

# Evaluating cubic equations of state for calculation of vapor–liquid equilibrium of CO<sub>2</sub> and CO<sub>2</sub>-mixtures for CO<sub>2</sub> capture and storage processes

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## ABSTRACT

Proper solution of vapor liquid equilibrium (VLE) is essential to the design and operation of CO<sub>2</sub> capture and storage system (CCS). According to the requirements of engineering applications, cubic equations of state (EOS) are preferable to predict VLE properties. This paper evaluates the reliabilities of five cubic EOSs, including PR, PT, RK, SRK and 3P1T for predicting VLE of CO<sub>2</sub> and binary CO<sub>2</sub>-mixtures containing CH<sub>4</sub>, H<sub>2</sub>S, SO<sub>2</sub>, Ar, N<sub>2</sub> or O<sub>2</sub>, based on the comparisons with the collected experimental data. Results show that SRK is superior in the calculations about the saturated pressure of pure CO<sub>2</sub>; while for the VLE properties of binary CO<sub>2</sub>-mixtures, PR, PT and SRK are generally superior to RK and 3P1T. The impacts of binary interaction parameter  $k_{ij}$  were also analyzed.  $k_{ij}$  has very clear effects on the calculating accuracy of an EOS in the property calculations of CO<sub>2</sub>-mixtures. In order to improve the calculation accuracy, the binary interaction parameter was calibrated for all of the studied EOSs regarding every binary CO<sub>2</sub>-mixture.

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## 1. Introduction

Carbon dioxide capture and storage (CCS), which involves the capture, transport and long-term storage of carbon dioxide, is a technology aimed at reducing greenhouse gas emissions from burning fossil fuels in industrial and energy-related processes. CCS is a critical technology amongst a portfolio of measures to limit climate change to a manageable level, along with improving energy efficiency, and switching to renewable energy resources. The importance of CCS has been highlighted in Fig. 1 as one of key elements in reducing greenhouse gas emissions [1].

The vapor liquid equilibrium (VLE) of CO<sub>2</sub> and CO<sub>2</sub>-mixtures is of great importance to the design and operation of many processes of CCS system, like separation, purification/liquefaction and transportation [2–4]. Since those processes cover a large range of operating conditions from normal atmosphere to supercritical state, and involve multi-components, the experimental data alone cannot satisfy the requirements of the engineering applications. Therefore, semi-empirical equations of state are usually used to predict those properties. Different EOSs and their reliabilities have been studied by previous investigators [5–7]. These studies have resulted in the general conclusion that their reliabilities vary for different properties, components and conditions. Due to rapid increasing research on CCS, there has been an increased interest in finding a proper EOS to predict VLE of CO<sub>2</sub> and CO<sub>2</sub>-mixtures.

However only a little work about it has been done so far, which cannot meet the demand of the applications in CCS systems. For example, Carroll studied Peng–Robinson (PR) [8] and Redlich–Kwong–Soave (SRK) EOSs [9] for the VLE calculations of CO<sub>2</sub>-mixtures including CH<sub>4</sub> and H<sub>2</sub>S [10–11].

EOSs can be divided into two categories: specialized EOSs, like Span's EOS [12] for CO<sub>2</sub>, and general EOSs, like van der Waals EOS [13]. Compared with the later, specialized equations have a better accuracy, but their applications are limited to certain substances. For example, Span's EOS can only be applied to CO<sub>2</sub>. The general equations can be further divided into two types: equations with simple structures (GESS), such as Redlich–Kwong (RK) EOS [14]; and equations with complex structures (GECS), such as Benedict–Webb–Rubin (BWR) EOS [15]. Although GECS may give better results, they contain more parameters, which may be not available for all of substances. And the complex structures of GECS make the calculation procedures on the thermodynamic properties more complicated, especially when calculating some derived properties like enthalpy and entropy. As a result, GECS is more difficult to be applied. In addition; also due to the complicated calculation procedure, if they are not included originally, GECS is more difficult to be integrated into some commercial simulation tools, like Aspen Plus [16] and IPSpro [17]. Thus from a viewpoint of engineering application, a GESS is preferable if it can provide a sufficient accuracy. The purpose of our study is to evaluate the reliabilities of cubic equations of state, which may be the simplest general equations, for predicting VLE of CO<sub>2</sub> and binary CO<sub>2</sub>-mixtures.

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### Nomenclature

$a, b, c$	constants in equations of state
$k_{ij}$	binary interaction parameter
$N$	number of experimental data
$P$	pressure
$R$	universal gas constant
$T$	temperature
$V$	molar volume
$x$	mole fraction in liquid phase
$X$	total mole fraction in mixtures
$y$	mole fraction in vapor phase
$z$	compressibility factor

### Abbreviations

AAD	absolute average deviation
Abs.	absolute
BWR	Benedict–Webb–Rubin
CCS	CO <sub>2</sub> capture and storage
DEV	deviation
EOR	enhanced oil recovery

EOS	equation of state
GECS	generalized equation with complex structure
GESS	generalized equation with simple structure
PR	Peng–Robinson
PT	Patel–Teja
RK	Redlich–Kwong
SRK	Redlich–Kwong–Soave
VLE	vapor liquid equilibrium

### Subscripts

boi	boiling
c	critical
cal	calculated value
con	condensing
exp	experimental value
g	gas
i, j	component index
l	liquid
s	saturated

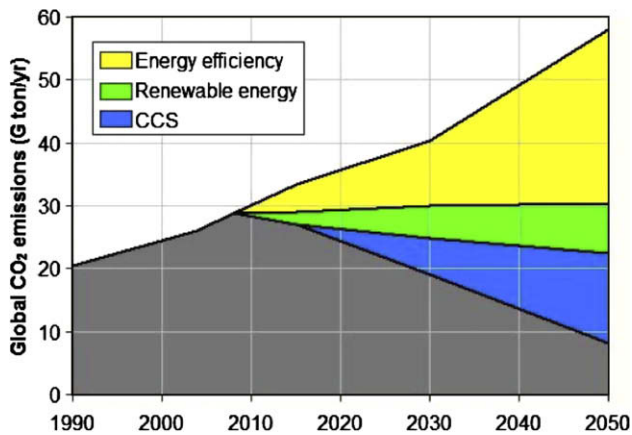


Fig. 1. The strategy to reduce global CO<sub>2</sub> emissions [1].

Since van der Waals proposed his EOS in 1873, numerous modified versions of cubic EOSs with two or more parameters have been developed to improve predictions of volumetric and phase equilibrium properties of fluids. It has been well established that a cubic EOS can model phase equilibrium satisfactorily. In our previous work [18], we compared several cubic EOSs with the preliminary results generated by Aspen Plus. However to obtain more accurate results, the calculated results must be compared with experimental data. In this paper the experimental data on VLE of CO<sub>2</sub> and CO<sub>2</sub>-mixtures were collected; with our self-programming codes, five cubic equations were studied; and the binary interaction parameter,  $k_{ij}$ , was also calibrated for all of the studied EOSs concerning different binary CO<sub>2</sub>-mixtures. Finally insights and guidelines were provided regarding the selection of equations of state for the VLE calculations involved in the design processes of CCS.

## 2. Equations of state

Five cubic EOSs widely used in gas industries are included in this study: RK, SRK, PR, Patel–Teja (PT) [19], and 3PIT [20]. All studied EOSs are summarized in Table 1 with the features as described below:

Table 1

Summary of studied EOSs for CO<sub>2</sub> and CO<sub>2</sub>-mixtures

EOS	Function Form	Year	Mixing Rule
RK	$P = \frac{RT}{V-b} - \frac{a(T)^{0.5}}{V(V+b)}$	1949	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$ ; $b = \sum_i x_i b_i$ ; $k_{ij} = k_{ji}$
SRK	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$	1972	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$ ; $b = \sum_i x_i b_i$ ; $k_{ij} = k_{ji}$
PR	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$	1976	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$ ; $b = \sum_i x_i b_i$ ; $k_{ij} = k_{ji}$
PT	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$	1982	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$ ; $b = \sum_i x_i b_i$ ; $c = \sum_i x_i c_i$ ; $k_{ij} = k_{ji}$
3PIT	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+c)+b(3V+c)}$	1987	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$ ; $b = \sum_i x_i b_i$ ; $c = \sum_i x_i c_i$ ; $k_{ij} = k_{ji}$

- RK EOS is the earliest modification of van der Waals EOS. It improved the intermolecular attraction term. It is suitable for the systems at low pressures.
- SRK EOS is a modification of RK EOS by introducing a temperature-dependent function to modify the attraction parameter. It was one of the most popular EOS in the hydrocarbon industry. SRK is quite capable of predicting VLE for liquid mixtures but it is not very satisfactory for predictions of liquid compressibility.
- PR EOS was proposed based on the previous RK EOS. It is capable of predicting the liquid density as well as vapor pressure in order to further improve VLE predictions. It is recommended for hydrocarbon processing applications, such as gas processing, refinery, and petrochemical processes.
- PT EOS has two substance dependent parameters which are obtained from the liquid density and vapor pressure data, and correlated with an acentric factor. The 3-parameter PT equation has been shown to give satisfactory results for both vapor pressure and density even for heavy and polar compounds. It is also recommended for hydrocarbon processing applications.
- 3PIT EOS is an equation of van der Waals type. It was primarily developed for non-polar compounds, however it was claimed to be able to be applied for polar substances as well [6].

## 3. Calculations of pure CO<sub>2</sub> properties

CO<sub>2</sub> is the major component in the mixtures of CCS system, and in some processes the mole fraction of CO<sub>2</sub> in CO<sub>2</sub>-fluids may

**Table 2**Summary of the experimental data about VLE of pure CO<sub>2</sub>

Source	Year	Temp (K)	Pressure (MPa)	Uncertainty
Holste et al. [21]	1987	215–448	0.1–50.0	P: ±0.01% T: ±0.01 K
Duschek [22]	1990	217–340	0.3–9.0	P: ±0.02% T: ±0.003 K
Gilgen et al. [23]	1992	220–360	0.3–13.0	V: ±(0.015–0.04)%
Brachthuser [24]	1993	233–523	0.8–30.1	V: ±(0.02–0.04)%
Klimeck et al. [25]	2001	240–470	0.5–30	P: ±0.016% T: ±0.004 K

exceed 95%. Therefore it is necessary to study the reliabilities of EOSs on the property calculations of pure CO<sub>2</sub>.

### 3.1. Summary of the experimental data

Since 1980s, many new experiments with better accuracy on VLE of CO<sub>2</sub> have been carried out. Table 2 lists those used for EOS evaluation.

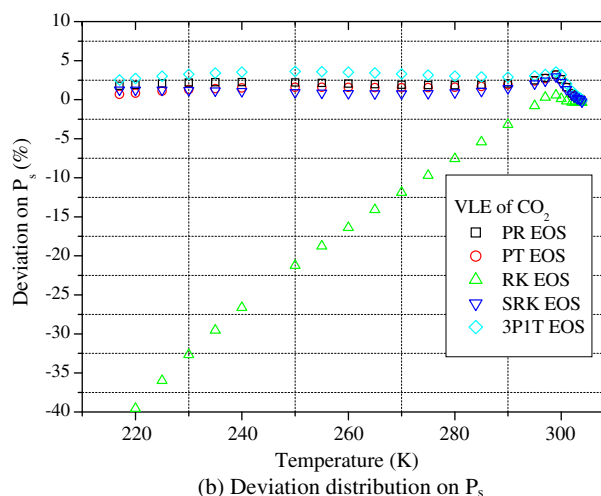
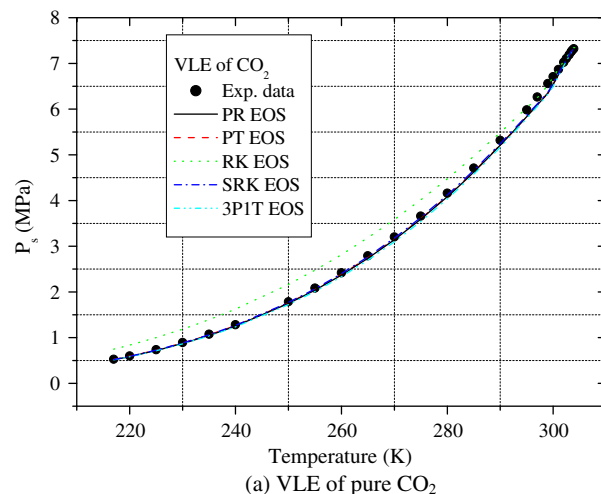
### 3.2. Calculated results

The comparison on VLE of pure CO<sub>2</sub> between experimental data and calculated results from different EOSs is shown in Fig. 2a. Except RK EOS, the equations are all capable of calculating the saturation pressure with an average absolute deviation (AAD) less than 3%. Here AAD is defined as:

$$\text{AAD} = \frac{\sum \text{abs} \left( \frac{M_{\text{cal}} - M_{\text{exp}}}{M_{\text{exp}}} \right)}{N} \times 100\%$$

SRK EOS was found to be more accurate than the others over the whole range of tested conditions, with AAD of 1.05%.

Fig. 2b shows the deviation distribution of the calculated results on the saturated pressure of CO<sub>2</sub>. We can see that cubic EOS's accuracy is independent on temperature, except RK EOS, which gets better along with the rise of temperature. As a conclusion, RK EOS is not appropriate for the VLE calculation of CO<sub>2</sub> if temperature is lower than 290 K.



**Fig. 2.** Calculated results on VLE of pure CO<sub>2</sub> and the deviation distribution on saturated pressure from different EOSs.

**Table 3**Summary of the experimental data for CO<sub>2</sub>-mixtures

Source	Year	Type	Mixture	T (K)	P (MPa)	Uncertainty
Caubet [29]	1901	TPVX	CO <sub>2</sub> /SO <sub>2</sub>	291–416	2.7–10.5	
Reamer et al. [30]	1944	TPxy	CO <sub>2</sub> /CH <sub>4</sub>	311–511	1.4–69	
Steckel [31]	1945	PTxy	CO <sub>2</sub> /H <sub>2</sub> S	221–288.15	0.1–3.6	
Bierlein et al. [32]	1953	PTVX	CO <sub>2</sub> /H <sub>2</sub> S	273–370	1.5–8.5	V: ±0.02% T: ±0.02 K P: ±0.1%
Donnelly et al. [33]	1954	TPxy	CO <sub>2</sub> /CH <sub>4</sub>	167–301	2.0–7.4	
Muirbrook et al. [34,35]	1965	TPxy	CO <sub>2</sub> /O <sub>2</sub> , CO <sub>2</sub> /N <sub>2</sub> , CO <sub>2</sub> /N <sub>2</sub> /O <sub>2</sub>	273.15	5.5–12	
Kestin et al. [36]	1966	TPVX	CO <sub>2</sub> /Ar	293.15–303.15	0.101–2.58	
Fredenslund et al. [37]	1970	TPxy	CO <sub>2</sub> /O <sub>2</sub>	223.15–283.15	1–13	P: ±0.5% T: ±0.02 K P: ±0.01 atm T: ±0.01 K P: ±0.01 atm T: ±0.01 K
Arai et al. [38]	1971	PVTx	CO <sub>2</sub> /N <sub>2</sub> , CO <sub>2</sub> /CH <sub>4</sub>	253–288	55–15	
Sarashina et al. [39]	1971	PVTx	CO <sub>2</sub> /Ar	288.15	5.69–9.77	
Davalos et al. [40]	1976	TPxy	CO <sub>2</sub> /CH <sub>4</sub>	230–250	0.9–8.5	
Altunin et al. [41]	1977	z	CO <sub>2</sub> /Ar	303.15	0.29–10.75	
Mraw et al. [42]	1978	TPxy	CO <sub>2</sub> /CH <sub>4</sub>	89–208	0.5–6.3	
Somait et al. [43]	1978	TPxy	CO <sub>2</sub> /N <sub>2</sub>	270	3–12	P: ±0.015 atm T: ±0.02 K
Dorau et al. [44]	1983	TPxy	CO <sub>2</sub> /N <sub>2</sub>	223.15–273.15	3–20	
Esper et al. [45]	1989	TPVX	CO <sub>2</sub> /N <sub>2</sub>	205–320	0.1–48	P: ±0.015% T: ±0.01 K

## 4. Calculation on the properties of CO<sub>2</sub>-mixture

### 4.1. Impurity

The requirements on CO<sub>2</sub> purity are defined by the requirements from CO<sub>2</sub> transport, storage environmental regulations and the cost. Depending on the CO<sub>2</sub> capture approaches, the purity of CO<sub>2</sub> stream varies from different CO<sub>2</sub> capture systems. Generally impurities may come from air, fuels and the products of combustion. The most common impurities in the flue gas include O<sub>2</sub>, N<sub>2</sub>, Ar, CH<sub>4</sub>, H<sub>2</sub>S, SO<sub>2</sub> and H<sub>2</sub>O. Because CO<sub>2</sub>/H<sub>2</sub>O has been studied intensively in previous studies [26–28], in this paper H<sub>2</sub>O is excluded and our attention is paid to CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, Ar and SO<sub>2</sub>.

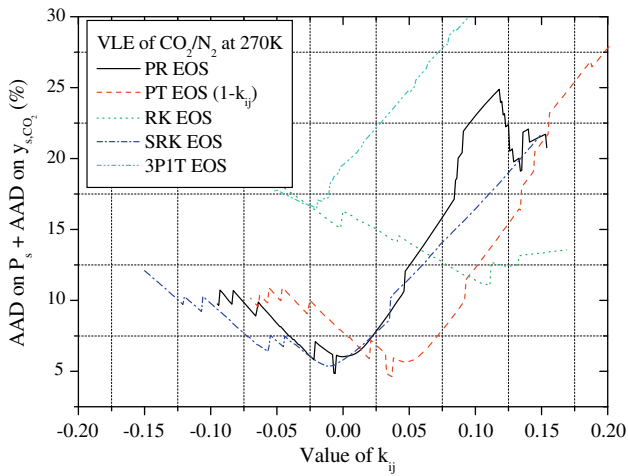


Fig. 3. Relationship between calculation accuracy and binary interaction parameter.

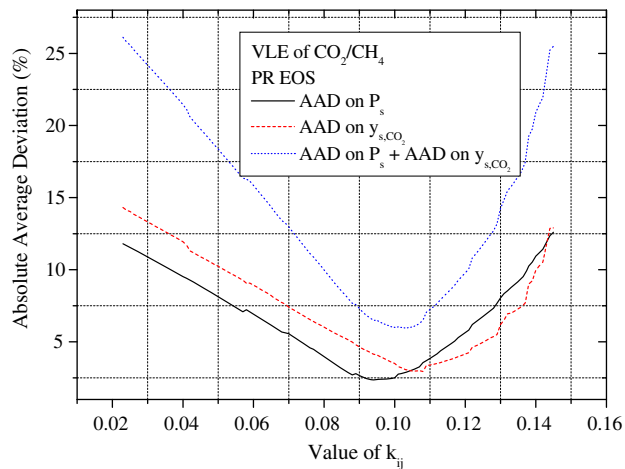


Fig. 4. AAD on  $P_s$ ,  $y_{s,CO_2}$  and  $P_s + y_{s,CO_2}$  of CO<sub>2</sub>/CH<sub>4</sub> at different  $k_{ij}$ .

Table 4  
Calibrated  $k_{ij}$  for different binary CO<sub>2</sub>-mixtures

	PR	PT	RK	SRK	3P1T
CO <sub>2</sub> /CH <sub>4</sub>	0.100	0.905	0.079	0.105	−0.034
CO <sub>2</sub> /O <sub>2</sub>	0.114	0.899	0.168	0.116	0.105
CO <sub>2</sub> /H <sub>2</sub> S	0.099	0.892	0.083	0.106	0.098
CO <sub>2</sub> /N <sub>2</sub>	−0.007	1.036	0.102	−0.014	−0.026
CO <sub>2</sub> /Ar	0.163	0.882	−0.076	0.180	0.140
CO <sub>2</sub> /SO <sub>2</sub>	0.046	0.952	−0.041	0.048	0.083

### 4.2. Survey of experimental data

For the thermodynamic properties of CO<sub>2</sub>-mixtures, many experimental investigations were carried out and focused mainly on the impurities like hydrocarbons, nitrogen and hydrogen sulfide. This was due to their importance for production and processing of natural gas resources and the use of the CO<sub>2</sub>-mixtures for

Table 5

AAD of EOSs on the calculated VLE properties of binary CO<sub>2</sub>-mixtures

		PR	PT	RK	SRK	3P1T
CO <sub>2</sub> /CH <sub>4</sub>	$P_s$	1.68	2.00	5.73	1.87	20.74
	$y_{s,CO_2}$	2.63	3.14	16.71	2.79	26.95
CO <sub>2</sub> /O <sub>2</sub>	$P_s$	4.17	3.62	4.08	4.02	3.50
	$y_{s,CO_2}$	2.89	2.74	14.90	3.44	14.13
CO <sub>2</sub> /H <sub>2</sub> S	$P_s$	1.22	1.48	3.41	1.32	3.32
	$y_{s,CO_2}$	4.54	4.28	9.28	4.49	4.79
CO <sub>2</sub> /N <sub>2</sub>	$P_s$	2.08	1.62	4.08	1.79	3.10
	$y_{s,CO_2}$	2.23	2.17	5.25	2.83	13.15
CO <sub>2</sub> /Ar	$P_s$	2.88	2.85	5.43	3.36	9.79
	$y_{s,CO_2}$	—	—	—	—	—
CO <sub>2</sub> /SO <sub>2</sub>	$P_s$	4.64	4.67	10.62	4.28	4.17
	$y_{s,CO_2}$	—	—	—	—	—

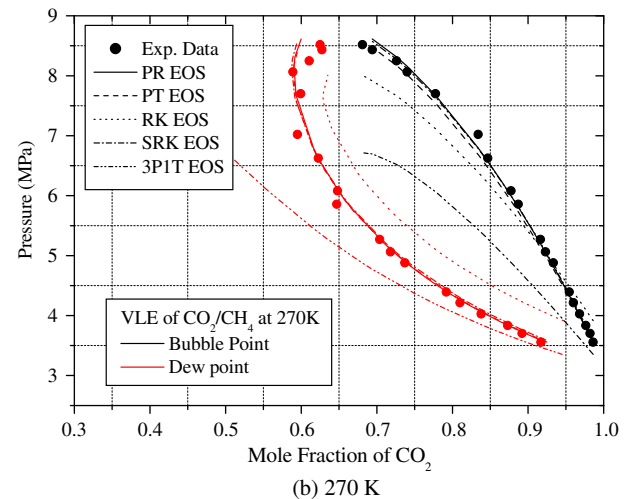
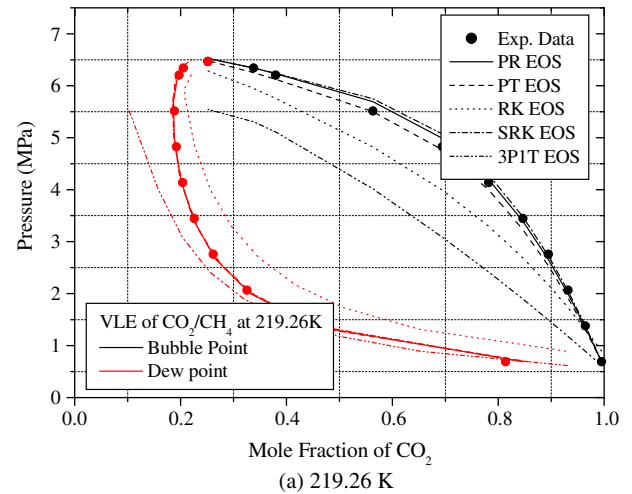


Fig. 5. Calculated results on VLE of CO<sub>2</sub>/CH<sub>4</sub> at 219.26 and 270 K.

enhanced oil recovery (EOR) process. As a result, there are many available experimental data about the mixtures of  $\text{CO}_2/\text{N}_2$ ,  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{H}_2\text{S}$ , which cover a wide range of temperature and pressure. However, the experimental data of  $\text{CO}_2$ -mixtures containing  $\text{O}_2$ , Ar and  $\text{SO}_2$  are limited. The experimental data collected from the literature are summarized in Table 3.

Examining Table 3, some gaps were identified between the available experimental data and the requirements of EOS evaluations. For example, there are few experimental data on VLE of  $\text{CO}_2/\text{SO}_2$  at temperatures lower than 290 K, and there are few experimental data on VLE of  $\text{CO}_2/\text{Ar}$ , except at the temperature 288.15 K and pressure 5–10 MPa. Moreover most of the experimental data are about binary  $\text{CO}_2$ -mixtures. Thus the experimental data of multi-component  $\text{CO}_2$ -mixtures are still necessary to further verify the reliabilities of EOSs.

#### 4.3. Mixing rules and binary interaction parameter

In general the semi-empirical EOSs were developed by using pure component data. The application of these equations has been extended to multi-component systems by defining mixing rules to evaluate the average parameters required in the EOS calculations. In this study, the conventional random van der Waals mixing rules are employed for all of EOSs. In the mixing rules, there is one very important parameter, the binary interaction parameter  $k_{ij}$ , which accounts for the attraction forces between pairs of non-similar molecules. Theoretically it is a modification of intermolecular attraction when calculating thermodynamic properties of mixtures.  $k_{ij}$  is more sensitive to derivative or partial properties such as fugacity coefficients than to total properties such as mixture molar volumes. For that reason, values of  $k_{ij}$  have most often been determined from VLE data.

Since the determination of  $k_{ij}$  requires a large amount of experimental data for a certain system, the calibrated binary interaction parameters are not known for all the binary systems and EOSs. If the calibrated  $k_{ij}$  is unknown, for approximate calculation we can ignore the difference of attraction forces which are between non-similar molecules and between similar molecules, and regard different molecules as the same. Thus, values of  $k_{ij}$  would be taken as zero (if  $(1 - k_{ij})$  is used in the mixing rules, such as RK EOS) or unity (if  $(k_{ij})$  is used in the mixing rules, such as PT EOS).

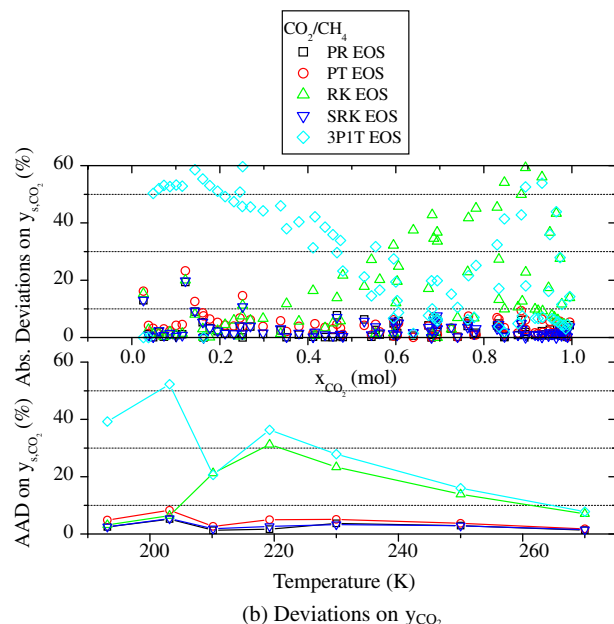
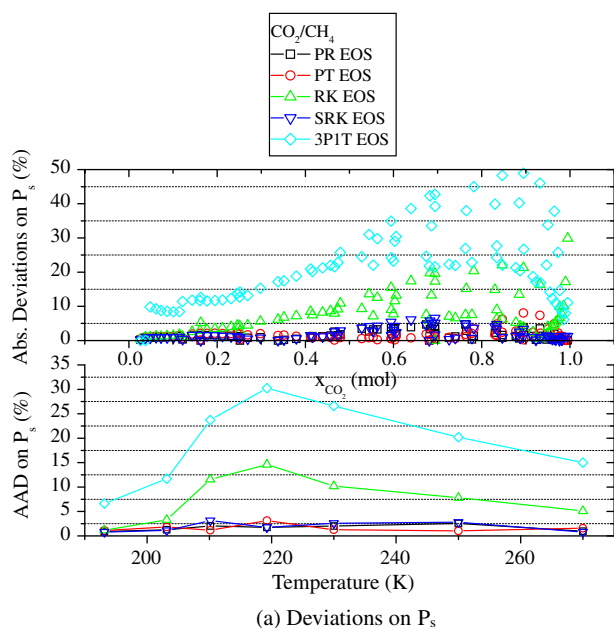


Fig. 6. Calculation deviations on  $P_s$  and  $y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{CH}_4$ .

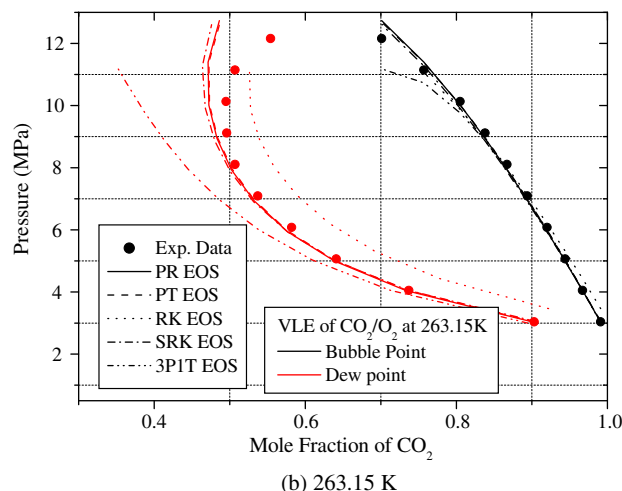
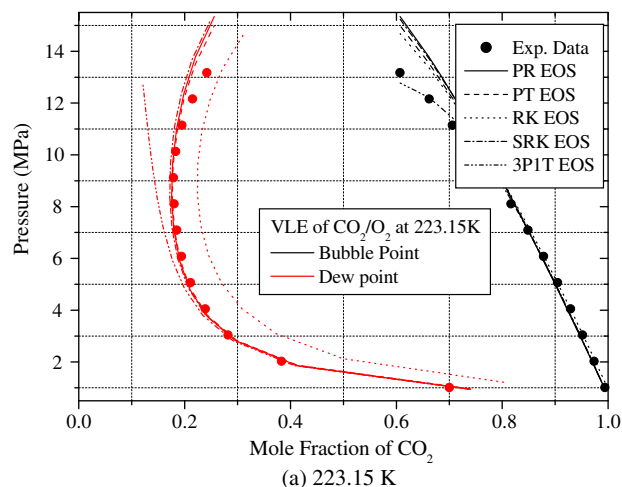


Fig. 7. Calculated results on VLE of  $\text{CO}_2/\text{O}_2$  at 223.15 and 263.15 K.



However an inappropriate  $k_{ij}$  may cause poor calculating accuracy of an EOS. Fig. 3 shows the sum of AAD on the saturated pressure and AAD on the saturated vapor fraction of  $\text{CO}_2$  ( $y_{s,\text{CO}_2}$ ) at different values of binary interaction parameter  $k_{ij}$  for  $\text{CO}_2/\text{CH}_4$ . It is quite clear that AAD changes with the variation of  $k_{ij}$ .

In order to improve cubic equations' accuracy and evaluate EOSs accurately, the binary interaction parameters of various binary  $\text{CO}_2$ -mixtures must be determined first. Usually the binary interaction parameter  $k_{ij}$  is considered to be independent of temperature, composition and density [46]. However, others have suggested there are also some different conclusions that  $k_{ij}$  is temperature and composition dependent [47–49]. As the interaction parameter is determined by matching the predicted values with experimental data, it should be considered as a fitting param-

eter only and not a rigorous physical parameter [6]. In this study the value of  $k_{ij}$  is still regarded as a constant.

The saturated pressures and saturated vapor compositions were calculated from the known saturated temperatures ( $T_s$ ) and saturated liquid compositions ( $x_s$ ). Fig. 4 shows the AAD of PR EOS on  $P_s$ ,  $y_{s,\text{CO}_2}$ , and  $P_s + y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{CH}_4$  at different  $k_{ij}$ . It clearly displays that for various properties, the right value of  $k_{ij}$  may be different. Since both saturated pressure and saturated vapor composition are important to CCS processes, here we calibrate  $k_{ij}$  as the value that makes the sum of AAD on  $P_s$  and  $y_{s,\text{CO}_2}$  minimum. For  $\text{CO}_2/\text{Ar}$  and  $\text{CO}_2/\text{SO}_2$ , because no  $x_s$  was known at dew points and no  $y_s$  was known at bubble points, no AAD on  $y_{s,\text{CO}_2}/x_{s,\text{CO}_2}$  was calculated. In these cases, the value of  $k_{ij}$  that makes the AAD on  $P_s$  minimum was chosen. Based on the experimental data listed in Table 3,  $k_{ij}$  was calibrated for every EOS concerning every binary mixture. Results are given in Table 4.

#### 4.4. VLE

With the new calibrated  $k_{ij}$ , VLE of different binary  $\text{CO}_2$ -mixtures were calculated using different EOSs; and the calculated results were compared with experimental data. Table 5 summarized the absolute average deviations of EOSs. In general, all of the studied EOS have various performances for various mixtures. Comparatively PR, PT and SRK are superior to RK and 3P1T for all

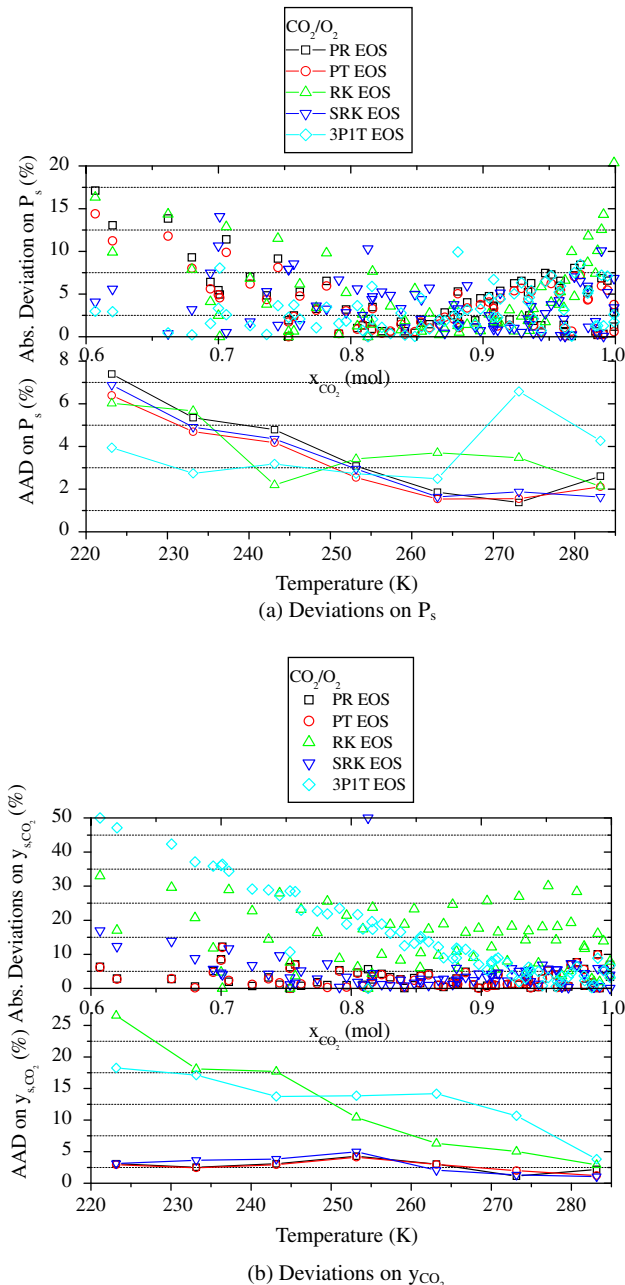


Fig. 8. Calculation deviations on  $P_s$  and  $y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{O}_2$ .

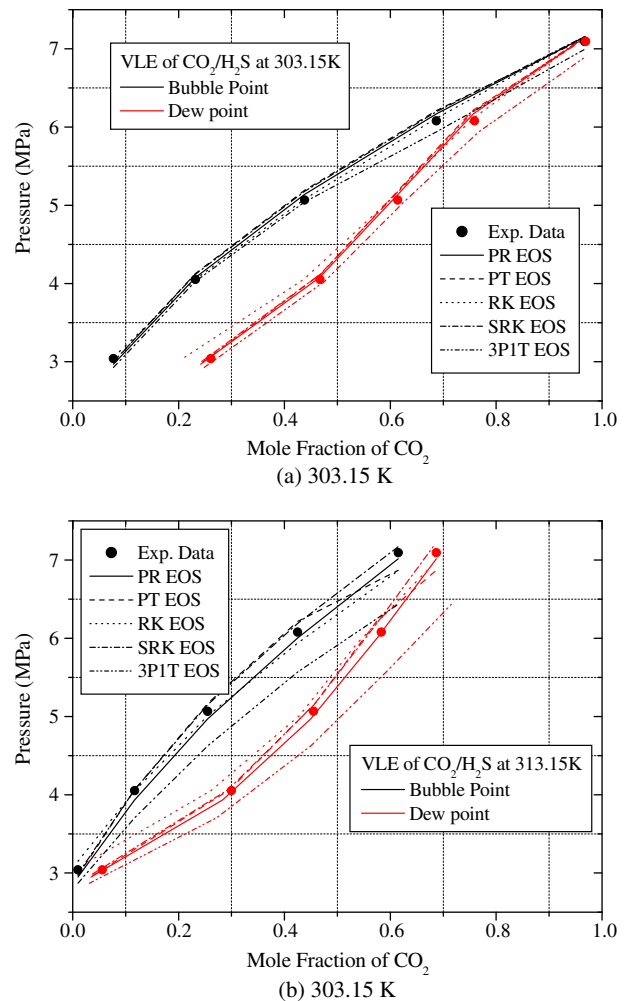


Fig. 9. Calculated results on VLE of  $\text{CO}_2/\text{H}_2\text{S}$  at 303.15 and 313.15 K.

of the studied mixtures, except  $\text{CO}_2/\text{SO}_2$ . It should be pointed out that although 3P1T is primarily developed for non-polar compounds, it does not show any advantages in the VLE calculations of  $\text{CO}_2/\text{CH}_4$ ,  $\text{CO}_2/\text{O}_2$ ,  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{Ar}$ . In the following, further analysis was carried out regarding every binary  $\text{CO}_2$ -mixture.

#### 4.4.1. Mixture of $\text{CO}_2/\text{CH}_4$

Fig. 5 shows the calculated VLE diagrams of  $\text{CO}_2/\text{CH}_4$  at 219.26 and 270 K. It is clear that the calculated results of PR, PT and SRK fit the experimental data well; and comparatively 3P1T has the worst accuracy. Given  $T$  and  $x_{s,\text{CO}_2}$ , RK may predict a lower, while 3P1T may predict a higher  $\text{CO}_2$  composition in vapor phase than the actual value. In addition, the performances of EOSs are normally getting worse as the conditions are approaching the critical points of mixtures. For example when  $x_{s,\text{CO}_2}$  is 68.1 mol%, 270 K is quite close to the critical temperature of  $\text{CO}_2/\text{CH}_4$  ( $T_c = 275.2$  K). At these

composition and temperature, except RK, cubic equations failed to calculate  $P_s$  and  $y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{CH}_4$  with an AAD within 30%. The big deviations might be caused by the appearance of the so-called trivial solution [50]. The trivial solution could be avoided by applying some novel algorithms or by making a better initial value [51–54]. In this paper the algorithm developed by Asselineau [51] was used.

Fig. 6 shows the deviation distributions of all EOSs on  $P_s$  and  $y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{CH}_4$ . PR, PT and SRK have similar accuracy on  $P_s$  and  $y_{s,\text{CO}_2}$ , and their performances do not vary clearly, nearly within 5%, at various temperature and  $x_{s,\text{CO}_2}$  of  $\text{CO}_2$ . Different from them, RK and 3P1T have much worse accuracy on  $y_{s,\text{CO}_2}$  than on  $P_s$ ; and their performances are affected by temperature and  $x_{s,\text{CO}_2}$  obviously. Their AADs on  $P_s$  and  $y_{s,\text{CO}_2}$  rise first and then drop along with the rise of temperature approximately; meanwhile RK has better accuracies on both  $P_s$  and  $y_{s,\text{CO}_2}$  but 3P1T has better accuracies on  $P_s$  at lower  $x_{s,\text{CO}_2}$ . Generally PR is more accurate than the other cubic EOSs in the calculations on  $P_s$  and  $y_{s,\text{CO}_2}$ , with respective AADs of 1.68% and 2.63%.

#### 4.4.2. Mixture of $\text{CO}_2/\text{O}_2$

Fig. 7 shows the calculated VLE diagrams of  $\text{CO}_2/\text{O}_2$  at 223.15 and 263.15 K. Compared with the calculations on  $\text{CO}_2/\text{CH}_4$ , PR, PT, RK and SRK have quite similar performances, but 3P1T has a better one, especially on the saturated pressure. Along with the increments of oxygen's mole fraction in liquid phase, the performances of all equations are getting worse. When  $x_{s,\text{O}_2}$  is high, they may generate higher saturated pressures at low temperatures, such as 223.15 K, while predict lower values of  $y_{s,\text{CO}_2}$ , except RK as high temperatures, like 263.15 K.

Fig. 8 shows the distributions of the absolute deviations on  $P_s$  and  $y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{O}_2$ . Comparatively temperature have quite regular impacts on the calculation accuracy of both  $P_s$  and  $y_{s,\text{CO}_2}$ . Except 3P1T's AAD on  $P_s$ , all equations' AADs on  $P_s$  and  $y_{s,\text{CO}_2}$  drop along with the increment of temperature. Moreover 3P1T's deviations on  $y_{s,\text{CO}_2}$  drop long with the increment of  $x_{s,\text{CO}_2}$ . Generally 3P1T is superior in the calculations on  $P_s$  with AAD of 3.50%, while PT is superior in the calculations on the saturated vapor composition where AAD is 2.74%.

#### 4.4.3. Mixture of $\text{CO}_2/\text{H}_2\text{S}$

Fig. 9 shows the calculated VLE diagrams of  $\text{CO}_2/\text{H}_2\text{S}$  at 303.15 and 313.15 K. Clearly the results of all cubic equations agree with the experimental data well except 3P1T at the high temperature. And the accuracy differences amongst all equations are much smaller, if compared with the VLE calculations of other binary

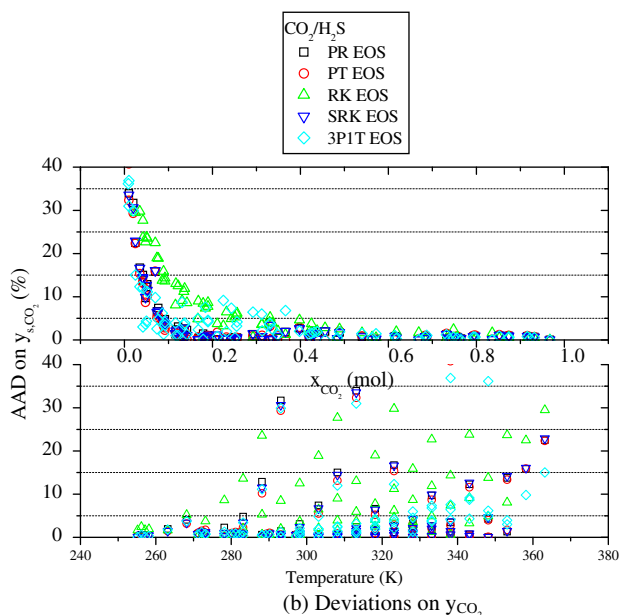
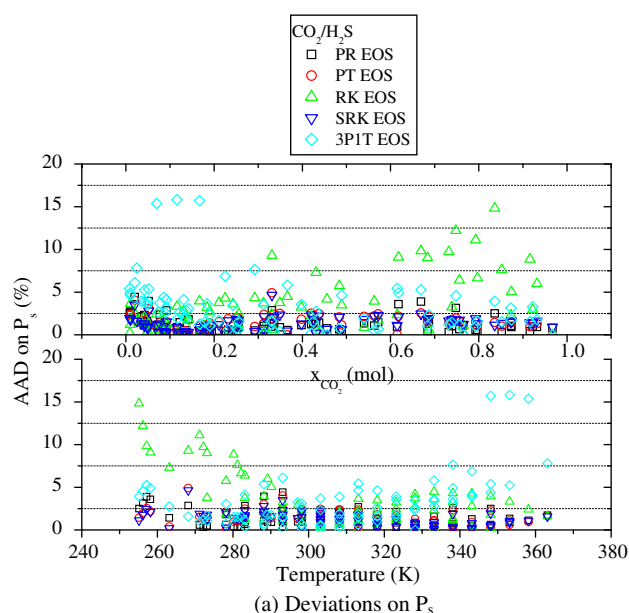


Fig. 10. Calculation deviations on  $P_s$  and  $y_{s,\text{CO}_2}$  of  $\text{CO}_2/\text{H}_2\text{S}$ .

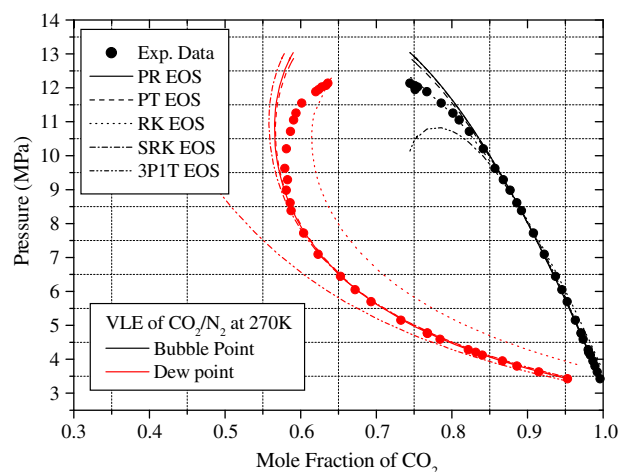


Fig. 11. Calculated results on VLE of  $\text{CO}_2/\text{N}_2$  at 270 K.

CO<sub>2</sub>-mixtures. Moreover 3P1T always got smaller saturated pressures than the experimental data at both low and high temperatures.

Fig. 10 shows the distributions of the absolute deviations on  $P_s$  and  $y_{s,CO_2}$  of CO<sub>2</sub>/H<sub>2</sub>S. Comparatively PR, PT and SRK's accuracies on  $P_s$  are not obviously affected by temperature and  $x_{s,CO_2}$ ; RK's accuracy on  $P_s$  becomes better while and 3P1T's becomes worse along with the increments of temperature and decrements of  $x_{CO_2}$ . As to the calculation accuracy on  $y_{s,CO_2}$ , all equations have better performance at lower temperatures and higher  $x_{s,CO_2}$ . Generally, PR is superior in the calculations on  $P_s$  with AAD at 1.22% and SRK is superior in the calculations on  $y_{s,CO_2}$ , where AAD is 4.49%.

#### 4.4.4. Mixture of CO<sub>2</sub>/N<sub>2</sub>

Fig. 11 shows the calculated VLE diagrams of CO<sub>2</sub>/N<sub>2</sub> at 270K. All equations have better accuracies on  $P_s$  than on  $y_{s,CO_2}$ . It is quite similar to the calculations on CO<sub>2</sub>/O<sub>2</sub> that the performances of all equations are getting worse at high  $x_{N_2}$ , except RK. Compared with experimental data, RK always predicts higher; while 3P1T predicts lower mole fraction of CO<sub>2</sub> in vapor phase.

Fig. 12 shows the distributions of the absolute deviations on  $P_s$  and  $y_{s,CO_2}$  of CO<sub>2</sub>/N<sub>2</sub>. Except RK, all equations have better accuracy on  $P_s$  and  $y_{s,CO_2}$  at high  $x_{s,CO_2}$ . For example, at 270 K, the deviations on  $P_s$  and  $y_{s,CO_2}$  of PR, PT and SRK are within 2.5% when  $x_{s,CO_2}$  is over 85%; however they may be larger than 5% when  $x_{s,CO_2}$  is less than 80%. Along with the increments of  $x_{s,CO_2}$ , RK's absolute deviations of on  $P_s$  drop first and then rise, while its absolute deviations on  $y_{s,CO_2}$  rise first and then drop. Generally PT is more accurate than the other cubic EOSs in the calculations on  $P_s$  and  $y_{s,CO_2}$ , with respective AADs of 1.62% and 2.17%.

#### 4.4.5. Mixture of CO<sub>2</sub>/Ar

Fig. 13 shows the calculated VLE diagrams of CO<sub>2</sub>/Ar at 288.15 K. PR, PT and SRK have quite similar calculated results, which agree well with the experimental data on condensing pressures, but not on boiling pressures when  $x_{Ar}$  is high. RK also has a better accuracy on condensing pressures. 3P1T's deviations on both dew and bubble points are very clear.

Fig. 14 shows the distributions of the absolute deviations on  $P_s$  of CO<sub>2</sub>/Ar. To the calculations on condensing pressures, the accura-

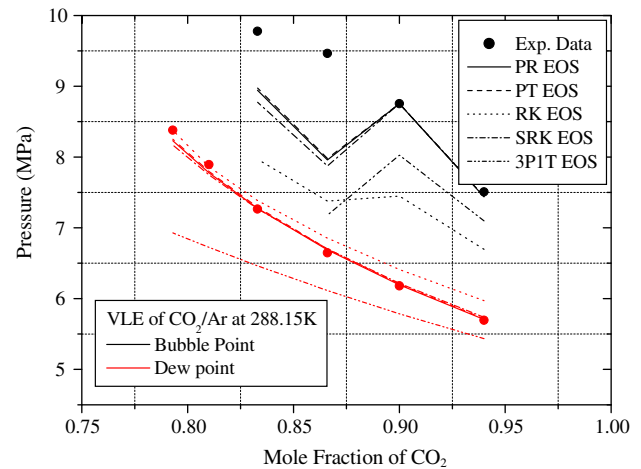


Fig. 13. Calculated results on VLE of CO<sub>2</sub>/Ar at 288.15 K.

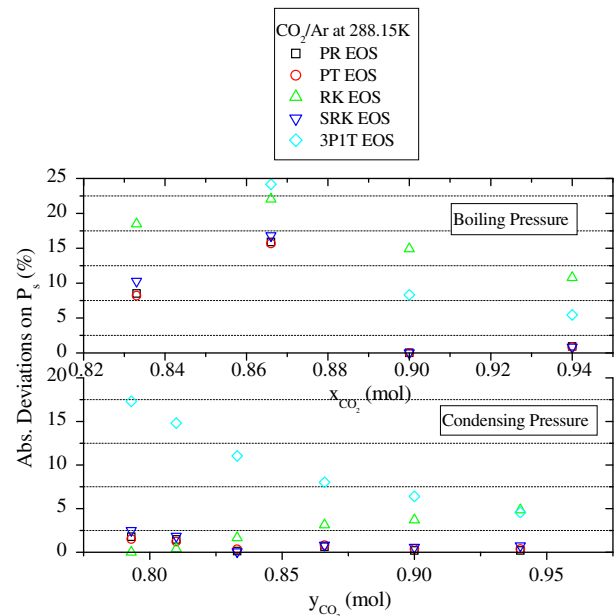


Fig. 14. The distributions of absolute deviations of on  $P_s$  of CO<sub>2</sub>/Ar.

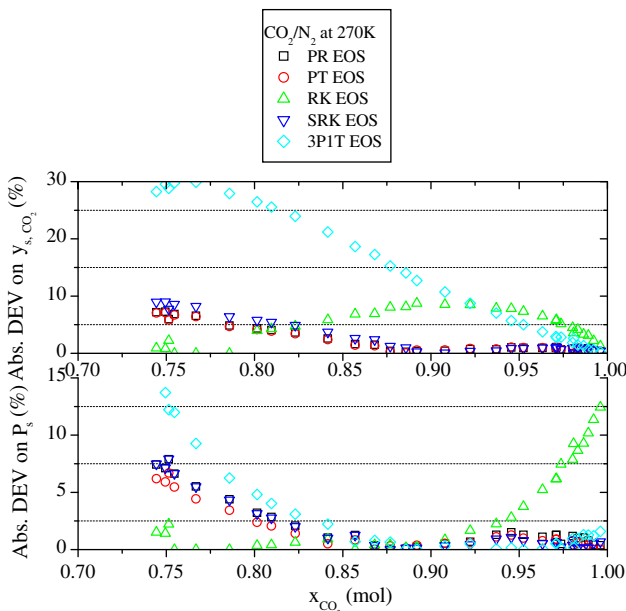


Fig. 12. The distributions of absolute deviations on  $P_s$  and  $y_{s,CO_2}$  of CO<sub>2</sub>/N<sub>2</sub>.

cies of PR, PT, SRK and 3P1T are getting better; while RK's accuracy is getting worse along with the increments of CO<sub>2</sub> mole fraction in vapor phase. Generally PT is superior to other equations, where AAD on  $P_s$  is 2.85%.

#### 4.4.6. Mixture of CO<sub>2</sub>/SO<sub>2</sub>

Fig. 15 shows the calculated VLE diagrams of CO<sub>2</sub>/SO<sub>2</sub> at  $X_{CO_2} = 62.13$  and 88.71 mol%. At low concentration of CO<sub>2</sub>, such as  $X_{CO_2} = 62.13$  mol%, PR, PT, SRK and 3P1T have better accuracy on VLE; while at high concentration of CO<sub>2</sub>, such as  $X_{CO_2} = 88.71$  mol%, RK's results agree with the experimental data better. Compared with the VLE calculations on other CO<sub>2</sub>-mixtures, 3P1T has much better performances on CO<sub>2</sub>/SO<sub>2</sub>.

Fig. 16 shows the distributions of the absolute deviations on  $P_s$  of CO<sub>2</sub>/SO<sub>2</sub>. Along with the rise of  $X_{SO_2}$ , PR, PT, SRK and 3P1T's accuracies on boiling pressures are getting worse, while their accuracies on condensing pressures are getting better except  $X_{SO_2}$  is lower than 10 mol%. RK performs in a similar way on boiling pres-



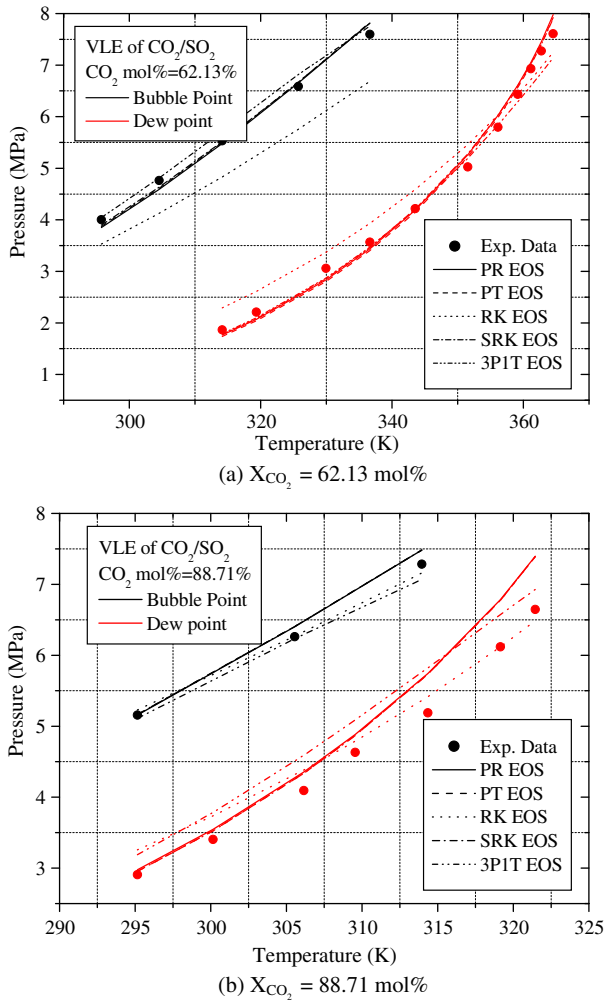


Fig. 15. Calculated results on VLE of CO<sub>2</sub>/SO<sub>2</sub> at X<sub>CO2</sub> = 62.13 and 88.71 mol%.

tures, but a reverse way on condensing pressures. Comparatively the accuracies of all cubic equations were not affected by temperature clearly. In general, 3P1T is more accurate than the other EOSs in the calculations on  $P_s$ , where AAD is 4.17%.

5. Further discussions on binary interaction parameter,  $k_{ij}$

Binary interaction parameter,  $k_{ij}$ , can also be found from the literature for some CO<sub>2</sub>-mixtures. Comparisons were carried out between the calculated results generated with the literature  $k_{ij}$  and the new calibrated  $k_{ij}$ . Absolute average deviations are listed in Table 6. Because the target function applied to the calibration

Table 6

AAD of EOSs with the literature  $k_{ij}$  and the new calibrated  $k_{ij}$

EOS		CO <sub>2</sub> /CH <sub>4</sub>		CO <sub>2</sub> /N <sub>2</sub>		CO <sub>2</sub> /H <sub>2</sub> S	
		$k_{ij}$	AAD on $P_s/y_{s,CO_2}$	$k_{ij}$	AAD on $P_s/y_{s,CO_2}$	$k_{ij}$	AAD on $P_s/y_{s,CO_2}$
PR	New calibrated	0.100	1.68/2.63	−0.007	2.08/2.23	0.099	1.22/4.54
	Literature [55]	0.0919	1.52/3.87	−0.017	2.11/2.38	0.0974	1.18/4.69
PT	New calibrated	0.905	2.00/3.14	—	—	—	—
	Literature [19]	0.907	1.93/3.24	—	—	—	—
RK	New calibrated	0.079	5.73/16.71	0.102	4.08/5.25	0.083	3.41/9.28
	Literature [16]	0.0933	4.73/18.41	−0.0315	16.76/11.98	0.0989	4.39/8.36
SRK	New calibrated	—	—	—	—	0.106	1.32/4.49
	Literature [10]	—	—	—	—	0.0989	1.14/5.00

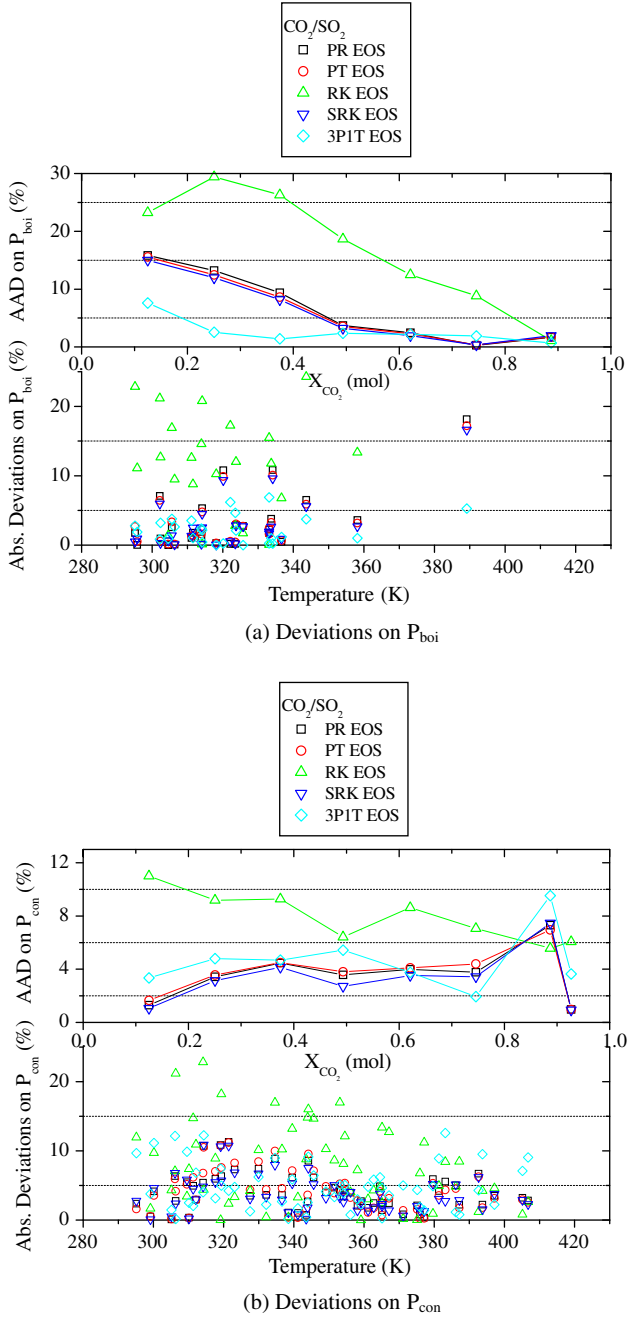


Fig. 16. The distributions of absolute deviations on condensing and boiling pressures of CO<sub>2</sub>/SO<sub>2</sub>.

of  $k_{ij}$  was defined to make the sum of deviations on  $P_s$  and  $y_{s,CO_2}$  minimum in this paper, the accuracies of EOSs on  $P_s$  may not be

improved with the new regressed  $k_{ij}$ . However the accuracies of EOSs on  $P_s + y_{s,CO_2}$  were remarkably improved.

Moreover, as mentioned above that the determination of  $k_{ij}$  requires a large amount of experimental data, the calibrated  $k_{ij}$  might be inappropriate, because the VLE experimental data of  $CO_2/Ar$  are limited. Therefore it is necessary to carry out more experiments to close the experimental gaps, in order to improve the EOS accuracy.

## 6. Conclusions

Based on the collected experimental data, this paper studied the reliability of five cubic equations of state on predicting vapor liquid equilibria of  $CO_2$  and binary  $CO_2$ -mixtures (including  $CH_4$ ,  $O_2$ ,  $H_2S$ ,  $N_2$ ,  $Ar$  and  $SO_2$ ). According to the results, we have the following conclusions on the various tested EOSs:

- (1) For the VLE properties of pure  $CO_2$ , SRK is superior in the calculations on saturated pressure with AAD of 1.05%. In general RK is not recommended for VLE calculations.
- (2) The experimental data on VLE were collected from literatures for all of studied binary  $CO_2$ -mixtures. Some experimental gaps were identified: there are few experimental data on VLE of  $CO_2/SO_2$  at temperatures lower than 290 K, and on VLE of  $CO_2/Ar$ , except at the temperature 288.15 K and pressure 5–10 MPa.
- (3) The binary interaction parameter has clear effects on the calculating accuracy of an EOS in the VLE calculations of  $CO_2$ -mixtures. In order to improve EOSs' accuracy,  $k_{ij}$  has to be calibrated based on experimental data for all of the EOSs regarding all of the binary  $CO_2$ -mixtures.
- (4) For the VLE properties of binary  $CO_2$ -mixtures, PR, PT and SRK are generally superior to RK and 3P1T. Comparatively PR is recommended to the calculations of  $CO_2/CH_4$  and  $CO_2/H_2S$ ; PT is recommended to the calculations of  $CO_2/O_2$ ,  $CO_2/N_2$  and  $CO_2/Ar$ ; while 3P1T is recommended to the calculations of  $CO_2/SO_2$ .
- (5) With the new calibrated  $k_{ij}$ , although EOSs accuracy on saturated pressure may not be improved, they have better accuracies on saturated vapor composition than with the values of  $k_{ij}$  available from the literature.

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