

Density Measurements of Styrene Solutions in Supercritical CO₂

Horng J. Dai

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

J. Michael Simonson

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Hank D. Cochran*

Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Densities of styrene solutions of a wide concentration range from (0.65 to 29.9) mol % in supercritical CO₂ have been measured isothermally at (40, 50, 60, and 70) °C at pressures to 34.47 MPa by a vibrating-tube densitometer. These results should aid in using supercritical CO₂ for separation or synthesis with styrene and improving the broad database supporting supercritical fluid technologies in general.

Introduction

Carbon dioxide is nonflammable, nontoxic, naturally occurring, and inexpensive. Above its critical point, supercritical CO₂ has properties intermediate between those of a gas and a liquid, that is, high density and low viscosity. Previous studies^{1,2} have shown that supercritical CO₂ has adjustable solvent power, enhanced mass transfer characteristics, and low surface tension. Because of these attributes, supercritical CO₂ promises to be an environmentally benign replacement for the organic solvents currently used in separation or synthesis. Today, there are ~60 chemical plants operating using supercritical CO₂ technologies.

Styrene is an important petrochemical raw material that is commonly produced by dehydrogenation of ethylbenzene. Separation of styrene from ethylbenzene, due to incomplete reaction, by use of supercritical CO₂ as a solvent may be an attractive method because the generally employed vacuum distillation is energy-consuming. Moreover, DeSimone and co-workers^{3–5} have successfully demonstrated the synthesis of polystyrene in supercritical CO₂ by heterogeneous polymerization using a diblock copolymer as an emulsifying agent. High-pressure thermodynamic data of styrene in CO₂, therefore, are among the important and fundamental parameters for supercritical fluid process design. In previous works,^{6,7} phase behavior, solubility, and vapor–liquid equilibrium of styrene in supercritical CO₂ have been reported. However, systematic density measurements of the styrene/CO₂ system have not been made. In this work, density data are reported of five styrene solutions in CO₂ obtained at (40, 50, 60, and 70) °C over the pressure range from (13.79 to 34.37) MPa.

Experimental Section

A detailed description of the experimental apparatus in this study can be found elsewhere,⁸ so it is only briefly described here. All of the results reported here were obtained as density difference, $\delta\rho$, between sample fluid and an appropriate reference fluid (pure CO₂) using a

vibrating-tube densitometer at the Oak Ridge National Laboratory. $\delta\rho$ 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. A stainless steel sample cell of 25 mL was used to prepare the solutions. The cell was initially loaded with a measured amount of styrene (Aldrich, 99% pure, used as received) and then immersed in an ice + water bath. CO₂ 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 styrene in CO₂. 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 pressure measurement.

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

$$\delta\rho = \rho_1 - \rho_2 = k(\tau_1^2 - \tau_2^2) \quad (1)$$

where ρ_i and τ_i are the density and oscillation period of material i , respectively, and the proportionality constant k is dependent on the temperature and pressure and may be determined by measuring τ for two reference fluids of known density by vibrating-tube densitometer at the appropriate temperature and pressure:

$$k = (\rho_0 - \rho_2)/(\tau_0^2 - \tau_2^2) \quad (2)$$

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 measured τ for the two fluids and on the accuracy of the reference-fluid densities ρ_0 and ρ_2 . Highly pure CO₂ was used as one density

* Corresponding author (e-mail hdc@ornl.gov).

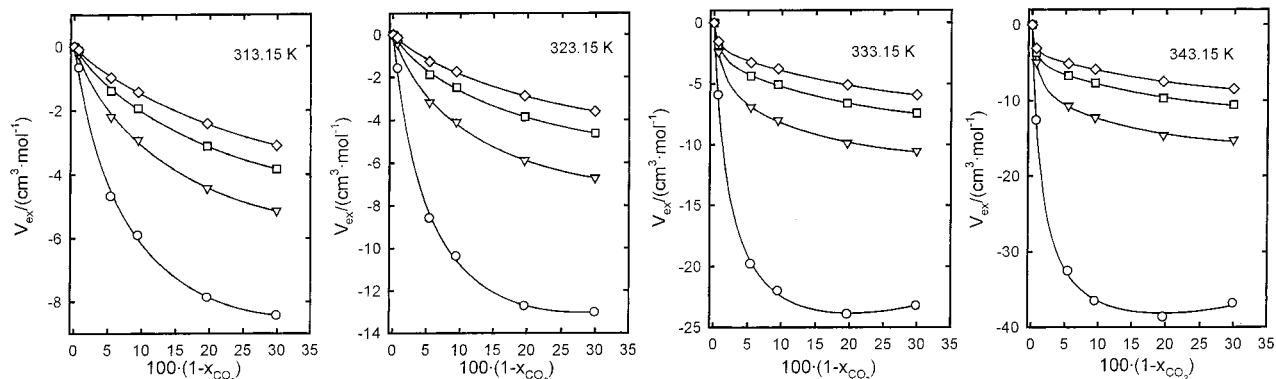


Figure 1. Excess molar volumes for $\{(1-x)\text{CO}_2 + x(\text{styrene})\}$ plotted against $100x$ at the temperatures indicated. Curves at experimental pressures trend from high pressure (upper curves) to low pressure at all temperatures.

Table 1. Density Results of Styrene (1) Solutions in CO₂ (2) at Various Concentrations and Temperatures

| x_1 | P/MPa | $\rho/\text{g}\cdot\text{cm}^{-3}$ | | | |
|--------|----------------|------------------------------------|--------------------------------|--------------------------------|--------------------------------|
| | | $t = 40\text{ }^\circ\text{C}$ | $t = 50\text{ }^\circ\text{C}$ | $t = 60\text{ }^\circ\text{C}$ | $t = 70\text{ }^\circ\text{C}$ |
| 0.0065 | 34.47 | 0.9336 | 0.8985 | 0.8863 | 0.8735 |
| | 27.58 | 0.8986 | 0.8580 | 0.8389 | 0.8186 |
| | 20.68 | 0.8510 | 0.7999 | 0.7670 | 0.7306 |
| | 13.79 | 0.7709 | 0.6853 | 0.6005 | 0.5177 |
| 0.0544 | 34.47 | 0.9432 | 0.9148 | 0.9138 | 0.9072 |
| | 27.58 | 0.9172 | 0.8853 | 0.8821 | 0.8699 |
| | 20.68 | 0.8839 | 0.8457 | 0.8385 | 0.8170 |
| | 13.79 | 0.8352 | 0.7818 | 0.7606 | 0.7051 |
| 0.0945 | 34.47 | 0.9452 | 0.9191 | 0.9199 | 0.9179 |
| | 27.58 | 0.9230 | 0.8941 | 0.8936 | 0.8878 |
| | 20.68 | 0.8951 | 0.8621 | 0.8593 | 0.8471 |
| | 13.79 | 0.8578 | 0.8153 | 0.8051 | 0.7747 |
| 0.1961 | 34.47 | 0.9474 | 0.9275 | 0.9330 | 0.9377 |
| | 27.58 | 0.9325 | 0.9111 | 0.9156 | 0.9196 |
| | 20.68 | 0.9152 | 0.8918 | 0.8952 | 0.8963 |
| | 13.79 | 0.8942 | 0.8674 | 0.8682 | 0.8623 |
| 0.2990 | 34.47 | 0.9446 | 0.9285 | 0.9360 | 0.9447 |
| | 27.58 | 0.9336 | 0.9166 | 0.9238 | 0.9315 |
| | 20.68 | 0.9211 | 0.9044 | 0.9097 | 0.9165 |
| | 13.79 | 0.9070 | 0.8878 | 0.8921 | 0.8949 |

standard at all conditions of this study, and Ar was used as the complementary reference fluid. Densities of CO₂ and Ar were obtained from NIST Thermophysical Properties of Pure Fluids Database.⁹ Values for k calculated from this pair were fit as a cubic function of temperature with reduced weight assigned to the $t = 40\text{ }^\circ\text{C}$ (CO₂ + Ar) pair due to lower confidence in the calculated density of CO₂ at this temperature. The calibration constant k for the apparatus used in this study was found to be independent of pressure within experimental uncertainty in the calibration measurements.

Results

Density data obtained at (40, 50, 60, and 70) °C from five styrene solutions with concentrations of (0.65, 5.44, 9.45, 19.61, and 29.90) mol % in CO₂ are shown in Table 1. Reproducibility of the results from repeated measurements of τ is generally within $\pm 3 \times 10^{-6}$ relative error, resulting in a density uncertainty of $\pm 0.0001\text{ g}\cdot\text{cm}^{-3}$. The reported data are the density calculated from the median of the upper and lower limits of frequency fluctuation.

Excess molar volumes were calculated from the results given in Table 1 using literature values for the molar volumes of pure CO₂ and styrene at the experimental conditions. Values for CO₂ were taken from the equation of state of Huang et al.,¹⁰ and those for styrene were

Table 2. Molar Volumes $V_m/(\text{cm}^3\cdot\text{mol}^{-1})$ for CO₂ at Experimental Conditions Calculated from the Equation of State of Huang et al.¹⁰

| T/K | $V_m/(\text{cm}^3\cdot\text{mol}^{-1})$ | | | |
|------------------|---|--------|--------|--------|
| 313.15 | 57.839 | 51.960 | 49.080 | 47.186 |
| 323.15 | 65.992 | 55.484 | 51.498 | 49.080 |
| 333.15 | 79.555 | 59.886 | 54.280 | 51.174 |
| 343.15 | 98.127 | 65.374 | 57.484 | 53.508 |
| $P/\text{MPa} =$ | 13.79 | 20.68 | 27.58 | 34.47 |

Table 3. Molar Volumes $V_m/(\text{cm}^3\cdot\text{mol}^{-1})$ for Styrene at Experimental Conditions Calculated from the Representation of Cibulka and Takagi¹¹

| T/K | $V_m/(\text{cm}^3\cdot\text{mol}^{-1})$ | | | |
|------------------|---|--------|--------|--------|
| 313.15 | 121.18 | 120.50 | 119.85 | 119.25 |
| 323.15 | 122.36 | 121.63 | 120.95 | 120.30 |
| 333.15 | 123.58 | 122.79 | 122.06 | 121.38 |
| 343.15 | 124.82 | 123.99 | 123.21 | 122.48 |
| $P/\text{MPa} =$ | 13.79 | 20.68 | 27.58 | 34.47 |

calculated from the correlation equations given by Cibulka and Takagi.¹¹ Reference fluid values for the experimental conditions are listed in Tables 2 and 3. Excess molar volumes V_{ex} calculated from the density results are shown in Figure 1. The excess molar volumes become more negative with increasing temperature at a given pressure; at all temperatures studied the values become more negative with decreasing pressure. Even given the limited range of mole fraction accessible in this system, it is clear that the plots of excess molar volume against mole fraction are highly asymmetric, particularly at the higher temperatures. These trends indicate a relatively strong attractive interaction between CO₂ and styrene, where the addition of small amounts of styrene to CO₂ leads to a significant decrease in the volume of the mixture.

Test fits of common expressions for the composition dependence of excess molar properties to isothermal, isobaric sets of experimental results indicated that simple treatments (e.g., the two- or three-suffix Margules equation¹²) were insufficiently flexible to represent the observed asymmetric composition dependence of V_{ex} , whereas more flexible representations such as the Wilson or Renon treatment¹² were not sufficiently constrained by the limited range and number of the present experimental results. A hybrid model of the form

$$V_{\text{ex}}/V_0 = -x_1x_2[C_1 + C_2\{L/(x_1 + Lx_2) - (1/L)/(x_2 + x_1/L)\}] \quad (3)$$

where $V_0 = 1\text{ cm}^3\cdot\text{mol}^{-1}$, x_1 and x_2 are the mole fractions of CO₂ and styrene, respectively, and C_1 , C_2 , and L are

Table 4. Values of Parameters of Equation 3

| T/K | | parameter values | | | |
|-----------|-------|------------------|----------|----------|----------|
| 313.15 | L | 14.2639 | 12.3929 | 14.0757 | 19.2879 |
| | C_1 | 15.0121 | 15.2199 | 14.3243 | 13.2267 |
| | C_2 | 9.3954 | 3.6152 | 1.4822 | 0.5371 |
| 323.15 | L | 19.0754 | 15.8265 | 15.9229 | 19.9600 |
| | C_1 | 17.1638 | 18.5602 | 15.9311 | 14.4635 |
| | C_2 | 15.9116 | 4.9319 | 2.2426 | 0.9481 |
| 333.15 | L | 41.8664 | 68.0576 | 120.1112 | 205.6403 |
| | C_1 | 24.0382 | 27.0167 | 23.1305 | 20.0943 |
| | C_2 | 28.0652 | 7.3906 | 3.8113 | 2.4841 |
| 343.15 | L | 63.3454 | 122.2022 | 229.0600 | 401.1370 |
| | C_1 | 43.7259 | 38.5502 | 31.6133 | 29.9225 |
| | C_2 | 42.0860 | 10.7447 | 5.8328 | 4.1160 |
| $P/MPa =$ | | 13.79 | 20.68 | 27.58 | 34.47 |

adjustable parameters, was applied to the experimentally obtained values of V_{ex} . Values of the parameters are listed in Table 4; smooth values of V_{ex} calculated from this treatment are shown in Figure 1.

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