa. The temperature is measured with an accuracy of  $\pm 0.5$  K and monitored with

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Table 1 (Continued)

| 323 K          |                         | 348 K          |                         | 373 K          |                         | 398 K          |                         | 423 K          |                         |
|----------------|-------------------------|----------------|-------------------------|----------------|-------------------------|----------------|-------------------------|----------------|-------------------------|
| $p/\text{MPa}$ | $\rho/\text{g cm}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{g cm}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{g cm}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{g cm}^{-3}$ | $p/\text{MPa}$ | $\rho/\text{g cm}^{-3}$ |
| $w_1 = 0$      |                         |                |                         |                |                         |                |                         |                |                         |
| 1.65           | 0.7581                  | 10.20          | 0.7421                  | 23.86          | 0.7346                  | 42.55          | 0.7341                  | 60.12          | 0.7346                  |
| 4.30           | 0.7613                  | 15.01          | 0.7482                  | 27.17          | 0.7384                  | 45.51          | 0.7375                  | 61.84          | 0.7361                  |
| 7.59           | 0.7654                  | 19.58          | 0.7535                  | 30.70          | 0.7423                  | 49.85          | 0.7429                  | 63.93          | 0.7375                  |
| 11.79          | 0.7704                  | 23.21          | 0.7581                  | 34.43          | 0.7468                  | 53.64          | 0.7463                  | 45.49          | 0.7399                  |
| 15.27          | 0.7730                  | 26.41          | 0.7629                  | 38.14          | 0.7509                  | 57.24          | 0.7495                  |                |                         |
| 19.13          | 0.7771                  | 30.82          | 0.7650                  | 42.00          | 0.7547                  | 61.09          | 0.7537                  |                |                         |
| 22.83          | 0.7815                  | 34.45          | 0.7697                  | 45.72          | 0.7581                  | 64.70          | 0.7564                  |                |                         |
| 26.55          | 0.7859                  | 38.15          | 0.7734                  | 49.62          | 0.7620                  |                |                         |                |                         |
| 30.61          | 0.7884                  | 42.11          | 0.7762                  | 53.45          | 0.7660                  |                |                         |                |                         |
| 34.66          | 0.7923                  | 45.84          | 0.7805                  | 57.07          | 0.7695                  |                |                         |                |                         |
| 38.23          | 0.7961                  | 49.72          | 0.7835                  | 61.04          | 0.7736                  |                |                         |                |                         |
| 42.41          | 0.7990                  | 53.53          | 0.7874                  | 64.61          | 0.7761                  |                |                         |                |                         |
| 45.97          | 0.8027                  | 57.15          | 0.7905                  |                |                         |                |                         |                |                         |
| 49.52          | 0.8055                  | 60.88          | 0.7939                  |                |                         |                |                         |                |                         |
| 53.51          | 0.8079                  | 64.61          | 0.7936                  |                |                         |                |                         |                |                         |
| 57.14          | 0.8102                  |                |                         |                |                         |                |                         |                |                         |
| 61.01          | 0.8131                  |                |                         |                |                         |                |                         |                |                         |
| 64.86          | 0.8169                  |                |                         |                |                         |                |                         |                |                         |

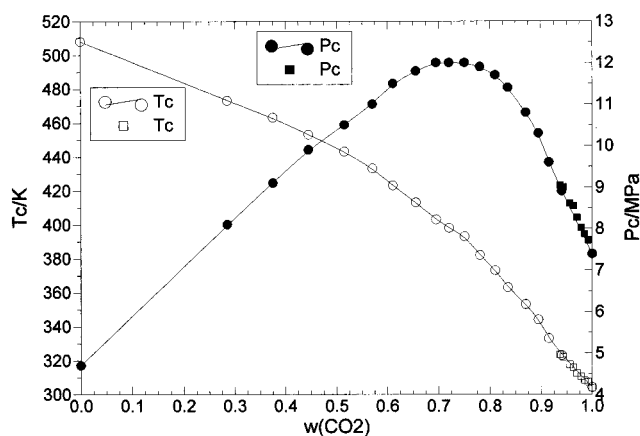
a resolution of  $\pm 0.1$  K. A linear variable differential transformer coil (LVDT) and a position readout unit (PRU) are used to monitor the position of a movable piston inside the variable volume part (VVP) of the cell. This is achieved with the aid of a ferromagnetic metal piece on a steel rod attached to the piston. When the piston is moved to a new position (with a pressurizing fluid from a pressure generator PGN), the LVDT coil is moved to sense the new location of the ferromagnetic element. The position readout unit gives the actual distance traveled from which the internal volume of the cell is determined at any given temperature and pressure. Once the cell is loaded with a known mass of fluid, its density is determined as a function of pressure at each temperature. As we reported earlier (Kiran, 1996b), with this system densities are determined with an accuracy of  $\pm 1.22\%$ , and volume changes are determined with an accuracy of  $\pm 0.0025$  cm<sup>3</sup>. The maximum internal volume of the cell is 22.43 cm<sup>3</sup>.

Density measurements were conducted for the pure fluids and for mixtures containing a total mass loading of about 15 g.

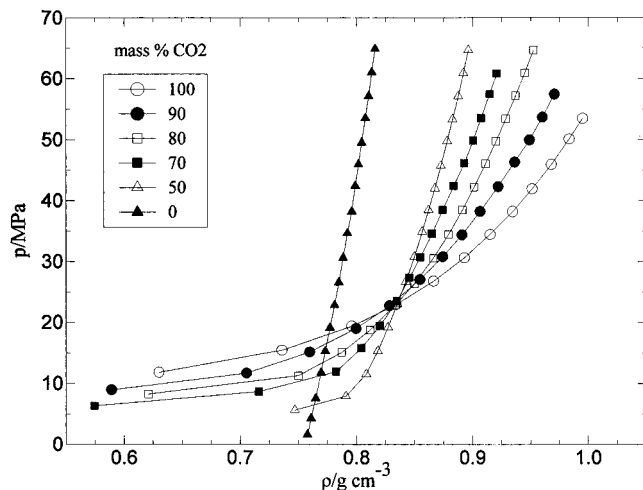
**Materials.** Carbon dioxide was bone-dry grade with a purity of 99.8% (Airco; supplied with an eductor tube). Acetone (99.9+% purity) was obtained from Sigma.

## Results and Discussion

**Density.** Table 1 summarizes the density data for pure carbon dioxide and acetone and for their binary mixtures containing 50, 70, 80, and 90 mass % carbon dioxide which were measured at 323, 348, 373, 398, and 423 K at pressures up to 70 MPa. At most of these conditions, the mixtures are either supercritical or exist as liquid mixtures. Figure 2 shows the variation of the critical pressure and temperature which has been generated using the limited data reported by Gurdial et al. (1993). For this mixture more complete experimental data on critical temperatures and pressures have been recently reported (Ziegler et al., 1996) without, however, compositional information. We have estimated the critical temperatures as a function of composition for these mixtures using the method of Li (1971). Using the composition-critical temperature relationship obtained, we then determined for each composition (temperature), the corresponding critical pressure using the critical temperature-pressure data of Ziegler. The results are included in the figure. The present density measurements have been mostly conducted at pressures which are higher than the critical pressures these mixtures display. Above about 12 MPa, the mixtures are all above the critical pressure. The mixtures with high carbon dioxide content



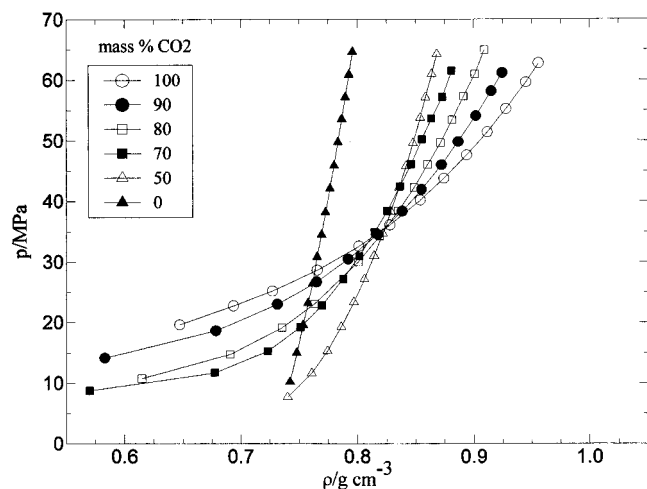
**Figure 2.** Critical temperature and pressure of the binary mixtures carbon dioxide (1) + acetone (2). Data are from Gurdial et al. (1993) (squares) and Ziegler et al. (1966) (circles). (Compositions corresponding to the critical  $P/T$  data of Ziegler et al. have been calculated from predictions of the critical temperatures using the method of Li (1971)).



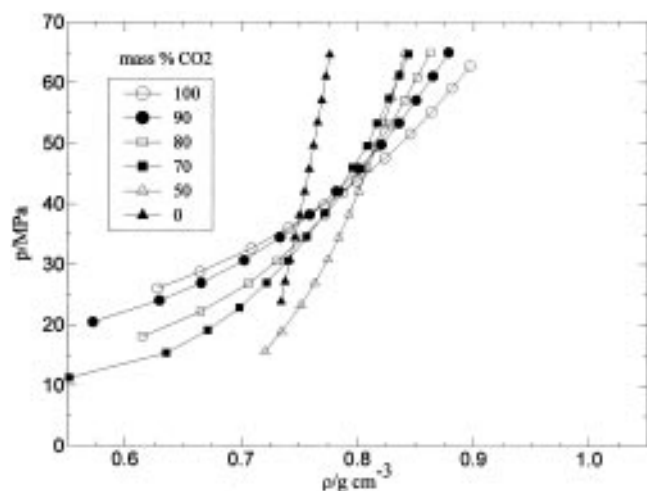
**Figure 3.** Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 323 K (compositions in mass percent).

were also above their respective critical temperatures and therefore were supercritical at the conditions evaluated.

Figure 3 shows the variation of density with pressure for each mixture at 323 K. As shown, acetone has a relatively low compressibility displayed by the steep increase in pressure to bring about even small changes in



**Figure 4.** Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 348 K (compositions in mass percent).



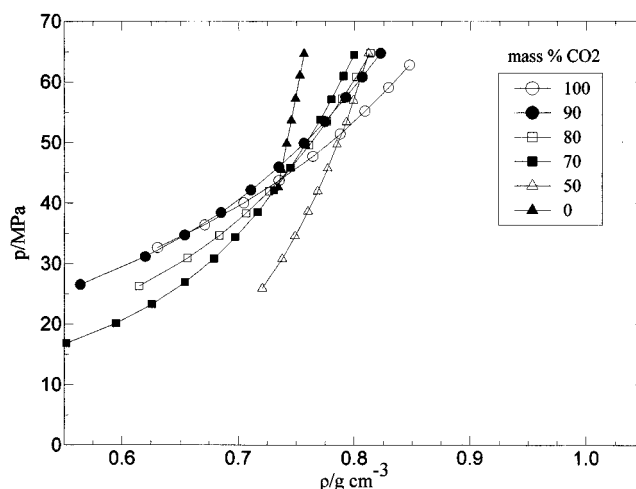
**Figure 5.** Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 373 K (compositions in mass percent).

the density of the fluid. The density changes from about 0.7704 to 0.8079 g/cm<sup>3</sup> when the pressure is changed from about 11.8 to 53.5 MPa, while in the same interval the density of carbon dioxide increases from 0.6292 to 0.9942 g/cm<sup>3</sup>. It is interesting to note that with increasing pressure, the density of carbon dioxide becomes greater than that of acetone at about 16 MPa. As shown in the figure, binary mixtures of carbon dioxide and acetone are also more compressible than acetone, and each mixture shows a density crossover (i.e., the density of the mixture becomes greater than that of pure acetone) at a characteristic pressure. Similar trends are observed in Figures 4–7 which show the variation of density with pressure at 348, 373, 398, and 423 K. The density crossover pressures shift, however, to higher pressures. As the temperature is increased, the density difference between acetone and carbon dioxide becomes smaller, and consequently for the mixtures, the spacing between isopleths becomes narrower.

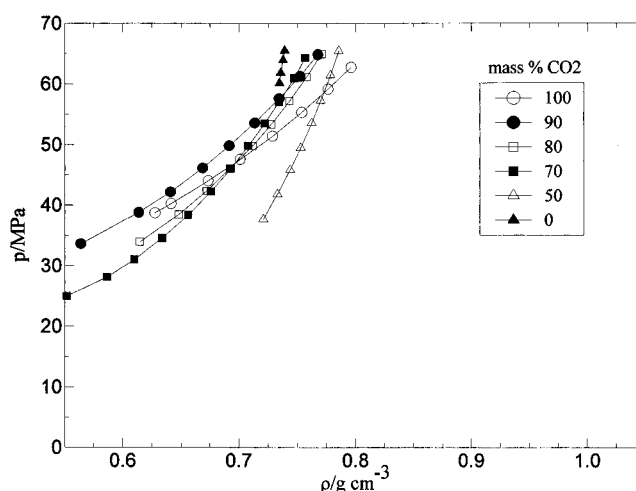
**Excess Volume.** The excess volumes for the mixtures were determined using the following relationship:

$$V^E = V^{\text{mix}} - (x_1 V_1 + x_2 V_2)$$

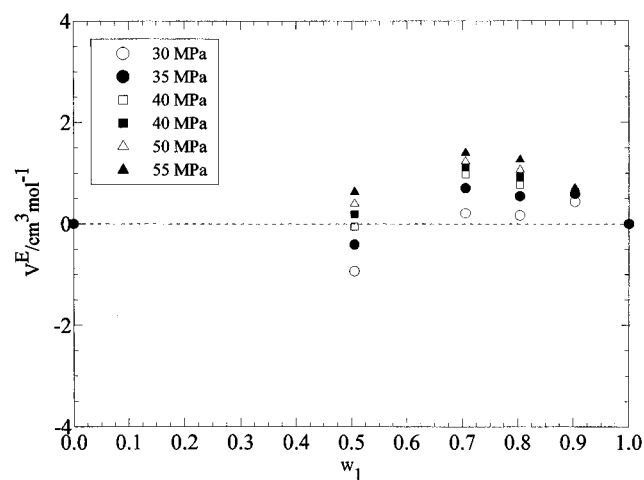
where  $V_1$  and  $V_2$  represent the pure component molar volumes and  $x_1$  and  $x_2$  are the mole fractions of carbon dioxide and acetone. In Figures 8 and 9 excess volumes



**Figure 6.** Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 398 K (compositions in mass percent).

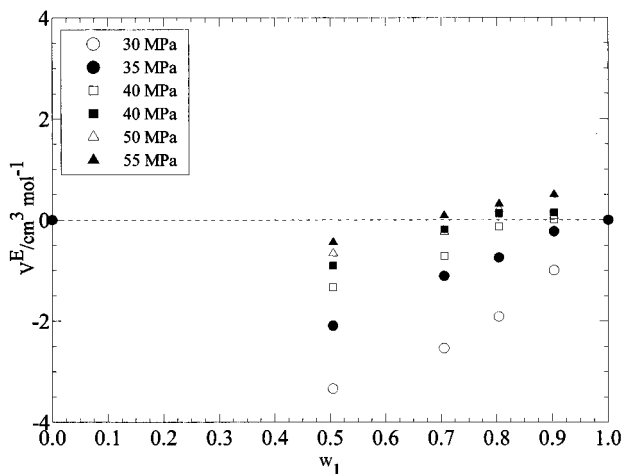


**Figure 7.** Pressure dependence of density for the binary mixtures of carbon dioxide and acetone at 423 K (compositions in mass percent).



**Figure 8.** Excess volume for carbon dioxide (1) + acetone (2) at 323 K.

are shown at 323 and 348 K for different pressures as a function of carbon dioxide mass fraction  $w_1$ . (In our laboratory, we are interested in compositional information based on mass fractions.) The error in excess volume for this system, depending upon the composition, was estimated to be in the range 6.9 to 15.6% with a mean value



**Figure 9.** Excess volume for carbon dioxide (1) + acetone (2) at 348 K.

of 9.6%. At 323 K (Figure 8)  $V^E$  appears to be mostly positive for these mixtures, though it is likely that the overall shape is sigmoidal with negative excess volumes displayed for mixtures with high acetone content. At 348 K,  $V^E$  becomes more negative. At both temperatures, excess volume becomes more positive with increasing pressure.

Excess volumes for carbon dioxide + acetone mixtures have not been previously reported in the literature. In fact, high-pressure excess volume data are available only for a limited number of systems (Battino, 1971; Seitz et al., 1996; Ott et al., 1996; Kiran et al., 1996b; Pöhler and Kiran, 1996). Carbon dioxide + organic solvent systems are the least studied. The present trends are more like the trends that we reported earlier for carbon dioxide + pentane mixtures (Kiran et al., 1996b). That the excess volume becomes more negative with increasing temperature and more positive with increasing pressure were also observed with carbon dioxide + toluene (Pöhler and Kiran, 1996), but for that system excess volumes were found to be negative for mixtures with high carbon dioxide content, which is in contrast with carbon dioxide + pentane or carbon dioxide + acetone systems.

## Conclusions

The density of carbon dioxide becomes greater than that of acetone above a characteristic pressure at a given temperature. Binary mixtures also display density crossover. Excess volumes are shown to decrease with temperature but increase with pressure.

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