

Impacts of equations of state (EOS) and impurities on the volume calculation of CO₂ mixtures in the applications of CO₂ capture and storage (CCS) processes

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ABSTRACT

Volume property is the necessary thermodynamic property in the design and operation of the CO₂ capture and storage system (CCS). Because of their simple structures, cubic equations of state (EOS) are preferable to be applied in predicting volumes for engineering applications. This paper evaluates the reliabilities of seven cubic EOS, including PR, PT, RK, SRK, MPR, MSRK and ISRK for predicting volumes of binary CO₂ mixtures containing CH₄, H₂S, SO₂, Ar and N₂, based on the comparisons with the collected experimental data. Results show that for calculations on the volume properties of binary CO₂ mixtures, PR and PT are generally superior to others for all of the studied mixtures. In addition, it was found that the binary interaction parameter has clear effects on the calculating accuracy of an EOS in the volume calculations of CO₂ mixtures. In order to improve the accuracy, k_{ij} was calibrated for all of the EOS regarding the gas and liquid phases of all the studied binary CO₂ mixtures, respectively.

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1. Introduction

Carbon dioxide capture and storage (CCS), which involves the processes of capture, transport and long-term storage of carbon dioxide, is a technology aimed at reducing greenhouse gas emissions from burning fossil fuels during industrial and energy-related processes. CCS has been verified as a key element in mitigating the climate change, along with other actions, such as improving energy efficiency, and switching to renewable energy resources reducing greenhouse gas emissions [1].

The volume property of CO₂ mixtures plays an important role in the design and operation of many processes of the CCS system, like compression, transportation and storage. For example, to transport a certain amount of CO₂ stream by pipeline, CO₂ mixtures with high densities are much desired to reduce the size of pipeline under the same operating conditions, because a high density implies a smaller volume [2]. In addition, since the impurities may change the volume of CO₂ mixtures, they would affect the storage capacity in mature natural gas fields. In storage depth of 1 km and 2 km, 5 mol% N₂ leads to a reduction of the storage capacity of 22% and 9%, respectively [3]. Therefore it is of great importance to have a good understanding about the volumes of CO₂ mixtures.

Since CCS processes cover a wide range of operating conditions from normal atmosphere to supercritical phase, and involve multi-

components, the experimental data cannot satisfy the requirements of the engineering applications. Therefore, semi-empirical equations of state are usually used to predict those properties. Due to the rapid increasing research on CCS, there has been an increased interest in finding a proper equation of state (EOS) to calculate the densities of CO₂ mixtures. GERG2004, which is developed by the Lehrstuhl für Thermodynamik at Ruhr-Universität Bochum, has attracted more and more interest for the property calculations of CO₂ mixtures. It has a formation based on a multi-fluid approximation, which is explicit in the reduced Helmholtz energy, dependent on the density, the temperature, and the composition. It is claimed to be able to calculate a number of thermodynamic properties of mixtures of natural gas components accurately [4]. However, as we have discussed in [6], the applications of GERG2004 are limited due to its complexity from the viewpoint of engineer. Moreover, it cannot be used for the mixtures containing SO₂. Based on our previous analysis [5–7], cubic equations of state are more preferable in the engineering applications, because they have simple structures and reasonable accuracy. We have evaluated the reliabilities of cubic EOS for predicting VLE of CO₂ mixtures and concluded that the reliabilities of different equations of state vary for different properties, components and conditions [6]. Meanwhile, results also show that calibrating the binary interaction parameter, k_{ij} , can be helpful to improve the accuracy of EOS. In this work, we are going to study different cubic EOS regarding the volume calculation of CO₂ mixtures, including the calibration of k_{ij} from experimental data.

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Nomenclature

k_{ij}	binary interaction parameter
N	number of experimental data
P	pressure
T	temperature
V	molar volume
x	mole fraction in liquid phase
X	total mole fraction in mixtures
y	mole fraction in gas phase
ξ_{ij}	binary interaction parameter

Abbreviation

AAD	absolute average deviation
Abs	absolute
CCS	CO ₂ capture and storage
Comp	compressibility
Dev	deviation
EOR	enhanced oil recovery

EOS	equation of state
ISRK	improved SRK
MPR	modified PR
MSRK	modified SRK
PR	Peng–Robinson
PT	Patel–Teja
RK	Redlich–Kwong
SRK	Redlich–Kwong–Soave
VLE	vapor liquid equilibrium

Subscript

cal	calculated value
exp	experimental value
g	gas
i, j	component labels
l	liquid

With the results, the insights and guidelines would be provided concerning the selection of equations of state for density calculations.

2. Equations of state

Seven cubic equations of state are included in this study: Peng–Robinson (PR) [8], Patel–Teja (PT) [9], Redlich–Kwong (RK) [10], Redlich–Kwong–Soave (SRK) [11], modified SRK (MRK) [12], modified PR (MPR) [13], and improved SRK (ISRK) [14]. All studied EOS are summarized in Table 1 with the features as described below:

- PR EOS is proposed based on RK EOS. It is capable of predicting the liquid density as well as gas 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 gas pressure data, and correlated with an acentric factor. The three-parameter PT equation has been shown to give satisfactory results for both gas pressure and density even for heavy and polar compounds. It is also recommended for hydrocarbon processing applications.
- RK EOS is the earliest modification of van der Waals EOS. It improved the intermolecular attraction. It is more applicable for the system at low pressures.
- SKR EOS is another 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.

- MSRK and MPR EOS include a translation along the volume axis. Applications of this improved method to pure liquid, mixtures of liquids or gases, and petroleum fluids show that markedly superior volume estimations are obtained, except in the neighborhood of the pure-component critical points; nonetheless, critical volumes for mixtures can be estimated correctly.
- ISRK EOS is another modification of SRK, by introducing a temperature dependent volume correction. ISRK can provide accurate densities for polar and non-polar pure substances both near to and far from the critical point. It can also be easily extended to mixtures, and the calculation results show that it can shift the critical locus towards experimental values and give good results for the liquid densities of mixtures.

3. Calculation on the volumes of CO₂ mixtures**3.1. Impurity**

The requirements on CO₂ purity are defined by the requirements from CO₂ transport, storage environmental regulations and the cost. Depending on the CO₂ capture approaches, the purity of CO₂ stream varies from different CO₂ capture systems. Generally impurities may come from air, fuels and the products of combustion. The most common impurities in the flue gas include O₂, N₂, Ar, CH₄, H₂S, SO₂ and H₂O. Because CO₂/H₂O has been studied intensively in previous studies [15], in this paper H₂O is excluded.

Table 1
Summary of studied EOS for volume calculations of CO₂ mixtures.

EOS	Function form	Mixing rule
PR	$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$; $b = \sum_i x_i b_i$; $k_{ij} = k_{ji}$
PT	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} \xi_{ij}$; $b = \sum_i x_i b_i$; $\xi_{ij} = \xi_{ji}$
RK	$P = \frac{RT}{V-b} - \frac{a(T)^{0.5}}{V(V+b)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$; $b = \sum_i x_i b_i$; $k_{ij} = k_{ji}$
SRK	$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$; $b = \sum_i x_i b_i$; $k_{ij} = k_{ji}$
MPR	$P = \frac{RT}{V-b} - \frac{a}{(V+c)(V+b+2c)+(b+c)(V-b)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$; $b = \sum_i x_i b_i$; $c = \sum_i x_i c_i$; $k_{ij} = k_{ji}$
MSRK	$P = \frac{RT}{V-b} - \frac{a}{(V+c)(V+b+2c)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$; $b = \sum_i x_i b_i$; $c = \sum_i x_i c_i$; $k_{ij} = k_{ji}$
ISRK	$P = \frac{RT}{V+c-b} - \frac{a(T)}{(V+c)(V+b+c)}$	$a = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$; $b = \sum_i \sum_j x_i x_j (\frac{b_i + b_j}{2})(1 - l_{ij})$; $c = \sum_i x_i c_i$; $k_{ij} = k_{ji}$; $l_{ij} = l_{ji}$

3.2. Survey of experimental data

For the volume property of CO₂ mixtures, many investigations were carried out and focused mainly on the impurities like hydrocarbons, nitrogen and hydrosulfide. This was due to their importance for production and processing of natural gas resources and using the CO₂ mixture for enhanced oil recovery (EOR) process. As a result, there are many available experimental data about the mixtures of CO₂/N₂, CO₂/CH₄ and CO₂/H₂S, which cover a wide range of temperature and pressure. However, the experimental data of CO₂ mixtures containing Ar are limited; and there are no experimental data about CO₂/O₂. As to the mixtures of CO₂/SO₂, although the measured points are plenty, their reliabilities remain unknown, because they were conducted long time ago and there are no other available sources, which can be used to further verify them. The experimental data collected from the literature are summarized in Table 2.

3.3. Mixing rules and binary interaction parameter

In general the semi-empirical equations of state were developed by using pure component data. The application of these equations has been extended to a multi-component system by defining mixing rules to evaluate the average parameters required in the EOS calculations. In the mixing rules, there is one very important parameter, binary interaction parameter k_{ij} , which accounts for the attraction forces between pairs of non-similar molecules. It has been verified that an inappropriate k_{ij} may cause poor calculating accuracy of an EOS [7].

Theoretically k_{ij} is a modification of intermolecular attraction when calculating thermodynamic properties of mixtures. It 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.

However, it does not mean the k_{ij} regressed from VLE data will definitely result in a good accuracy on the density calculation as well. Fig. 1 shows the absolute average deviations (AAD), which is defined as: $AAD = \frac{\sum \left| \frac{V_{calc} - V_{exp}}{V_{exp}} \right| \times 100\%}{N}$, of PR EOS on the saturated

pressure, the saturated gas fraction of CO₂ (y_{s,CO_2}), the gas volume and liquid volume of CO₂/CH₄ at different values of binary interaction parameter k_{ij} . It is quite clear that the right values of k_{ij} are different for various properties.

In order to improve cubic equations' accuracy and evaluate EOS accurately, the binary interaction parameters of various binary CO₂ mixtures were calibrated regarding both gas and liquid volumes based on the experimental data. As the interaction parameter is determined by matching the predicted values with experimental

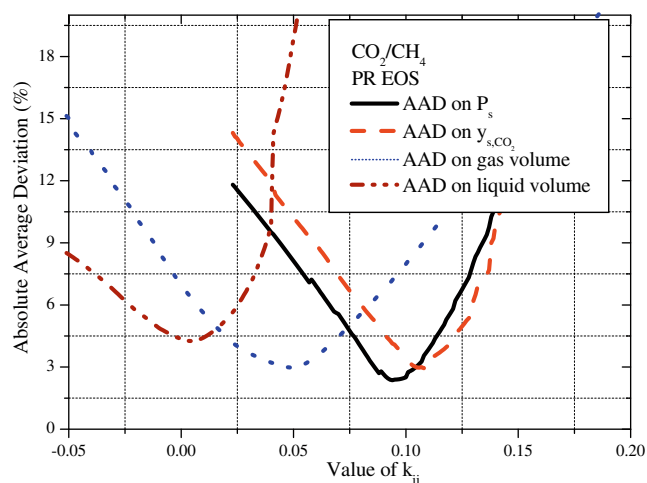


Fig. 1. AAD of PR EOS on P_s , y_{s,CO_2} , gas volume and liquid volume of CO₂/CH₄ at different k_{ij} .

data, k_{ij} is considered to be independent of temperature, composition and volume [27,28]. Hence, in this study the value of k_{ij} is still regarded as a constant. Results on correlated k_{ij} are given in Table 3.

With the new correlated k_{ij} , volumes of different binary CO₂ mixtures were calculated using different EOS with our self-programming codes. The calculated results were compared with experimental data, and Table 4 summarized the absolute average deviations of EOS on both gas and liquid volumes of CO₂ mixtures. It should be pointed out that the volumes of saturated liquid and gas were calculated without vapor liquid equilibrium estimation. In general, all of the studied EOS have various performances for various mixtures. If k_{ij} is properly calibrated, cubic EOS may have even better accuracy on liquid volume than on gas volume. Comparatively PR and PT are superior to others in volume calculations. In the following, further analysis was conducted regarding every binary CO₂ mixture.

3.3.1. CO₂/CH₄

Fig. 2 shows the comparison between the calculated results and experimental data on both liquid and gas volumes of CO₂/CH₄. All of cubic EOS have a better accuracy on gas volumes than on liquid volumes. Meanwhile they are more likely to predict a higher value in those low liquid volume cases; while a lower value in those high liquid volume cases, compared to experimental data. Generally, ISRK has the worst accuracies on both V_g and V_l ; and PT is superior in the calculations on V_g and V_l with AAD of 2.34% and 3.70%, respectively.

Table 2

Summary of the experimental data of binary-CO₂-mixture volumes.

Source	Year	Type	Mixture	T (K)	P (MPa)	Uncertainty
Caubet [15]	1901	TPVX	CO ₂ /SO ₂	291–416	2.7–10.5	
Reamer et al. [16]	1944	TPxy	CO ₂ /CH ₄	311–511	1.4–69	
Bierlein et al. [17]	1953	PTVX	CO ₂ /H ₂ S	273–370	1.5–8.5	V: ±0.02%, T: ±0.02 K
Donnelly et al. [18]	1954	TPxy	CO ₂ /CH ₄	167–301	2.0–7.4	
Kestin et al. [19]	1966	TPVX	CO ₂ /Ar	293.15–303.15	0.101–2.58	
Arai et al. [20]	1971	PVTx	CO ₂ /N ₂ , CO ₂ /CH ₄	253–288	5–15	P: ±0.01atm, T: ±0.01K
Sarashina et al. [21]	1971	PVTx	CO ₂ /Ar	288.15	5.69–9.77	P: ±0.01 atm, T: ±0.01 K
Davalos et al. [22]	1976	TPxy	CO ₂ /CH ₄	230–250	0.9–8.5	
Altunin et al. [23]	1977	Comp	CO ₂ /Ar	303.15	0.29–10.75	
Mraw et al. [24]	1978	TPxy	CO ₂ /CH ₄	89–208	0.5–6.3	
Dorau et al. [25]	1983	TPxy	CO ₂ /N ₂	223.15–273.15	3–20	
Esper et al. [26]	1989	TPVX	CO ₂ /N ₂	205–320	0.1–48	P: ±0.015%, T: ±0.01 K

Table 3Correlated k_{ij} for different binary CO₂ mixtures based on volume experimental data.

		PR	PT	RK	SRK	MPR	MSRK	ISRK ^a
CO ₂ /CH ₄	G	0.049	0.963	0.008	0.018	−0.006	−0.032	0.033/0.189
	L	0.008	1.002	−0.077	−0.056	−0.120	−0.192	−2.225/−0.375
CO ₂ /H ₂ S	G	0.038	0.960	0.031	0.033	−0.014	−0.015	−0.055/0.125
	L	0.012	1.004	−0.073	−0.064	−0.082	−0.181	−0.900/−0.085
CO ₂ /N ₂	G	−0.001	1.015	−0.019	−0.037	−0.053	−0.095	−0.104/0.099
	L	−0.017	1.029	−0.129	−0.104	−0.154	−0.258	−0.490/0.050
CO ₂ /Ar	G	0.027	0.990	0.0	0.007	−0.031	−0.043	0.015/0.320
	L	0.002	1.015	−0.077	−0.065	−0.124	−0.200	−0.015/0.335
CO ₂ /SO ₂	G	−0.085	1.090	−0.091	−0.092	−0.148	−0.156	−0.500/−0.500
	L	0.004	0.996	−0.026	−0.026	−0.122	−0.175	−0.700/−0.115

^a k_{ij}/I_{ij} .**Table 4**AAD of different EOS on both gas and liquid volumes of various binary CO₂ mixtures.

		PR	PT	RK	SRK	MPR	MSRK	ISRK
CO ₂ /CH ₄	V _g	2.95	2.34	2.56	2.56	4.49	3.97	7.42
	V _l	4.17	3.70	5.19	5.12	5.50	6.08	8.33
CO ₂ /H ₂ S	V _g	4.71	5.57	8.84	7.34	3.37	4.26	7.21
	V _l	3.03	2.43	4.95	4.18	4.30	4.97	4.99
CO ₂ /N ₂	V _g	1.58	0.98	1.47	1.50	2.85	2.59	5.17
	V _l	1.74	1.77	5.97	4.99	3.79	6.16	7.46
CO ₂ /Ar	V _g	5.96	6.08	6.43	6.45	7.21	7.16	6.24
	V _l	2.37	2.12	4.86	4.66	3.99	5.48	4.64
CO ₂ /SO ₂	V _g	13.02	13.06	14.26	14.00	11.64	12.76	8.83
	V _l	9.43	9.28	11.96	10.84	10.51	12.15	13.21

Fig. 3 shows the calculation deviations on V_g and V_l of CO₂/CH₄. For their performances on V_g , except ISRK, all cubic EOS do not vary clearly at various temperatures and y_{CO_2} , but become poor at high pressures; while for their performances on V_l , their AAD first drop, then rise along with the increase of x_{CO_2} , but do not vary regularly at various pressures.

3.3.2. CO₂/H₂S

Fig. 4 shows the comparison between the calculated results and experimental data on both liquid and gas volumes of CO₂/H₂S. Comparatively cubic equations of state have a better accuracy on liquid volumes than on gas volumes. For the calculations of liquid

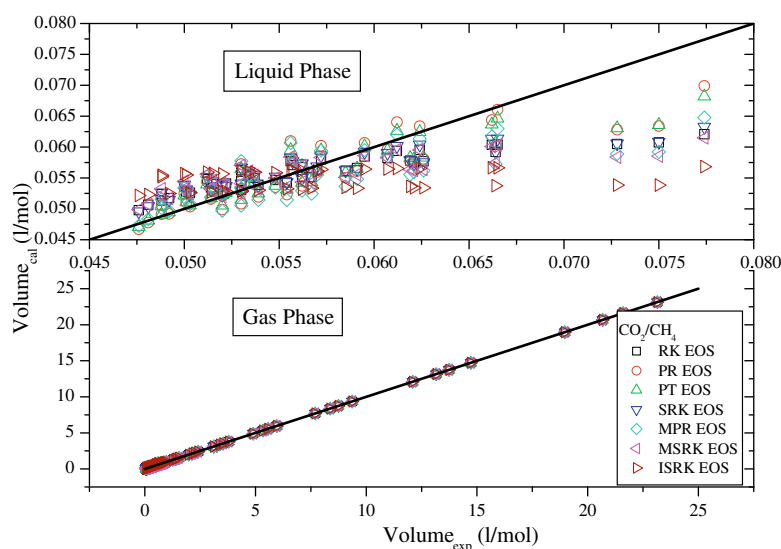
volume, the deviations of all EOS become large in those large volume cases, especially those of ISRK; while for the calculations of gas volume, the deviations of all EOS become small in those large volume cases. Generally, ISRK has the worst accuracies on both V_g and V_l ; MPR is superior in the calculations on V_g with AAD at 3.37%; and PT is superior in the calculations on V_l , where AAD is 2.43%.

Fig. 5 shows the calculation deviations on V_g and V_l of CO₂/H₂S. Approximately the performances on V_g and V_l of all cubic EOS are not affected clearly by temperatures, but become poor at high pressures. Moreover, the accuracies of EOS become comparatively poor at high concentrations of CO₂ in the calculation of gas volume; while they are not affected by concentrations of CO₂ in the calculation of liquid volume, except that of MPR.

3.3.3. CO₂/N₂

Fig. 6 shows the comparison between the calculated results and experimental data on both liquid and gas volumes of CO₂/N₂. It is quite similar to the calculations on CO₂/CH₄. Comparatively, the calculated results of PR and PT agree well with the experimental data especially in the liquid phase. Generally, ISRK has the worst accuracies on both V_g and V_l ; PT is superior in the calculations on V_g with AAD at 0.98%; and PR is superior in the calculations on V_l , where AAD is 1.74%.

Fig. 7 shows the calculation deviations on V_g and V_l of CO₂/N₂. For the calculation on gas volume, RK, PR, PT and SRK have quite

**Fig. 2.** Comparison between calculated results and experimental data on both liquid and gas volumes of CO₂/CH₄.

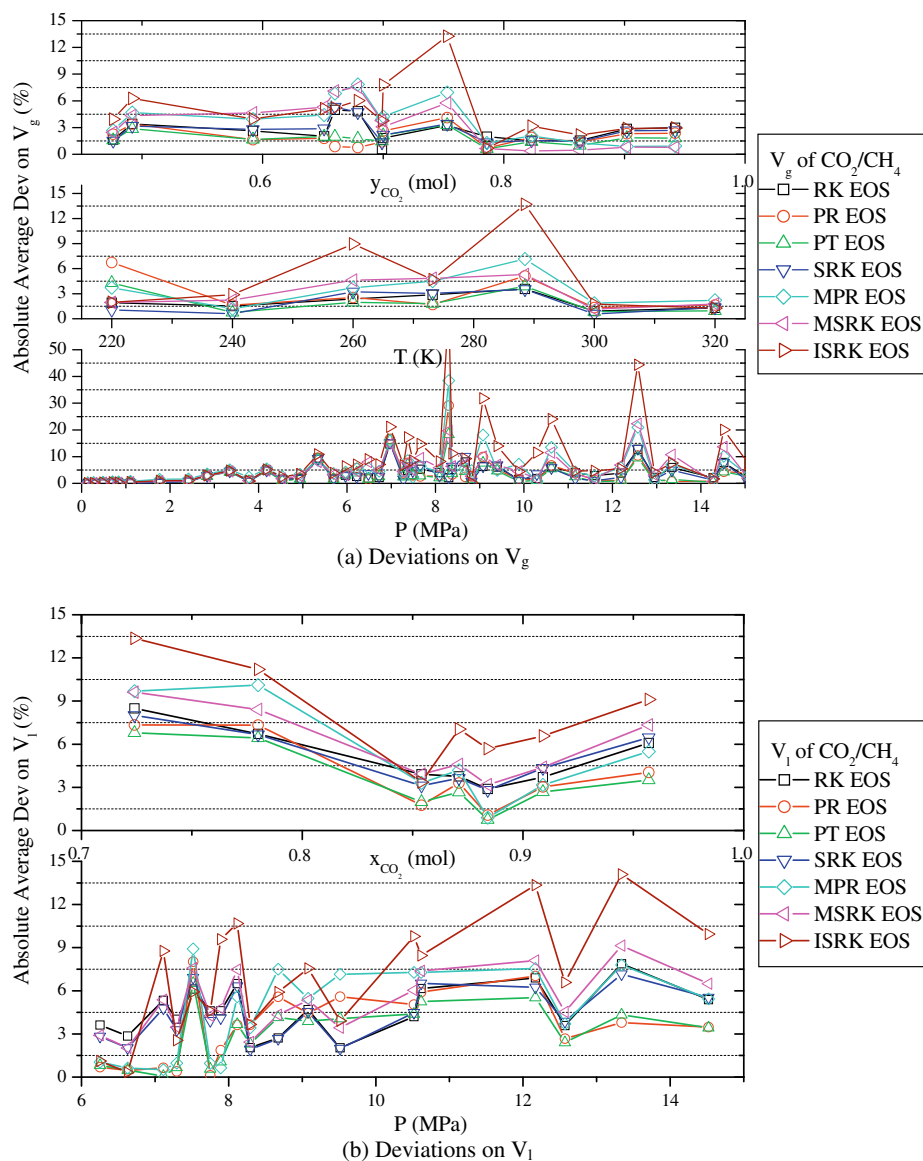


Fig. 3. Calculation deviations on V_g and V_l of CO_2/CH_4 .

similar performances, and they are not impacted by pressure, temperature and CO_2 concentration very much. Except several points, their absolute deviations and AAD are always within 3% in the whole experimental ranges. MPR and MSRK have quite big AAD as y_{CO_2} is around 80 mol%; while ISRK has big AAD as T is around 290 K or P is between 8 and 16 MPa. For the calculation on liquid volume, pressure and CO_2 concentration do not have a regular impact on the accuracies of EOS. However, the AAD of ISRK is large, maybe up to 20%, if x_{CO_2} is low.

3.3.4. CO_2/Ar

Fig. 8 shows the comparison between the calculated results and experimental data on both liquid and gas volumes of CO_2/Ar . As same as the calculations of $\text{CO}_2/\text{H}_2\text{S}$, cubic equations of state have a better accuracy on liquid volumes than on gas volumes. For the calculations of gas volume, the big deviations of all EOS appear when the concentrations of Ar are very low. Generally, PR is superior in the calculations on V_g with AAD at 5.96%; and PT is superior in the calculations on V_l , where AAD is 2.12%.

Fig. 9 shows the calculation deviations on V_g and V_l of CO_2/Ar . It is easy to see that the concentration of CO_2 and pressure have quite

clear impacts on the accuracies of EOS. Approximately along with the increment of CO_2 concentration, the AAD on V_g of all EOS drops, while the AAD on V_l drops first and then rises. Along with the increment of pressure, the AAD on V_g of all EOS first drops and then rises; while the AAD on V_l rises first and then drops, except ISRK.

3.3.5. CO_2/SO_2

Fig. 10 shows the comparison between the calculated results and experimental data on both liquid and gas volumes of CO_2/SO_2 . Comparatively all EOS have the worst accuracies on CO_2/SO_2 amongst all of the studied binary CO_2 mixtures. And except ISRK, all EOS have a better accuracy on liquid volumes than on gas volumes. Moreover although ISRK has the best performance on the gas volumes, it has the worst performance on the liquid volumes. Generally ISRK is superior in the calculations on V_g with AAD at 8.83%; and PT is superior in the calculations on V_l , where AAD is 9.28%.

Fig. 11 shows the calculation deviations on V_g and V_l of CO_2/SO_2 . Temperature does not have regular impacts on the calculations of V_g and V_l . However, at high pressures the AAD of EOS on V_g become large; while the AAD of EOS on V_l become small. In addition, the

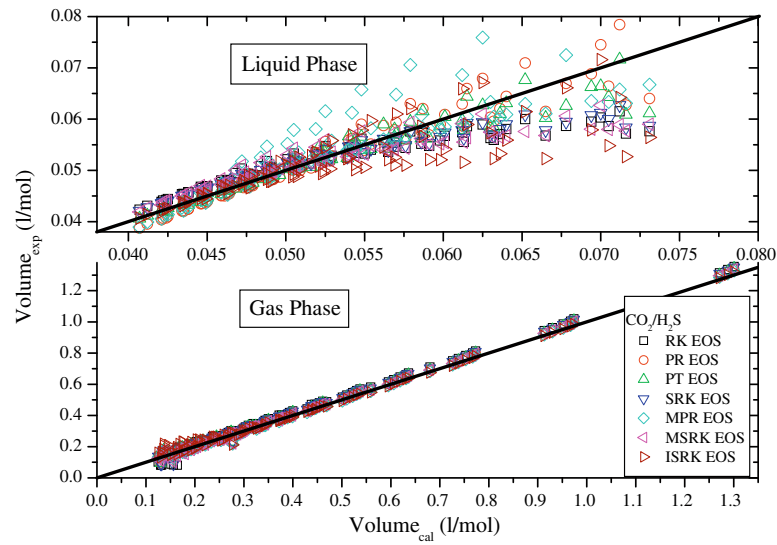


Fig. 4. Calculated comparison between calculated results and experimental data on both liquid and gas volumes of $\text{CO}_2/\text{H}_2\text{S}$.

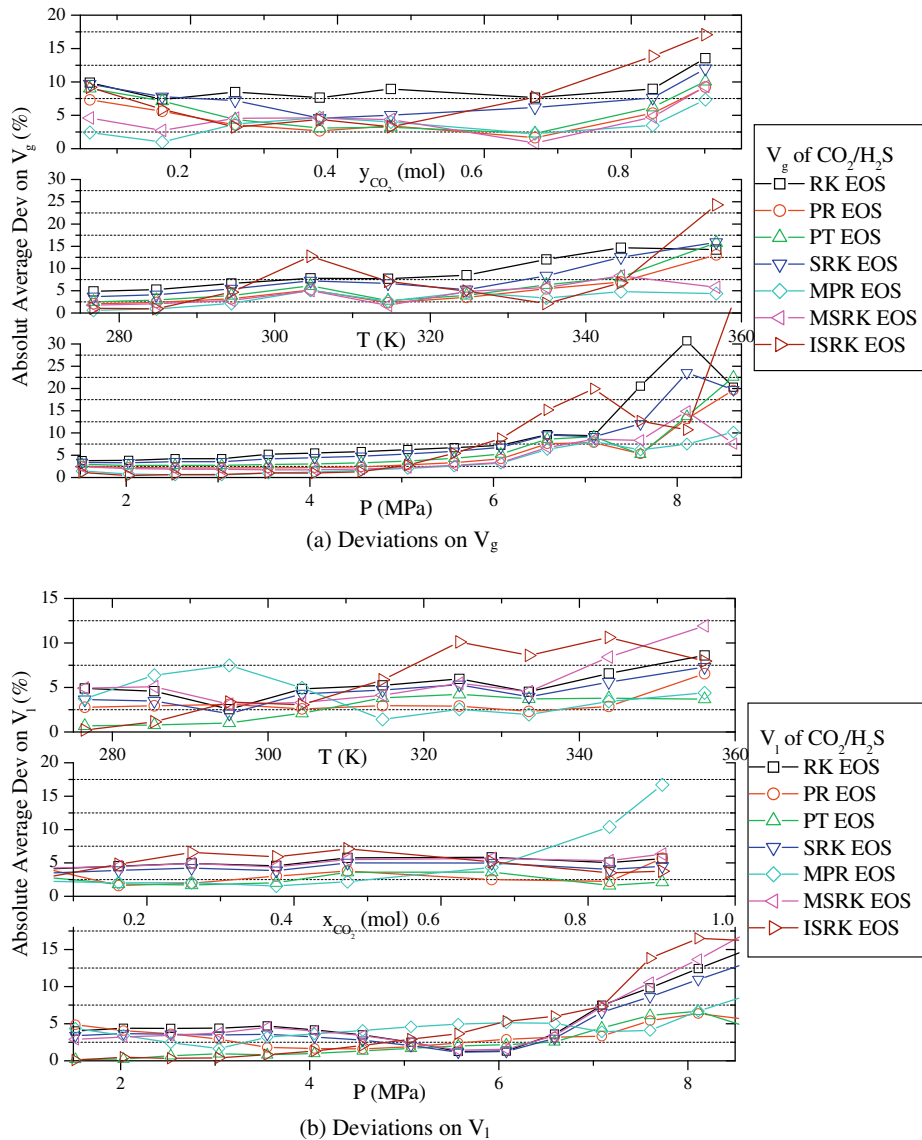


Fig. 5. Calculation deviations on V_g and V_l of $\text{CO}_2/\text{H}_2\text{S}$.

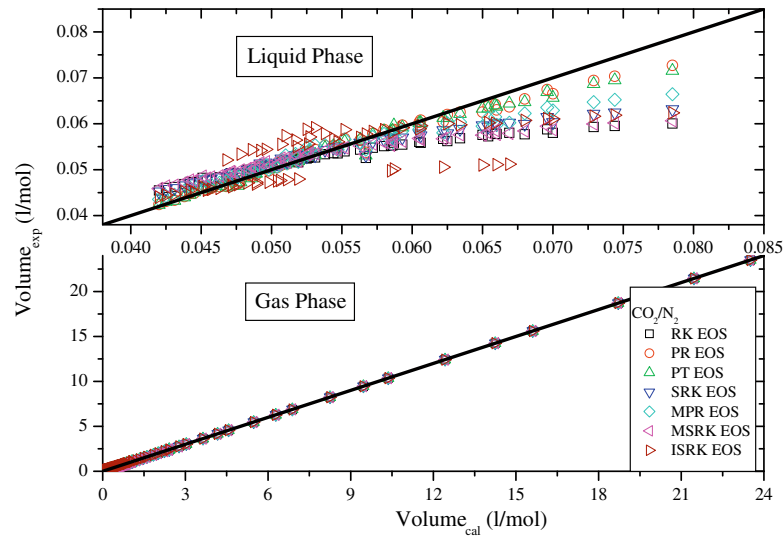


Fig. 6. Comparison between calculated results and experimental data on both liquid and gas volumes of CO_2/N_2 .

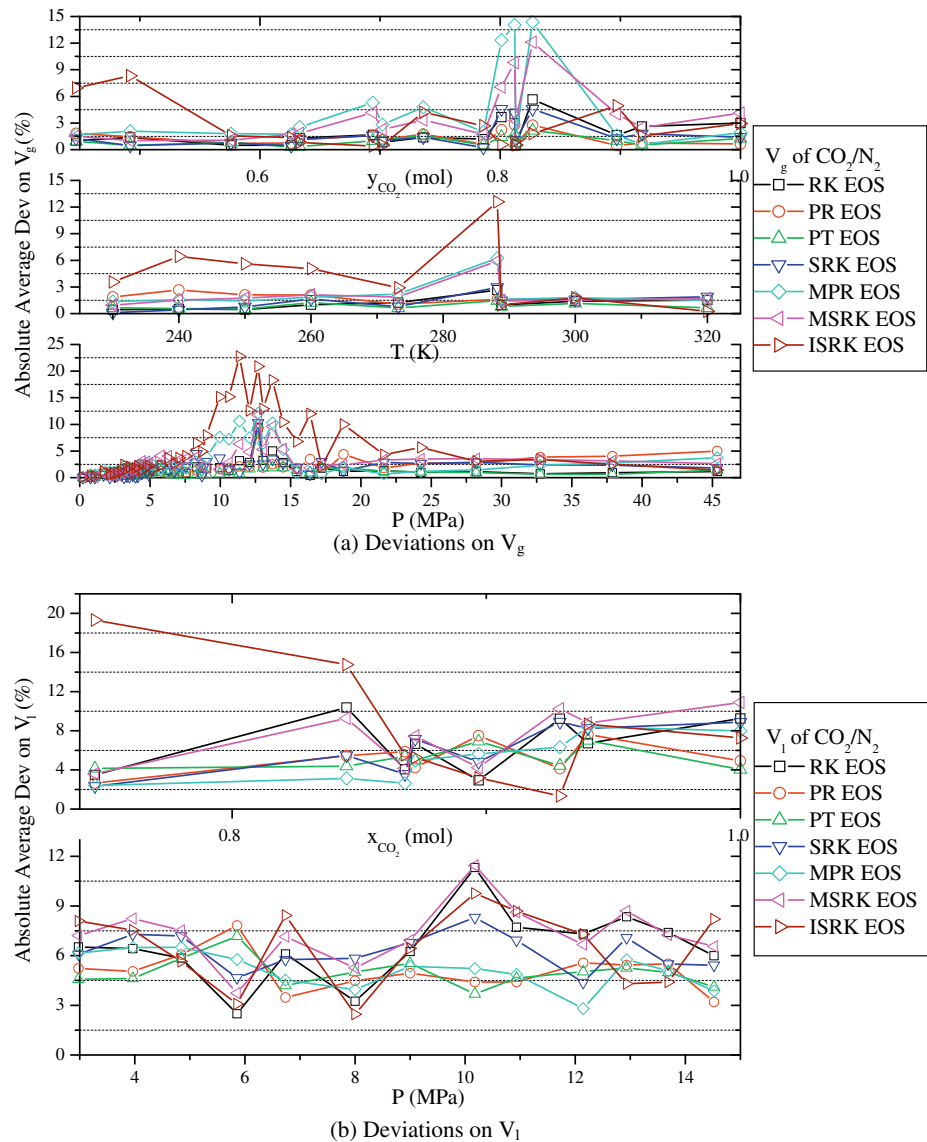


Fig. 7. Calculation deviations on V_g and V_l of CO_2/N_2 .

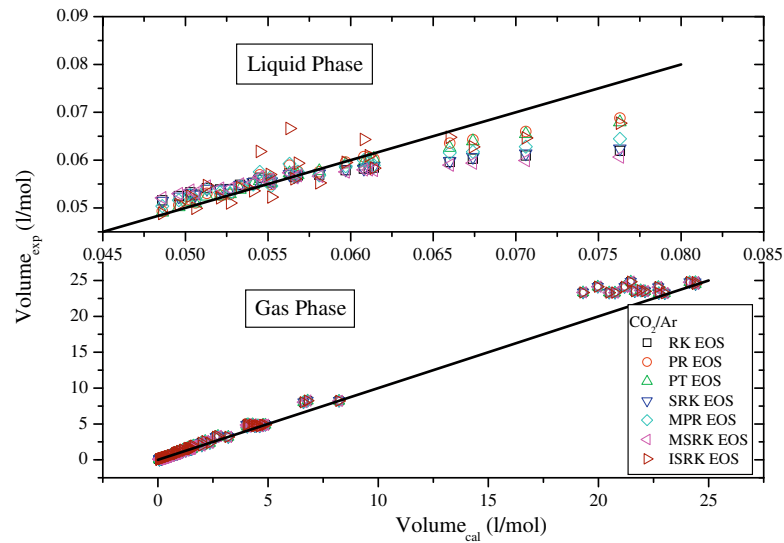


Fig. 8. Comparison between calculated results and experimental data on both liquid and gas volumes of CO_2/Ar .

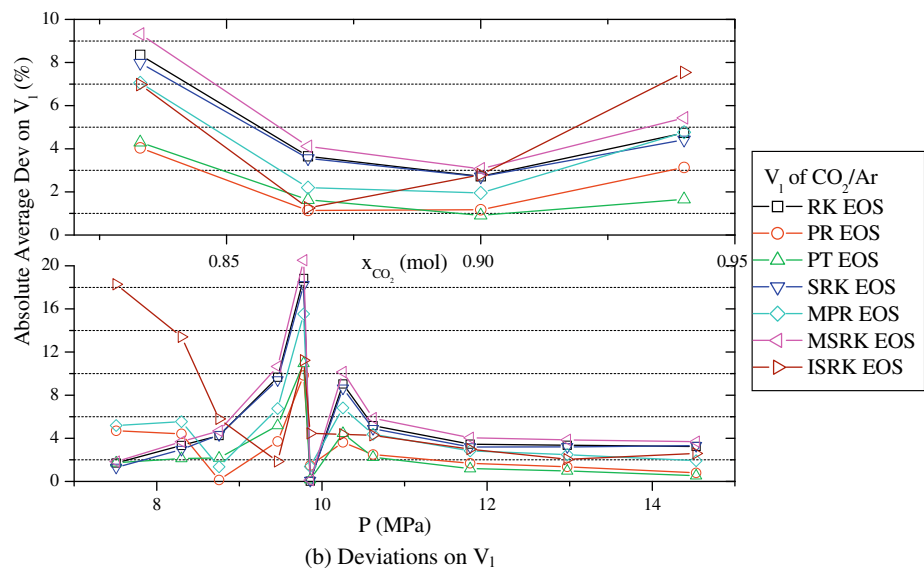
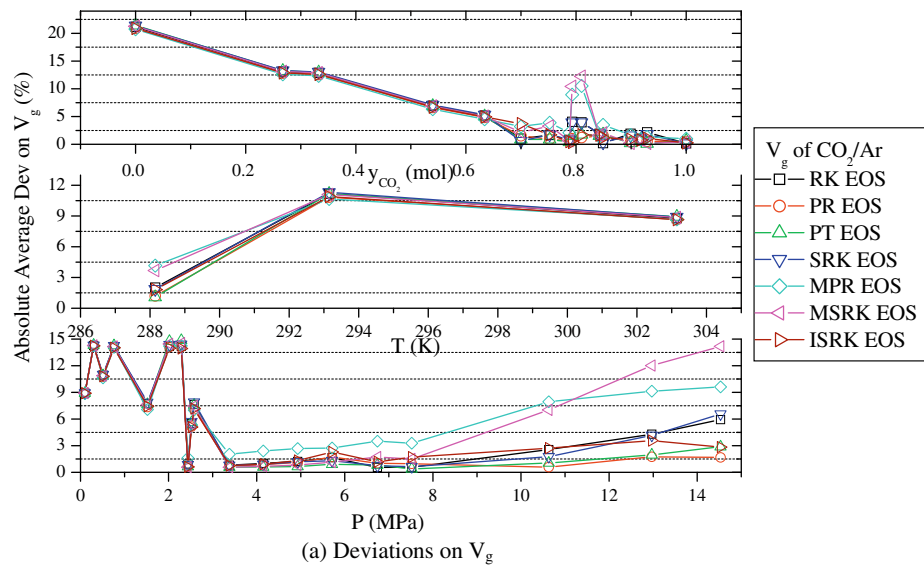


Fig. 9. Calculation deviations on V_g and V_l of CO_2/Ar .

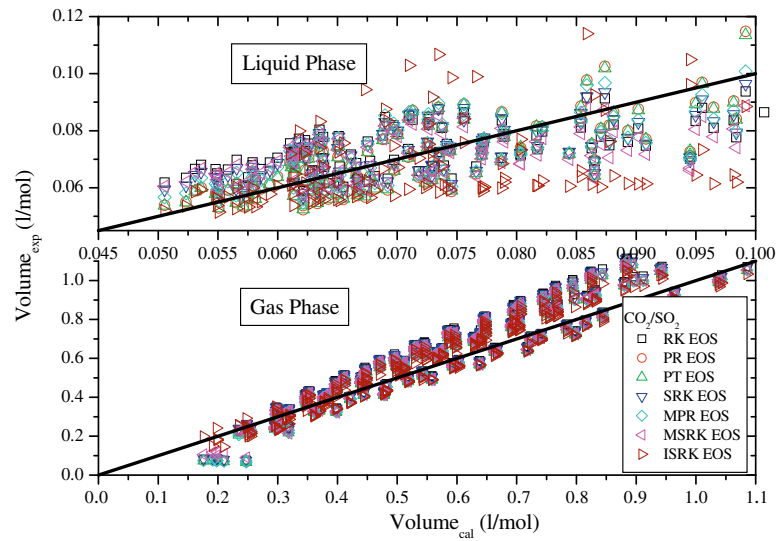


Fig. 10. Comparison between calculated results and experimental data on both liquid and gas volumes of CO_2/SO_2 .

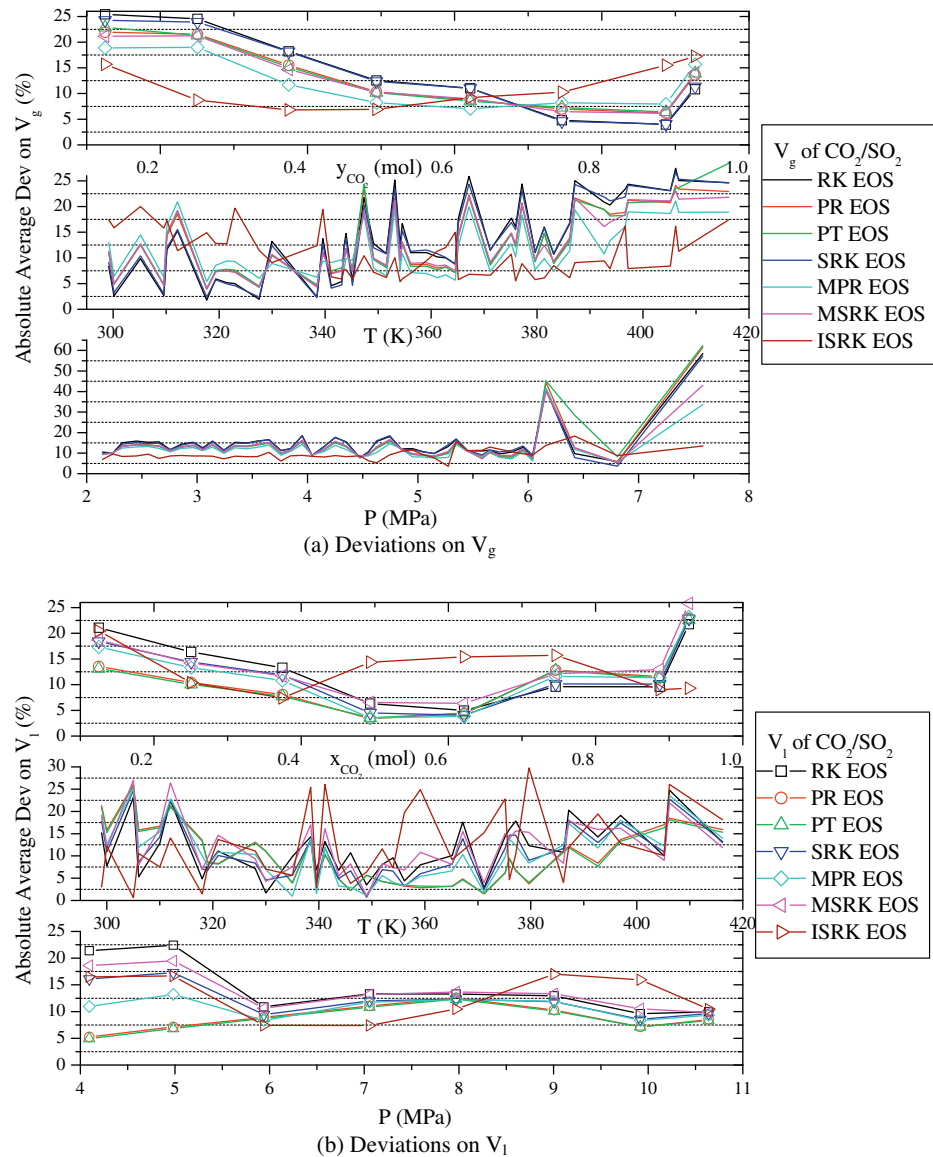


Fig. 11. Calculation deviations on V_g and V_l of CO_2/SO_2 .

Table 5AAD of EOS on the calculated gas volumes of binary CO₂ mixtures at different values of k_{ij} (%).

	k_{ij}	PR	PT	RK	SRK	MPR	MSRK	ISRK
CO ₂ /CH ₄	0 ^a	5.95	5.26	2.77	3.44	4.55	5.33	15.67
	k_{ij-Vg}	2.95	2.34	2.56	2.56	4.49	3.97	7.42
	k_{ij-Vl}	5.95	5.53	12.09	11.02	16.09	19.56	49.80
CO ₂ /H ₂ S	0 ^a	15.81	15.94	13.53	13.49	4.04	5.56	18.16
	k_{ij-Vg}	4.71	5.57	8.84	7.34	3.37	4.26	7.21
	k_{ij-Vl}	10.69	18.04	35.55	35.49	30.23	52.07	78.58
CO ₂ /N ₂	0 ^a	1.59	1.73	2.41	3.84	5.08	8.10	13.63
	k_{ij-Vg}	1.58	0.98	1.47	1.50	2.85	2.59	5.17
	k_{ij-Vl}	2.40	1.54	9.65	7.08	9.71	14.52	24.31
CO ₂ /Ar	0 ^a	7.57	6.47	6.43	6.50	8.13	9.26	15.45
	k_{ij-Vg}	5.96	6.08	6.43	6.45	7.21	7.16	6.24
	k_{ij-Vl}	7.42	7.56	12.36	12.05	12.67	15.99	8.55
CO ₂ /SO ₂	0 ^a	14.79	14.74	16.80	16.82	16.19	18.11	19.43
	k_{ij-Vg}	13.02	13.06	14.26	14.00	11.64	12.76	8.83
	k_{ij-Vl}	14.95	14.90	15.44	15.44	11.80	13.07	51.99

^a $k_{ij}=1$ (for PT EOS).**Table 6**AAD of EOS on the calculated liquid volumes of binary CO₂ mixtures at different values of k_{ij} (%).

	k_{ij}	PR	PT	RK	SRK	MPR	MSRK	ISRK
CO ₂ /CH ₄	0 ^a	4.51	3.72	12.17	9.26	37.55	42.51	108.11
	k_{ij-Vg}	17.55	9.62	14.01	12.63	34.50	28.94	57.77
	k_{ij-Vl}	4.17	3.70	5.19	5.12	5.50	6.08	8.33
CO ₂ /H ₂ S	0 ^a	3.76	2.47	11.02	9.25	96.59	79.80	440.71
	k_{ij-Vg}	60.41	64.61	66.58	65.46	134.81	104.74	141.71
	k_{ij-Vl}	3.03	2.43	4.95	4.18	4.30	4.97	4.99
CO ₂ /N ₂	0 ^a	3.40	5.50	16.88	15.02	63.39	56.19	133.78
	k_{ij-Vg}	3.20	2.56	12.70	8.17	30.03	18.70	51.65
	k_{ij-Vl}	1.74	1.77	5.97	4.99	3.79	6.16	7.46
CO ₂ /Ar	0 ^a	2.39	3.30	13.08	10.67	38.16	42.26	111.51
	k_{ij-Vg}	12.66	10.99	18.37	17.50	29.06	31.12	16.47
	k_{ij-Vl}	2.37	2.12	4.86	4.66	3.99	5.48	4.64
CO ₂ /SO ₂	0 ^a	9.54	9.42	13.20	12.37	66.17	66.57	129.76
	k_{ij-Vg}	20.27	20.66	16.12	15.74	14.57	15.99	93.78
	k_{ij-Vl}	9.43	9.28	11.96	10.84	10.51	12.15	13.21

^a $k_{ij} = 1$ (for PT EOS).

accuracies of EOS become poor at low and high CO₂ concentrations in both gas and liquid phases, except ISRK accuracy on V_l .

4. Further discussions on k_{ij}

As mentioned above, the right values of k_{ij} are different for various properties. Therefore the binary interaction parameter was calibrated regarding gas volumes and liquid volumes, respectively. Table 5 and 6 summarize the AAD of on the calculated gas and liquid densities of binary CO₂ mixtures at different values of k_{ij} . Here, k_{ij-Vg}/k_{ij-Vl} is k_{ij} calibrated from the experimental data of vapor/liquid volumes. It is clear that the AAD could be very huge, especially in the calculations of liquid volumes, if a wrong value of k_{ij} is applied. In addition, those AAD over 50% happen when involving the calculations on saturated gas and liquid volumes. It implies the liquid/gas volumes were obtained when calculating the saturated gas/liquid volumes, because no VLE estimation is conducted before calculating volumes.

Moreover, it is well known that the determination of k_{ij} requires a large amount of experimental data. If there are not enough experimental data to calibrate k_{ij} , the value of '0' ('1' for PT EOS) should be used, which means ignores the difference of attraction forces. Checking the performances of EOS with $k_{ij} = 0/1$, it is clear that PR and PT are generally superior to other equations.

5. Conclusions

Based on the collected experimental data, this paper studied the reliabilities of seven cubic equations of state on predicting gas and liquid volumes of binary CO₂ mixtures (including CH₄, H₂S, N₂, Ar and SO₂). According to the results, we have the following conclusions on the various tested EOS:

- (1) Binary interaction parameter has clear effects on the calculating accuracy of an EOS in the volume calculations of CO₂ mixtures. In order to improve the accuracy, k_{ij} was calibrated for all of the EOS regarding the gas and liquid phases of all the studied binary CO₂ mixtures, respectively. The AAD of an EOS could be very huge, especially in the calculations of liquid volumes, if a wrong value is applied.
- (2) For calculations on the volume properties of binary CO₂ mixtures, PR and PT are generally superior to others for all of the studied mixtures. Comparatively PT is recommended to the calculations of CO₂/CH₄, V_l of CO₂/H₂S, CO₂/Ar and CO₂/SO₂, and V_g of CO₂/N₂; PR is recommended to the calculations of V_l of CO₂/N₂ and V_g of CO₂/Ar; MPR and ISRK are recommended to the calculations of V_l of CO₂/H₂S and V_g of CO₂/SO₂, respectively.

- (3) If the calibrated k_{ij} is not available, generally PR and PT are more likely to give accurate results for the density of both vapor and liquid phases than other EOS studied in this paper.

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References

- [1] Intergovernmental Panel on Climate Change (IPCC). IPCC special report on carbon dioxide capture and storage. Cambridge University Press; 2005.
- [2] Li H, Yan J. Impacts of impurities in CO₂-fluids on CO₂ transport process. In: Proceedings of the ASME turbo Expo 2006, Barcelona, Spain May 8–11th 2006. Paper No. GT2006-90954.
- [3] Schoneich S, May F, Vosteen HD. Influence of impurities in CO₂-rich gas mixtures on the storage capacity of mature natural gas fields. DGMK/OGEW-Frühjahrstagung 2007. Celle: Fachbereich Aufsychung und Gewinnung.
- [4] GERG2004. <http://www.ruhr-uni-bochum.de/thermo/Software/Seiten/GERG_2004-eng.htm>.
- [5] Li H, Ji X, Yan J. A new modification on RK EOS for gaseous CO₂ and gaseous mixtures of CO₂ and H₂O. Int J Energy Res 2006;30:135–48.
- [6] Li H, Yan J. Evaluating cubic equations of state for calculation of vapor–liquid equilibrium of CO₂ and CO₂-mixtures for CO₂ capture and storage processes. Appl Energy 2009;86(6):826–36.
- [7] Li H, Yan J, Anheden M. Impurity impacts on the purification process in oxy-fuel combustion based CO₂ capture and storage system. Appl Energy 2009;86(2):202–13.
- [8] Peng DY, Robinson DB. A new two-constant equation of state. Int Eng Chem Fundam 1976;15:59–64.
- [9] Patel NC, Teja AS. A new cubic equation of state for fluids and fluid mixtures. Chem Eng Sci 1982;37(3):463–73.
- [10] Redlich O, Kwong JNS. On the thermodynamics of solutions. Chem Rev 1949;44:233–44.
- [11] Soave G. Equilibrium constants for modified Redlich–Kwong equation of state. Chem Eng Sci 1972;27:1196–203.
- [12] Peneloux A, Rauzy E. A consistent correction for Redlich–Kwong–Soave volumes. Fluid Phase Equilibr 1982;8:7–23.
- [13] Ji W, Lempe DA. Density improvement of the SRK equation of state. Fluid Phase Equilibr 1997;130(12):49–63.
- [14] Hu J, Duan Z, Zhu C, Chou I-M. PVTx properties of the CO₂–H₂O and CO₂–H₂O–NaCl systems below 647 K: assessment of experimental data and thermodynamic models. Chem Geol 2007;238:249–67.
- [15] Caubet F. Liquéfaction des mélanges gazeux. Université de Bordeaux; 1901.
- [16] Reamer HH, Olds RH, Sage BH, Lacey WN. Phase equilibria in hydrocarbon systems: methane–carbon dioxide system in the gaseous region. Ind Eng Chem 1944;35(1):88–90.
- [17] Bierlein JA, Kay WB. Phase-equilibrium properties of system carbon dioxide–hydrogen sulfide. Ind Eng Chem 1953;45(3):618–24.
- [18] Donnelly HG, Katz DL. Phase equilibria in the carbon dioxide–methane system. Ind Eng Chem 1954;46(3):511–7.
- [19] Kestin J, Kobayashi Y, Wood RT. The viscosity of four binary gaseous mixtures at 20 and 30 °C. Phys Amsterdam 1966;32:1065–89.
- [20] Arai Y, Kaminishi G, Saito S. The experimental determination of the P – V – T – X relations for the carbon dioxide–nitrogen and the carbon dioxide–methane system. J Chem Eng Jpn 1971;4(2):113–22.
- [21] Sarashina E, Arai Y, Saito S. The P – V – T – X relation for the carbon dioxide–methane system. J Chem Eng Jpn 1971;4:379–81.
- [22] Davalos J, Anderson WR, Phelps RE, Kldnay AJ. Liquid–gas equilibria at 250.00 K for systems containing methane, ethane, and carbon dioxide. J Chem Eng Data 1976;21(1):81–4.
- [23] Altunin VV, Koposhilov OD. An experimental study of thermal properties of gaseous mixtures of carbon dioxide with argon. Teploenergetika 1977;24(8):80–3.
- [24] Mrav SC, Hwang S, Kobayashi R. Gas–liquid equilibrium of the CH₄–CO₂ system at low temperature. J Chem Eng Data 1978;23(2):135–9.
- [25] Dorau W, Al-Wakeel IM, Knapp H. VLE data for CO₂–CF₂Cl₂, N₂–CO₂, N₂–CF₂Cl₂ and N₂–CO₂–CF₂Cl. Cryogenics 1983;29:35.
- [26] Esper GJ, Bailey DM, Holste JC, Hall KR. Volumetric behavior of near-equimolar mixtures for CO₂ + CH₄ and CO₂ + N₂. Fluid Phase Equilibr 1989;49:35–47.
- [27] Prausnitz JM, Lichtenthaler RN, de Azevedo EG. Molecular thermodynamics of fluid-phase equilibria. 2nd ed. Prentice-Hall; 1986.
- [28] Danesh A, Xu D-H, Todd AC. Comparative study of cubic equations of state for predicting phase behavior and volumetric properties of injection gas-reservoir oil systems. Fluid Phase Equilibr 1991;63:259–78.