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# Volumetric Properties of Pentane + Carbon Dioxide at High Pressures

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The volumetric behavior of carbon dioxide + pentane has been investigated 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 fluid mixtures containing 10, 20, 35, 50, 62, 72, 80, and 88% by weight carbon dioxide are presented as a function of pressure at each temperature. With increasing pressure (above 20 MPa) the density of carbon dioxide becomes greater than that of pentane, and mixture densities show a crossover with composition. At a given temperature and pressure, under a majority of the conditions evaluated, the excess volume for the mixtures shows a sigmoidal variation with composition, being negative at low carbon dioxide content and becoming positive with increasing carbon dioxide content. With increasing pressure, excess volumes become less negative.

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## Introduction

Binary fluid mixtures are important for a number of applications involving supercritical fluids. The interest in such fluids stems from the fact that using binary mixtures, one can (a) adjust the critical temperature and/or pressure of the mixture and thus the actual operational conditions, (b) reduce the amount of less desirable solvents for a given process application, (c) improve selectivity toward certain compounds, for example, in extractions, (d) introduce reactivity toward certain compounds as in reactive extractions, or simply (e) facilitate postprocessing and removal of residual active solvents.

At the University of Maine, we have been exploring binary fluid mixtures for regulation of solubility and processing of polymers, to conduct polymerization reactions, and to extract compounds from multicomponent complex matrices such as synthetic or natural polymer mixtures (Kiran, 1994). We have already reported the solubility of polyolefins in mixtures of carbon dioxide and pentane (Kiran *et al.*, 1993; Xiong and Kiran, 1994a) or butane (Xiong and Kiran, 1994b). We have also reported polymerization of styrene in these fluids (Kiran and Gokmenoglu, 1994).

Even though phase equilibria and critical properties of carbon dioxide + pentane mixtures have been reported in the literature (Cheng *et al.*, 1989; Leu and Robinson, 1987; Wu *et al.*, 1988), there is essentially no information on the densities of these mixtures at high pressures. The density is an important scaling factor in many aspects of the supercritical fluid processing. We have undertaken the present study to document the volumetric behavior of these mixtures over the full composition range at pressures up to 70 MPa. The excess volumes for these mixtures and their variation with composition, temperature, and pressure have also been determined. Volumetric properties of other mixtures are also being investigated (Gokmenoglu *et al.*, 1995; Pohler and Kiran, 1995).

## Experimental Section

***Variable-Volume View Cell.*** A specially designed variable-volume view cell initially developed for investigation of the solubility of polymers (Kiran *et al.*, 1993) has been used for measurements of the densities at high pressures. Figure 1 shows the overall system arrangement including the fluid delivery, pressure generation lines, and the view cell itself. The details of the view cell are shown in Figure 2. It is operable at pressures up to 70 MPa and temperatures up to 473 K. The maximum internal volume of the cell is (22.43 ± 0.05) $cm^3$ as determined by charging water at ambient conditions. Two sapphire windows (W) permit visual or optical observation of the cell content. The window sealing is accomplished by gold foils on the wetted side. Mixing of the cell content is achieved with a magnetic stirrer (MS). The variable-volume part (VVP) is sealed with Teflon O-rings. An linear-variable differential transformer (LVDT) coil is used to monitor the position of the movable piston (P) in the variable-volume part. The methodology was initially developed and employed in our laboratory in a unique instrument for simultaneous measurement of density and viscosity at high pressures (Sen and Kiran, 1990; Sen and Kiran, 1991; Sen, 1991; Kiran and Sen, 1992, 1993). Its modifications and automated versions are in use in our laboratory for the study of pressure−volume−temperature (PVT) behavior and phase separation processes in high-pressure solutions (Kiran and Zhuang, 1994; Zhuang and Kiran, 1995). For position sensing, the movable piston (P) is attached to a steel rod with a ferromagnetic metal piece acting as the sensing element. This metal piece moves with the piston and induces a current in the LVDT coil. To determine the exact position of the piston, the LVDT coil is moved with the piston locator screw (PLS) until the digital readout unit (DRU) shows zero. At this point, the position readout unit (PRU) is set to zero also. When the piston is moved to a new position (using the pressure generator, PGN), the LVDT coil is moved to sense its new location. The reading from the PRU unit gives the actual distance traveled by the piston with an accuracy of 0.013 mm. Knowing the initial cell volume and the cross-sectional area of the piston (1.99 $cm^2$) permits determination of the volume change or the volume of the cell content at any other temperature or pressure.

Four cartridge heating elements (HE) are used to heat the cell. Temperature is controlled with an Omega controller using a platinum resistance temperature detector (RTD) probe and monitored with a resolution of ±0.1 K. The pressure is measured to an accuracy of ±0.06 MPa using

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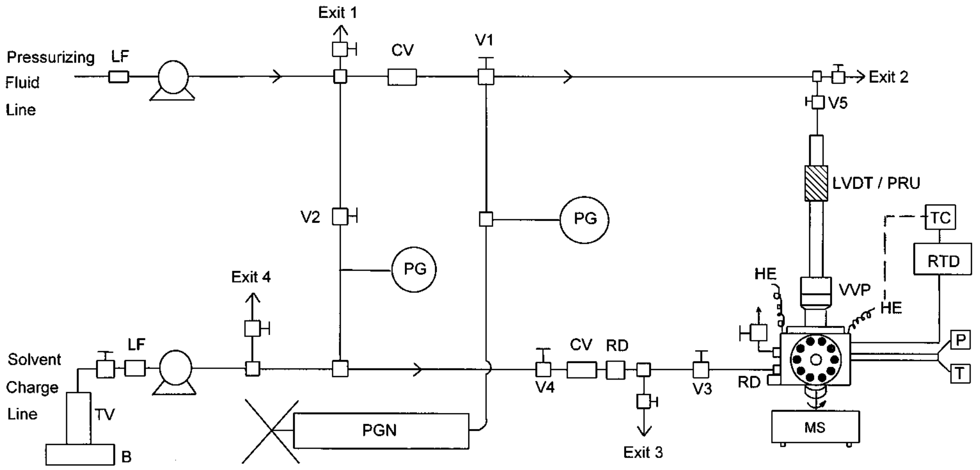

**Figure 1.** Overall diagram of the experimental system (TV = transfer vessel; B = balance; PG = pressure gauge; PGN = pressure generator; LVDT/PRU = piston position readout unit; VVP = variable-volume part; HE = heating elements; RD = rupture disk; MS = magnetic stirrer; TC = temperature controller).

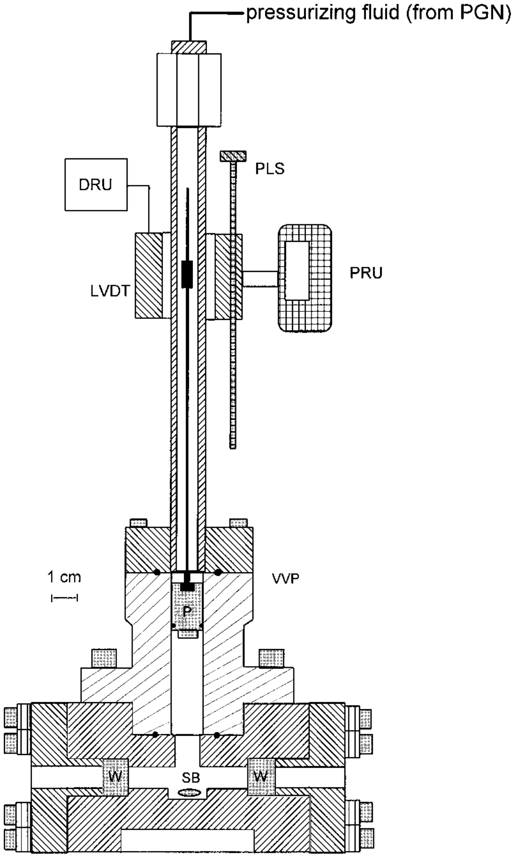

**Figure 2.** Variable-volume view cell with piston position readout unit (LVDT = linear-variable differential transformer; PLS = position locator screw; DRU = digital voltage readout unit; PRU = position readout unit; W = sapphire window; SB = stirring bar; P = piston).

a Dynisco flush mount type transducer and read with a resolution of ±0.007 MPa. The temperature is measured with an accuracy of ±0.5 K.

***Operational Procedure.*** The system is designed for direct loading of the cell with different fluids using a transfer vessel and monitoring the change in mass of the transfer vessel during loading with a sensitive balance (Mettler Model 6100 with an accuracy of ±0.01 g). The cell is first flushed with carbon dioxide to remove any air, and then charged with the desired amount of pentane. The exact amount actually charged is further verified by disconnecting the cell from valves 3 and 5 (Figure 1), and weighing it on a Sartorius balance (16 kg capacity with 0.1 g accuracy). The cell is then connected to the system, and carbon dioxide is now charged from another transfer vessel (TV) which has been previously filled with liquid carbon dioxide. During carbon dioxide charge, the pump head (Milton Roy) is cooled to avoid cavitation. The amount of carbon dioxide charged to the cell is monitored by the change in the total mass of the transfer vessel. After charging, the cell which is now loaded with both fluids is again disconnected from the system line and the total cell content is weighed.

During the charging process no pressure is applied from the pressure generator to ensure that the experiments are started with the piston being at the top, i.e., cell at its maximum volume. The zero position of the piston, corresponding to the initial maximum volume position, is determined by the LVDT as described above. Then, the pressurizing fluid is pumped to fill the pressure generator line on the other side of the piston. (Essentially any fluid can be used in the pressure generation line, but fluids that are not very compressible are easier to work with. In these experiments, we have used pentane). The whole cell is then heated to a desired temperature, and the cell content is stirred with the magnetic stirrer. When temperature equilibrium is reached, the pressure in the cell is changed by moving the piston to different positions, and the corresponding cell volumes or the densities are determined. The mapping is continued for all temperatures of interest for a given fluid mixture.

***Materials.*** Carbon dioxide was bone-dry grade with a purity of 99.8% (Airco, supplied with an eductor tube). Pentane (99.9% purity) was obtained from Aldrich.

***Reproducibility and Errors.*** The resolution of the LVDT position sensor is such that the volume changes are determined with an accuracy of ±0.0025 $cm^3$. Density measurements are accurate to ±1.2% as verified by comparisons with data reported in the literature at similar conditions. The error stems primarily from charging of the fluid to the cell, rather than determination of the changes in volume after the cell is loaded.

## Results and Discussion

***a. Density.*** Densities of pure carbon dioxide and pentane and of binary mixtures containing 10, 20, 35, 50, 62, 72 , 80, and 88 mass % carbon dioxide have been determined at 323, 348, 373, 398, and 423 K over a pressure range from 10 to 70 MPa. Table 1 shows the tabulated data. At these conditions, the mixtures are either in the one-phase liquid or supercritical fluid state. Figure 3 shows the variation of both the critical temper-

**Table 1. Densities of Carbon Dioxide and Pentane Mixtures (Mixture Compositions Are Based on Mass)**

| 323 K | | 348 K | | 373 K | | 398 K | | 423 K | |
|---|---|---|---|---|---|---|---|---|---|
| pressure /MPa | density /(g/cm$^3$) | pressure /MPa | density /(g/cm$^3$) | pressure/ MPa | density/ (g/cm$^3$) | pressure/ MPa1 | density/(g/ cm$^3$) | pressure/ MPa | density/ (g/cm$^3$) |
| Carbon Dioxide/Pentane = 100/0 | | | | | | | | | |
| 11.83 | 0.6292 | 19.63 | 0.6475 | 26.05 | 0.6282 | 32.64 | 0.6298 | 38.73 | 0.6281 |
| 15.46 | 0.7348 | 22.74 | 0.6932 | 28.78 | 0.6644 | 36.40 | 0.6711 | 40.26 | 0.6410 |
| 19.40 | 0.7954 | 25.19 | 0.7271 | 32.63 | 0.7087 | 40.06 | 0.7053 | 44.03 | 0.6726 |
| 22.96 | 0.8343 | 28.61 | 0.7648 | 36.11 | 0.7408 | 43.74 | 0.7346 | 47.57 | 0.7014 |
| 26.79 | 0.8659 | 32.55 | 0.8010 | 39.82 | 0.7710 | 47.73 | 0.7644 | 51.40 | 0.7293 |
| 30.59 | 0.8925 | 36.08 | 0.8270 | 43.79 | 0.7986 | 51.41 | 0.7881 | 55.33 | 0.537 |
| 34.45 | 0.9145 | 40.17 | 0.8534 | 47.56 | 0.8232 | 55.19 | 0.8088 | 59.16 | 0.7757 |
| 38.21 | 0.9347 | 43.74 | 0.8743 | 51.54 | 0.8454 | 59.08 | 0.8289 | 62.76 | 0.7962 |
| 41.93 | 0.9595 | 47.59 | 0.8927 | 55.13 | 0.8634 | 62.78 | 0.8472 | | |
| 45.94 | 0.9655 | 51.39 | 0.9123 | 59.11 | 0.8808 | | | | |
| 50.09 | 0.9837 | 55.22 | 0.9284 | 62.75 | 0.8974 | | | | |
| 53.45 | 0.9942 | 59.12 | 0.9502 | | | | | | |
| Carbon Dioxide/Pentane = 88/12 | | | | | | | | | |
| 9.55 | 0.6133 | 16.51 | 0.6142 | 23.10 | 0.6111 | 30.61 | 0.6144 | 38.07 | 0.6131 |
| 11.66 | 0.6746 | 19.22 | 0.6584 | 26.83 | 0.6504 | 34.54 | 0.6462 | 41.68 | 0.6377 |
| 15.46 | 0.7334 | 23.01 | 0.7021 | 30.66 | 0.6836 | 38.16 | 0.6738 | 45.69 | 0.6644 |
| 19.22 | 0.7677 | 26.62 | 0.7328 | 34.44 | 0.7107 | 41.96 | 0.6984 | 49.47 | 0.6862 |
| 22.99 | 0.7962 | 30.63 | 0.7613 | 38.15 | 0.7346 | 45.73 | 0.7177 | 53.11 | 0.7049 |
| 26.76 | 0.8191 | 34.48 | 0.7827 | 41.99 | 0.7572 | 49.42 | 0.7360 | 57.04 | 0.7227 |
| 30.56 | 0.8370 | 38.10 | 0.8015 | 45.68 | 0.7750 | 53.31 | 0.7536 | 60.92 | 0.7390 |
| 34.31 | 0.8539 | 41.78 | 0.8181 | 49.48 | 0.7909 | 57.75 | 0.7702 | 64.53 | 0.7528 |
| 38.23 | 0.8688 | 46.02 | 0.8350 | 53.28 | 0.8064 | 60.89 | 0.7850 | | |
| 41.99 | 0.8822 | 49.47 | 0.8479 | 57.14 | 0.8203 | 64.49 | 0.7909 | | |
| 45.74 | 0.8941 | 53.24 | 0.8601 | 61.03 | 0.8328 | | | | |
| 49.42 | 0.9035 | 57.27 | 0.8728 | 64.76 | 0.8439 | | | | |
| 53.24 | 0.9145 | 60.68 | 0.8827 | | | | | | |
| 57.14 | 0.9254 | 64.52 | 0.8933 | | | | | | |
| 61.48 | 0.9361 | | | | | | | | |
| 64.61 | 0.9420 | | | | | | | | |
| Carbon Dioxide/Pentane = 80/20 | | | | | | | | | |
| 9.71 | 0.6532 | 19.33 | 0.6622 | 26.83 | 0.6491 | 34.35 | 0.6409 | 42.02 | 0.6421 |
| 11.67 | 0.6837 | 22.94 | 0.6968 | 30.63 | 0.6784 | 38.20 | 0.6654 | 45.77 | 0.6617 |
| 15.40 | 0.7254 | 26.74 | 0.7242 | 34.36 | 0.7012 | 41.88 | 0.6863 | 49.61 | 0.6009 |
| 19.20 | 0.7541 | 30.69 | 0.7460 | 38.15 | 0.7216 | 45.61 | 0.7055 | 53.40 | 0.6672 |
| 23.05 | 0.7769 | 34.39 | 0.7641 | 41.90 | 0.7404 | 49.45 | 0.7237 | 57.03 | 0.7121 |
| 26.87 | 0.7956 | 38.22 | 0.7803 | 45.69 | 0.7548 | 53.39 | 0.7392 | 60.82 | 0.7256 |
| 30.49 | 0.8110 | 42.46 | 0.7971 | 49.48 | 0.7706 | 57.09 | 0.7534 | 64.61 | 0.7402 |
| 34.31 | 0.8263 | 45.71 | 0.8080 | 53.28 | 0.7848 | 60.73 | 0.7651 | | |
| 38.24 | 0.8394 | 49.45 | 0.8188 | 57.03 | 0.7972 | 64.62 | 0.7775 | | |
| 42.02 | 0.8507 | 53.41 | 0.8306 | 61.06 | 0.8094 | | | | |
| 45.97 | 0.8618 | 57.12 | 0.8408 | 64.83 | 0.8190 | | | | |
| 49.56 | 0.8713 | 60.89 | 0.8511 | | | | | | |
| 53.13 | 0.8794 | 64.66 | 0.8603 | | | | | | |
| 57.13 | 0.8890 | | | | | | | | |
| 60.87 | 0.8967 | | | | | | | | |
| Carbon Dioxide/Pentane = 72/28 | | | | | | | | | |
| 14.66 | 0.7149 | 22.74 | 0.7023 | 29.59 | 0.6956 | 38.18 | 0.6955 | 46.21 | 0.6964 |
| 19.29 | 0.7372 | 26.80 | 0.7211 | 31.42 | 0.7045 | 42.25 | 0.7116 | 49.49 | 0.7076 |
| 22.78 | 0.7512 | 30.65 | 0.7378 | 34.66 | 0.7193 | 45.86 | 0.7258 | 53.54 | 0.7232 |
| 26.67 | 0.7664 | 34.29 | 0.7506 | 38.30 | 0.7336 | 49.57 | 0.7390 | 57.09 | 0.7350 |
| 30.25 | 0.7776 | 38.18 | 0.7635 | 42.17 | 0.7484 | 53.17 | 0.7511 | 61.02 | 0.7469 |
| 34.34 | 0.7901 | 41.90 | 0.7762 | 45.85 | 0.7600 | 56.94 | 0.7634 | 64.92 | 0.7594 |
| 38.11 | 0.8004 | 45.60 | 0.7860 | 49.46 | 0.7713 | 60.64 | 0.7738 | | |
| 41.82 | 0.8087 | 49.31 | 0.7959 | 53.42 | 0.7819 | 64.31 | 0.7831 | | |
| 45.55 | 0.8165 | 53.07 | 0.8050 | 57.22 | 0.7927 | | | | |
| 49.37 | 0.8261 | 56.81 | 0.8133 | 61.15 | 0.8019 | | | | |
| 53.26 | 0.8330 | 60.77 | 0.8217 | 64.55 | 0.8110 | | | | |
| 56.96 | 0.8411 | 64.71 | 0.8304 | | | | | | |
| 60.67 | 0.8468 | | | | | | | | |
| 64.73 | 0.8552 | | | | | | | | |
| Carbon Dioxide/Pentane = 62/38 | | | | | | | | | |
| 17.64 | 0.7032 | 26.95 | 0.7029 | 36.49 | 0.7033 | 46.26 | 0.7030 | | |
| 19.83 | 0.7105 | 30.51 | 0.7156 | 39.57 | 0.7134 | 49.67 | 0.7129 | | |
| 23.26 | 0.7230 | 34.04 | 0.7255 | 42.43 | 0.7218 | 53.43 | 0.7234 | | |
| 26.68 | 0.7326 | 38.34 | 0.7406 | 46.15 | 0.7316 | 57.56 | 0.7342 | | |
| 30.67 | 0.7444 | 41.96 | 0.7510 | 49.84 | 0.7420 | 61.35 | 0.7439 | | |
| 34.26 | 0.7539 | 45.92 | 0.7611 | 53.44 | 0.7514 | 64.71 | 0.7517 | | |
| 38.21 | 0.7618 | 49.54 | 0.7694 | 57.41 | 0.7608 | | | | |
| 42.02 | 0.7711 | 53.36 | 0.7775 | 61.08 | 0.7689 | | | | |
| 45.86 | 0.7784 | 57.15 | 0.7856 | 64.73 | 0.7758 | | | | |
| 49.71 | 0.7861 | 60.91 | 0.7942 | | | | | | |
| 53.51 | 0.7930 | 64.42 | 0.8003 | | | | | | |
| 57.46 | 0.7989 | | | | | | | | |
| 60.97 | 0.8054 | | | | | | | | |
| 65.01 | 0.8119 | | | | | | | | |
| Carbon Dioxide/Pentane = 50/50 | | | | | | | | | |
| 13.54 | 0.6831 | 25.25 | 0.6832 | 35.73 | 0.6827 | 44.62 | 0.6832 | 53.70 | 0.6830 |
| 16.40 | 0.6945 | 28.02 | 0.6919 | 38.56 | 0.6922 | 49.45 | 0.6958 | 57.28 | 0.6924 |
| 19.67 | 0.7045 | 31.06 | 0.7014 | 42.38 | 0.7020 | 53.63 | 0.7068 | 61.11 | 0.7008 |

**Table 1 (Continued)**

| 323 K | | 348 K | | 373 K | | 398 K | | 423 | |
|---|---|---|---|---|---|---|---|---|---|
| pressure/ MPa | density/ (g/cm$^3$) | pressure/ MPa | density /(g/cm$^3$) | pressure /MPa | density/ (g/cm$^3$) | pressure /MPa | density/ (g/cm$^3$) | pressure /MPa | density/ (g/cm$^3$) |
| Carbon Dioxide/Pentane = 50/50 | | | | | | | | | |
| 23.18 | 0.7148 | 34.62 | 0.7112 | 46.14 | 0.7108 | 57.40 | 0.7161 | 64.94 | 0.7104 |
| 27.05 | 0.7251 | 38.38 | 0.7201 | 49.81 | 0.7198 | 61.13 | 0.7240 | | |
| 30.99 | 0.7353 | 42.19 | 0.7290 | 53.53 | 0.7283 | 64.90 | 0.7316 | | |
| 34.49 | 0.7433 | 46.17 | 0.7368 | 57.22 | 0.7364 | | | | |
| 38.28 | 0.7510 | 49.97 | 0.7449 | 61.45 | 0.7437 | | | | |
| 41.94 | 0.7578 | 53.70 | 0.7522 | 64.71 | 0.7535 | | | | |
| 45.82 | 0.7654 | 57.47 | 0.7591 | | | | | | |
| 49.86 | 0.7717 | 61.29 | 0.7646 | | | | | | |
| 53.63 | 0.7776 | 64.79 | 0.7712 | | | | | | |
| 57.03 | 0.7838 | | | | | | | | |
| 60.60 | 0.7887 | | | | | | | | |
| 64.45 | 0.7950 | | | | | | | | |
| Carbon Dioxide/Pentane = 35/65 | | | | | | | | | |
| 12.23 | 0.6631 | 26.98 | 0.6631 | 40.44 | 0.6631 | 53.79 | 0.6631 | | |
| 15.83 | 0.6733 | 30.37 | 0.6704 | 43.74 | 0.6702 | 57.40 | 0.6688 | | |
| 19.07 | 0.6805 | 34.61 | 0.6801 | 46.11 | 0.6736 | 60.85 | 0.6757 | | |
| 22.75 | 0.6887 | 38.12 | 0.6884 | 49.89 | 0.6808 | 64.77 | 0.6821 | | |
| 26.70 | 0.6982 | 42.15 | 0.6939 | 53.29 | 0.6866 | | | | |
| 30.50 | 0.7050 | 46.10 | 0.7013 | 57.04 | 0.6937 | | | | |
| 34.94 | 0.7126 | 49.34 | 0.7070 | 61.00 | 0.7001 | | | | |
| 38.29 | 0.7188 | 53.47 | 0.7125 | 64.18 | 0.7053 | | | | |
| 41.98 | 0.7246 | 57.18 | 0.7185 | | | | | | |
| 45.92 | 0.7310 | 60.83 | 0.7241 | | | | | | |
| 49.58 | 0.7362 | 64.48 | 0.7294 | | | | | | |
| 53.51 | 0.7421 | | | | | | | | |
| 57.09 | 0.7457 | | | | | | | | |
| 60.85 | 0.7511 | | | | | | | | |
| 64.51 | 0.7555 | | | | | | | | |
| Carbon Dioxide/Pentane = 20/80 | | | | | | | | | |
| 13.22 | 0.6453 | 28.41 | 0.6453 | 42.45 | 0.6453 | 56.98 | 0.6453 | | |
| 17.40 | 0.6521 | 30.91 | 0.6487 | 45.64 | 0.6485 | 59.82 | 0.6478 | | |
| 19.95 | 0.6559 | 34.66 | 0.6532 | 49.68 | 0.6550 | 62.53 | 0.6516 | | |
| 23.24 | 0.6617 | 38.18 | 0.6586 | 53.54 | 0.6601 | 65.02 | 0.6546 | | |
| 26.95 | 0.6673 | 41.97 | 0.6645 | 56.93 | 0.6643 | | | | |
| 30.50 | 0.6720 | 46.08 | 0.6701 | 60.84 | 0.6691 | | | | |
| 34.45 | 0.6766 | 49.50 | 0.6740 | 64.51 | 0.6734 | | | | |
| 38.05 | 0.6817 | 53.30 | 0.6791 | | | | | | |
| 41.75 | 0.6855 | 56.87 | 0.6827 | | | | | | |
| 45.89 | 0.6910 | 61.01 | 0.6877 | | | | | | |
| 49.41 | 0.6953 | 64.68 | 0.6906 | | | | | | |
| 53.21 | 0.6992 | | | | | | | | |
| 56.96 | 0.7030 | | | | | | | | |
| 61.12 | 0.7071 | | | | | | | | |
| 64.82 | 0.7105 | | | | | | | | |
| Carbon Dioxide/Pentane = 10/90 | | | | | | | | | |
| 8.60 | 0.6214 | 23.09 | 0.6214 | 36.65 | 0.6214 | 51.14 | 0.6214 | | |
| 11.64 | 0.6271 | 26.73 | 0.6268 | 39.40 | 0.6254 | 54.09 | 0.6246 | | |
| 15.26 | 0.6328 | 30.48 | 0.6316 | 42.31 | 0.6290 | 57.27 | 0.6288 | | |
| 19.27 | 0.6387 | 34.55 | 0.6366 | 45.87 | 0.6326 | 61.19 | 0.6326 | | |
| 22.88 | 0.6436 | 38.12 | 0.6428 | 49.62 | 0.6377 | 64.60 | 0.6370 | | |
| 26.78 | 0.6502 | 41.97 | 0.6480 | 53.25 | 0.6416 | | | | |
| 30.63 | 0.6554 | 45.69 | 0.6521 | 57.19 | 0.6485 | | | | |
| 34.20 | 0.6586 | 49.87 | 0.6574 | 60.97 | 0.6509 | | | | |
| 37.99 | 0.6635 | 53.31 | 0.6608 | 64.67 | 0.6546 | | | | |
| 42.05 | 0.6676 | 57.01 | 0.6647 | | | | | | |
| 45.68 | 0.6716 | 60.87 | 0.6681 | | | | | | |
| 49.47 | 0.6760 | 64.89 | 0.6724 | | | | | | |
| 53.51 | 0.6803 | | | | | | | | |
| 57.27 | 0.6837 | | | | | | | | |
| 60.63 | 0.6859 | | | | | | | | |
| 64.40 | 0.6904 | | | | | | | | |
| Carbon Dioxide/Pentane = 0/100 | | | | | | | | | |
| | | 8.07 | 0.5856 | 15.94 | 0.5764 | 23.68 | 0.5677 | 33.39 | 0.5677 |
| | | 11.80 | 0.5912 | 19.59 | 0.5810 | 26.71 | 0.5711 | 36.17 | 0.5702 |
| | | 15.83 | 0.5960 | 23.35 | 0.5846 | 30.93 | 0.5760 | 38.60 | 0.5734 |
| | | 19.39 | 0.6004 | 27.17 | 0.5902 | 34.33 | 0.5806 | 41.82 | 0.5776 |
| | | 23.25 | 0.6036 | 30.70 | 0.5944 | 38.57 | 0.5848 | 46.33 | 0.5825 |
| | | 26.71 | 0.6066 | 34.47 | 0.5966 | 41.94 | 0.5888 | 49.47 | 0.5864 |
| | | 30.89 | 0.6109 | 38.29 | 0.6007 | 45.42 | 0.5926 | 53.22 | 0.5903 |
| | | 34.69 | 0.6152 | 42.03 | 0.6049 | 49.42 | 0.5974 | 57.19 | 0.5950 |
| | | 38.40 | 0.6181 | 46.01 | 0.6086 | 53.60 | 0.6011 | 60.82 | 0.5984 |
| | | 42.23 | 0.6206 | 49.77 | 0.6115 | 57.48 | 0.6052 | 64.71 | 0.6021 |
| | | 45.83 | 0.6244 | 53.94 | 0.6157 | 61.39 | 0.6085 | | |
| | | 49.73 | 0.6273 | 56.93 | 0.6181 | 64.52 | 0.6116 | | |
| | | 53.73 | 0.6298 | 60.73 | 0.6213 | | | | |
| | | 57.11 | 0.6325 | 64.52 | 0.6237 | | | | |
| | | 61.01 | 0.6360 | | | | | | |
| | | 64.75 | 0.6399 | | | | | | |

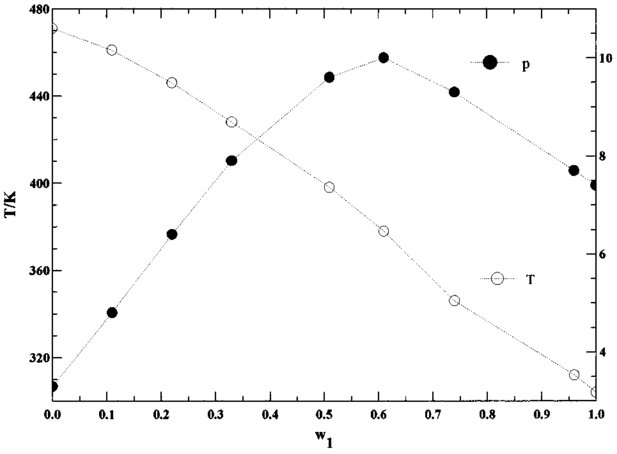

**Figure 3.** Critical temperature and pressure of binary mixtures of carbon dioxide (1) + pentane (2). Data are from Cheng *et al.* (1989).

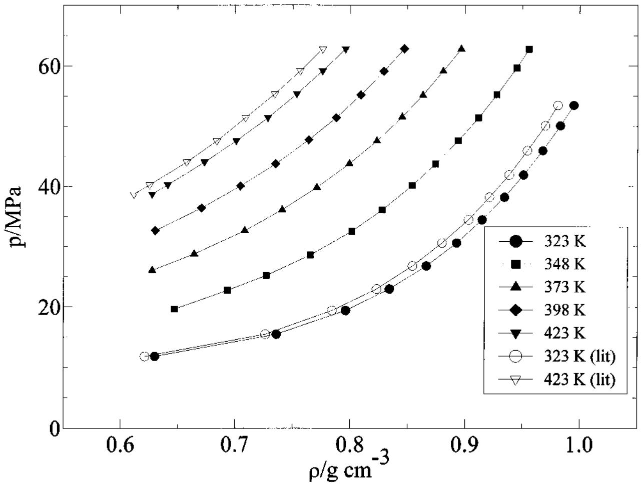

**Figure 4.** Pressure dependence of the density of carbon dioxide at different temperatures. Literature values are from Vargaftik (1975).

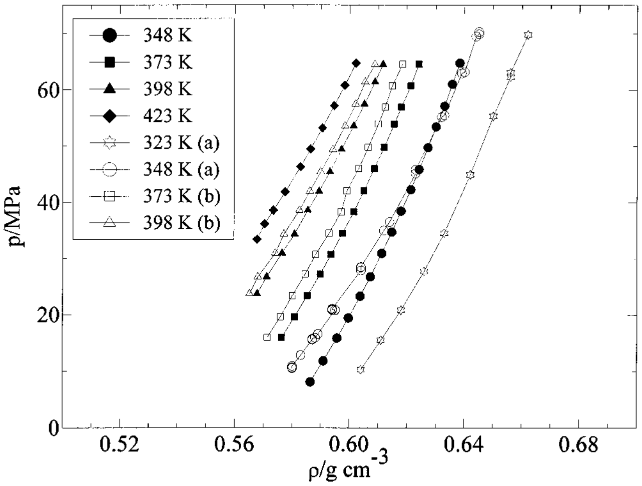

**Figure 5.** Pressure dependence of the density of pentane at different temperatures. Literature values are from (a) Kiran and Sen (1992) and (b) Sage and Lacey (1950).

ature and pressure for these mixtures based on data reported in the literature (Cheng *et al.*, 1989). The present measurements are all at pressures above the maximum critical pressure for the mixtures.

Figures 4 and 5 show the densities of the pure fluids. As would be expected, the densities decrease with temperature and increase with pressure. Results are compared with literature data at similar temperatures and pressures for carbon dioxide (Vargaftik, 1975) and pentane (Kiran and Sen, 1992; Sage and Lacey, 1950). When not at the same temperature, literature data were interpolated to match the temperatures. The density data for pentane are within ±0.5−0.9% of the literature values. Carbon dioxide densities are within ±1.3% of the literature values at low temperatures, and within ±2.5% at higher temperatures. Comparisons with recent literature data of high accuracy on carbon dioxide (Duschek et al., 1990) could not be made since that set of data is limited to pressures less then 9 MPa, and temperatures less then 340 K. (The present measurements cover a range from about 10 to 65 MPa). On the average, the density determinations are estimated to be accurate within ±1.2% of the literature values.

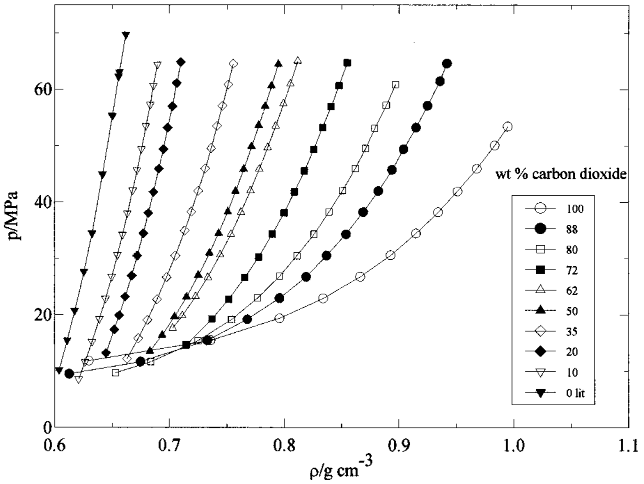

**Figure 6.** Pressure dependence of the density for the binary mixtures of carbon dioxide (1) and pentane (2) at 323 K. Compositions are on a mass basis. Pure pentane data at this temperature are from Kiran and Sen (1992).

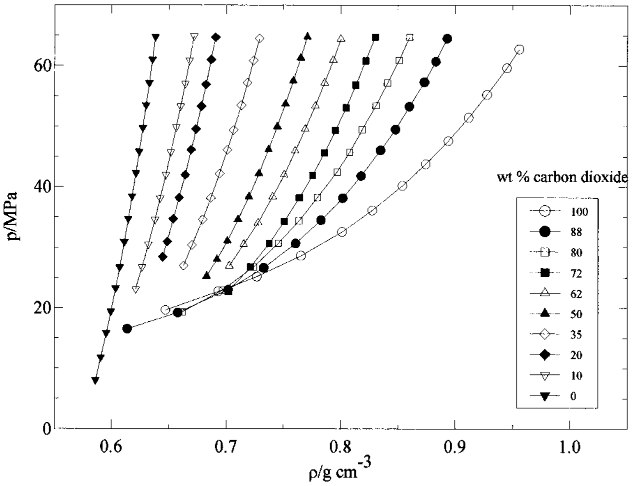

**Figure 7.** Pressure dependence of the density for the binary mixtures of carbon dioxide (1) and pentane (2) at 348 K. Compositions are on a mass basis.

An interesting feature displayed in these figures is that pentane has a lower density than carbon dioxide at pressures above about 20 MPa. In the 20−70 MPa interval, carbon dioxide densities vary in the range from 0.3 to 1.0 g/cm$^3$, while for pentane, the range is from about 0.55 to 0.67 g/cm$^3$. (That carbon dioxide may have higher densities than pentane is clearly understandable, but is against common *a priori* intuition). The figures also demonstrate the less compressible nature of pentane for which the pressure versus density curves are much steeper.

Figures 6−10 show the comparative densities of the binary mixtures at different temperatures. At 323 K, above 20 MPa there is a smooth transition to higher densities

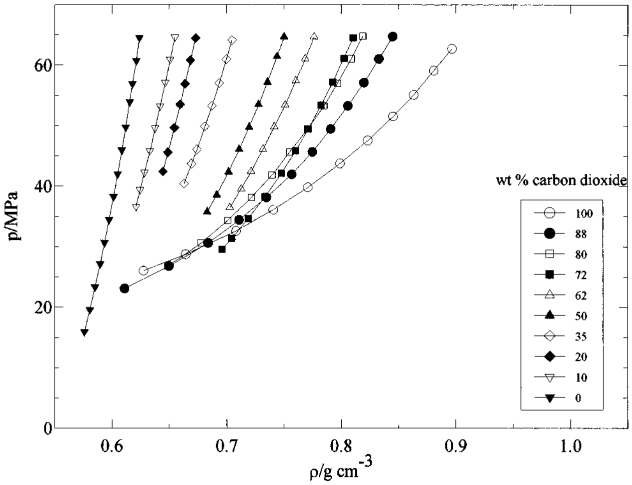

**Figure 8.** Pressure dependence of the density for the binary mixtures of carbon dioxide (1) and pentane (2) at 373 K. Compositions are on a mass basis.

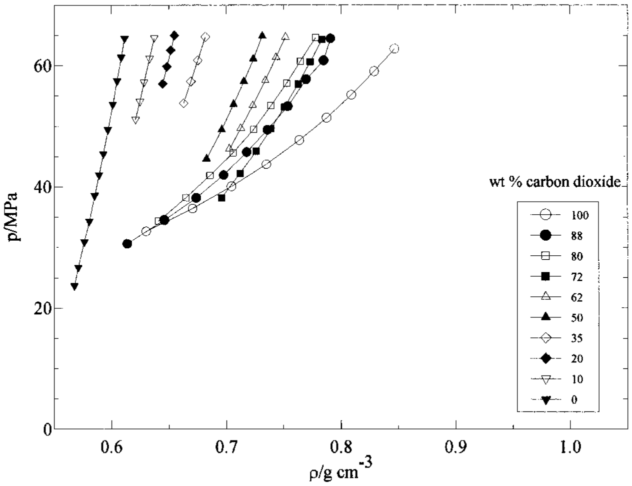

**Figure 9.** Pressure dependence of the density for the binary mixtures of carbon dioxide (1) and pentane (2) at 398 K. Compositions are on a mass basis.

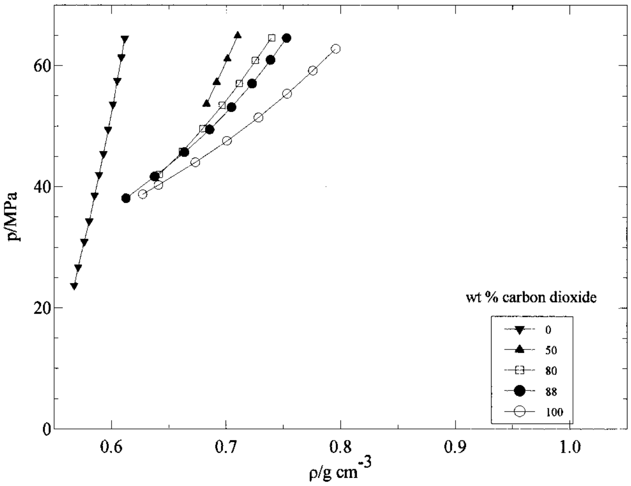

**Figure 10.** Pressure dependence of the density for the binary mixtures of carbon dioxide (1) and pentane (2) at 423 K. Compositions are on a mass basis.

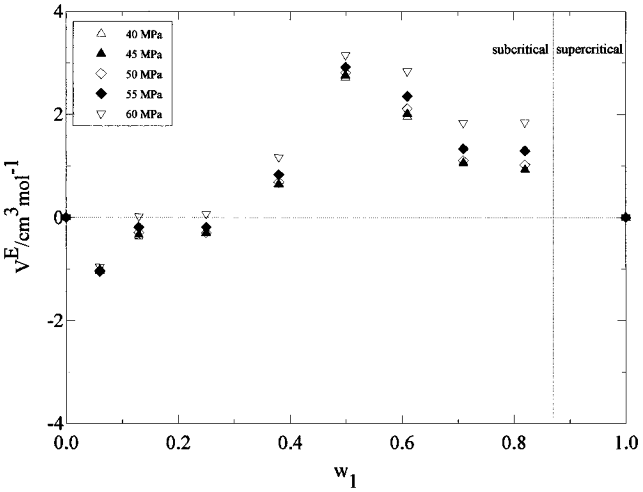

**Figure 11.** Excess volume for binary mixtures of carbon dioxide (1) with pentane (2) at 323 K.

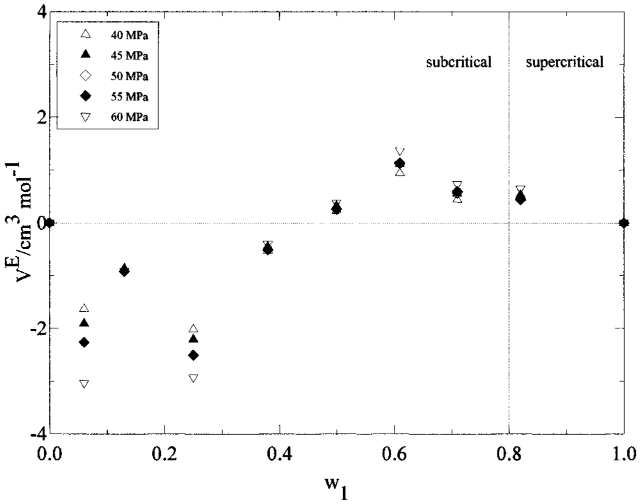

**Figure 12.** Excess volume for binary mixtures of carbon dioxide (1) with pentane (2) at 348 K.

with increasing carbon dioxide content of the mixture. The density range covers values from 0.6 to 1.0 g/cm$^3$. At lower pressures, there appears to be a crossover region where the density for mixtures with high carbon dioxide content becomes lower than the density for mixtures with lower carbon dioxide content. The same trend is observed also at 348 K, but smooth trends are observed above about 30 MPa. The crossover pressure becomes higher at higher temperatures. At 373 K and above, the full density range also narrows. At 423 K densities are limited to a range of values from about 0.58 to 0.8 g/cm$^3$.

***b. Excess Volume.*** Specific volume $V^{sp} = 1/\rho$ versus pressure data were fitted with third-order polynomials, and the excess volume ($V^E$) of the mixtures were determined at any given temperature for different pressures and compositions according to

$$V^E = V^{mix} - [x_1V_1 + x_2V_2]$$

where $x_1$ and $x_2$ are the mole fractions of carbon dioxide and pentane. The results are shown in Figures 11−13 for excess volumes of the mixtures at 323, 348, and 373 K. The error in the excess volume data shown in the figures is estimated to be about 11%. At each temperature, the excess volume per mole of mixture is plotted as a function of pressure and the mass fraction of carbon dioxide in the mixture. (Even though excess volumes are normally plotted as a function of mole fraction, in our laboratory, we are more interested in direct information on compositions based on mass).

In these figures, the compositions for which the mixtures are supercritical at the indicated pressures and temperatures are also noted. As already pointed out, pressures are all above the critical pressures of all the mixtures. Thus,

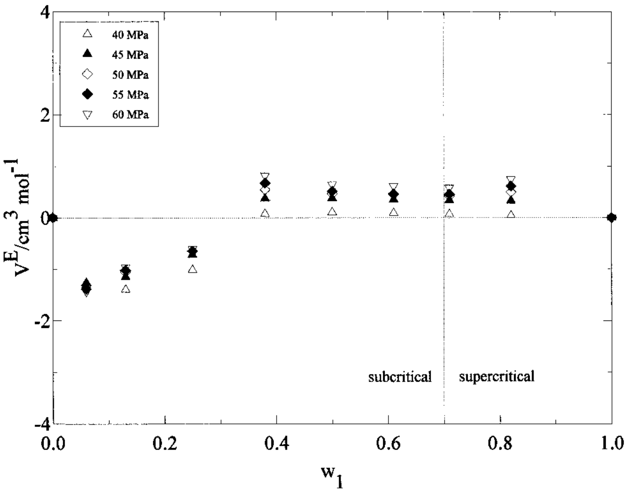

**Figure 13.** Excess volume for binary mixtures of carbon dioxide (1) with pentane (2) at 373 K.

the mixtures, even when they are at temperatures below the critical temperature of the mixture, are one-phase homogeneous liquids at these conditions.

As shown, excess volume data display sigmoidal variation with composition. At 323 K (Figure 11), at low carbon dioxide additions, mixtures display a negative excess volume which then becomes positive and goes through a maximum at around 0.5 mass fraction carbon dioxide at all pressures evaluated. For mixtures with high carbon dioxide content which are supercritical at this temperature, excess volumes remain positive. With increasing pressure excess volumes appear to become slightly more positive. At 348 K (Figure 12) similar behavior is observed, but the excess volumes tend to be more negative at this temperature. At even higher temperatures, at 373 K (Figure 13), sigmoidal behavior is still retained, but positive deviations now appear to be much smaller. At all temperatures, increasing the pressure makes the excess volume slightly more positive.

Excess volumes for pentane + carbon dioxide mixtures have not been previously reported in the literature. In fact, literature on excess volumes at high pressures is very limited. Depending upon the system investigated, both negative and positive excess volumes have been reported. For example, $V^E$ in 3-methylpyridine + water at high pressures (up to 250 MPa) is negative and highly skewed toward high methylpyridine concentrations, while for neon + nitrogen mixtures (up to 40 MPa) it is negative but more symmetrical (Battino, 1971). The excess volume in either system becomes less negative with increasing pressure. For water + ethanol at pressures up to 15 MPa (Ott et al., 1993) and for *n*-butylamine + alcohol up to 34 MPa (Papaioannou et al. 1993) excess volumes are negative and decrease (become less negative) with increasing pressure. In contrast, for mixtures of ethylbenzene with octanol, nonanol, and dodecanol, in the 50−100 °C range at pressures up to 7.5 MPa, $V^E$ is reported to be positive for all conditions (Garg and Ahluwalia, 1995). Excess volumes of mixtures of carbon dioxide and methane at 200 °C and 1000 bar are reported to be positive and symmetric (Seitz et al. 1994). For mixtures of carbon dioxide, methane, and nitrogen at these conditions the excess volumes are also positive.

The present observations on the pressure effect for carbon dioxide + pentane, that is, excess volume becoming less negative with increasing pressure, is consistent with the literature. However, unlike carbon dioxide + methane, the present system shows sigmoidal variation with composition.

It should be noted that sigmoidal variation is more often reported with systems containing a polar component at low pressures. For example, at ambient conditions, excess volumes in toluene + propanol (Yadav et al., 1993) and tetralin + alcohol (Yu and Tsai, 1994) are reported to be sigmoidal. In these systems, the positive contribution to $V^E$ is explained as arising from the breaking of hydrogen bonds in the self-associated alkanol and from disruptions in the favorable orientational order of the aromatic hydrocarbon. Negative contributions are attributed to changes of free volumes in the mixtures and to the presence of electron donor−acceptor interactions between alkanols and aromatic hydrocarbons (aromatic hydrocarbons are indicated to behave like electron donors). Competition of such opposing forces (i.e., positive contributions arising from disruption of order, and negative contributions arising from free-volume or packing effects) is given as the cause of the sigmoidal behavior in these systems.

The present system is a mixture of a nonpolar molecule (pentane) with a molecule having a quadrupole moment (carbon dioxide). Sigmoidal variation in $V^E$ is suggestive of competing factors which may involve free-volume or packing effects, as well as disruption of order such as disruption of the quadrupole−quadrupole interactions in carbon dioxide in the mixtures. Quantitatively, it is possible to analyze the effectiveness of different equations of state in their ability to predict the experimental excess volumes, and hence provide insight into the relative importance of the attractive and repulsive contributions to the excess volume (Tomlins and Marsh, 1977). Such analyses have not been conducted at this time.

## Conclusions

It is shown that the densities of mixtures of carbon dioxide and pentane display a crossover phenomenon which is a consequence of the density of carbon dioxide becoming greater than that of pentane at high pressures (at pressures above 20 MPa). Excess volumes for the mixtures show a sigmoidal variation with composition, being negative at low carbon dioxide levels, but becoming positive as the carbon dioxide content is increased.

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