Fluid Phase Equilibria 418 (2016) 94–99

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Accurate density measurements on a binary mixture (carbon dioxide + methane) at the vicinity of the critical point in the supercritical state by a single-sinker densimeter

Xiaoxian Yang, Zhe Wang*, Zheng Li

State Key Laboratory of Power Systems, Department of Thermal Engineering, Tsinghua University, Beijing, 100084, PR China

ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form
24 August 2015
Accepted 27 August 2015
Available online 2 September 2015

Keywords:
Single-sinker densimeter
Binary mixture
Carbon dioxide
Methane
Critical point

ABSTRACT

Pressure, density, and temperature measurements on a binary mixture (carbon dioxide + methane) with the composition 0.950 mol fraction carbon dioxide were carried out at the vicinity of the critical point in the supercritical state using a single-sinker magnetic suspension densimeter. The expanded measurement uncertainties ($k = 2$) were 35 mK for temperature, 3.4 kPa for pressure, and 0.033% for density. The mixture sample was prepared gravimetrically with the expanded uncertainty in the composition less than 0.001 mol fraction. Relative deviations of the experimental densities at temperature 301.15 K with pressures from (2.0–12.0) MPa from the values calculated by the GERG-2008 equation of state were generally within approximately 1.0%, and these experimental data agreed well with the experimental results from other groups. The relative deviations from the results calculated by the GERG-2008 equation of state for the experimental data measured at temperatures from (300.15–313.15) K with pressures from (8.0–10.0) MPa were within 5.0%. The absolute values of the relative deviations first increased and then decreased with increasing pressure for each isotherm, and the pressure of the peaking point was close to the pressure of the maximum value of $(\partial\rho/\partial T)_p$, calculated using the experimental data, on the same isotherm.

1. Introduction

At the vicinity of the critical point in the supercritical state, the density of a fluid ρ changes significantly with a tiny variation in the temperature T or pressure p. Based on this characteristic, fluids in this special region have been adopted in various industrial applications, *e.g.*, supercritical fluid extraction, refrigerating engineering, and carbon capture and storage. Meanwhile, safety issues such as plug flow in pipeline transportation should also be carefully considered when fluids are in this region. In industry, fluid densities are normally estimated by equations of state (EOSs). Nonetheless, it is a challenge for an EOS to accurately predict the fluid density in this particular region because the values of $(\partial\rho/\partial T)_p$ and $(\partial\rho/\partial p)_T$ are significantly larger than those in most other regions. Therefore, to evaluate the accuracy of the EOS and further improve its performance in this region, comprehensive density measurements in this region are necessary and significant.

To the best of our knowledge, experimental density data for binary mixtures at the vicinity of the critical point in the supercritical state are rare, and the available data generally lack accuracy. In the present project, we focused on the binary mixture (carbon dioxide + methane). The available experimental data for this binary mixture are summarized in Table 1. Mixtures with high carbon dioxide concentrations have attracted attention in the field of carbon capture and storage. However, only a small quantity of data is available at the vicinity of the critical point in the supercritical state for this binary mixture with compositions about 0.950 mol fraction carbon dioxide. To fill this data gap, comprehensive density measurements at temperatures from (300.15–313.15) K and pressures from (8.0–10.0) MPa were carried out utilizing a single-sinker magnetic suspension densimeter (SSD).

2. Experimental

2.1. Apparatus

The fluid density was measured according to the Archimedes buoyancy principle using the SSD. A sinker was weighed twice, *i.e.*,

* Corresponding author.
E-mail address: zhewang@tsinghua.edu.cn (Z. Wang).

http://dx.doi.org/10.1016/j.fluid.2015.08.029
0378-3812/

Table 1
Review of volumetric measurements on the binary system (carbon dioxide + methane).[a]

T/K	p/MPa	x/mole fraction of CO_2	Uncertainties[b] of T; p; ρ	Author	Year
311–478	1.4–68.9	0.15, 0.39, 0.59, 0.80	n/a; n/a; 0.1%	Reamer et al. [1]	1944
293–453	4.1–19.3	0.20, 0.40, 0.60, 0.80	n/a; n/a; n/a	Beer [2]	1969
253–288	2.4–14.5	0.45–0.96	0.01 K; 0.1 MPa; n/a	Arai et al. [3]	1971
283–322	4.7–20.7	0.91[c]	n/a; n/a; n/a	Simon et al. [4]	1977
225–400	2.1–35.8	0.98	0.03 K; 0.01%; 0.1%	Magee and Ely [5]	1988
300–320	0.2–9.8	0.1, 0.3, 0.68, 0.90	0.005 K; 0.005%–0.015%; n/a	Brugge et al. [6]	1989
323.15	8.1–12.6	0.001	0.01 K; 0.1%; n/a	McElroy et al. [7]	1989
205–320	0.1–48.4	0.47608	0.01 K; 0.005%–0.015% p; n/a	Esper et al. [8], Bailey et al. [9]	1989
473.15	100.0	0.10–0.90	0.01 K; 0.01 MPa; n/a	Seitz et al. [10]	1994
673.15	19.9–99.9	0.10–0.90	0.05 K; 0.02 MPa; 1 kg m^{-3}	Seitz and Blencoe [11]	1996
323–573	9.9–99.9	0.10–0.90	0.05 K; 0.02 MPa; 1 kg m^{-3}	Seitz et al. [12]	1996
225–350	1.8–69.5	0.10, 0.29, 0.30, 0.67, 0.90	0.005 K; 0.006 MPa; 0.1%	Hwang et al. [13]	1997
250–400	1.0–20.0	0.20, 0.40, 0.60	less than 0.004 K; 0.005 MPa; 0.07 kg m^{-3} ($k = 2$)	Mondejar et al. [14]	2012

[a] There are also data in the GERG databank (Jaeschke and Humphreys [15] and Jaeschke et al. [16]), yet the original data were unavailable to us.
[b] The uncertainties listed are just for information purpose. From the current point of view, they may not be reliable because i) the confidence probability was not provided in the original paper; ii) there was no general standard to declare the measurement uncertainty at that time; or iii) no complete analysis on the measurement uncertainty was performed for these apparatuses. The uncertainty guidance we followed is GUM [17].
[c] In total, the mixture contained a 0.0062 mol fraction of impurities, including nitrogen, ethane, and propane.

W_{vac} in the evacuated environment and W_{fluid} when immersed in the fluid sample. The density of the fluid sample can be calculated by

$$\rho(T,p) = \frac{W_{vac}(T) - W_{fluid}(T,p)}{V_{sinker}(T,p)}, \quad (1)$$

where $V_{sinker}(T, p)$ is the volume of the sinker at temperature T and pressure p. The sinker adopted in our apparatus (type: FluiDENS, Rubotherm, Germany) was made of monocrystalline silicon. $V_{sinker}(T, p)$ was related to T and p as follows:

$$V_{sinker}(T,p) = V_0 \cdot \left[1 + 3 \cdot \overline{\alpha}\Big|_{T_0}^{T} \cdot (T - T_0) - \frac{1}{K(T)} \cdot (p - p_0)\right], \quad (2)$$

where V_0 is the volume of the sinker at the reference state ($p_0 = 0.10135$ MPa and $T_0 = 293.15$ K); $\overline{\alpha}\Big|_{T_0}^{T}$ is the average value of the linear thermal expansion coefficient, $\alpha(T)$, in the temperature range from T_0 to T; and $K(T)$ is the isothermal compression modulus. The value of $\alpha(T)$ for the monocrystalline silicon from $T = (293–1000)$ K was given by Watanabe et al. [18], and $K(T)$ can be calculated by

$$K(T) = \frac{c_{11}(T) + 2 \cdot c_{12}(T)}{3}, \quad (3)$$

where $c_{11}(T)$ and $c_{12}(T)$ are elastic moduli, with values obtained from the literature [19,20]. Detailed descriptions of our apparatus, the general experimental procedure, and the data analysis method were given by Yang et al. [21], and only a brief introduction concerning the measurement uncertainties is given here. The temperatures of the fluid samples were measured using a calibrated 25 Ω platinum resistance thermometer. The resistance of the thermometer was measured using a precision AC resistance thermometry bridge (type: F700, ASL, U.K.) in reference to a calibrated bridge internal resistor. Pressure measurements were conducted using a calibrated Digiquartz intelligent pressure transmitter (type: 9000-6k-101, Paroscientific, U.S.A.). The sinker ($V \approx 17.3$ cm^3, $m \approx 40.0$ g, $\rho \approx 2.31$ g/cm^3) was weighed inside the high-pressure measuring cell using a magnetic suspension coupling with an analytical balance (type: XP205, Mettler Toledo, Switzerland). The expanded measurement uncertainties ($k = 2$) for the temperature $u(T)$, pressure $u(p)$, and density $u_M(\rho)/\rho$ are 35 mK, 3.4 kPa, and 0.033%, respectively [21].

2.2. Fluid samples

The binary mixture sample (carbon dioxide + methane) with the composition 0.950 mol fraction carbon dioxide was provided by Beijing Beiwen Gas, China. The pure nitrogen (0.999999 mol fraction) used as a calibration fluid, as explained in a previous paper [21], was provided by the same provider. The pure components are described in Table 2. The mixture sample was prepared gravimetrically by the supplier with the expanded uncertainty ($k = 2$) in the composition less than 0.001 mol fraction. At the vicinity of the critical point in the supercritical state and where $(\partial\rho/\partial T)_p$ is large, a tiny composition change would yield a significant variation in density. The contribution of the composition uncertainty to the uncertainty in the density determination $u_x(\rho)$ was roughly estimated by

$$u_x(\rho) = \rho_{GERG}(T, p, \mathbf{x} + \Delta\mathbf{x}) - \rho_{GERG}(T, p, \mathbf{x}), \quad (4)$$

where $\rho_{GERG}(T, p, \mathbf{x})$ is the density calculated by the GERG-2008 EOS [22] at temperature T, pressure p, and composition $\mathbf{x}$. The GERG-2008 EOS is an internationally accepted standard for calculating the thermodynamic properties of natural-gas mixtures, as implemented in the NIST REFPROP database [23]. The value of $\mathbf{x}$ is (0.095, 0.050) mole fraction for the mixture under study. A possible maximal error in the composition was assigned to the value of $\Delta\mathbf{x}$, *i.e.* $\Delta\mathbf{x} = (0.001, -0.001)$ mole fraction.

Table 2
Sample information.

Chemical name	Source	Purification method	Purity/mole fraction	Analysis method
Nitrogen	Beijing Beiwen Gas	None	0.999999	Gas chromatography
Carbon dioxide	Beijing Beiwen Gas	None	0.999995	Gas chromatography
Methane	Beijing Beiwen Gas	None	0.999990	Gas chromatography