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**The phase equilibrium and density studies of the ternary mixtures of CO<sub>2</sub> + Ar + N<sub>2</sub> and CO<sub>2</sub> + Ar + H<sub>2</sub>, systems relevance to CCS technology**

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## Abstract

The  $p$ - $T$  phase diagrams of two ternary systems ( $\text{CO}_2 + \text{Ar} + \text{N}_2$  and  $\text{CO}_2 + \text{Ar} + \text{H}_2$ ) have been measured at temperatures between 268 and 303 K using a fibre-optic phase equilibrium analyser.  $\text{CO}_2$ , which is the major component, has a mole fraction ranging from 0.90 to 0.98 in both systems. The molar ratio of the two minor components is  $\text{Ar}:\text{N}_2 = 1:1$  and  $\text{Ar}:\text{H}_2 = 2:3$ , respectively for the two ternary systems. In addition, the density of a ternary mixture with  $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$  is reported at 293.15 K, 303.15 K, 313.15 K and 333.15 K and pressures up to 23 MPa. The new experimental phase equilibrium and density data have also been used to evaluate the GERG-2008/EOS-CG, gSAFT and Peng-Robinson equations of state. Among these equations, EOS-CG exhibits the best predictions on both the  $p$ - $T$  phase diagrams and densities of  $\text{CO}_2 + \text{Ar} + \text{N}_2$ ; and gSAFT gives the lowest average absolute deviation between the predicted and the measured bubble-point pressures of  $\text{CO}_2 + \text{Ar} + \text{H}_2$ .

Keywords: carbon capture and storage, carbon dioxide, argon, nitrogen, hydrogen, vapour-liquid equilibrium, density, equation of state.

# 1. Introduction

Carbon Capture and Storage (CCS) is one of the few carbon mitigation technologies that offers a balance of scale, feasibility, grid stability and energy security (Metz et al., 2005). In the long term, if the least-cost trajectory to the 2 °C temperature-rise limit cannot be maintained, more stringent measures will have to be taken to constrain the cumulative CO<sub>2</sub> emissions in the second half of the 21st century. CCS may also be the only way to achieve zero/negative emissions when, for example, using biomass as fuel (IPCC, 2013).

The major obstacle for CCS deployment on a large scale is the high cost for both infrastructure and operation. The cost at the capture stage can be reduced by tolerating more impurities in CO<sub>2</sub> streams at the price of lower storage capacity and decreased efficiency for compression and transportation. The design, optimisation and full economic evaluation of the compression, transportation and injection stages need to be conducted for CO<sub>2</sub> streams with a range of impurities at different concentrations. The captured CO<sub>2</sub> stream is a multi-component mixture. The major component is CO<sub>2</sub> often at a mole fraction between 95% and 99%; and the minor components are N<sub>2</sub>, Ar, H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, SO<sub>2</sub>, CO, H<sub>2</sub>S and H<sub>2</sub>O at the composition range from several hundred ppm to several percent (de Visser et al., 2008; Metz et al., 2005). The key binaries are those between CO<sub>2</sub> and one of the minor components, e.g. CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>O.

Accurate thermodynamic properties of impure CO<sub>2</sub> systems are critical information for the computational design and modelling of the CCS processes. Recently, much attention has been given to studies of the thermodynamic properties, such as vapour-liquid equilibrium (VLE) and density of CO<sub>2</sub> mixtures with impurities. A number of research groups have studied some of these key binaries, such as CO<sub>2</sub>/N<sub>2</sub> (Fandino et al., 2015; Mantovani et al., 2012; Tenorio et al., 2015; Westman et al., 2016b), CO<sub>2</sub>/Ar (Coquelet et al., 2008; Köpke and Eggers, 2007; Mantovani et al., 2012; Yang et al., 2015a), CO<sub>2</sub>/H<sub>2</sub> (Cipollina et al., 2007; Fandino et al., 2015; Sanchez-Vicente et al., 2013; Tenorio et al., 2015), CO<sub>2</sub>/O<sub>2</sub> (Mantovani et al., 2012; Westman et al., 2016a), CO<sub>2</sub>/SO<sub>2</sub> (Coquelet et al., 2014; Köpke and Eggers, 2007), CO<sub>2</sub>/CO (Cipollina et al.,

2007), CO<sub>2</sub>/H<sub>2</sub>S (Chapoy et al., 2013a) and CO<sub>2</sub>/H<sub>2</sub>O (Hou et al., 2013; Valtz et al., 2004), which either focused on the binaries with an insufficient amount of data under the conditions relevant to CCS or aimed at reducing experimental uncertainties. A comprehensive data survey of the available thermodynamic properties of binary systems with CO<sub>2</sub> can be found in the monograph by Kunz et al. (2007) and in the recent reviews by Munkejord et al. (2016) and Li et al. (2011).

The data for the binary systems are primarily used for fitting the binary interaction parameters required by the equation of state (EoS) to calculate the thermodynamic properties of mixtures. When applying these binary interaction parameters to predict the thermodynamic properties of the systems with three or more components, rigorous validation is necessary because (i) the parameters fitted from binaries are applicable to limited ranges of temperature, pressure and composition, which may be different from the conditions of various CCS processes; and (ii) the optimised binary interaction parameters between the pair of the two minor components are not always available with high quality and hence it is essential to examine how these parameters affect the overall predictive ability of the EoSs. However, unlike the binary systems, only a handful of multi-component CO<sub>2</sub> systems closely relevant to CCS have been previously studied experimentally in the literature. Table 1 summarises the work on the ternary and quaternary CO<sub>2</sub> systems with permanent gases as the impurities.

As the third most common gas (0.93 vol%) in the Earth's atmosphere, argon cannot be eliminated completely from an oxygen stream with an economically viable technology for oxy-fuel combustion processes, resulting in a concentration of up to 4.5 vol% in the CO<sub>2</sub> stream generated from a power plant (IEAGHG, 2005, 2011; Lovseth et al., 2013). Compared to the CO<sub>2</sub> + N<sub>2</sub> binary system with ~5000 density and >400 VLE data points available, CO<sub>2</sub> + Ar has ~1100 density and ~170 VLE data points reported in the literature. It has also been pointed out by Gernert and Span (2016) that the density data sets of CO<sub>2</sub> + Ar are less accurate than the best data sets for CO<sub>2</sub> + N<sub>2</sub>. Therefore, new ternary data containing CO<sub>2</sub> and Ar are required for

independent tests on the predictive ability of the EoSs and the parameter(s) fitted merely from the binary data of CO<sub>2</sub> + Ar.

In this paper we report the  $p$ - $T$  phase diagrams of two ternary systems (CO<sub>2</sub> + Ar + N<sub>2</sub> and CO<sub>2</sub> + Ar + H<sub>2</sub>) with  $x_{\text{CO}_2}$  between 0.90 and 0.98 (mole fraction), together with the density data for the CO<sub>2</sub> + Ar + N<sub>2</sub> mixture with  $x_{\text{Ar}} = 0.05$  and  $x_{\text{N}_2} = 0.05$ . Both our VLE and density measurements are focused on the critical region, which is not only of great importance to CO<sub>2</sub> compression, transportation and injection, but also a challenging region in terms of modelling with EoSs. To avoid sampling difficulties in the critical region, VLE data were determined in this study with the synthetic approach (Dohrn and Brunner, 1995; Dohrn et al., 2010; Fonseca et al., 2011), which is a complementary method to the analytical approach. In the modelling part of this paper, the evaluation of the different EOSs – Peng-Robinson, gSAFT and GERG2008/EOS-CG was carried out against the new ternary data.

## 2. Experimental Section

### 2.1. Methods

The  $p$ - $T$  phase boundary and the density data were measured separately using two pieces of high-pressure apparatus. The first apparatus is a fibre-optic phase equilibrium analyser, which monitors the change in the refractive index of fluid phases when the phase transition occurs at the vapour–liquid phase boundary. The second is a vibrating tube densitometer based on the principle of the mass-spring model. Detailed descriptions of both pieces of apparatus, and the corresponding sample preparation and measurement procedures have been published previously (Sanchez-Vicente et al., 2013). Only a brief explanation of the two methods used to carry out the measurements is given below.

A synthetic approach (Dohrn and Brunner, 1995; Dohrn et al., 2010; Fonseca et al., 2011) was employed to determine the  $p$ - $T$  phase boundary of the mixtures. The fluid phase transitions were monitored by using a silica-based, single-mode optical fibre sensor (Avdeev et

al., 2004). For a mixture with a known composition, the most convenient way to map the phase envelope over a wide temperature range is performing a series of isothermal measurements. Two configurations (Configuration A and Configuration B) were used in this work in accordance with the requirement of the two operating modes (decreasing and increasing the system pressure at a constant temperature). Configuration A (decreasing the system pressure) was mainly for determining the bubble-point curve, whereas Configuration B (increasing the system pressure) was more suitable for the dew-point measurements. Because the shape of the recorded isotherm (reflective coefficient versus  $p$ ) can be used to differentiate between the bubble-point and dew-point transition (Ke et al., 2014), the actual assignment of the bubble-point and dew-point did not rely on which configuration had been used.

Since for some CO<sub>2</sub>-permanent gas mixtures the isothermal measurements may not be the most efficient method to determine the highest temperature (maxcondentherm temperature,  $T_{\max}$ ) on the phase envelope, the isobaric searching method was used instead to measure  $T_{\max}$ . To determine  $T_{\max}$  isobarically, several isotherms near  $T_{\max}$  were first measured in order to give an approximate pressure of the maxcondentherm point. Then a fresh fluid sample was prepared in the equilibrium cell (Ke et al., 2014) and the system temperature was brought to 2–4 K above  $T_{\max}$ . Finally, the temperature of the equilibrium cell was gradually decreased at a rate of 0.03 K/min until phase separation was observed by using the optical fibre sensor. During the measurement the system pressure was maintain at the pre-determined pressure by using a computer-controlled, high-pressure syringe pump (Teledyne ISCO 260D).

The high-pressure vibrating tube densitometer used in this work was Anton Paar Model DMA-HP with DMA 4500 for measuring the period of oscillation. Calibrations were carried out by using nitrogen and degassed water as the two reference substances at twelve temperatures from 288 to 378 K and at pressures up to 23 MPa. At each temperature, the calibration curve was fitted to the reference density obtained from the NIST standard reference database (NIST, 2012) as a function of the measured system pressure ( $p$ ) and the period of oscillation ( $\tau$ ), see equation 1 (Sanchez-Vicente et al., 2013).



$$\rho = (a + bp + cp^2) + (d + ep + fp^2)\tau^2 \quad (1)$$

where  $\rho$  represents the density and coefficients  $a$  to  $f$  are constants at a given temperature.

The density of the ternary mixtures was recorded at constant temperature from high to low pressure at an interval of  $\sim 0.5$  MPa. Between two data points, the system pressure was decreased by opening an electronic valve for  $\sim 5$  s and then waiting for sufficient time until the period of oscillation was re-stabilised.

Both the phase equilibrium and density apparatus were interfaced with a purpose-built sample mixing and delivery unit (Ke et al., 2014) to ensure that the composition of the mixture being measured is the same as the composition of the bulk mixture. For the phase equilibrium measurements, the mixture of the permanent gases (either Ar + N<sub>2</sub> or Ar + H<sub>2</sub>) was first introduced into the sample mixing and delivery unit as a premixed gas from the cylinder. The molar ratio of both Ar/N<sub>2</sub> and Ar/H<sub>2</sub> was primarily dependent on the composition of the gas mixtures in the cylinders, which were prepared using a balance by the supplier (BOC). The mass of the gas mixtures (i.e. Ar + N<sub>2</sub> and Ar + H<sub>2</sub>) can be calculated from the temperature, pressure and volume of the sample mixer using the NIST Standard Reference Data (Lemmon et al., 2007). The mass of CO<sub>2</sub> was determined by weighing the sample cylinder before and after transferring CO<sub>2</sub> into the mixing and delivery unit. For the density measurements, the Ar + N<sub>2</sub> mixtures were made in-house with a nominal molar ratio of Ar:N<sub>2</sub> of 1:1. The accurate mass of Ar, N<sub>2</sub> and CO<sub>2</sub> present in the mixing and delivery unit was determined using a gravimetric method.

## 2.2. Uncertainties

### 2.2.1 $p$ - $T$ phase boundary measurements

The temperature of the equilibrium cell was measured by a precision thermometer (ASL Ltd, F252) with a Pt-100 RTD probe with the measurement uncertainty of 0.02 K after calibrating against a standard platinum RTD probe. Considering the temperature homogeneity

and stability of the water bath, the standard uncertainty of the reported temperature on the phase boundary was estimated to be less than 0.1 K for all of our measurements.

The phase transition pressure was measured by the pressure transducer (RDP Electronics Ltd, model Super-TJE, 0-34.5 MPa) with a resolution of 0.0007 MPa (0.1 psi). After a calibration against a Mensor pressure transducer (Series 6100, 0-13.8 MPa), the uncertainty of the RDP pressure transducer is  $\sim 0.007$  MPa (1 psi). The combined standard uncertainty of the reported bubble/dew-point pressures was estimated less than 0.05 MPa, taking into account that there are other sources of uncertainty, such as the sample composition in both the equilibrium cell and the mixing and delivery unit, the temperature homogeneity of the water bath, and the sensitivity of detecting the phase transition by the optical fiber sensor in the near critical conditions.

### **2.2.2 Density measurements**

The temperature of the sample in the vibrating tube densitometer was measured by a built-in Pt100 temperature sensor with a temperature uncertainty of 0.05 K as stated in the operation manual. The sample pressure was measured by the pressure transducer (Mensor, series 6100, 0-34.5 MPa) with an uncertainty of 0.0035 MPa after factory calibration.

According to manufacturer's specifications, the Anton Paar densitometer (DMA-HP + DMA 4500) has an uncertainty in the density of  $0.1 \text{ kg m}^{-3}$  at ambient pressure and temperature and  $1 \text{ kg m}^{-3}$  at extreme pressure and temperature (e.g. 70 MPa and 473 K). In our density calibrations, the standard deviation of the linear regression of the calibration curves was less than  $0.04 \text{ kg m}^{-3}$ . When separate experiments were run on the same sample at the same temperature and pressure, the standard deviation of the mean was  $\sim 0.2 \text{ kg m}^{-3}$  for the measured density. Considering all sources of uncertainties, the combined standard uncertainties were estimated to be less than  $1 \text{ kg m}^{-3}$ , except for several data points at conditions close to the critical point (e.g.  $T = 313.15 \text{ K}$  and  $8 \text{ MPa} < p < 13 \text{ MPa}$ , where the combined standard uncertainty increased to about  $2 \text{ kg m}^{-3}$ ). Since the density measured by a vibrating tube

densitometer has high relative uncertainty for low pressure gases, no data are reported for the ternary mixtures at pressure below 1.5 MPa.

### 2.2.3 Composition of the ternary mixtures

The mass of CO<sub>2</sub>, N<sub>2</sub> and Ar was determined using Mettler-Toledo precision balances (MS1003S and XP5003S with the linearity of 0.0002 g and 0.006 g, respectively). The relative standard uncertainty for the mass of CO<sub>2</sub> was better than 0.1%. For the pre-mixed Ar + N<sub>2</sub> mixtures used the density measurements, the relative standard uncertainty for the mass of either Ar or N<sub>2</sub> was better than 0.5%.

The mass of the permanent gas (i.e. N<sub>2</sub>, H<sub>2</sub> and Ar) introduced into the sample mixing unit was calculated from the temperature, pressure and volume of the mixing unit, together with the composition of the pre-mixed permanent gasses in the cylinder using the NIST database (Lemmon et al., 2007). The relative standard uncertainties of the temperature and volume were 0.17% and 0.09%, respectively. The relative uncertainty of the molar composition of the pre-mixed samples was better than 0.5%. The pressure of the gas sample in the mixing and delivery unit was measured by the pressure transducer (Mensor, Series 6100, 0–2.1 MPa) with an uncertainty of 0.0002 MPa, according to the calibration certificate.

Applying the uncertainty propagation model (Bevington and Robinson, 1992), it was estimated that for each sample the relative standard uncertainty of the mole fraction of the permanent gases (i.e.  $x_{Ar}$ ,  $x_{N2}$  and  $x_{H2}$ ) is no more than 0.6%.

## 2.3. Chemicals

Carbon dioxide (99.99%), argon (99.998%) nitrogen (99.9992%) and hydrogen (99.995%) were supplied by BOC and were used without further purification. Two premixed gas mixtures of Ar + N<sub>2</sub> and Ar + H<sub>2</sub> were prepared and supplied by BOC with compositions of 50.00% Ar / 50.00% N<sub>2</sub> and 40.00% Ar / 60.00% H<sub>2</sub> (mole fraction), respectively.

### 3. Results and Discussion

#### 3.1. The $p$ - $T$ phase boundary of the $\text{CO}_2 + \text{Ar} + \text{N}_2$ and $\text{CO}_2 + \text{Ar} + \text{H}_2$ mixtures

The  $p$ - $T$  phase boundary of the ternary system of  $\text{CO}_2 + \text{Ar} + \text{N}_2$  was measured at a fixed molar ratio of  $\text{Ar}:\text{N}_2$  (1:1) but with two levels of  $\text{CO}_2$  compositions, i.e.  $x_{\text{CO}_2} = 0.900$  for the first mixture and  $x_{\text{CO}_2} = 0.980$  for the second mixture, respectively. The temperature, pressure and sample composition are listed in Table 2. Figure 1 shows both the bubble-point and dew-point lines of the two ternary mixtures, together with the vapour-pressure of pure  $\text{CO}_2$ .

For both of the mixtures, the two-phase region, which is enclosed by the bubble-point and dew-point lines, is located above the vapour-pressure curve of  $\text{CO}_2$ , see Figure 1. The bubble-point line is particularly important because it defines the lower limit for the pipeline transport of  $\text{CO}_2$  mixtures in a homogeneous dense phase. Clearly, at a given temperature the bubble-point pressure increases with increasing the mole fraction of the impurities ( $x_{\text{Ar}} + x_{\text{N}_2}$ ) in the mixture. Using the data shown in Table 2, it is calculated that the bubble-point pressure is 5.98 MPa for the 98% $\text{CO}_2 + 1\% \text{Ar} + 1\% \text{N}_2$  mixture and 8.88 MPa for the 90% $\text{CO}_2 + 5\% \text{Ar} + 5\% \text{N}_2$  mixture, corresponding to an increase of 17% and 74%, respectively, from the vapour pressure of pure  $\text{CO}_2$  (5.09 MPa) at 288.15 K. Furthermore, due to the high concentration of impurities in the mixture, the bubble point line exhibits a shallow maximum at 292 K and 9.0 MPa for the mixture with  $x_{\text{CO}_2} = 0.900$ , whereas the bubble-point line increases monotonically as temperature increases for the mixture with  $x_{\text{CO}_2} = 0.980$ .

The maxcondentherm point, defined as the maximum temperature on the  $p$ - $T$  envelope was experimentally determined in this study. To locate the maxcondentherm temperature, we carried out the isothermal searching at three temperatures (i.e. 298.10 K, 297.09 K and 296.70 K) for the 90% $\text{CO}_2 + 5\% \text{Ar} + 5\% \text{N}_2$  mixture. Since no phase separations can be observed from these three temperatures, an isobaric searching was then made at 8.11 MPa and the phase transition was found at 296.43 K. For the mixture of 98% $\text{CO}_2 + 1\% \text{Ar} + 1\% \text{N}_2$ , two tests were

made at 302.75 K and 302.59 K without observation of any phase separation. Due to the shape of the phase envelope of the diluted mixtures (98% CO<sub>2</sub> mixture), no tests were carried out isobarically to locate the maxcondentherm point. Considering all of the phase transition data along the phase envelopes and the separate tests listed above, we estimated  $T_{\max}$  to be 296.4±0.2 K for the 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> mixture and 302.5±0.2 K for the 98%CO<sub>2</sub> + 1%Ar + 1%N<sub>2</sub> mixture, respectively (see Table 3). As can be seen from the table, the  $T_{\max}$  decreases as the concentration of the impurities increases in the CO<sub>2</sub> mixture.

Figure 2 shows the  $p$ - $T$  phase boundary of the binary mixture of CO<sub>2</sub> + N<sub>2</sub> with  $x_{\text{N}_2} = 0.100$ , which was measured by using the same method as that for the ternary systems (see Section 2). The tabulated data for this mixture can be found from Table S1 in the Electronic Supplementary Material. The phase transition pressures for the CO<sub>2</sub> + Ar mixture with  $x_{\text{Ar}} = 0.100$  were obtained by interpolating the  $p$ - $x$  phase diagrams reported in the literature (Coquelet et al., 2008; Kaminishi et al., 1968; Köpke and Eggers, 2007; Sarashina et al., 1971a) at four temperatures (273 K, 283 K, 288 K and 295 K). As can be seen from Figure 2, the dew-point lines are almost superimposed on each other for the three mixtures with the same total mole fraction of impurity, i.e. 90%CO<sub>2</sub> + 5%N<sub>2</sub> + 5%Ar, 90%CO<sub>2</sub> + 10%N<sub>2</sub> and 90%CO<sub>2</sub> + 10%Ar. The bubble-point pressures are close to each other for the three mixtures in the near critical region ( $T > 295$  K). As the temperature decreases, the bubble-point lines start to diverge. At approximately 273.15 K, the bubble-point pressure of 90%CO<sub>2</sub> + 5%N<sub>2</sub> + 5%Ar is 0.18 MPa lower than that of 90%CO<sub>2</sub> + 10%N<sub>2</sub>, but 0.29 MPa higher than that of 90%CO<sub>2</sub> + 10%Ar. For comparison, we have also included in Figure 2 the bubble-point line of the quaternary mixture (90%CO<sub>2</sub> + 5%O<sub>2</sub> + 2%Ar + 3%N<sub>2</sub>) reported by Chapoy et al. (2013b). The total mole fraction of the three impurities in the quaternary mixture is approximately 10%. It can be seen from the Figure that the bubble-point pressures of the quaternary mixture are slightly lower than those of the 90%CO<sub>2</sub> + 5%N<sub>2</sub> + 5%Ar mixture, except for the bubble point at 293.35 K.

Furthermore, similar comparisons are made for binary and ternary mixtures containing 98% of CO<sub>2</sub>, see Figure S1 in the Electronic Supplementary Material. As expected, the

differences in both the bubble- and dew-point pressures are within experimental uncertainty between 98%CO<sub>2</sub> + 1%Ar + 1% N<sub>2</sub>, 98%CO<sub>2</sub> + 2%N<sub>2</sub> and 98%CO<sub>2</sub> + 2%Ar because of the low mole fraction of the impurities in the mixtures.

The second ternary system presented in this study is 95%CO<sub>2</sub> + 2%Ar + 3%H<sub>2</sub>, the composition of which was selected for direct comparison with the 95%CO<sub>2</sub> + 5%H<sub>2</sub> and 95%CO<sub>2</sub> + 2%N<sub>2</sub> + 3%H<sub>2</sub> mixtures measured in our previous studies (Tenorio et al., 2015). Similar to those binary and ternary system containing 3-9% H<sub>2</sub> (mole fraction), the two-phase region in the  $p$ - $T$  space is much larger than those mixtures without H<sub>2</sub> as the impurity, see Figure 3. Moreover, the bubble point line is rather flat over temperatures between 273 K and 300 K. At the benchmark temperature of 288.15 K (15°C), the bubble-point pressure is 8.90 MPa, which is about 75% higher than the vapour pressure of pure CO<sub>2</sub>.

Figure 3 also shows the  $p$ - $T$  phase envelopes of 95%CO<sub>2</sub> + 5%H<sub>2</sub> (Tenorio et al., 2015), 94.5% CO<sub>2</sub> + 5.5% Ar (Ahmad et al., 2014) and 95%CO<sub>2</sub> + 2%N<sub>2</sub> + 3%H<sub>2</sub> (Tenorio et al., 2015), reported in the literature. For all the four mixtures, the mole fraction of CO<sub>2</sub> is similar to each other (95%). But the ratio of H<sub>2</sub> to the other permanent gas (Ar or N<sub>2</sub>) varies from 0:5 to 3:2, and then to 5:0. As the ratio increases, the bubble-point lines shifted significantly to high-pressure. Therefore, the amount of H<sub>2</sub> is the predominant factor in determining the shift in the bubble-point pressures of these CO<sub>2</sub> mixtures. In terms of the phase behaviour over the temperature range of 273-300 K, it is not important whether the third impurity is Ar or N<sub>2</sub> because the results show that the  $p$ - $T$  phase envelopes of the two ternary systems (i.e. 95%CO<sub>2</sub> + 3%H<sub>2</sub> + 2%N<sub>2</sub> and 95%CO<sub>2</sub> + 3%H<sub>2</sub> + 2%Ar) are almost identical.

The  $T_{\max}$  of 95%CO<sub>2</sub> + 2%Ar + 3%H<sub>2</sub> was determined by using the isobaric searching method, giving a  $T_{\max}$  of 301.6±0.2 K. An additional experiment was carried out at a constant temperature of 301.74 K and no phase separation was observed between 7.2 MPa and 10.3 MPa. The maxcondentherm temperatures of all three ternary mixtures are listed in Table 4. Because the three ternary mixtures in this study contains low-concentration of permanent gases, it is

expected that the temperature difference between the critical point and maxcondentherm point is small. As a result, retrograde condensation could only happen in a very narrow temperature region. The effects of retrograde condensation on CO<sub>2</sub> compression and transportation processes is remained unclear.

### 3.2. The density of the CO<sub>2</sub> + Ar + N<sub>2</sub> mixtures

Density measurements on the ternary mixture (CO<sub>2</sub> + Ar + N<sub>2</sub>) with  $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$  were made at four temperatures, i.e. 293.15 K, 303.15 K, 313.15 and 333.15 K, and pressures up to 23 MPa. The results are presented in Table S2 in the Electronic Supplementary Material. The VLE data for this mixture were measured in this work and were given in Section 3.1 above, showing that the  $T_{\text{max}}$  is at 296.4 K. Since the measured isotherm of 293.15 K was below the  $T_{\text{max}}$ , the data collection was carried out at pressures above 10 MPa at this temperature to ensure that the reported density data are from homogeneous phases. Figure 4 shows four isotherms of our measured density data, together with the data reported recently by Yang et al. (2015b) for the CO<sub>2</sub> + Ar + N<sub>2</sub> system with the same composition as this work but at 323.15 K. The density isotherms exhibit the commonly observed characteristics of dilute CO<sub>2</sub> mixtures in the near-critical region.

The mass densities at 313.15 K for 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> were also converted to the molar density for comparison with the densities of pure CO<sub>2</sub> and the two binary mixtures of 90%CO<sub>2</sub> + 10%H<sub>2</sub> and 90%CO<sub>2</sub> + 10%N<sub>2</sub>, see Figure 5. The densities of pure CO<sub>2</sub> were calculated by using the Span-Wagner equation of state (Span and Wagner, 1996) and the densities of the CO<sub>2</sub> + H<sub>2</sub> mixture were taken from our previous work (Sanchez-Vicente et al., 2013). The density data for the 90%CO<sub>2</sub> + 10%N<sub>2</sub> mixture were measured in this study and the data can be found from Table S3 in the Electronic Supplementary Material.

Figure 5a shows that the density isotherm for 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> is almost overlapped with that of 90%CO<sub>2</sub> + 10%N<sub>2</sub>. It is also can be seen from the Figure that the density of 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> is much lower than that of pure CO<sub>2</sub>, but slightly higher

than that of 90%CO<sub>2</sub> + 10%H<sub>2</sub> at pressures above 6 MPa. The relative differences between the molar density of the mixture and pure CO<sub>2</sub> are plotted in Figure 5b as a function of pressure. The large relative differences for all of the three mixtures can be seen in the supercritical region (7–12 MPa). For example, the densities of both 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> and 90%CO<sub>2</sub> + 10%N<sub>2</sub> mixtures are approximately 47% lower than that of pure CO<sub>2</sub> at 9.5 MPa. H<sub>2</sub> has a slightly stronger effect on the density than N<sub>2</sub> or Ar, resulting in a decrease of 51% in the mixture density at 10 MPa for 90%CO<sub>2</sub> + 10%H<sub>2</sub>.

### 3.3. Modelling

#### 3.3.1. Equations of state (EoS) and parameters

The GERG-2008, EOS-CG, gSAFT and Peng-Robinson (PR) EoS were examined by using both the VLE and density data for the ternary mixtures measured in this study. The GERG-2008/EOS-CG EoS is an empirical multi-parameter model explicit in the Helmholtz free energy, representing the most accurate and sophisticated equations to calculate the thermodynamic properties of the mixtures containing small molecules, such as CH<sub>4</sub>, N<sub>2</sub> and CO<sub>2</sub>. The PR EoS is a simple, flexible and computationally fast cubic equation, which has been applied for modelling a variety of CCS processes, such as CO<sub>2</sub> pipeline networks (Wetenhall et al., 2014), and CO<sub>2</sub> storage capacity in deep saline aquifers (Kumar et al., 2005). The SAFT equation of state gives realistic representation of the interactions between like and unlike molecules, including those with association sites, such as water and alkanolamine. The selection of the three equations of state represents the different requirements on different parts of the CCS chain, from computational fluid dynamics modelling of CO<sub>2</sub> pipelines (Wareing et al., 2013) to calibration of flow-meters.

For the PR EoS (Peng and Robinson, 1976), the parameters ( $a$  and  $b$ ) for mixtures were calculated from the van der Waals one-fluid mixing rules, see equations (2) and (3).

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij}) (a_{ii} a_{jj})^{0.5} \quad (2)$$



$$b = \sum_i x_i b_i \quad (3)$$

where  $k_{ij}$  is the binary interaction parameter for  $i$ - $j$  pairs and  $x_i$  and  $x_j$  represents the mole fraction of component  $i$  and  $j$ , respectively. The terms  $a_{ii}$  (or  $a_{jj}$ ) and  $b_i$  are the pure component parameters, which can be calculated from the critical temperature ( $T_c$ ), critical pressure ( $p_c$ ) and acentric factor ( $\omega$ ) of pure substances. Table S4 in the Electronic Supplementary Material lists the values of  $T_c$ ,  $p_c$  and  $\omega$  used in this study for  $\text{CO}_2$ , Ar,  $\text{N}_2$  and  $\text{H}_2$ .

Five binary interaction parameters (i.e.  $k_{\text{CO}_2\text{-Ar}}$ ,  $k_{\text{CO}_2\text{-N}_2}$ ,  $k_{\text{CO}_2\text{-H}_2}$ ,  $k_{\text{Ar-N}_2}$  and  $k_{\text{Ar-H}_2}$ ) are required to model the two ternary systems of  $\text{CO}_2 + \text{Ar} + \text{N}_2$  and  $\text{CO}_2 + \text{Ar} + \text{H}_2$ . In this work,  $k_{\text{CO}_2\text{-N}_2}$  and  $k_{\text{CO}_2\text{-H}_2}$  were taken from the literature (Li and Yan, 2009a) and our previous work (Tenorio et al., 2015), respectively. Both  $k_{\text{Ar-N}_2}$  and  $k_{\text{Ar-H}_2}$  were set to a default value of 0 because either Ar,  $\text{N}_2$  or  $\text{H}_2$  are minor components (mole fraction  $< 0.05$ ) in the two ternary mixtures.  $k_{\text{CO}_2\text{-Ar}}$  was initially fitted by using the VLE data reported by Ahmad et al. (2014), Coquelet et al. (2008), Kaminishi et al. (1968), Köpke and Eggers (2007) and Sarashina et al. (1971a). The obtained temperature-independent parameter was 0.1343. We noticed that this binary interaction parameter was very different from the value ( $k_{\text{CO}_2\text{-Ar}} = -0.031$ ) reported in the literature (Mantovani et al., 2012), which was regressed against the density data of the binary mixture of  $\text{CO}_2 + \text{Ar}$ . For comparison, both values of  $k_{\text{CO}_2\text{-Ar}}$  were used in the following calculation of the ternary systems. In this paper, the two sets of the binary interaction parameters with  $k_{\text{CO}_2\text{-Ar}} = 0.1343$  and  $k_{\text{CO}_2\text{-Ar}} = -0.031$  are denoted with PR-1 and PR-2, respectively. All of the binary interaction parameters for the PR EoS can be found from Table 5.

PSE's gSAFT physical properties package provides robust and efficient implementations of two different SAFT variants, namely the SAFT-VR SW (Gil-Villegas et al., 1997) and SAFT-g Mie (Papaioannou et al., 2014) equations of state. The latter, as employed for the calculations presented here, is one of the most advanced SAFT-based group contribution

technologies available to date, being the first to be able to accurately predict both phase equilibrium and second-derivative properties (heat capacities, speed of sound) of complex fluids. Moreover, it is based on a group contribution approach that allows pure components and mixtures to be modelled accurately with little (or sometimes, no) reliance on experimental data. The parameters used in this publication can be found from the gSAFT property package (PSE, 2016).

The formulae and the parameters of the GERG-2008 EoS can be found in the original publications by Kunz et al. (Kunz et al., 2007; Kunz and Wagner, 2012). The parameters reported by Kunz et al. are briefly summarised as follows: among the 5 binaries for modelling the two ternary systems of CO<sub>2</sub> + Ar + N<sub>2</sub> and CO<sub>2</sub> + Ar + H<sub>2</sub>, the binary parameters ( $\beta_{v,ij}$ ,  $\gamma_{v,ij}$ ,  $\beta_{T,ij}$  and  $\gamma_{T,ij}$ ) are available for only 4 pairs (namely, CO<sub>2</sub>-Ar, CO<sub>2</sub>-N<sub>2</sub>, CO<sub>2</sub>-H<sub>2</sub> and Ar-N<sub>2</sub>) to calculate the reduced mixture density and the inverse reduced mixture temperature. For the Ar-H<sub>2</sub> pair  $\beta_{v,ij}$ ,  $\gamma_{v,ij}$ ,  $\beta_{T,ij}$  and  $\gamma_{T,ij}$  were set to the default value of 1. In addition, the specific departure function of the CO<sub>2</sub>-N<sub>2</sub> pair was developed by Kunz et al. using a combination of polynomial and exponential terms with 34 adjustable parameters. The departure functions were set to 0 for the rest of the 4 binaries. The calculations with the GERG-2008 model were carried out using software purchased from NIST (Lemmon et al., 2007).

The EOS-CG model (Gernert and Span, 2016) has the same mathematical structure as the GERG-2008 model, but with new binary parameters and departure functions specially developed for CO<sub>2</sub>-rich mixtures and humid gases. The new parameters relevant to the two ternary systems in this work are the binary parameters ( $\beta_{v,ij}$ ,  $\gamma_{v,ij}$ ,  $\beta_{T,ij}$  and  $\gamma_{T,ij}$ ) for CO<sub>2</sub>-Ar and N<sub>2</sub>-Ar, and the specific departure function the CO<sub>2</sub>-Ar pair. The parameters for the remaining three pairs (CO<sub>2</sub>-N<sub>2</sub>, CO<sub>2</sub>-H<sub>2</sub> and Ar-H<sub>2</sub>) are identical to those used in GERG-2008. The detailed description of the EOS-CG model and the parameters can be found in the recent publication and the TREND software by Span and his co-workers (Gernert and Span, 2016; Span et al., 2015).

### 3.3.2 Modelling the $p$ - $T$ phase boundary of the ternary mixtures containing CO<sub>2</sub> and Ar

The calculated  $p$ - $T$  phase boundaries for the 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> mixture are shown in Figure 6a, together with the experimental data reported in this work. The dew-point line calculated with the 5 models (i.e. GERG-2008, EOS-CG, gSAFT, PR-1 and PR-2) are almost overlaid with each other. For the bubble-point line, GERG-2008 correctly reproduces most of the bubble points except for the three points near  $T_{\max}$ . However, a significant improvement on the predictions of these three bubble points can be seen from EOS-CG. gSAFT also gives the best prediction near  $T_{\max}$ , but slightly under-predicts the bubble-point pressures at low temperatures, e.g. 273 K. Using the  $k_{\text{CO}_2\text{-Ar}}$  optimised from the binary VLE data, PR-1 behaves almost as well as EOS-CG and gSAFT, whereas the predictions of PR-2 are about 0.8 MPa below the experimental bubble-point pressures between 273 K and 293 K because the  $k_{\text{CO}_2\text{-Ar}}$  has been optimised for the binary density data, showing how sensitive the choice of  $k_{\text{CO}_2\text{-Ar}}$  is for the VLE prediction of the multi-component mixtures containing CO<sub>2</sub> and Ar using the PR EoS.

The average absolute deviation (AAD) and the average absolute relative deviation (AARD) between the experimental data and model predictions are listed in Table 6 for both the bubble- and dew-point pressures. For clarity and importance, only the relative deviations are shown in Figure 6b for each bubble-point pressure. As can be seen from Figure 6b, although EOS-CG, gSAFT and PR-1 all have the good agreement with the experimental data for the 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> mixture, EOS-CG gives the lowest relative deviations (within 1.3%) between 273 K and 293 K and the relative deviations increase up to 3.1% near  $T_{\max}$ .

Similar evaluations were applied to the ternary mixture of 98%CO<sub>2</sub> + 1%Ar + 1%N<sub>2</sub>, see Table 6 and Figure S3 in the Electronic Supplementary Material. The general trend in the relative deviations of the predicted bubble-point pressures is as follows: EOS-CG  $\approx$  GERG-2008 < PR-1 < gSAFT < PR-2. For the very dilute CO<sub>2</sub>-permanent gas mixture, it is expected

that the GERG-2008/EOS-CG would have the best performance because the pure fluid contributions that are calculated from highly accurate reference Helmholtz energy equations play major parts in the total Helmholtz energy in the mixture model.

The VLE modelling of the binary system of CO<sub>2</sub> + Ar was previously reported in the literature (Ahmad et al., 2014; Diamantonis et al., 2013; Li and Yan, 2009) by using a range of equations of states. For example, Diamantonis et al. correlated the experimental data at 288.15 K, showing that the AARD for the bubble-point pressures is 2.32% and 2.81% for PR and PC-SAFT, respectively. Gernert and Span reported that the AARD is between 0.42-0.67% for the liquid composition (Gernert, 2013; Gernert and Span, 2016). We also calculated the bubble-point pressures of CO<sub>2</sub> + Ar at the experimental temperatures between 273 K and 299 K for direct comparison with our ternary mixtures. The obtained AARD of the bubble-point pressures is 2.4% for GERG-2008 and 1.9% for EOS-CG, respectively. Clearly, the lowest AARD obtained from the EOS-CG for the ternary mixture of 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> benefits from the high quality specific departure function for the CO<sub>2</sub>-Ar pair.

Figure 7 depicts the modelling results for the ternary mixture of 95%CO<sub>2</sub> + 2%Ar + 3% H<sub>2</sub>. As can be seen from the figure, the predicted bubble-point lines show clear difference between the 5 models.

Both GERG-2008 and EOS-CG under-predict the bubble-point pressures by 0.5-0.9 MPa between 273 K and 293 K. The AARD between the predicted and the experimental bubble-point pressures are 7.3% and 7.7% for GERG-2008 and EOS-CG, respectively. Recalling that the AARD calculated from the GERG-2008 model is 7.6% for the bubble-point line of the 97%CO<sub>2</sub> + 3% H<sub>2</sub> mixture (Tenorio et al., 2015), the high AARD for 95%CO<sub>2</sub> + 2%Ar + 3% H<sub>2</sub> is due to the lack of the departure function for the CO<sub>2</sub>-H<sub>2</sub> pair in either GERG-2008 or EOS-CG. Therefore, two key pairs, i.e. CO<sub>2</sub>-Ar and CO<sub>2</sub>-H<sub>2</sub> are both important in the ternary mixture of 95%CO<sub>2</sub> + 2%Ar + 3% H<sub>2</sub>. The additional departure function of the CO<sub>2</sub>-Ar pair in the EOS-CG model is not sufficient to improve overall predictions of this mixture

because there is only 2% Ar in CO<sub>2</sub>. Nonetheless, the improvement can still be seen near  $T_{\max}$  for the phase boundary predicted by EOS-CG. The similar level of AARD obtained from the CO<sub>2</sub> + H<sub>2</sub> and CO<sub>2</sub> + Ar + H<sub>2</sub> mixtures also suggests that the departure function between the two minor components (Ar-H<sub>2</sub>) does not have predominant effects on the overall predictive ability of GERG-2008/EOS-CG for the multi-component mixtures.

Both PR-1 and PR-2 under-predict the bubble-point pressures, but they provide better predictions than GERG-2008 and EOS-CG. As expected, PR-1 (with the AAD of 0.27 MPa for bubble points) is more accurate than PR-2 (AAD = 0.51 MPa) because  $k_{\text{CO}_2\text{-Ar}}$  is optimised from the binary VLE data for PR-1 rather than from the density data for PR-2.

gSAFT is the most accurate model to predict the VLE of the 95%CO<sub>2</sub> + 2%Ar + 3% H<sub>2</sub> mixture among the 5 models used in this study. The AAD between the experimental and the calculated bubble-point pressures is 0.15 MPa, corresponding to the AARD of 1.7%. The relative deviation calculated from the 5 models can be found in Figure 7b for each individual bubble-point.

For the dew-point line of 95%CO<sub>2</sub> + 2%Ar +3% H<sub>2</sub>, the predictions from all of the 5 models are superimposed on each other, except for the temperatures very close  $T_{\max}$  (above 300 K), see Figure 7a. Moreover, the AARD between the experimental and the calculated dew-point pressure is in range of 0.4-0.6%, which are similar to the AARD of the two CO<sub>2</sub> + Ar + N<sub>2</sub> mixtures. The AAD and AARD between the measured data and the model calculations are also listed in Table 6 for the 95%CO<sub>2</sub> + 2%Ar +3% H<sub>2</sub> mixture.

A further comparison of the behaviour of the 5 models was made on the special point, i.e. the maxcondentherm point at the phase envelopes. The temperature at the maxcondentherm point is often 0.5–3 K above the  $T_c$  for the dilute CO<sub>2</sub>–permanent gas mixtures (Ke et al., 2005; Ke et al., 2004; Tenorio et al., 2015). Since our experimental methods allow  $T_{\max}$  to be determined with low uncertainty (~0.2 K), our  $T_{\max}$  data provide a simple assessment on how well the models work in the critical region. Figure 8 plots the calculated  $T_{\max}$  against the

experimental  $T_{\max}$  of the three ternary mixtures in this study, together with 8 binary and ternary mixtures containing CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>. We can see that almost all of the models over-predict  $T_{\max}$  of the dilute CO<sub>2</sub>-permanent gas mixtures. The only exception is that the GERG-2008 under-predicts the  $T_{\max}$  by 0.5 K for the mixture of 86%CO<sub>2</sub> + 14%N<sub>2</sub>.

Although the maximum deviation between the calculated  $T_{\max}$  and the experimental  $T_{\max}$  is small (< 2.2 K) for these mixtures, the general trend reveals that the PR EoS has low deviations and the GERG-2008 EoS often has high deviations. Compared with GERG-2008, the improvement from EOS-CG can also be clearly observed for the three ternary mixtures containing Ar.

### 3.3.3 Modelling the density of the ternary mixture of CO<sub>2</sub> + Ar + N<sub>2</sub>

The density of the ternary mixture of CO<sub>2</sub> + Ar + N<sub>2</sub> was calculated by 5 models, namely GERG-2008, EOS-CG, gSAFT, PR-1 and PR-2. The calculated isotherms for the densities at 293.15 K, 303.15, 313.15 K and 333.15 K are shown in Figure S3 in the Electronic Supplementary Material; the corresponding relative deviations between the calculated and experimental values are presented in Figure 9.

Considering all of the 4 temperatures of the reported density data in this work, GERG-2008 and EOS-CG are almost equally good at predicting the density of 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> with the AARD of 0.5%, see Table 6. Examining each individual isotherm, the AARD obtained by using EOS-CG is slightly better than, or as good as, that obtained by using GERG-2008 at 293.15 K and 303.15 K; whereas for the isotherms at 313.15 K and 333.15 K, GERG-2008 provided slightly better predictions than EOS-CG. The modelling on the same mixture carried out by Yang et al. (2015b) concluded that GERG-2008 gave a lower deviation than EOS-CG using their experimental data between 323.15 K and 423.15 K. Our results are consistent with their studies when the temperature is above 323.15 K. The calculations on the two low-temperature isotherms (293.15 K and 303.15 K) further reveal that EOS-CG produces better density predictions at the temperature near the  $T_c$  of the 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub>

mixture ( $T_c = 296.4$  K, calculated by using EOS-CG). It is worth pointing out that, for GERG-2008, a large portion of the experimental data (~98%) used to fit the adjustable parameter of the CO<sub>2</sub>-Ar pair are density data. Therefore, GERG-2008 works well for the density calculations even without a specific departure function, particularly in the region away from the  $T_c$ .

We also carried out the density calculation using PR-1 and PR-2. As can be seen from Table 6, the AARD of all of the measured density data across four different temperatures is 2.2% for PR-1 and 1.7% for PR-2, respectively, indicating that the PR EoS is much less accurate than GERG-2008/EOS-CG for the density prediction of the ternary mixture of CO<sub>2</sub> + Ar + N<sub>2</sub> even though using the value of  $k_{Ar-N_2}$  fitted to the binary CO<sub>2</sub>-Ar density data. In addition, for the PR EoS, the relative deviation between the predicted and experimental values exhibits both a maximum and a minimum along pressure, see Figure 9b-9d. The maximum represents the largest positive deviation, which is ~3% at ~8 MPa. The largest negative deviation is found to be ~2% in pressure range of 12 to 18 MPa. The AARDs calculated by using gSAFT are slightly better than those obtained from PR-1 and PR-2, see Table 6. Detailed examination of the relative deviations shows that gSAFT provides much better predictions at low pressures (<7 MPa) for the 90%CO<sub>2</sub> + 5%Ar + 5%N<sub>2</sub> mixture than PR-1 and PR-2. But the relative deviations increase to 2-4% when the pressure is above 12 MPa, see Figure 9.

## 4. Conclusions

New  $p$ - $T$  phase diagrams are reported for the two ternary systems of CO<sub>2</sub> + Ar + N<sub>2</sub> and CO<sub>2</sub> + Ar + H<sub>2</sub> over the temperature range 268 to 303 K and at pressures up to 9 MPa. The molar ratio between the two minor components is Ar:N<sub>2</sub> = 1:1 for the CO<sub>2</sub> + Ar + N<sub>2</sub> system and Ar:H<sub>2</sub> = 2:3 for the CO<sub>2</sub> + Ar + H<sub>2</sub> system, respectively. The total mole fraction of the impurities in the ternary system is between 0.02 and 0.10, covering the composition range of the streams expected to be produced from oxy-fuel capture technology.

Compared to the vapour pressure of pure CO<sub>2</sub> at the same temperature, the bubble-point pressure, which is the minimum pressure required to form a homogeneous dense phase

increases significantly in the presence of a mixed gas of Ar and N<sub>2</sub> (or Ar and H<sub>2</sub>), even though the total mole fraction of the impurity is less than 0.10. Among the three impurities in the two ternary systems (i.e. N<sub>2</sub>, Ar and H<sub>2</sub>), H<sub>2</sub> has the largest effect on the bubble-point pressure.

The density data of the ternary mixture of 90% CO<sub>2</sub> + 5% Ar + 5% N<sub>2</sub> shows a substantial decrease in the molar density at the conditions near the critical point (e.g. 47% lower than the pure CO<sub>2</sub> density at 313 K and 9.5 MPa). Regarding the effects of different permanent gases on the molar density of CO<sub>2</sub> mixtures, the difference between Ar and N<sub>2</sub> is insignificant for 10% impurity mixtures, whereas the density differences between mixtures containing 10% H<sub>2</sub> and 5% Ar + 5% N<sub>2</sub> as the impurities can be clearly observed.

The predictions from the GERG-2008, EOS-CG, g-SAFT and PR EoS agree well with the experimental  $p$ - $T$  phase boundary of the CO<sub>2</sub> + Ar + N<sub>2</sub> mixtures. For the bubble-point lines, the AAD in pressure is less than 0.17 MPa between the calculated and the measured values. The PR EoS is very sensitive to the choice of the binary interaction parameter, i.e.  $k_{\text{CO}_2\text{-Ar}}$ . Good predictions in the VLE data can only be achieved by using values of  $k_{\text{CO}_2\text{-Ar}}$  fitted from the binary VLE data in a similar temperature range. When considering both the VLE and density, EOS-CG is the best model among the four models for calculation of the thermodynamic properties of the CO<sub>2</sub> + Ar + N<sub>2</sub> system.

For the VLE data of 95% CO<sub>2</sub> + 2% Ar + 3% H<sub>2</sub> mixture, gSAFT gives excellent predictions of the bubble-point pressures with the AAD of 0.15 MPa. GERG-2008 and EOS-CG has the AAD of 0.64 MPa and 0.67 MPa, respectively for the bubble-point pressures, indicating the importance of the optimised departure function for the key binary (CO<sub>2</sub>-H<sub>2</sub>) for the overall performance of the empirical multi-parameter models.

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Table 1

VLE and density data available in the literature for the multi-component CO<sub>2</sub> systems with permanent gases.

System	Type of property	Data range			Data points	References
		T/K	p/MPa	$x_{\text{CO}_2}$		
CO <sub>2</sub> + N <sub>2</sub> + H <sub>2</sub>	VLE	253-302	2.1-8.7	0.93-0.95	36	(Tenorio et al., 2015)
CO <sub>2</sub> + N <sub>2</sub> + O <sub>2</sub>	VLE	218-273	5.2-11	0.15-0.92	64	(Zenner and Dana, 1963)
	VLE	273	5.2-11	0.60-0.96	12	(Muirbrook and Prausnitz, 1965)
CO <sub>2</sub> + N <sub>2</sub> + Ar	density	323-423	3-31	0.90-0.95	132	(Yang et al., 2015b)
CO <sub>2</sub> + N <sub>2</sub> + CH <sub>4</sub>	VLE	233-273	6.1-10	0.25-0.95	53	(Sarashina et al., 1971b)
	VLE	270	4.6-11	0.56-0.98	48	(Somait and Kidnay, 1978)
	VLE	220-250	6.1-12	0.15-0.89	88	(Al-Sahhaf, 1990; Al-Sahhaf et al., 1983)
	VLE	293-298	6.0-8.3	0.86-0.99	80	(Xu et al., 1992a, b)
CO <sub>2</sub> + Ar + O <sub>2</sub>	density	323-573	20-100	0.1-0.8	271	(Seitz et al., 1996)
	VLE	253-293	2.3-7.6	0.54-0.99	28	(Coquelet et al., 2014)
CO <sub>2</sub> + H <sub>2</sub> + CO	VLE	233-283	5.1-20	0.53-0.98	31	(Kaminishi et al., 1968)
	VLE	254-302	4.0-8.8	0.97-0.99	52	(Yokoyama et al., 1988)
	VLE(critical point)	282-303	8.4-14	0.71-0.96	15	(Ke et al., 2001)
CO <sub>2</sub> + N <sub>2</sub> + O <sub>2</sub> + Ar	VLE	253-293	7.1-9.0	0.90	4	(Chapoy et al., 2013b)
	density	273-423	1-125	0.90	43	(Chapoy et al., 2013b)

Table 2

Experimental  $p$ - $T$  phase boundary of the binary mixtures of CO<sub>2</sub> + Ar + N<sub>2</sub>.

$x_{N_2}$	$x_{Ar}$	$T / K$	$p / MPa$	phase transition <sup>c</sup>	$x_{N_2}$	$x_{Ar}$	$T / K$	$p / MPa$	phase transition <sup>c</sup>
0.0503	0.0503	267.94 <sup>a</sup>	3.52	dp	0.0102	0.0102	267.94 <sup>a</sup>	3.10	dp
0.0503	0.0503	270.43 <sup>a</sup>	3.81	dp	0.0102	0.0102	270.45 <sup>a</sup>	3.32	dp
0.0503	0.0503	272.89 <sup>a</sup>	4.07	dp	0.0102	0.0102	272.90 <sup>a</sup>	3.55	dp
0.0503	0.0503	275.38 <sup>a</sup>	4.36	dp	0.0102	0.0102	275.39 <sup>a</sup>	3.79	dp
0.0503	0.0503	277.90 <sup>a</sup>	4.65	dp	0.0102	0.0102	277.90 <sup>a</sup>	4.05	dp
0.0504	0.0504	280.44 <sup>a</sup>	4.99	dp	0.0102	0.0102	280.41 <sup>a</sup>	4.32	dp
0.0504	0.0504	282.96 <sup>a</sup>	5.34	dp	0.0102	0.0102	282.94 <sup>a</sup>	4.60	dp
0.0496	0.0496	284.97	5.78	dp	0.0102	0.0102	285.46 <sup>a</sup>	4.90	dp
0.0504	0.0504	285.48 <sup>a</sup>	5.73	dp	0.0102	0.0102	287.99 <sup>a</sup>	5.22	dp
0.0496	0.0496	285.97	5.94	dp	0.0102	0.0102	290.51 <sup>a</sup>	5.56	dp
0.0496	0.0496	286.98	6.09	dp	0.0101	0.0101	293.03 <sup>a</sup>	5.92	dp
0.0499	0.0499	287.99 <sup>a</sup>	6.16	dp	0.0101	0.0101	295.05 <sup>a</sup>	6.22	dp
0.0496	0.0496	288.99	6.38	dp	0.0102	0.0102	295.40	6.29	dp
0.0495	0.0495	290.50 <sup>a</sup>	6.60	dp	0.0101	0.0101	297.06 <sup>a</sup>	6.53	dp
0.0495	0.0495	293.02 <sup>a</sup>	7.10	dp	0.0101	0.0101	299.08 <sup>a</sup>	6.81	dp
0.0500	0.0500	294.07	7.28	dp	0.0100	0.0100	301.07 <sup>a</sup>	7.22	dp
0.0494	0.0494	295.03	7.57	dp	0.0100	0.0100	302.09 <sup>a</sup>	7.45	dp
0.0496	0.0496	295.55	7.77	dp	0.0100	0.0100	302.31	7.63	dp
0.0500	0.0500	296.08	7.83	dp	0.0100	0.0100	302.50 <sup>d</sup>	7.66	dp
0.0502	0.0502	296.43 <sup>b</sup>	8.11	dp	0.0100	0.0100	273.20 <sup>a</sup>	4.49	bp
0.0500	0.0500	273.14 <sup>a</sup>	8.01	bp	0.0100	0.0100	275.67	4.71	bp
0.0501	0.0501	275.66	8.17	bp	0.0100	0.0100	278.15	4.93	bp
0.0500	0.0500	278.13	8.31	bp	0.0100	0.0100	280.62	5.17	bp
0.0501	0.0501	280.63	8.46	bp	0.0100	0.0100	283.09	5.45	bp
0.0500	0.0500	283.12	8.61	bp	0.0100	0.0100	285.61	5.70	bp
0.0501	0.0501	285.62	8.76	bp	0.0100	0.0100	288.14 <sup>a</sup>	5.99	bp
0.0500	0.0500	288.12	8.88	bp	0.0100	0.0100	290.64	6.26	bp
0.0500	0.0500	290.63	8.96	bp	0.0100	0.0100	293.16	6.60	bp
0.0501	0.0501	293.13	8.96	bp	0.0100	0.0100	295.69	6.89	bp
0.0502	0.0502	295.17	8.78	bp	0.0100	0.0100	298.19	7.20	bp
0.0502	0.0502	296.19	8.58	bp	0.0100	0.0100	300.71	7.52	bp
					0.0100	0.0100	302.24	7.66	bp

<sup>a</sup> Values averaged from repeated measurements.<sup>b</sup> Measured by using Configuration A with the isobaric searching method.<sup>c</sup> bp and dp represent bubble-point and dew-point, respectively.<sup>d</sup> Measured by using Configuration A

Table 3

Experimental and calculated maxcondentherm temperature ( $T_{\max}$ ) on the  $p$ - $T$  phase envelop.

System	$x_{\text{Ar}}$	$x_{\text{N}_2}$	$x_{\text{H}_2}$	$T_{\max} / \text{K}$					
				Experimental	GERG-2008	EOS-CG	PR-1	PR-2	gSAFT
$\text{CO}_2 + \text{Ar} + \text{N}_2$	0.0500	0.0500	-	296.4±0.2	298.6	297.2	297.6	297.6	297.5
$\text{CO}_2 + \text{Ar} + \text{N}_2$	0.0101	0.0101	-	302.5±0.2	303.5	303.2	302.9	302.9	303.6
$\text{CO}_2 + \text{Ar} + \text{H}_2$	0.0201	-	0.0301	301.6±0.2	303.7	303.0	302.2	302.2	302.6



Table 4

Experimental  $p$ - $T$  phase boundary of the binary mixtures of CO<sub>2</sub> + Ar + H<sub>2</sub>.

$x_{\text{N}_2}$	$x_{\text{Ar}}$	$T / \text{K}$	$p / \text{MPa}$	phase transition <sup>c</sup>	$x_{\text{N}_2}$	$x_{\text{Ar}}$	$T / \text{K}$	$p / \text{MPa}$	phase transition <sup>c</sup>
0.0302	0.0201	267.97 <sup>a</sup>	3.26	dp	0.0301	0.0201	300.58 <sup>a</sup>	7.85	dp
0.0302	0.0201	270.47 <sup>a</sup>	3.49	dp	0.0300	0.0200	301.59 <sup>b</sup>	8.32	dp
0.0302	0.0201	272.93 <sup>a</sup>	3.73	dp	0.0300	0.0200	273.16 <sup>a</sup>	8.56	bp
0.0302	0.0201	275.42 <sup>a</sup>	3.99	dp	0.0300	0.0200	275.67	8.59	bp
0.0302	0.0201	277.92 <sup>a</sup>	4.26	dp	0.0300	0.0200	278.14	8.65	bp
0.0302	0.0201	280.44 <sup>a</sup>	4.56	dp	0.0300	0.0200	280.59	8.66	bp
0.0302	0.0201	282.96 <sup>a</sup>	4.87	dp	0.0300	0.0200	283.10	8.72	bp
0.0302	0.0201	285.48 <sup>a</sup>	5.20	dp	0.0300	0.0200	285.62	8.78	bp
0.0302	0.0201	288.01 <sup>a</sup>	5.56	dp	0.0300	0.0200	288.12	8.90	bp
0.0302	0.0202	290.52 <sup>a</sup>	5.93	dp	0.0300	0.0200	290.66	8.95	bp
0.0301	0.0201	292.89	6.34	dp	0.0300	0.0200	293.17	9.03	bp
0.0302	0.0202	295.56 <sup>a</sup>	6.77	dp	0.0300	0.0200	295.19	9.08	bp
0.0302	0.0202	298.08 <sup>a</sup>	7.25	dp	0.0300	0.0200	298.20	9.03	bp
0.0300	0.0200	299.08 <sup>a</sup>	7.37	dp	0.0300	0.0200	300.73	8.91	bp
0.0301	0.0201	300.08 <sup>a</sup>	7.71	dp					bp

<sup>a</sup> Values averaged from repeated measurements.<sup>b</sup> Measured by using Configuration A with the isobaric searching method.<sup>c</sup> bp and dp represent bubble-point and dew-point, respectively.

Table 5

The binary interaction parameters ( $k_{ij}$ ) used in the PR EoS

Equation of state	i-j pair	$k_{ij}$
PR-1/PR-2	CO <sub>2</sub> -N <sub>2</sub>	-0.007 <sup>a</sup>
PR-1/PR-2	CO <sub>2</sub> -H <sub>2</sub>	$-0.2884758 + 0.001953019 \times (T / \text{K})$ <sup>b, c</sup>
PR-1/PR-2	Ar-N <sub>2</sub>	0.0 <sup>d</sup>
PR-1/PR-2	Ar-H <sub>2</sub>	0.0 <sup>d</sup>
PR-1	CO <sub>2</sub> -Ar	0.1343 <sup>e</sup>
PR-2	CO <sub>2</sub> -Ar	-0.031 <sup>f</sup>

<sup>a</sup> Reported by Li et al. (2009).<sup>b</sup> Reported by Tenorio et al. (2015).<sup>c</sup>  $T$  represents temperature in the unit of K.<sup>d</sup> default.<sup>e</sup> fitted to the experimental VLE data reported in the literature.<sup>f</sup> reported by Mantovani et al. (2012) (fitted to the experimental density data).

Table 6

Average absolute deviation (AAD) and average absolute relative deviation (AARD) between the experimental data and the values calculated using the GERG-2008, EOS-CG, PR-1, PR-2, gSAFT equations of state for CO<sub>2</sub> + Ar + N<sub>2</sub> and CO<sub>2</sub> + Ar + H<sub>2</sub> mixtures.

$x_{Ar}$	$x_{N_2}$	$x_{H_2}$	Data	N <sup>a</sup>	AAD <sup>b</sup>	AARD <sup>c</sup>	AAD <sup>b</sup>	AARD <sup>c</sup>	AAD <sup>b</sup>	AARD <sup>c</sup>	AAD <sup>b</sup>	AARD <sup>c</sup>	AAD <sup>b</sup>	AARD <sup>c</sup>
					GERG-2008	EOS-CG	PR-1	PR-2	gSAFT					
0.050	0.050	-	dp <sup>d</sup> (VLE)	20	0.066	1.0%	0.042	0.7%	0.049	0.8%	0.088	1.5%	0.12	2.0%
0.050	0.050	-	bp <sup>d</sup> (VLE)	11	0.15	1.7%	0.11	1.3%	0.17	2.0%	0.58	6.8%	0.13	1.6%
0.050	0.050	-	All (VLE)	31	0.096	1.3%	0.066	0.9%	0.091	1.2%	0.26	3.4%	0.12	1.8%
0.010	0.010	-	dp (VLE)	19	0.036	0.6%	0.036	0.6%	0.033	0.5%	0.032	0.5%	0.043	0.6%
0.010	0.010	-	bp (VLE)	13	0.014	0.2%	0.013	0.2%	0.067	1.1%	0.18	3.2%	0.093	1.6%
0.010	0.010	-	All (VLE)	32	0.027	0.5%	0.027	0.5%	0.047	0.8%	0.092	1.6%	0.064	1.0%
0.020	-	0.030	dp (VLE)	17	0.044	0.6%	0.038	0.6%	0.038	0.6%	0.028	0.4%	0.043	0.6%
0.020	-	0.030	bp (VLE)	12	0.64	7.3%	0.67	7.7%	0.27	3.0%	0.51	5.8%	0.15	1.7%
0.020	-	0.030	All (VLE)	29	0.29	3.4%	0.30	3.5%	0.13	1.6%	0.23	2.6%	0.088	1.1%
0.050	0.050	-	293 K (density)	35	4.7	0.6%	3.0	0.4%	12	1.6%	7.2	0.9%	-	-
0.050	0.050	-	303 K (density)	36	2.8	0.7%	2.8	0.7%	11	2.3%	6.2	1.8%	7.6	1.3%
0.050	0.050	-	313 K (density)	34	1.4	0.4%	2.3	0.5%	12	2.6%	6.4	2.0%	8.6	1.7%
0.050	0.050	-	333 K (density)	38	0.58	0.2%	0.94	0.3%	7.4	2.1%	5.4	1.9%	7.3	1.8%
0.050	0.050	-	All (density)	143	2.4	0.5%	2.2	0.5%	10	2.2%	6.3	1.7%	7.8 <sup>e</sup>	1.6% <sup>e</sup>

<sup>a</sup> Number of data point.

<sup>b</sup>  $AAD = \frac{1}{N} \sum_{i=1}^N |p_{calc} - p_{exp}|$ , in the unit of MPa for the VLE calculations or  $AAD = \frac{1}{N} \sum_{i=1}^N |\rho_{calc} - \rho_{exp}|$  in the unit of kg m<sup>-3</sup> for the density calculations.

<sup>c</sup>  $AARD = \frac{1}{N} \sum_{i=1}^N \frac{|p_{calc} - p_{exp}|}{p_{exp}}$  for the VLE calculations or  $AARD = \frac{1}{N} \sum_{i=1}^N \frac{|\rho_{calc} - \rho_{exp}|}{\rho_{exp}}$  for the density calculations

<sup>d</sup> bp and dp represent bubble-point and dew-point, respectively.

<sup>e</sup> The total number of data points is 108.

## Figure Captions

Fig. 1. The measured  $p$ - $T$  phase boundaries of the ternary system of  $\text{CO}_2 + \text{Ar} + \text{N}_2$ . (●) and (○) represent the bubble-point and dew-point line, respectively, for the mixture with  $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$ . (◆) and (◇) represent the bubble-point and dew-point line, respectively, for the mixture with  $x_{\text{Ar}} = 0.010$  and  $x_{\text{N}_2} = 0.010$ . The solid line is the vapour-pressure curve of pure  $\text{CO}_2$  (Span and Wagner, 1996).

Fig. 2. Comparison of the  $p$ - $T$  phase boundaries of the ternary system of  $\text{CO}_2 + \text{Ar} + \text{N}_2$  with the literature data. (●) and (○) represent the bubble- and dew-point, respectively, for the ternary mixture with  $x_{\text{CO}_2} = 0.900$ ,  $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$ . The solid and dashed lines represent the unsmoothed bubble- and dew-point line of  $\text{CO}_2 + \text{N}_2$  with  $x_{\text{N}_2} = 0.100$ . For the  $\text{CO}_2 + \text{Ar}$  system, the phase transition pressures at  $x_{\text{Ar}} = 0.100$  are interpolated from the  $p$ - $x$  diagrams reported in the literature: (□) Köpke and Eggers (2007), (△) Sarashina et al. (1971a), (▽) Kaminishi et al. (1968), (◇) Coquelet et al. (2008). (×)  $\text{CO}_2 + \text{Ar} + \text{N}_2 + \text{O}_2$  with  $x_{\text{CO}_2} = 0.8983$ ,  $x_{\text{Ar}} = 0.0205$ ,  $x_{\text{N}_2} = 0.0307$  and  $x_{\text{O}_2} = 0.0505$  (Chapoy et al., 2013b).

Fig. 3. The  $p$ - $T$  phase boundaries of the ternary system of  $\text{CO}_2 + \text{Ar} + \text{H}_2$ . (●) and (○) represent the bubble- and dew-point, respectively, for the mixture with  $x_{\text{Ar}} = 0.020$  and  $x_{\text{H}_2} = 0.030$ . The lines in blue represent the unsmoothed bubble-point (solid) and dew-point (dashed) of the  $\text{CO}_2 + \text{N}_2 + \text{H}_2$  mixture with  $x_{\text{Ar}} = 0.020$  and  $x_{\text{H}_2} = 0.030$ . The lines in green are the unsmoothed bubble-point (solid) and dew-point (dotted) line of the  $\text{CO}_2 + \text{H}_2$  mixture with  $x_{\text{H}_2} = 0.050$ . (Tenorio et al., 2015) (■) and (□) are the bubble- and dew-point, respectively, for  $\text{CO}_2 + \text{Ar}$  with  $x_{\text{Ar}} = 0.055$  (Ahmad et al., 2014). The solid line represents the vapour-pressure curve of pure  $\text{CO}_2$  (Span and Wagner, 1996).

Fig. 4. Experimental densities of the ternary mixture of  $\text{CO}_2 + \text{Ar} + \text{N}_2$  with  $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$  at four temperatures: (□) 293.15 K, (○) 303.15 K, (△) 313.15 K, (◇) 333.15 K. The tabulated data can be found in Table S2 in the Electronic Supplementary Material. (⊕) 323.15 K, reported by Yang et al. (2015b) The line is merely to guide the eyes.

Fig. 5. Comparison of the density of the ternary mixture, 90.10% $\text{CO}_2 + 4.96\%\text{Ar} + 4.94\%\text{N}_2$  (○) with the densities of pure  $\text{CO}_2$  (solid line), 90.45% $\text{CO}_2 + 9.55\%\text{N}_2$  (◇) and 90.0% $\text{CO}_2 + 10.0\%\text{H}_2$  (dashed line): (a) molar density; (b) relative difference between the densities of the mixtures and  $\text{CO}_2$ , calculated from the data shown in (a). The temperature of the data shown in both figures is 313.15 K.

Fig. 6. Comparison of the experimental data for the ternary mixture of  $\text{CO}_2 + \text{Ar} + \text{N}_2$  ( $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$ ) with the phase transition pressures calculated from the gSAFT, GERG-2008, EOS-CG and PR EoS. (a) The  $p$ - $T$  phase diagram: experimental bubble-point ( $\circ$ ), experimental dew-point ( $\bullet$ ), phase boundaries calculated from gSAFT (green solid line), GERG-2008 (blue solid line), EOS-CG (magenta solid line), PR-1 (red dash-dotted line) and PR-2 (black dotted line). (b) Relative deviations of the calculated bubble points: gSAFT ( $\times$ , in green), GERG-2008 ( $\circ$ , in blue), EOS-CG ( $\circ$ , in magenta), PR-1 ( $+$ , in red) and PR-2 ( $+$ , in black).  $p_c$  represents the phase-transition pressure calculated from the equations of state, and  $p_e$  is the experimental phase-transition pressure reported in this work.

Fig. 7. Comparison of the experimental data of the ternary mixture of  $\text{CO}_2 + \text{Ar} + \text{H}_2$  ( $x_{\text{Ar}} = 0.020$  and  $x_{\text{H}_2} = 0.030$ ) with the phase transition pressures calculated from the gSAFT, GERG-2008, EOS-CG and PR EoS. (a) The  $p$ - $T$  phase diagram: experimental bubble-point ( $\circ$ ), experimental dew-point ( $\bullet$ ), phase boundaries calculated from gSAFT (green solid line), GERG-2008 (blue solid line), EOS-CG (magenta solid line), PR-1 (red dash-dotted line) and PR-2 (black dotted line). (b) Relative deviations of the calculated bubble points: gSAFT ( $\times$ , in green), GERG-2008 ( $\circ$ , in blue), EOS-CG ( $\circ$ , in magenta), PR-1 ( $+$ , in red) and PR-2 ( $+$ , in black).  $p_c$  represents the phase-transition pressure calculated from the equations of state, and  $p_e$  is the experimental phase-transition pressure reported in this work.

Fig. 8. The calculated maxcondentherm ( $T_{\text{max,cal}}$ ) on the  $p$ - $T$  phase envelope for the binary and ternary mixtures containing  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$  and Ar. The equations of states used are gSAFT ( $\circ$ ), GERG-2008 ( $\square$ ), EOS-CG ( $\diamond$ ) and PR ( $\times$ ).  $T_{\text{max,exp}}$  represents the experimental maxcondentherm on the  $p$ - $T$  phase envelope for a mixture with a given composition. The tabulated values of  $T_{\text{max,exp}}$  and  $T_{\text{max,cal}}$  can be found from Table 4 and from our previous work (Tenorio et al., 2015).

Fig. 9. The relative deviations between the calculated and experimental densities for the ternary mixture of  $\text{CO}_2 + \text{Ar} + \text{N}_2$  with  $x_{\text{Ar}} = 0.050$  and  $x_{\text{N}_2} = 0.050$  at four temperatures at (a) 293.15 K, (b) 303.15, (c) 313.15 K and (d) 333.15 K. The equations of state used are gSAFT ( $\triangle$ , in magenta), GERG-2008 ( $+$ , in black), EOS-CG ( $\circ$ , in green), PR-1 ( $\times$ , in red) and PR-2 ( $*$ , in blue).  $\Delta\rho = \rho_c - \rho_e$ , where  $\rho_c$  represents the density calculated from the equations of state, and  $\rho_e$  is the experimental density reported in this work.