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Density characteristics of CO₂ - CH₄ binary mixtures at temperatures from (300 to 308.15) K and pressures from (2 to 18) MPa

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Abstract

The accurate densities of CO₂ – CH₄ binary mixtures with CO₂ mole fraction of 0.0998, 0.2017, 0.3997, 0.6015, 0.7985 and 0.8988 at temperatures from (300 to 308.15) K and pressures from (2 to 18) MPa were measured using a high-precision magnetic suspension balance. The combined standard uncertainties of temperature and pressure were estimated as 0.02 K and 0.001 MPa, respectively. The density measurement uncertainty of MSB was estimated as 0.029 kg·m⁻³. Taking the effect of composition uncertainty and sorption into account, the combined standard uncertainties in the density measurement of CO₂ – CH₄ mixtures were around 0.30% with CO₂ mole fraction lower than 0.60 while they increased up to 0.96% with CO₂ mole fraction higher than 0.80 at pressure of 9.0 ~ 11.0 MPa. The measured densities were compared with the calculation from GERG-2008 EOS. It showed relatively good agreements between the GERG-2008 EOS and the measured densities with CO₂ mole fraction lower than 0.60 at 300 K as the relative deviations were generally within 2.0%. When CO₂ mole fraction was higher than 0.80 at 300 K, the relative deviations firstly increased to the maximum 3.73% in the vicinity of critical pressure and then decreased close to zero with the increasing pressure. The experimental data at other temperatures have the similar variation trends. Thus it's difficult to apply GERG-2008 EOS to predict the density characteristics of CO₂ – CH₄ binary mixtures with high CO₂ mole fraction in the vicinity of the critical point accurately.

Keywords: density; magnetic suspension balance; carbon dioxide; methane; GERG-2008 EOS

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1. Introduction

The accurate thermal physical properties of fluid play significant roles in various scientific and industrial applications. Due to the supercritical characteristic of CO₂, the temperature – pressure – density - composition (T, p, ρ, x) properties of CO₂ and its mixtures have numerous applications in geoscience research, refrigerating engineering, fossil fuel industries, and supercritical fluid extraction, especially the carbon capture, utilization and sequestration (CCUS). Generally, the thermal physical properties are described by the equation of state (EOS). To improve the accuracy of the EOS, the reliable and accurate experimental measurements of the (T, p, ρ, x) properties are necessary.

Table 1. Review of T - p - ρ - x measurements of CO₂ - CH₄ binary mixtures.

x^a	T/K	p/MPa	Number of the points	Author	Year
0.15, 0.39, 0.59, 0.80	311-478	1.4-68.9	560	Reamer et al.[1]	1944
0.20, 0.40, 0.60, 0.80	293-453	4.1-19.3	28	Beer[2]	1969
0.45-0.96	253-288	2.4-14.5	179	Arai et al.[3]	1971
0.8994 ^b	9.4-48.9	4.7-20.7	65	Simon et al.[4]	1977
0.4574, 0.5104	381-452	8.0-12.9	24	Tong and Liu[5]	1984
0.98	225-400	2.1-35.8	91	Magee and Ely[6]	1988
0.10, 0.30, 0.68, 0.90	300-320	0.2-9.8	155	Brugge et al.[7]	1989
0.47608	205-320	0.1-48.4	119	Esper et al.[8]	1989
0.001	323.15	8.1-12.6	11	McElroy et al.[9]	1989
0.4820	323.15-423.15	6.5	56	Mallu and Viswanath[10]	1990
0.10-0.90	473.15	100.0	9	Seitz et al.[11]	1994
0.10-0.90	673.15	19.9-99.9	44	Seitz and Blencoe[12]	1996
0.10-0.90	323-573	9.9-99.9	194	Seitz et al.[13]	1996
0.10, 0.29, 0.30, 0.67, 0.90	225-350	1.8-69.5	228	Hwang et al.[14]	1997
0.997	308.15	5.4-12.1	22	Zhang et al.[15]	2002
0.20, 0.40, 0.60	250-400	1.0-20.0	248	Mondejar et al.[16]	2012
0.8525, 0.9719, 0.9809, 0.9902, 0.9932, 0.9961	253.15-333.15	0.1-20.0	49 000	Blanco et al.[17]	2012
0.95	300.15-313.15	2.0-12.0 ^c	181	Yang et al.[18]	2016

a. The mole fraction of CO₂; b. the methane mole fraction was 0.0944, and other components were N₂ and C₂-C₆;

c. The majority of the experimental points were concentrated on pressure range of 8.0-10.0 MPa in the vicinity of critical pressure of CO₂ in Yang et al.[18].

In recent years, CO₂ sequestration with enhanced oil or gas recovery attracts increasing attentions due to its increasing hydrocarbon production and geological sequestering CO₂

simultaneously. During the application of CO₂ geological sequestration with enhanced gas recovery, the density and volumetric characteristics of CO₂ – CH₄ mixtures have significant influences on the estimation of fluid flow and CO₂ storage safety. To our knowledge, there were a number of reported experimental density data of CO₂ - CH₄ binary mixtures, listed in Table 1. However, except Yang et al.[18] measured the density of CO₂ - CH₄ with CO₂ mole fraction of 0.950 at temperature from (300.15 to 313.15) K and the supercritical pressure from (8.0 to 10.0) MPa, the available data in the vicinity of the critical point of CO₂ was still scarce. Therefore, in this work, we measured the densities of CO₂ - CH₄ binary mixtures with CO₂ mole fraction from of 0.0998, 0.2017, 0.3997, 0.6015, 0.7985 and 0.8988, temperatures from (300 to 308.15) K and pressures from (2 to 18) MPa using a high-precision magnetic suspension balance (MSB).

2. Experiment Apparatus

2.1 Material

The CH₄, CO₂ and N₂ were provided by Dalian Special Gases Co., LTD, China, with all the nominal purity of 0.99999 mole fraction, respectively. Simultaneously, six CO₂ - CH₄ binary mixtures with CO₂ mole fraction of 0.0998, 0.2017, 0.3997, 0.6015, 0.7985 and 0.8988 were prepared gravimetrically by the same provider, and the combined uncertainty in the composition was less than 0.001 mole fraction. The details of the pure components were described in Table 2.

Table 2. Details of the pure components

Chemical name	Source	CAS number	Purity/ mole fraction	Molar mass/g·mol ⁻¹
Nitrogen	Dalian Special Gases	7727-37-9	0.99999	28.0134
Carbon dioxide	Dalian Special Gases	124-38-9	0.99999	44.0095
Methane	Dalian Special Gases	74-82-8	0.99999	16.0425

2.2 Apparatus and procedure

A magnetic suspension balance manufactured by Rubotherm Präzisionsmesstechnik GmbH was applied to measure the density of CO₂ - CH₄ mixture in this work. The schematic diagram was shown in Fig. 1, and the detailed equipment parts of the MSB and the working states were similar as Klimeck et al.[19]. The density measurement using MSB was based on the Archimedes' principle, which was presented in our previous research [20; 21] in detail. The fluid density was obtained by weighing the sinker made of titanium in the measured fluid, whose volume was known.

$$\rho(T, p) = \frac{m - m_{\text{fluid}}(T, p)}{V(T, p)} \quad (1)$$

where, m , $m_{\text{fluid}}(T, p)$, $V(T, p)$ and $\rho(T, p)$ were the true mass (mass in the vacuum) of the sinker, the apparent mass (weighed in the measuring fluid) of the sinker, the volume of the sinker and the density of the measuring fluid, respectively, on the condition of temperature T and pressure p . $V(T, p)$ can be obtained from the volume V_0 on the reference condition at (T_0, p_0) , from the following equation.

$$V(T, p) = V_0 \left[1 + \alpha_T(T - T_0) - \frac{1}{K_T}(p - p_0) \right] \quad (2)$$

Where α_T and K_T were the isobaric thermal expansion coefficient and the isothermal compressibility module, both of which were functions of temperature and stated by the manufacturer. The reproducibility (standard deviation), resolution and uncertainty in density of the MSB were $\pm 30 \mu\text{g}$, $8 \cdot 10^{-4} \text{ kg} \cdot \text{m}^{-3}$ and $\pm(0.1\% + 4 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3})$, respectively.

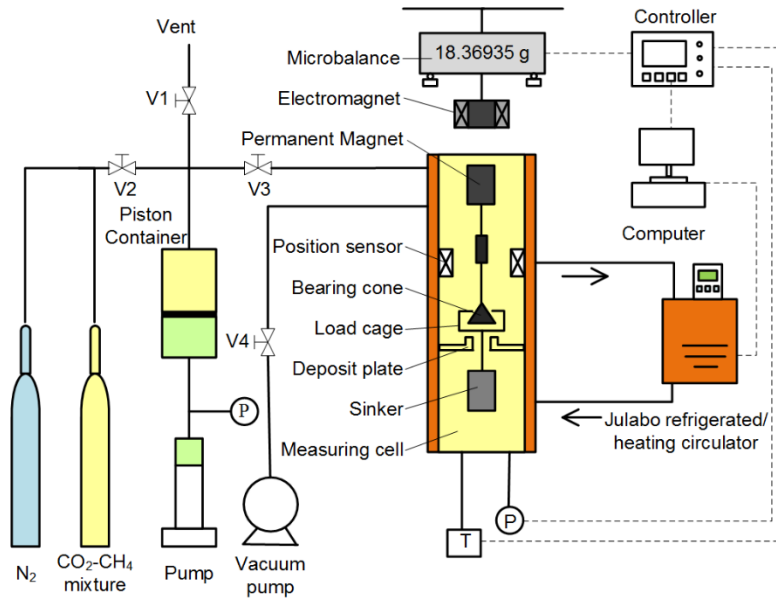


Fig. 1 Schematic diagram of the experiment system.

Outside the measuring cell, a double-walled thermostatic jacket was connected with a refrigerated/heating circulator (Julabo, FP 50-ME) to control the temperature of the target gas in the measuring cell to the required value, and the temperature was detected by a resistance thermometer (Pt100). The target gas was pressurized and stabilized by the piston container and pump, and measured by a pressure sensor (Druck, PMP 4010) up to 20 MPa, with the reproducibility of 0.08%.

The leakage detection of the whole system was examined by N₂ up to 19 MPa to assure no leakage of CO₂ - CH₄ binary mixture during measurement.

Table 3. The measured density data of N₂ by MSB and the corresponding uncertainties at pressure of 2.6 - 18.3 MPa and temperature of 304 - 305 K.

T/K	P/MPa	$\rho_{\text{NIST}}/\text{kg}\cdot\text{m}^{-3}$	$\rho_{\text{exp}}/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{NIST}} - \rho_{\text{exp}})}{\rho_{\text{NIST}}}$	u_T/K	u_p/MPa	$\frac{u_M(\rho)}{\rho}$
304.03	17.990	190.600	190.640	-0.021	0.013	0.0008	0.00008
304.10	16.877	179.950	180.004	-0.030	0.011	0.0016	0.00017
304.15	15.984	171.250	171.278	-0.016	0.007	0.0011	0.00008
304.16	14.927	160.800	160.840	-0.025	0.009	0.0011	0.00011
304.17	13.944	150.930	150.964	-0.023	0.011	0.0011	0.00008
304.11	12.948	140.820	140.851	-0.022	0.011	0.0009	0.00011
304.15	11.901	129.970	129.994	-0.019	0.008	0.0006	0.00006
304.16	10.861	119.060	119.075	-0.013	0.008	0.0008	0.00005
304.23	9.837	108.160	108.209	-0.045	0.007	0.0009	0.00007
304.13	8.812	97.195	97.213	-0.018	0.023	0.0009	0.00027
304.15	7.820	86.448	86.489	-0.048	0.019	0.0009	0.00014
304.11	6.796	75.276	75.316	-0.053	0.016	0.0015	0.00034
304.12	5.782	64.132	64.151	-0.030	0.010	0.0006	0.00027
304.14	4.379	48.624	48.633	-0.019	0.010	0.0010	0.00033
304.15	2.926	32.498	32.502	-0.012	0.006	0.0008	0.00016
304.88	18.305	192.920	192.939	-0.010	0.013	0.0007	0.00006
304.73	16.296	173.890	173.901	-0.006	0.008	0.0008	0.00006
304.77	14.270	153.860	153.864	-0.002	0.008	0.0006	0.00004
304.75	12.245	133.230	133.207	0.017	0.014	0.0006	0.00004
304.78	10.988	120.110	120.097	0.011	0.013	0.0006	0.00005
304.83	10.043	110.100	110.076	0.022	0.013	0.0006	0.00005
304.75	8.937	98.317	98.306	0.011	0.015	0.0008	0.00004
304.83	8.012	88.307	88.260	0.053	0.011	0.0006	0.00004
304.66	7.983	88.046	88.017	0.033	0.009	0.0008	0.00004
304.69	7.136	78.835	78.822	0.016	0.014	0.0008	0.00004
304.89	6.933	76.558	76.521	0.048	0.011	0.0006	0.00005
304.82	5.885	65.100	65.065	0.054	0.012	0.0006	0.00004
305.04	4.986	55.155	55.132	0.041	0.012	0.0008	0.00004
305.17	4.987	55.146	55.120	0.047	0.015	0.0012	0.00007
304.77	4.983	55.180	55.145	0.063	0.014	0.0006	0.00004
304.66	3.534	39.175	39.150	0.064	0.015	0.0006	0.00006
304.88	3.013	33.375	33.353	0.067	0.009	0.0006	0.00007
304.80	3.016	33.416	33.394	0.067	0.016	0.0007	0.00012
304.55	2.607	28.903	28.885	0.062	0.011	0.0008	0.00011

Prior to the experiment, the mass and volume of the sinker was calibrated to ensure the accuracy of measurement. The accuracy and reliability of the system were tested by the density measurement of N_2 , and the details can refer to the previous study [21]. In this work, the densities of N_2 at pressure of 2.6 - 18.3 MPa and temperature of 304 - 305 K were measured, and the results were in good accordance with the standard values from database of National Institute of Standards and Technology (NIST) [22] with a maximum deviation 0.07%. The detailed density data of N_2 and corresponding uncertainties were presented in Table 3. The thermodynamics properties of N_2 in NIST database were determined using the equation of state of Span et al.[23] and auxiliary model of Jacobsen et al.[24], and the uncertainty in density calculated by Span et al.[23] is 0.02% at pressures less than 30 MPa. As a result, the measured density using MSB is accurate.

Due to the scarcity of density data of CO_2 - CH_4 binary mixture in the vicinity of the critical point of CO_2 , the experimental temperatures were set as 300, 303.15, 305.15 and 308.15 K, and pressure in the range of 2 to 18 MPa, shown in Fig. 2, with CO_2 mole fraction of 0.10, 0.20, 0.40, 0.60, 0.80 and 0.90. One set of verification measurements were scheduled on the condition of 0.10 CO_2 mole fraction and 300 K with the same pressures of Brugge et al. [7] and Hwang et al. [14] to verify the experiment reliability.

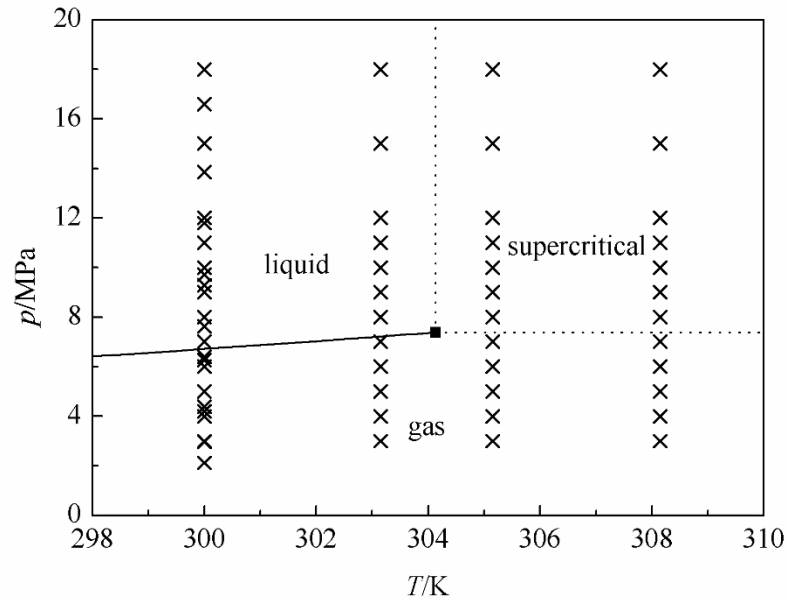


Fig. 2 The experimental temperature and pressure range for the density measurement of CO_2 - CH_4 binary mixtures in this work, ■, the critical point of CO_2 , —, the vapor-liquid phase boundary of CO_2 , · · ·, the supercritical phase boundary of CO_2 , and ×, the measuring points.

3. Results and Discussion

3.1 Uncertainty

The measurement uncertainty of the density using MSB $u_M(\rho)$ was calculated by the following equation.

$$u_M(\rho) = \sqrt{\left(\frac{\partial \rho}{\partial m}\right)^2 u_m^2 + \left(\frac{\partial \rho}{\partial m_{\text{fluid}}}\right)^2 u_{m_{\text{fluid}}}^2 + \left(\frac{\partial \rho}{\partial V}\right)^2 u_V^2} \quad (3a)$$

where, m , m_{fluid} , and V were the same as Eq. 1, and meanwhile, u_m , $u_{m_{\text{fluid}}}$ and u_V represented the uncertainties of the measured density caused by m , m_{fluid} , and V , respectively. According to Eq. 2, the volume uncertainty can be expressed as follows.

$$u_V = \sqrt{\left(\frac{\partial V}{\partial T}\right)^2 u_T^2 + \left(\frac{\partial V}{\partial p}\right)^2 u_p^2} \quad (3b)$$

where, u_T and u_p were combined standard uncertainty of temperature T and pressure p , estimated as follows[25].

$$u_i = \sqrt{u_{Ai}^2 + u_{Bi}^2} \quad (3c)$$

where, i denoted the temperature T or pressure p , and u_{Ai} and u_{Bi} were Type A standard uncertainty and Type B standard uncertainty for temperature T or pressure p , respectively. The combined standard uncertainties of temperature T and pressure p were estimated as $u_T = 0.02$ K and $u_p = 0.001$ MPa in this work, respectively, and the detailed u_T and u_p of every experiment point were listed in Table 4. Therefore, according to the estimation of volume uncertainty in Eq. 3b, the temperature uncertainty and pressure uncertainty were taken into account in the density measurement of CO₂-CH₄ binary mixture of this work. As a result, the average measurement uncertainty $u_M(\rho)$ was estimated as 0.029 kg·m⁻³.

The sorption of gas-mixture components on the internal surfaces of the measuring cell would influence the accuracy of density measurement. The sorption effect on the density uncertainty using MSB $u_s(\rho)/\rho$ was considered to be 0.1% as suggested by Richter and Kleinrahm [26].

The densities of CO₂ - CH₄ binary mixtures were measured in the vicinity of the critical

temperature of CO₂ where a tiny change of composition could cause a significant density variation. Therefore, the density uncertainty caused by the composition uncertainty $u_x(\rho)$ must be taken into consideration, which was estimated by the following equation [18].

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

where $\rho_{\text{GERG}}(T, p, x)$ was the density calculated using GERG-2008 EOS[27], and Δx was the composition uncertainty. GERG-2008 EOS is a widely adopted EOS for the thermodynamic properties of natural gases based on 21 natural gas components, including CH₄ and CO₂. Kunz et al. [27] reported that the uncertainties of GERG-2008 in gas-phase density were 0.1 % over the temperature range from (250 to 450) K at pressures up to 35 MPa, and in liquid phase density were (0.1 to 0.5) % up to 40 MPa, respectively, for a broad variety of natural gases and related mixtures. As for the two selected natural gas mixtures containing CO₂ mole fractions of about 0.14 and 0.20, the deviations in density were larger than others but never exceed 0.5 %. The uncertainty of GERG-2008 in compressed-liquid densities was also estimated as (0.1 to 0.2) % for some binary mixtures, such as methane–nitrogen, methane–ethane and so on. Simultaneously, the experimental density data in CO₂ - CH₄ mixture of Reamer et al.[1], Brugge et al.[7], Seitz and Blencoe[12], Seitz et al.[13] and Hwang et al.[14] were taken into account to determine the binary parameter of CO₂ - CH₄ in GERG-2008 [28]. It was claimed that GERG-2008 described the thermodynamic properties of many binary mixtures accurately, such as CO₂-CH₄, and the typical deviations were within (0.5 to 1) % in density. Due to the scarce experimental data around critical point of CO₂, the uncertainty of GERG-2008 in the critical region need to be further researched. Therefore, the contribution of the composition uncertainty to the density uncertainty was estimated by GERG-2008 EOS using Eq. 4. The composition uncertainty Δx was in the range of (-0.001, 0.001) mole fraction according to the data supplied by Dalian Special Gases Co., LTD.

Overall, in the density measurement of CO₂ - CH₄ binary mixture, the combined standard uncertainty $u_c(\rho)$, would be composed of measurement uncertainty $u_M(\rho)$, composition uncertainty effect $u_x(\rho)$ and adsorption effect $u_s(\rho)$ as the following equation.

$$u_c(\rho) = \sqrt{u_M(\rho)^2 + u_x(\rho)^2 + u_s(\rho)^2} \quad (5)$$

The combined standard density uncertainties $u_c(\rho)$ at different experimental conditions were

determined using Eq. 5. The $u_c(\rho)/\rho$, listed in Table 4, changed very little with pressure with CO₂ mole fraction of 0.0998, 0.2017, 0.3997 and 0.6015, around 0.30%, while the $u_c(\rho)/\rho$ with CO₂ mole fraction of 0.7985 and 0.8988 peaked at pressure of 9.0 ~ 11.0 MPa, with the maximum value 0.96%. Furthermore, $u_x(\rho)$ was the major contribution to $u_c(\rho)$ while the measurement uncertainty $u_M(\rho)$ was small, with the average value 0.029 kg·m⁻³.

3.2 Discussion of the Results

The experiment results (T, p, ρ, x) of CO₂ – CH₄ binary mixtures were listed in Table 4. In addition, the combined standard uncertainties $u_c(\rho)/\rho$ and the relative deviation of the measured densities and densities calculated from GERG-2008 EOS were assessed and shown in Table 4.

The comparison between the experimental densities of the verification measurements and the reported experimental data of Brugge et al.[7] and Hwang et al.[14] with CO₂ mole fraction of 0.10 at temperature of 300 K were illustrated in Fig. 3. The comparison with Mondejar et al. [16] at 300 K and Simon et al. [4] at 305 K were also plotted. Additionally, the density data of Yang et al.[18] at 300 and 305 K were presented as well for reference due to its temperature-pressure close to the critical point, although the CO₂ mole fraction was 0.950. It's shown that the measured density data in verification measurements of this work had good agreements with the reported experiment data of Brugge et al.[7] and Hwang et al.[14]. The variation trends of the measured density of this work at 300 K with CO₂ mole fraction of 0.20, 0.40 and 0.60 were also the same as the reported experimental data of Mondejar et al. [16]. However, the data with CO₂ mole fraction of 0.90 at 305 K of this work and Simon et al. [4] did not match so well. At pressure of 15 and 18 MPa, the measured densities of this work were bigger than that of Simon et al. [4] while the measured densities were smaller than that of Simon et al. [4] at other pressures. Through the comparison of Yang et al.[18] and this work, it's shown that the density variation gradient with pressure is larger in the vicinity of critical point at the high CO₂ mole fraction than that at low mole fraction in the vicinity of critical point.

Simultaneously, the corresponding relative deviations between the measured density and the calculated values from GERG-2008 EOS were shown in Fig. 4. The calculated results of GERG-2008 excellently agreed with the reported data of Brugge et al.[7], Hwang et al.[14], Mondejar et al. [16] with CO₂ mole fraction of 0.10, 0.20 and 0.40 at 300 K as the relative

deviations were very small. The density data of this work on the same condition above were also predicted accurately by GERG-2008 with very small relative deviations. And the relative deviations of Brugge et al.[7] were small with CO₂ mole fraction of 0.90 at pressure of 0.2-6.4 MPa. With CO₂ mole fraction of 0.90, the relative deviations of Hwang et al.[14] increased firstly and then decreased with pressure at 300 K, and reached to the maximum at pressure of 8.0-10.0 MPa, in the vicinity of the critical pressure of CO₂. On this condition, the deviation tendency of this work was similar to Hwang et al.[14], but the maximum deviations, 3.37% at 9.0 MPa, was a little bigger than that of Hwang et al.[14], 2.22% at 8.7 MPa, while the experiment data of Brugge et al.[7] and Hwang et al.[14] were applied for the optimization on the binary parameters of CO₂-CH₄ of the GERG-2008[28]. The deviations of Simon et al. [4] at 305 K increased from -8.78% at 9.0 MPa to 2.79% at 17.9 MPa. Nevertheless, the deviation tendency of this work at 305 K was similar to that at 300 K, and the maximum was 3.81% at 10.0 MPa. Except for the pressure in the range of 8.0-12.0 MPa, the relative deviations of this work at 300 K and 305 K at other pressures were within 2.0%. The data of Yang et al.[18] with CO₂ mole fraction of 0.950 also had large relative deviation, about 3.45%, when the experimental pressure close to the critical pressure, and then the relative deviation decreased with pressure. In consequence, the measured density data agreed with the reported experimental densities of Brugge et al.[7] and Hwang et al.[14] at 0.10 CO₂ mole fraction at 300 K and the relative deviations tendencies with the calculation of GERG-2008 were within 2.0 % except for the pressure range in 8.0-12.0 MPa with maximum deviation of 3.81% at 300 K and 305 K.

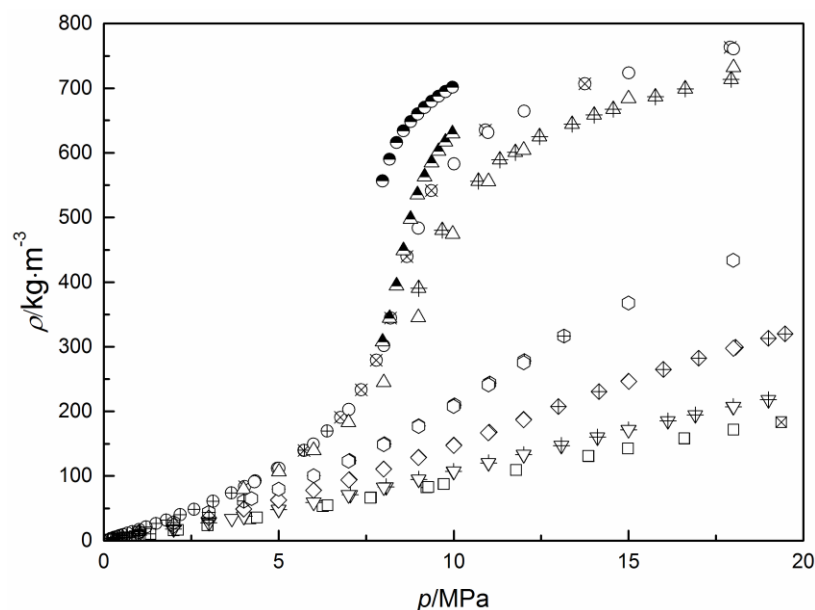


Fig. 3 The density comparison of the experimental results of this work and the reported data at 300 K: \boxplus and \oplus , Brugge et al. [7] at $T=300$ K, $x=0.09990$ and $x=0.90112$; \boxtimes and \boxtimes , Hwang et al. [14] at $T=300$ K, $x=0.09826$ and $x=0.90112$; ∇ , \diamond and \oplus , Mondejar et al. [16] at $T=300$ K, $x=0.199778$, $x=0.400637$ and $x=0.601623$; \bullet , Yang et al.[18] at $T=300.15$ K, $x=0.950$; \square , ∇ , \diamond , \square , and \circ , this work at $T=300$ K, $x=0.0998$, $x=0.2017$, $x=0.3997$ and $x=0.6015$ and $x=0.8988$; and at 305 K: \triangle , Simon et al. [4] at $T=305.37$ K, $x=0.8994$; \blacktriangle , Yang et al.[18] at $T=305.15$ K, $x=0.950$; \triangle , this work at $T=305.15$ K, $x=0.8988$.

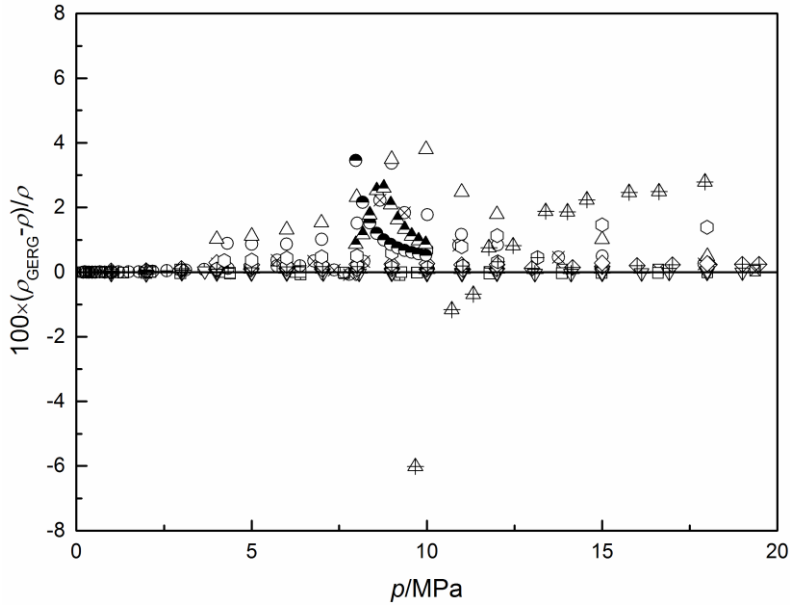


Fig. 4 The relative deviation between the calculated results from GERG-2008 and the experimental densities for $\text{CO}_2 - \text{CH}_4$ binary mixtures at 300 K: \boxplus and \oplus , Brugge et al. [7] at $T=300$ K, $x=0.09990$ and $x=0.90112$; \boxtimes and \boxtimes , Hwang et al. [14] at $T=300$ K, $x=0.09826$ and $x=0.90112$; ∇ , \diamond and \oplus , Mondejar et al. [16] at $T=300$ K, $x=0.199778$, $x=0.400637$ and $x=0.601623$; \bullet , Yang et al.[18] at $T=300.15$ K, $x=0.950$; \square , ∇ , \diamond , \square , and \circ , this work at $T=300$ K, $x=0.0998$, $x=0.2017$, $x=0.3997$ and $x=0.6015$ and $x=0.8988$; and at 305 K: \triangle , Simon et al. [4] at $T=305.37$ K, $x=0.8994$; \blacktriangle , Yang et al.[18] at $T=305.15$ K, $x=0.950$; \triangle , this work at $T=305.15$ K, $x=0.8988$.

The relative deviations between measured densities and the calculated values from GERG-2008 EOS changed with pressure at CO_2 mole fraction of 0.0998, 0.2017, 0.3997, 0.6015, 0.7985 and 0.8988 at 300 K, which were illustrated in Fig. 5. The variation curves at other temperatures were similar. Firstly, the relative deviations with CO_2 mole fraction of 0.0998, 0.2017 and 0.3997 at 300 K were comparatively small, no more than 0.5%. However, on the condition of high CO_2 mole fraction, 0.7985 and 0.8988, the variation trend of the relative deviations firstly increase and then decrease with the increasing pressure. Obviously, the relative deviations increased to the maximum up to 2.21% at pressure of 11.0 MPa with 0.7985 CO_2 mole fraction and 3.37% at

pressure of 9.0 MPa with 0.8988 CO₂ mole fraction, and then decreased. It was supposed that the large deviations appeared in the vicinity of critical point, and the details were analyzed in the next paragraph. In addition, the relative deviations were approximately within 2.0% at 0.7985 and 0.8988 CO₂ mole fraction except in the vicinity of critical pressure, 8.0-12.0 MPa. When CO₂ mole fraction was 0.6015, the changing tendency of relative deviations increase slowly with pressure, but the relative deviations were generally within 2.0%.

Table 4. Experimental densities of CO₂ - CH₄ binary mixtures and density deviations calculated from GERG-2008 EOS.^a

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state ^b
0.0998 CO ₂ + 0.9002 CH ₄							
299.98	2.118	16.647	-0.002	0.014	0.0006	0.0032	G
300.02	2.964	23.652	0.083	0.008	0.0006	0.0030	G
299.99	4.192	34.275	-0.004	0.013	0.0007	0.0029	G
299.98	4.383	35.981	-0.030	0.012	0.0007	0.0029	G
300.04	6.260	53.190	0.002	0.015	0.0006	0.0028	SC
300.00	6.399	54.523	-0.004	0.014	0.0006	0.0029	SC
300.00	7.624	66.394	-0.008	0.013	0.0006	0.0028	SC
300.07	9.277	82.984	-0.004	0.010	0.0007	0.0028	SC
299.98	9.722	87.624	-0.022	0.015	0.0008	0.0028	SC
300.03	11.790	109.201	-0.042	0.011	0.0009	0.0029	SC
299.97	13.852	130.843	-0.033	0.012	0.0008	0.0030	SC
299.99	14.986	142.483	-0.030	0.015	0.0010	0.0030	SC
300.07	16.598	158.420	-0.026	0.014	0.0009	0.0030	SC
300.02	18.000	171.730	-0.015	0.017	0.0023	0.0031	SC
303.12	3.001	23.673	0.046	0.025	0.0007	0.0030	G
303.18	4.002	32.139	0.058	0.008	0.0006	0.0029	G
303.15	5.000	40.895	0.038	0.012	0.0007	0.0028	G
303.16	6.006	50.034	-0.011	0.021	0.0008	0.0029	SC
303.19	7.000	59.247	0.089	0.010	0.0006	0.0028	SC
303.14	8.002	68.892	0.053	0.014	0.0009	0.0029	SC
303.11	9.000	78.724	0.038	0.013	0.0015	0.0029	SC
303.15	10.004	88.738	0.064	0.013	0.0011	0.0029	SC
303.12	11.000	98.851	0.066	0.014	0.0017	0.0030	SC
303.10	12.003	109.095	0.078	0.010	0.0008	0.0029	SC
303.17	14.997	139.317	0.092	0.015	0.0013	0.0030	SC
303.11	18.001	167.945	0.109	0.014	0.0012	0.0030	SC
305.16	3.003	23.496	0.057	0.012	0.0006	0.0030	G
305.16	4.003	31.879	0.066	0.017	0.0009	0.0030	G
305.23	5.002	40.525	0.046	0.011	0.0008	0.0029	G
305.11	5.997	49.434	0.088	0.019	0.0007	0.0028	SC
305.13	6.992	58.605	0.053	0.008	0.0008	0.0028	SC
305.15	7.998	68.122	0.043	0.009	0.0010	0.0028	SC
305.13	9.002	77.799	0.102	0.014	0.0010	0.0028	SC
305.17	10.003	87.669	0.063	0.012	0.0012	0.0029	SC
305.17	10.999	97.609	0.058	0.011	0.0009	0.0029	SC
305.09	12.002	107.694	0.096	0.012	0.0009	0.0029	SC
305.16	14.996	137.438	0.110	0.011	0.0007	0.0029	SC
305.17	18.001	165.624	0.128	0.015	0.0015	0.0030	SC
308.15	3.000	23.193	0.075	0.014	0.0006	0.0030	G

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state
0.0998 CO ₂ + 0.9002 CH ₄							
308.17	3.998	31.420	0.111	0.011	0.0006	0.0029	G
308.21	5.001	39.985	0.056	0.009	0.0008	0.0029	G
308.19	6.002	48.761	0.098	0.010	0.0009	0.0029	SC
308.15	6.999	57.796	0.054	0.014	0.0007	0.0028	SC
308.24	8.000	67.015	0.082	0.008	0.0008	0.0029	SC
308.17	9.004	76.501	0.120	0.008	0.0008	0.0028	SC
308.18	9.999	86.118	0.061	0.012	0.0006	0.0028	SC
308.13	11.000	95.867	0.088	0.011	0.0011	0.0028	SC
308.16	11.997	105.588	0.125	0.013	0.0008	0.0028	SC
308.15	14.997	134.770	0.119	0.015	0.0009	0.0029	SC
308.12	18.004	162.496	0.120	0.012	0.0009	0.0030	SC
0.2017 CO ₂ + 0.7983 CH ₄							
300.00	3.662	34.438	0.034	0.012	0.0006	0.0026	G
299.99	4.000	37.902	0.033	0.016	0.0006	0.0026	G
300.01	5.001	48.462	0.005	0.016	0.0008	0.0026	G
299.99	6.002	59.460	0.011	0.015	0.0008	0.0026	G
299.97	6.997	70.838	0.016	0.016	0.0008	0.0026	SC
299.96	7.999	82.733	0.000	0.012	0.0006	0.0026	SC
299.95	9.002	95.030	-0.004	0.012	0.0008	0.0027	SC
299.99	10.005	107.622	-0.005	0.012	0.0007	0.0027	SC
300.01	11.000	120.384	-0.013	0.008	0.0008	0.0028	SC
299.99	12.000	133.357	0.002	0.014	0.0011	0.0028	SC
300.00	14.999	171.971	0.001	0.012	0.0008	0.0029	SC
299.99	18.001	207.683	0.044	0.012	0.0014	0.0030	SC
303.13	3.999	37.359	0.056	0.012	0.0007	0.0026	G
303.17	4.998	47.685	0.032	0.019	0.0006	0.0026	G
303.17	6.001	58.474	0.028	0.016	0.0007	0.0026	G
303.13	6.999	69.612	0.051	0.011	0.0006	0.0026	SC
303.18	7.999	81.148	0.043	0.014	0.0009	0.0027	SC
303.17	9.001	93.089	0.037	0.012	0.0006	0.0026	SC
303.22	9.998	105.223	0.039	0.008	0.0009	0.0027	SC
303.20	10.996	117.650	0.033	0.008	0.0008	0.0027	SC
303.13	11.999	130.323	0.038	0.008	0.0010	0.0028	SC
303.19	15.005	167.871	0.028	0.007	0.0010	0.0029	SC
303.11	17.996	202.897	0.028	0.012	0.0019	0.0030	SC
305.18	4.001	37.030	0.093	0.013	0.0006	0.0026	G
305.18	5.001	47.235	0.105	0.012	0.0006	0.0026	G
305.22	6.000	57.810	0.121	0.015	0.0007	0.0026	G
305.19	7.000	68.786	0.151	0.017	0.0007	0.0026	SC
305.16	8.002	80.173	0.161	0.013	0.0007	0.0026	SC
305.19	9.001	91.841	0.162	0.015	0.0006	0.0026	SC

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state
0.2017 CO ₂ + 0.7983 CH ₄							
305.20	10.000	103.792	0.162	0.012	0.0011	0.0027	SC
305.15	11.001	116.026	0.174	0.018	0.0009	0.0028	SC
305.15	11.998	128.322	0.171	0.012	0.0010	0.0028	SC
305.18	14.999	165.099	0.180	0.011	0.0009	0.0029	SC
305.16	18.000	199.543	0.223	0.013	0.0010	0.0029	SC
308.16	4.002	36.486	0.313	0.014	0.0007	0.0027	G
308.14	5.002	46.531	0.270	0.012	0.0007	0.0026	G
308.18	6.001	56.895	0.271	0.014	0.0006	0.0026	G
308.18	6.999	67.631	0.260	0.017	0.0007	0.0026	SC
308.11	7.996	78.731	0.242	0.017	0.0008	0.0026	SC
308.13	9.004	90.207	0.251	0.016	0.0007	0.0027	SC
308.13	10.002	101.870	0.237	0.013	0.0010	0.0028	SC
308.14	11.000	113.723	0.228	0.016	0.0011	0.0027	SC
308.20	11.998	125.636	0.232	0.016	0.0012	0.0028	SC
308.16	15.001	161.570	0.216	0.013	0.0009	0.0028	SC
308.12	18.001	195.388	0.229	0.013	0.0008	0.0029	SC
0.3997 CO ₂ + 0.6003 CH ₄							
299.99	4.003	48.763	0.298	0.034	0.0007	0.0024	G
300.06	5.002	62.850	0.231	0.008	0.0009	0.0026	G
299.93	5.997	77.827	0.218	0.013	0.0008	0.0024	G
299.96	7.003	93.846	0.239	0.016	0.0008	0.0025	G
299.97	8.000	110.726	0.244	0.009	0.0006	0.0025	G
299.98	8.997	128.548	0.245	0.010	0.0008	0.0027	SC
300.21	10.004	147.143	0.263	0.015	0.0008	0.0027	SC
300.00	10.995	166.796	0.225	0.012	0.0006	0.0028	SC
299.96	12.001	186.929	0.235	0.006	0.0007	0.0028	SC
300.02	15.007	246.022	0.283	0.012	0.0011	0.0030	SC
300.05	18.002	297.591	0.266	0.014	0.0015	0.0030	SC
303.16	4.001	48.004	0.305	0.010	0.0015	0.0028	G
303.13	4.999	61.796	0.245	0.012	0.0007	0.0024	G
303.18	5.999	76.379	0.259	0.018	0.0007	0.0024	G
303.18	6.996	91.801	0.262	0.010	0.0010	0.0025	G
303.16	8.000	108.241	0.265	0.009	0.0008	0.0025	G
303.20	8.999	125.402	0.271	0.010	0.0008	0.0027	SC
303.21	9.999	143.458	0.245	0.013	0.0007	0.0026	SC
303.20	10.993	162.067	0.230	0.017	0.0010	0.0028	SC
303.15	12.001	181.298	0.296	0.010	0.0006	0.0029	SC
303.29	15.006	237.974	0.373	0.013	0.0008	0.0029	SC
303.21	17.999	288.435	0.514	0.008	0.0009	0.0030	SC
305.10	4.001	47.504	0.434	0.007	0.0007	0.0024	G
305.18	4.996	60.999	0.411	0.010	0.0006	0.0023	G

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state
0.3997 CO ₂ + 0.6003 CH ₄							
305.18	6.000	75.426	0.405	0.009	0.0008	0.0024	G
305.18	7.002	90.651	0.383	0.010	0.0006	0.0024	G
305.22	8.006	106.718	0.370	0.008	0.0006	0.0025	G
305.16	8.998	123.489	0.351	0.011	0.0006	0.0025	SC
305.18	9.997	141.056	0.335	0.009	0.0006	0.0026	SC
305.08	11.001	159.477	0.329	0.008	0.0007	0.0027	SC
305.15	12.006	178.104	0.330	0.010	0.0008	0.0028	SC
305.13	14.994	233.750	0.320	0.016	0.0008	0.0029	SC
305.24	17.994	283.653	0.360	0.008	0.0008	0.0029	SC
308.26	4.003	46.849	0.412	0.007	0.0006	0.0024	G
308.16	5.006	60.225	0.399	0.013	0.0008	0.0024	G
308.14	6.001	74.193	0.434	0.011	0.0012	0.0025	G
308.22	7.001	88.937	0.436	0.009	0.0011	0.0026	G
308.13	8.003	104.538	0.470	0.015	0.0006	0.0024	G
308.15	8.996	120.739	0.440	0.015	0.0007	0.0025	SC
308.17	9.994	137.721	0.395	0.008	0.0006	0.0026	SC
308.08	10.996	155.394	0.409	0.014	0.0007	0.0027	SC
308.23	12.000	173.174	0.426	0.017	0.0010	0.0027	SC
308.14	14.996	227.135	0.436	0.008	0.0006	0.0029	SC
308.16	17.997	276.178	0.499	0.009	0.0006	0.0029	SC
0.6015 CO ₂ + 0.3985 CH ₄							
299.61	4.220	65.102	0.356	0.010	0.0007	0.0022	G
299.96	5.002	79.746	0.376	0.013	0.0008	0.0022	G
299.94	6.004	100.404	0.438	0.013	0.0006	0.0023	G
299.98	7.000	123.126	0.476	0.016	0.0008	0.0026	G
299.98	8.002	148.650	0.502	0.015	0.0013	0.0027	G
300.01	9.002	176.866	0.591	0.012	0.0017	0.0031	SC
300.02	9.996	207.768	0.683	0.011	0.0007	0.0031	SC
300.03	10.998	241.279	0.781	0.010	0.0008	0.0033	SC
299.99	12.004	275.504	1.130	0.011	0.0007	0.0035	SC
300.04	14.998	367.750	1.461	0.006	0.0006	0.0034	SC
300.00	17.997	433.882	1.388	0.013	0.0006	0.0031	SC
303.14	3.995	59.469	1.055	0.012	0.0006	0.0022	G
303.16	5.009	77.914	0.922	0.015	0.0007	0.0022	G
303.23	6.005	97.567	0.999	0.014	0.0006	0.0023	G
303.14	7.004	119.411	1.044	0.013	0.0009	0.0025	G
303.15	8.006	143.460	1.112	0.008	0.0006	0.0026	G
303.16	8.999	169.770	1.160	0.007	0.0006	0.0027	SC
303.15	9.999	198.747	1.223	0.006	0.0006	0.0029	SC
303.10	11.000	229.981	1.310	0.016	0.0008	0.0031	SC
303.19	12.002	261.850	1.423	0.015	0.0008	0.0033	SC

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state
0.6015 CO ₂ + 0.3985 CH ₄							
303.22	15.003	352.168	1.562	0.013	0.0007	0.0033	SC
303.14	17.999	420.157	1.362	0.009	0.0008	0.0031	SC
305.15	3.979	58.587	1.035	0.018	0.0006	0.0022	G
305.14	5.001	76.729	1.079	0.015	0.0006	0.0022	G
305.15	6.000	96.024	1.174	0.013	0.0007	0.0023	G
305.17	6.999	117.142	1.266	0.016	0.0006	0.0024	G
305.18	8.000	140.462	1.287	0.011	0.0007	0.0025	G
305.15	9.004	165.984	1.428	0.012	0.0007	0.0028	SC
305.22	10.006	193.541	1.541	0.008	0.0006	0.0029	SC
305.13	11.012	223.400	1.716	0.012	0.0007	0.0031	SC
305.19	12.005	253.791	1.823	0.011	0.0008	0.0032	SC
305.16	15.000	340.932	2.237	0.014	0.0007	0.0033	SC
305.10	17.995	408.107	2.225	0.017	0.0015	0.0032	SC
308.16	4.004	57.940	1.346	0.011	0.0008	0.0022	G
308.22	5.006	75.217	1.397	0.008	0.0008	0.0022	G
308.14	5.997	93.812	1.472	0.017	0.0007	0.0023	G
308.11	7.002	114.280	1.576	0.013	0.0006	0.0024	G
308.12	8.003	136.504	1.649	0.013	0.0007	0.0025	G
308.14	8.998	160.546	1.730	0.012	0.0007	0.0027	SC
308.16	10.002	186.699	1.820	0.010	0.0008	0.0028	SC
308.13	11.001	214.588	1.915	0.007	0.0006	0.0029	SC
308.14	12.002	243.454	2.061	0.014	0.0010	0.0032	SC
308.13	15.007	328.628	2.141	0.009	0.0008	0.0033	SC
308.19	18.000	395.269	2.220	0.012	0.0009	0.0031	SC
0.7985 CO ₂ + 0.2015 CH ₄							
300.02	3.999	74.633	0.456	0.013	0.0008	0.0021	G
299.99	4.997	99.658	0.527	0.014	0.0006	0.0022	G
299.97	5.996	129.225	0.618	0.011	0.0008	0.0025	G
300.02	6.996	165.378	0.726	0.012	0.0008	0.0029	G
300.00	8.000	212.092	0.987	0.008	0.0006	0.0035	G
300.01	8.998	274.617	1.271	0.012	0.0007	0.0046	SC
299.98	10.003	353.847	1.936	0.014	0.0006	0.0055	SC
299.98	10.997	428.638	2.211	0.008	0.0006	0.0052	SC
300.04	12.001	485.736	1.886	0.008	0.0006	0.0046	SC
300.07	14.999	584.129	1.131	0.011	0.0007	0.0034	SC
300.06	17.999	637.414	0.788	0.011	0.0010	0.0030	SC
303.16	4.000	73.078	0.641	0.016	0.0008	0.0021	G
303.20	5.001	97.235	0.649	0.016	0.0008	0.0022	G
303.13	6.004	125.434	0.739	0.016	0.0006	0.0024	G
303.21	7.002	158.820	0.874	0.015	0.0006	0.0027	G
303.16	7.994	200.301	0.980	0.011	0.0010	0.0032	G

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state
0.7985 CO ₂ + 0.2015 CH ₄							
303.11	9.001	254.341	1.226	0.012	0.0006	0.0040	SC
303.12	10.001	320.908	1.720	0.011	0.0007	0.0048	SC
303.15	11.003	391.279	2.139	0.011	0.0008	0.0051	SC
303.13	11.860	444.556	1.946	0.010	0.0006	0.0047	SC
303.15	14.998	561.073	1.280	0.009	0.0008	0.0035	SC
303.10	18.071	621.015	0.897	0.012	0.0008	0.0030	SC
305.11	3.997	72.035	0.828	0.008	0.0006	0.0021	G
305.12	5.006	95.778	0.888	0.007	0.0006	0.0022	G
305.11	6.003	122.855	0.982	0.012	0.0007	0.0024	G
305.17	7.000	154.794	1.086	0.009	0.0008	0.0027	G
305.24	8.000	193.790	1.164	0.014	0.0009	0.0031	G
305.19	9.001	243.070	1.298	0.008	0.0006	0.0037	SC
305.23	10.000	303.258	1.585	0.007	0.0006	0.0044	SC
305.20	11.001	369.844	1.971	0.016	0.0006	0.0048	SC
305.18	11.999	429.815	2.059	0.011	0.0008	0.0046	SC
305.14	14.994	546.063	1.323	0.011	0.0010	0.0036	SC
305.18	18.002	608.035	0.944	0.015	0.0012	0.0031	SC
308.16	4.006	70.911	0.885	0.013	0.0006	0.0021	G
308.17	5.006	93.740	0.885	0.018	0.0006	0.0021	G
308.19	6.002	119.651	0.951	0.014	0.0008	0.0024	G
308.21	7.002	149.932	1.016	0.011	0.0006	0.0026	G
308.18	8.000	185.875	1.181	0.007	0.0007	0.0029	G
308.16	9.001	229.843	1.320	0.012	0.0006	0.0034	SC
308.22	10.003	282.745	1.509	0.009	0.0007	0.0040	SC
308.14	11.000	342.357	1.961	0.009	0.0009	0.0045	SC
308.12	11.997	401.005	1.994	0.008	0.0008	0.0045	SC
308.13	15.001	523.511	1.389	0.010	0.0014	0.0037	SC
308.17	18.002	590.479	1.024	0.013	0.0015	0.0032	SC
0.8988 CO ₂ + 0.1012 CH ₄							
300.10	4.310	90.75	0.894	0.008	0.0008	0.0022	G
300.04	5.006	112.11	0.864	0.011	0.0006	0.0023	G
300.03	5.996	149.39	0.864	0.011	0.0009	0.0027	G
299.98	7.004	203.10	1.015	0.007	0.0007	0.0037	G
299.96	8.008	302.14	1.511	0.010	0.0007	0.0077	G
299.98	8.997	483.35	3.373	0.015	0.0012	0.0095	SC
300.02	10.011	582.85	1.772	0.014	0.0010	0.0055	SC
299.97	10.986	631.42	1.166	0.013	0.0008	0.0042	SC
299.99	12.017	664.34	0.846	0.013	0.0009	0.0049	SC
299.95	15.006	723.66	0.495	0.013	0.0010	0.0040	SC
300.03	17.999	760.57	0.370	0.012	0.0009	0.0035	SC
303.11	4.004	80.36	1.254	0.013	0.0007	0.0022	G

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\frac{100(\rho_{\text{GERG}} - \rho)}{\rho}$	u_T/K	u_p/MPa	$\frac{u_c(\rho)}{\rho}$	Phase state
0.8988 CO ₂ + 0.1012 CH ₄							
303.17	5.005	108.149	1.630	0.013	0.0008	0.0022	G
303.26	6.002	141.868	2.187	0.015	0.0008	0.0026	G
303.18	7.001	186.521	3.100	0.011	0.0008	0.0033	G
303.16	8.016	253.316	5.530	0.014	0.0006	0.0053	G
303.16	8.992	374.284	7.532	0.012	0.0006	0.0096	SC
303.07	10.005	522.742	2.664	0.008	0.0007	0.0066	SC
303.07	11.007	588.449	2.011	0.011	0.0009	0.0048	SC
303.29	11.998	626.792	1.518	0.009	0.0015	0.0042	SC
303.21	15.000	701.018	0.573	0.008	0.0008	0.0032	SC
303.17	18.000	742.988	0.438	0.008	0.0008	0.0029	SC
305.12	3.998	79.325	1.018	0.013	0.0007	0.0022	G
305.20	5.004	106.835	1.121	0.015	0.0010	0.0024	G
305.23	6.002	139.912	1.317	0.016	0.0010	0.0027	G
305.13	6.994	182.804	1.529	0.013	0.0008	0.0031	G
305.04	7.997	244.829	2.326	0.013	0.0008	0.0045	G
305.21	8.996	345.688	3.492	0.008	0.0008	0.0077	SC
305.06	9.978	474.418	3.805	0.014	0.0009	0.0074	SC
305.16	10.996	555.932	2.480	0.008	0.0013	0.0054	SC
305.20	11.998	604.408	1.792	0.011	0.0020	0.0045	SC
305.21	15.000	683.999	1.010	0.016	0.0018	0.0034	SC
305.01	18.003	732.397	0.488	0.014	0.0012	0.0029	SC
308.23	4.004	78.335	0.478	0.014	0.0006	0.0020	G
308.22	5.002	104.568	0.769	0.012	0.0007	0.0021	G
308.23	5.998	135.871	0.972	0.014	0.0008	0.0024	G
308.06	6.995	175.453	1.211	0.008	0.0007	0.0030	G
308.05	7.997	229.008	1.545	0.008	0.0007	0.0040	G
308.09	8.982	306.981	2.192	0.009	0.0008	0.0059	SC
308.16	9.993	417.764	2.814	0.009	0.0007	0.0074	SC
308.24	11.004	513.225	1.722	0.008	0.0007	0.0059	SC
308.34	11.928	563.033	2.024	0.011	0.0008	0.0048	SC
308.26	14.998	660.797	1.137	0.010	0.0011	0.0036	SC
308.11	18.002	711.774	0.889	0.010	0.0016	0.0032	SC

a. The combined standard uncertainties were $u_T = 0.02$ K, $u_p = 0.001$ MPa and $u_M(\rho) = 0.029$ kg·m⁻³, and the mixture samples were prepared gravimetrically with the composition uncertainty less than 0.001 mole fraction. $u_c(\rho)$ was the combined standard uncertainty of the measured density with taking the measurement uncertainty, composition uncertainty effect and sorption effect into consideration; b. The phase states mean: G, gaseous state; SC, supercritical state.

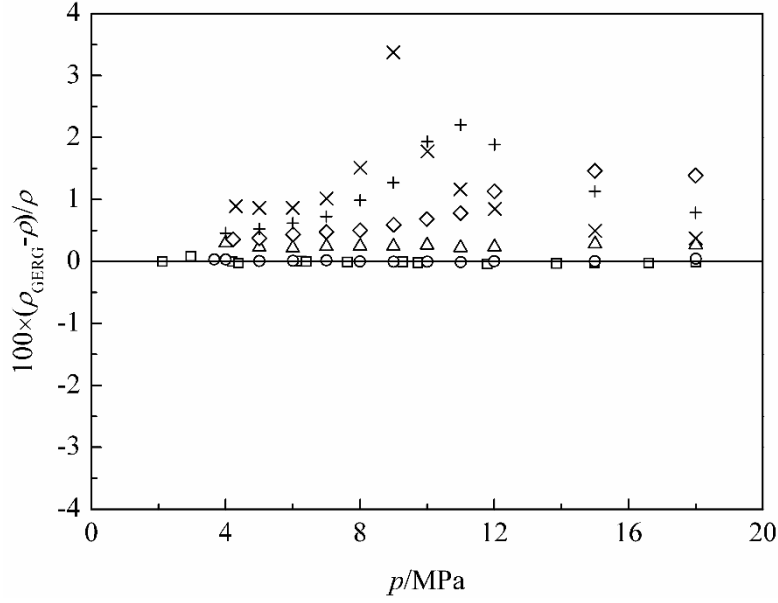


Fig. 5 The relative deviations of experimental densities and calculated values from GERG-2008 for the CO₂ – CH₄ binary mixtures change with pressure at 300 K with CO₂ mole fraction of: □, $x=0.0998$; ○, $x=0.2017$; △, $x=0.3997$; ◇, $x=0.6015$; +, $x=0.7985$; ×, $x=0.8988$.

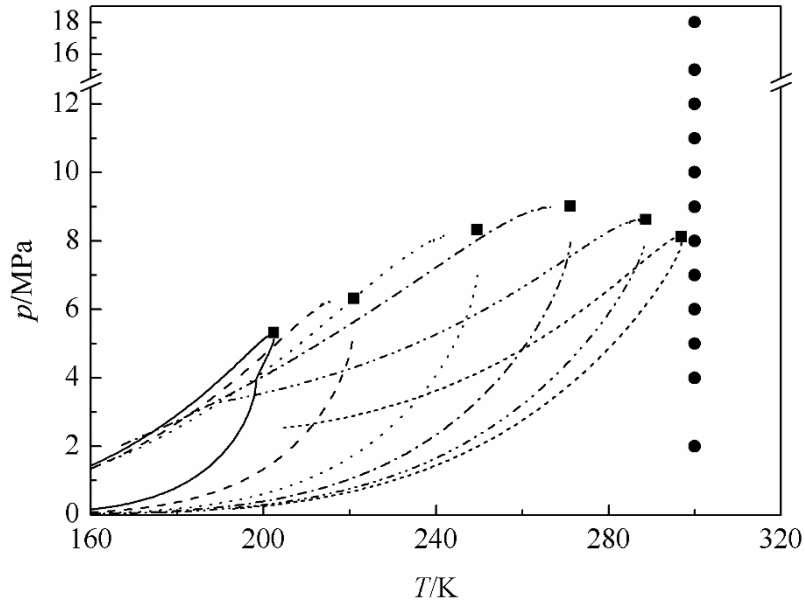


Fig. 6 The vapor-liquid saturation lines and possible critical points of six types of CO₂-CH₄ mixtures, estimated using REFPROP according to GERG-2004: ●, the experimental points; ■, the possible critical points estimated using REFPROP; the different kinds of lines representing the vapor-liquid saturation lines for CO₂-CH₄ mixtures with CO₂ mole fraction of: —, $x=0.0998$; ---, $x=0.2017$; ····, $x=0.3997$; -·-·, $x=0.6015$; -·-·-·, $x=0.7985$; -·-·-·-·, $x=0.8988$.

The vapor saturation lines and liquid saturation lines of the six types of the CO₂-CH₄ mixtures were estimated using the NIST software (REFPROP 9.0), illustrated in Fig. 6. In REFPROP 9.0, the

thermal physical properties of the CO₂-CH₄ mixtures were calculated using GERG-2004 EOS [28]. GERG-2008 was developed and improved from GERG-2004 EOS, and the binary parameters and prediction accuracies of these two EOSs were same for density and vapor-liquid equilibrium of CO₂ - CH₄ mixtures. The critical points were obtained by extending the vapor saturation line and liquid saturation line along the trend of the two lines to end at the meeting-point. Therefore, the critical points were estimated based on vapor saturation line and liquid saturation line and plotted in Fig. 6, and the experimental temperature-pressure points were also figured. Additionally, the phase state of every measured experimental point was added in Table 4 accordingly. The critical temperatures for CO₂-CH₄ mixtures with CO₂ mole fraction of 0.7985 and 0.8988 are close to 300 K, while the critical temperatures of other mixtures are much smaller than 300 K. Simultaneously, the critical pressures are about 8.0-10.0 MPa for CO₂-CH₄ mixtures with CO₂ mole fraction of 0.7985 and 0.8988, respectively. The large deviations of CO₂-CH₄ mixtures with CO₂ mole fraction of 0.7985 and 0.8988 at 300 K may be due to the proximity to the critical point. Because the point of 300 K and 9.0 MPa is more close to the critical point for CO₂-CH₄ mixture with 0.8988 CO₂ mole fraction than the point of 300 K and 11.0 MPa to the critical point for CO₂-CH₄ mixture with 0.7985 CO₂ mole fraction, the deviation is much larger. In conclusion, the deviation becomes larger in the vicinity of critical point than that at other states.

The GERG-2008 EOS had relatively satisfying prediction abilities to describe the densities of CO₂ – CH₄ binary mixtures with CO₂ mole fraction no more than 0.60 at the majority of pressure of 2.0 – 18.0 MPa. Simultaneously, the densities of CO₂ – CH₄ binary mixtures at high CO₂ mole fraction were difficult to be described in the vicinity of critical point.

4. Conclusion

The accurate densities of CO₂ – CH₄ binary mixtures with CO₂ mole fraction of 0.0998, 0.2017, 0.3997, 0.6015, 0.7985 and 0.8988 at temperatures from (300 to 308.15) K and pressures from (2 to 18) MPa were measured using a high-precision magnetic suspension balance. The combined standard uncertainties of temperature and pressure were estimated as 0.02 K and 0.001 MPa, respectively. Without considering other effects, the density measurement uncertainty of MSB was estimated as 0.029 kg·m⁻³. Taking the composition uncertainty effect and sorption effect into account, the combined uncertainties in the density measurement of the CO₂ – CH₄ binary mixtures were around 0.30% with CO₂ mole fraction lower than 0.60 while they increased up to 0.96% at

pressure of 9.0 ~ 11.0 MPa at CO₂ mole fraction higher than 0.80. The composition uncertainty played a dominant role on the combined uncertainty of mixture density.

The measured densities had good agreements with the reported experimental data of Brugge et al.[7] and Hwang et al.[14] with CO₂ mole fraction of 0.10 and 0.90 at temperature of 300 K. Additionally the measured densities were compared with the densities calculated from GERG-2008 EOS. It showed a relatively satisfying agreement between the GERG-2008 EOS and the measured density with CO₂ mole fraction no more than 0.60 as the relative deviations were generally within 2.0%. The relative deviations were approximately within 2.0% except few data points with CO₂ mole fraction higher than 0.80 in the vicinity of critical pressure. The relative deviations firstly increased up to maximum in the vicinity of critical pressure and then decreased close to zero with the increasing pressure. Thus, the density prediction abilities of GERG-2008 EOS in the vicinity of critical pressure at high CO₂ concentrations were not as good as low CO₂ concentration conditions. According to the density data of CO₂ – CH₄ binary mixtures in this work, the model should be improved to enhance the accurate prediction of the thermophysical characteristics of CO₂ – CH₄ binary mixture in the vicinity of critical point, and this would be the future focus of our study.

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