# Density Measurements of 2-Propanol Solutions in Supercritical CO₂

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Using a vibrating-tube densitometer, densities of 2-propanol solutions with compositions between (0.72 and 1.89) mol % in supercritical $CO_2$ have been measured isothermally at (40, 50, 60, and 70) °C at pressures to 34.47 MPa. These measurements span the temperature and pressure ranges of earlier neutron scattering studies of the supercritical $CO_2$ fluids, and density data are needed to interpret the results. In addition, these results should aid in using supercritical $CO_2$ for separation or processing with 2-propanol and for improving the broad database supporting supercritical fluid technologies in general.

## Introduction

Carbon dioxide is nonflammable, nontoxic, naturally occurring, and inexpensive. Above its critical pressure ($P_c$ = 7.3 MPa) and temperature ($T_c$ = 31 °C), $CO_2$ has properties intermediate between those of a gas and a liquid, that is, high density and low viscosity. Because of these attributes, supercritical fluid (SCF) $CO_2$ has been proposed as an environmentally benign replacement for the organic solvents currently used in many industrial synthesis and separation processes. High-pressure thermodynamic data, especially densities of low-volatile compounds in a supercritical fluid, are among the important and fundamental parameters for SCF process design but have not been investigated for many systems of interest. The low molecular weight alcohols are among the most important compounds in separation processes. They are often used as entrainers to control the polarity of a SCF solvent in extraction applications and are also used as modifiers in SCF chromatography. In particular, the application of supercritical gases to separate alcohol from water[1,2] has received some attention because the conventional distillation methods are very energy intensive.

In previous studies,[3,4] the solubilities and vapor−liquid equilibria of the low molecular weight alcohols in supercritical $CO_2$ have been reported. However, systematic measurements of the density of these systems have not been made. These results are important in applying supercritical $CO_2$ for separation or processing with these compounds.

## Experimental Section

Since a detailed description of the experimental apparatus in this study can be found elsewhere,[5] it is only briefly described here. All of the results reported here were obtained as density difference, $\delta\rho$, between SCF and an appropriate reference fluid (pure $CO_2$) using a vibrating-tube densitometer at Oak Ridge National Laboratory (ORNL). $\delta\rho$ was measured with a Paar DMA 60 and 512 HP remote cell with a stainless steel jacket through which thermostated water was circulated. The temperature of the densitometer was maintained within ±0.1 °C and monitored with a calibrated 100 Ω platinum resistance thermometer (RTD). A stainless steel sample cell of 25 mL was used to prepare the solutions. The cell was initially loaded with a measured amount of 2-propanol (IPA) (Aldrich, 99% pure, used as received) and then immersed in an ice + water bath. $CO_2$ was transferred into the cell until the desired concentration was reached. Before delivering the solution to the densitometer, the pressure of the sample cell was measured at the experimental temperature to ensure supercritical solution and miscibility of IPA in $CO_2$. A transducer from Precise Sensors with an accuracy of $\delta p/p_{max} = 10^{-3}$, where $p_{max}$ is the upper pressure bound of the transducer (103.4 MPa), was used for the pressure measurement.

The difference in density $\delta\rho$ of fluids contained in the vibrating tube is related to the oscillation period $\tau$ of the densitometer as

$$\delta\rho = \rho_1 - \rho_2 = \kappa(\tau_1{}^2 - \tau_2{}^2) \tag{1}$$

where $\rho_i$ and $\tau_i$ are the density and oscillation period of material $i$, respectively, and the proportionality constant $\kappa$ is dependent on the temperature and pressure and may be determined by measuring $\tau$ for two reference fluids of known density with a vibrating-tube densitometer at the

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**Table 1. Density Results of 2-Propanol (1) Solutions in $CO_2$ (2) at Various Concentrations and Temperatures**

| | | $\rho/g\cdot cm^{-3}$ | | | |
|---|---|---|---|---|---|
| $x_1$ | $P$/MPa | $T = 40\ °C$ | $T = 50\ °C$ | $T = 60\ °C$ | $T = 70\ °C$ |
| 0.0072 | 34.47 | 0.9322 | 0.8965 | 0.8606 | 0.8233 |
| | 27.58 | 0.8969 | 0.8554 | 0.8128 | 0.7681 |
| | 20.68 | 0.8490 | 0.7963 | 0.7403 | 0.6693 |
| | 13.79 | 0.7674 | 0.6782 | 0.5674 | 0.4653 |
| | 10.34 | 0.6704 | 0.4548 | 0.3235 | 0.2699 |
| | 6.89 | 0.1984 | 0.1699 | 0.1539 | 0.1421 |
| 0.0102 | 34.47 | 0.9318 | 0.8964 | 0.8605 | 0.8235 |
| | 27.58 | 0.8968 | 0.8558 | 0.8134 | 0.7693 |
| | 20.68 | 0.8491 | 0.7974 | 0.7417 | 0.6826 |
| | 13.79 | 0.7685 | 0.6816 | 0.5722 | 0.4640 |
| | 10.34 | 0.6743 | 0.4663 | 0.3289 | 0.2714 |
| | 6.89 | | 0.1716 | 0.1550 | 0.1428 |
| 0.0152 | 34.47 | 0.9311 | 0.8964 | 0.8611 | 0.8242 |
| | 27.58 | 0.8969 | 0.8566 | 0.8151 | 0.7712 |
| | 20.68 | 0.8507 | 0.8000 | 0.7458 | 0.6868 |
| | 13.79 | 0.7740 | 0.6890 | 0.5833 | 0.4746 |
| | 10.34 | 0.6841 | 0.4907 | 0.3389 | 0.2773 |
| | 6.89 | | 0.1730 | 0.1563 | 0.1436 |
| 0.0187 | 34.47 | 0.9307 | 0.8962 | 0.8608 | 0.8245 |
| | 27.58 | 0.8970 | 0.8568 | 0.8152 | 0.7720 |
| | 20.68 | 0.8515 | 0.8009 | 0.7468 | 0.6890 |
| | 13.79 | 0.7766 | 0.6935 | 0.5891 | 0.4788 |
| | 10.34 | 0.6937 | 0.5036 | 0.3444 | 0.2775 |
| | 6.89 | | 0.1744 | 0.1581 | 0.1453 |

appropriate temperature and pressure:

$$\kappa = (\rho_0 - \rho_2)/(\tau_0^2 - \tau_2^2) \qquad (2)$$

The vibrating-tube densitometer gives the relative density between a fluid of unknown density and a reference fluid, so the accuracy of the density measurements is dependent both on the accuracy of the measured $\tau$ for the two fluids and on the accuracy of the reference-fluid densities $\rho_0$ and $\rho_2$. Highly pure $CO_2$ was used as one density standard at all conditions of this study while Ar was used as the complementary reference fluid. Densities of $CO_2$ and Ar were obtained from the *NIST Thermophysical Properties of Pure Fluids Database*.[6] Values for $\kappa$ calculated from this pair were fit as a cubic function of temperature with reduced weight assigned to the $T = 40$ °C ($CO_2$ + Ar) pair due to lower confidence in the calculated density of $CO_2$ at this temperature. The calibration constant $\kappa$ for the apparatus used in this study was found to be independent of pressure within experimental uncertainty in the calibration measurements. As a result, the following relationship was found to best fit our calibration data:

$$\kappa = (1.635 - 2.34 \times 10^{-9})T^3 \qquad (3)$$

where $T$ is in Kelvin.

### Results

Density data obtained at (40, 50, 60, and 70) °C from four 2-propanol solutions with concentrations of (0.72, 1.02,
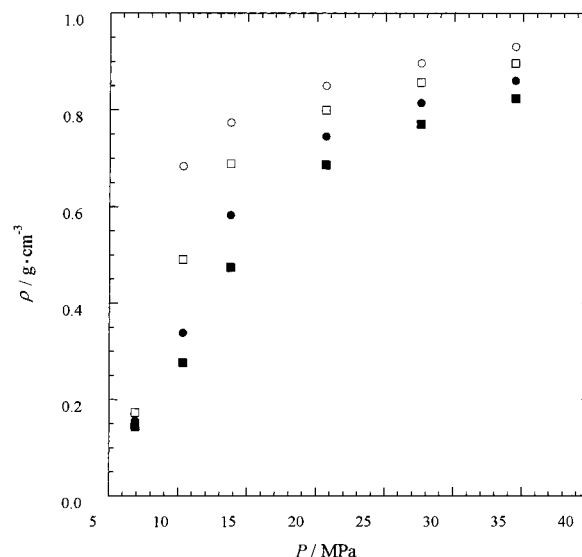


**Figure 1.** Density results of 1.52 mol % 2-propanol solution in $CO_2$: ○, 40 °C; □, 50 °C; ●, 60 °C; ■, 70 °C.

1.52, and 1.87) mol % in $CO_2$ are shown in Table 1, and typical density isotherms of the solutions are shown in Figure 1, where densities of 1.52 mol % solution are plotted as a function of pressure. The reproducibility of the results from repeated measurements of $\tau$ is generally within $\pm 3 \times 10^{-6}$, resulting in a density uncertainty of $\pm 0.0001$ g·cm$^{-3}$. The reported data are the average of the upper and lower limits of the calculated density. In addition, measurements were also made at 6.89 MPa, which is below the critical pressure of $CO_2$.

### Acknowledgment

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