

An improved PR equation of state for CO₂-containing gas compressibility factor calculation



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ABSTRACT

Peng-Robinson equation of state (PR EoS) is a reliable and widely used cubic EoS to predict natural gases thermodynamic properties. However, large deviations between the calculated compressibility factor values and the realistic values are observed when it is applied to the high volume CO₂-content natural gas. In order to enhance its applicability, a new correction parameter associated with three-parameters (the reduced temperature T_r , reduced pressure P_r and CO₂ volume content) is introduced into the attractive term of PR EoS by fitting the deviations between 267 groups of experimental compressibility factors and corresponding calculation values. The results reveal that the average absolute deviation between experimental data and predicted compressibility factors from the improved PR EoS is 2.708% when the pressures range from 3 MPa to 15 MPa, temperatures range from 263.15 K to 313.15 K and CO₂ volume contents range from 9.84% to 100%. The deviation is reduced by 9.61% when compared to that of the original PR EoS. The results also demonstrate that this improved PR EoS has better performance than PRSV, PRTwu BWRS EoSs, and is essentially comparable in predictability to PC-SAFT EoS.

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1. Introduction

Currently, many gas fields containing high volume content of CO₂ have been found in China, i.e., the Huangqiao Gas Field (CO₂ volume content from 90 to 99%), Sanshui gas field (CO₂ volume content from 84 to 99%), Jiyang gas field (CO₂ volume content from 68 to 93%), Wanjinta gas field (CO₂ volume content from 90 to 99%) (Heidaryan et al., 2013). Besides, many natural gas fields which are under exploration also contain CO₂, i.e., Changbei gas field (CO₂ volume content from 5.321 to 10%), CNOOC Dongfang gas field (CO₂ volume content from 55 to 71%). There are some new challenges during the gathering, transportation and processing of the high CO₂-content natural gas due to its physical properties are quite different from regular natural gas. These physical properties include compressibility factor, density, heat capacity, enthalpy, entropy and so on, in which the compressibility factor is the most

essential one because it is the basis to compute other related properties (Dranchuk et al., 1973).

In the past years, many scholars have presented a lot of compressibility factor correlations. One type of these correlations is built for the regular natural gas with no acid components, such as the Dranchuk-Abu-Kassem (Obeida et al., 1997), Dranchuk-Purvis-Robinson (Elsharkawy and Elkamel, 2000), Beggs and Brill (Huang et al., 2011) and Li XiangFang Correlations (Dranchuk and Kassem, 1975). The other type of correlations modifies the calculation method of pseudocritical parameters so that they can be applied to acid gases, i.e., the GXQ model, Wichert-Aziz model and Carr-Kobayshi-Burrows model (Abudour et al., 2012). Due to these correlations are limited in the specific pressure, temperature and composition ranges, accordingly we cannot always get satisfactory results by using them to compute the compressibility factor of high CO₂-content natural gases (Fouad and Berrouk, 2013).

On contrary, the cubic equations of state is applicable to wider pressures, temperatures and gas compositions ranges (Hosseiniifar and Jamshidi, 2016). Not only the compressibility factor, but also the models of the enthalpy, entropy, heat capacity can also be built from the EoS. Among many existing cubic EoSs, Peng-Robinson EoS is preferable in the field of natural gas properties computation because of its simple form and high accuracy for gas with no

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components. However, large deviations between the calculated compressibility factors and experimental data may be observed if the PR EoS is applied to the high CO₂-content natural gas mixtures, especially for the system that the mole fraction of CO₂ is higher than 10%. Since compressibility factor is the basis of other physical parameters computation, its inaccuracy may cause larger deviations for other parameters (Abovsky, 2014).

The improvements for the PR EoS fall into three categories (Cismondi and Mollerup, 2005). The first method is to modify the attractive parameters in the temperature function, such as the PRSV2, PRD and PR-Twu EoSs. The second one focuses on improvements of the binary interaction coefficients based on the experimental data or group contribution method, such as the PRN, Predictive PR78 (PPR78) EoSs (Jaubert et al., 2010; Vitu et al., 2008). The last one is the volume-translated PR EoS, whose basic principle is subtracting a volume correction term in the liquid and gas specific volume term simultaneously (Gibbons and Laughton, 1984), such as the PR-Peneloux EoS. Although these improved PR EoSs have better performance on density and volume predictions of both liquid and vapor phases, there are rarely literature reporting the compressibility factor predictions with regard to high CO₂ volume content natural gases (Stryjek and Vera, 1986).

In this paper, the compressibility factors of six natural gas samples are firstly measured by using the experimental method. The mole fractions of CO₂ in six samples are equal to 9.84%, 28.86%, 50.99%, 70.98%, 91.77% and 100% respectively. These experiments cover the pressures from 3 MPa to 15 MPa, and the temperatures from 263.15 K to 313.15 K. By fitting the deviations between calculated compressibility factors and experimental values, a new four-parameters correlation is introduced into the attractive term of original PR EoS. As a result, the accuracy of compressibility factor prediction is enhanced significantly.

2. Experimental compressibility factors of high CO₂ volume content gases

2.1. The experimental instrument and methods

The mercury free DBR- JEFRI PVT instrument made in Canada is utilized to test the compressibility factors of seven gas samples (Pedersen et al., 1989). The instrument is consist of a PVT vessel of approximately 135 mL capacity, an automatic pump, a gas chromatograph, a gasometer, a constant temperature air bath, a flash separator and a ground separator. The experimental methods are outlined by the Chinese code "Test method for reservoir fluid physical properties (SY/T 5542-2009)" (Bian et al., 2011). The compositions of these samples are listed in Table 1, in which the mole fractions of CO₂ (V_c) are equal to 9.84%, 28.86%, 50.99%, 70.98%, 91.77% and 100%, respectively.

Table 1
Compositions of gas mixtures with CO₂.

Component	Samples					
	1	2	3	4	5	6
CO ₂	100	91.77	70.98	50.99	28.86	9.84
N ₂	—	0.58	1.14	0.83	1.24	2.05
CH ₄	—	—	27.32	46.54	67.73	86.02
C ₂ H ₆	—	7.6	0.46	1.16	1.59	1.67
C ₃ H ₈	—	—	0.08	0.33	0.42	0.31
iC ₄	—	0.02	0.01	0.05	0.06	0.04
nC ₄	—	—	0.01	0.06	0.07	0.05
iC ₅	—	—	0.01	0.02	0.03	0.01
nC ₅	—	—	—	0.01	0.01	—
C ₆ +	—	0.02	—	0.01	—	—

Table 2
Experimental z factors of Sample 6.

Pressure (MPa)	T (K)					
	313.15	303.15	293.15	283.15	273.15	263.15
15	0.8692	0.8409	0.8140	0.7779	0.7471	0.7180
13	0.8700	0.8429	0.8153	0.7774	0.7484	0.7160
11	0.8737	0.8489	0.8189	0.7839	0.7548	0.7254
9	0.8791	0.8563	0.8270	0.7971	0.7693	0.7420
7	0.8911	0.8701	0.8438	0.8202	0.7957	0.7710
5	0.9078	0.8932	0.8763	0.8548	0.8339	0.8087
3	0.9323	0.9237	0.9122	0.8960	0.8831	0.8713

2.2. Experimental results

Table 2–7 listed the experimental results with regard to the compressibility factors (z factors) of the sample gas. These experiments cover the pressures from 3 MPa to 15 MPa, and temperatures from 263.15 K to 313.15 K.

3. Accuracy of the calculated compressibility factor based on PR EoS

3.1. PR EoS

The basic form of the original PR Eos is expressed by Eq. (1) (Peng and Robinson, 1976):

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \quad (1)$$

Where, P is the absolute pressure, Pa; T is the temperature, K; R is gas constant, 8.314 J/(mol·K); V is the specific volume, mol/m³; a , b are parameters expressed by Eqs. (2) and (3), respectively.

For single-component gas.

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha \quad (2)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha^{0.5} = 1 + \left(1 - T_r^{0.5}\right) \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right) \quad (4)$$

$$T_r = \frac{T}{T_c} \quad (5)$$

Where, α is the attractive parameter; T_r is the reduced temperature; T_c is the critical temperature, K; P_c the critical pressure, Pa and ω is

Table 3
Experimental z factors of Sample 5.

Pressure (MPa)	Temperature (K)					
	313.15	303.15	293.15	283.15	273.15	265.65
15.00	0.7050	0.6500	0.5882	0.5510	0.5211	0.4877
13.00	0.7284	0.6729	0.6176	0.5543	0.5095	0.4584
11.00	0.7637	0.7161	0.6606	0.5966	0.5229	0.4697
9.00	0.8057	0.7610	0.7179	0.6524	0.5761	0.5089
7.00	0.8516	0.8158	0.7761	0.7367	0.6810	0.6170
6.00	0.8715	0.8485	0.8252	0.7944	0.7514	0.6950
5.00	0.9025	0.8911	0.8718	0.8515	0.8209	0.7766
4.21				0.8892	0.8505	

Table 4
Experimental z factors of Sample 4.

Pressure (MPa)	Temperature (K)				
	313.15	303.15	293.15	283.15	275.85
15.00	0.5760	0.5302	0.5000	0.4774	0.4487
13.00	0.5977	0.5535	0.5117	0.4710	0.4319
11.00	0.6458	0.5932	0.5483	0.4908	0.4285
9.00	0.7410	0.6733	0.6177	0.5602	0.4916
7.00	0.8246	0.7703	0.7203	0.6600	0.6110
6.00	0.8707	0.8217	0.7731	0.7230	0.6872
5.00	0.9005	0.8770	0.8353	0.7949	0.7674
4.50	0.9128	0.8987	0.8859	0.8574	0.8386

Table 5
Experimental z factors of Sample 3.

Pressure (MPa)	Temperature (K)					
	313.1	303.15	293.15	283.15	273.15	265.15
15.00	0.4739	0.4529	0.4417	0.4089	0.4062	0.3947
13.00	0.4806	0.4296	0.4103	0.3714	0.3638	0.3493
11.00	0.5300	0.4748	0.4047	0.346	0.3248	0.3038
9.00	0.6397	0.5904	0.464	0.342	0.2853	0.2662
8.52					0.2731	
8.00			0.5299	0.3955		
7.79						0.234
7.00	0.7580	0.7104	0.6172	0.5057	0.4006	0.2906
6.00	0.8222	0.7783	0.7051	0.6247		0.4438
5.00	0.8668	0.8338	0.7795	0.7044		
4.08					0.7218	
4.00						0.6779

the acentric factor. These critical parameters and acentric factors for specific components are obtained from the API Technical Data Book (API, 2005), their values are listed in Table 8.

For gas mixtures, the parameters a , b should be calculated by certain mixing rules according to pure component's values. In this paper, the mixing rule expressed by Eqs. (6) and (7) are adopted.

$$a_m = \sum_{i=1}^n \sum_{j=1}^n y_i y_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (6)$$

Table 6
Experimental z factors of Sample 2.

P(MPa)	T (K)					
	313.15	303.15	293.15	283.15	273.15	265.15
15.00	0.4056	0.3926	0.3588	0.3407	0.2799	0.2691
14.00			0.3465			
13.00	0.4140	0.3527	0.3325	0.3120	0.2506	0.2404
12.00			0.3139			
11.00	0.4415	0.3443	0.2923	0.2706	0.2228	0.2084
10.00			0.2798			
9.00	0.5794	0.4113	0.2719	0.2298	0.1927	0.1730
8.73						0.1694
8.00	0.6526	0.5320	0.2682			
7.53				0.2123		
7.00	0.7424	0.6459				0.1467
6.76					0.1615	
6.00	0.7953	0.7409	0.5527		0.2169	
5.75						0.1384
5.00	0.8464	0.8247				
4.90				0.5781		
4.00				0.7060		
3.52					0.7075	
3.17						0.6822

Table 7
Experimental z factors of Sample 1.

Pressure (MPa)	Temperature (K)				
	313.15	304.15	283.15	273.15	267.15
*15.00	0.2387	0.2329	0.2049	0.1967	0.1909
13	0.223	0.2085	0.1883	0.1779	0.1705
12	0.2158				
11	0.206	0.1849	0.1633	0.1526	0.1464
10	0.1989				
9	0.2006	0.1613	0.1361	0.1266	0.1215
8	0.4295	0.1495			
7	0.5863		0.1084	0.1004	0.0959
5	0.7596		0.0797	0.0736	0.0695

$$b_m = \sum_{i=1}^n y_i b_i \quad (7)$$

Where, y_i (y_j) is the mole fraction of component i (j); n is the total number of components; k_{ij} refers to the binary interaction parameters (BIP) (Li and Guo, 1991) which are collected from the ASPEN HYSYS 2006 and listed in Table 9.

Based on the original PR EoS, the compressibility factor model can be written as Eq. (8), so that the compressibility factor is easily to be solved.

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad (8)$$

$$A = \frac{aP}{R^2 T^2} \quad (9)$$

$$B = \frac{bP}{RT} \quad (10)$$

It should be noted that the binary interaction parameters may have significant influences on computations of the compressibility factors. Many researcher have presented new algorithms regarding the BIPs, such as the Nishiumi correlation (Nishiumi et al., 1988), Jaubert correlation (Jaubert et al., 2010). Especially, Nishiumi correlation was extended for many complicated systems, which have the C₁–C₂₀ alkanes, carbon dioxide-alkane, nitrogen-alkane and hydrogen sulfide-alkane components. Thus, we researched the accuracy of the improved PR EoS with using Nishiumi correlation. Nishiumi BIPs correlation is expressed by Eqs.(11)–(13).

Table 8
Critical parameters and acentric factors.

Component	T _c (K)	P _c (MPa)	ω
CH ₄	190.58	4.544	0.0126
C ₂ H ₆	305.42	4.816	0.0978
C ₂ H ₄	282.36	4.966	0.1010
C ₃ H ₈	369.82	4.194	0.1541
C ₃ H ₆	364.75	4.550	0.1500
nC ₄ H ₁₀	408.14	3.747	0.2015
iC ₄ H ₁₀	425.18	3.600	0.1840
nC ₅ H ₁₂	469.65	3.325	0.2524
iC ₅ H ₁₂	460.39	3.381	0.2286
H ₂	33.25	1.280	–0.2190
CO	132.95	3.453	0.0442
O ₂	154.33	4.971	0.0200
N ₂	125.97	3.349	0.0372
CO ₂	304.25	7.290	0.2667
H ₂ S	373.55	8.890	0.0920
air	132.40	3.725	
H ₂ O	647.00	21.83	0.3434

Table 9
The binary interaction parameters.

Component	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	iC ₄ H ₁₀	nC ₄ H ₁₀	iC ₅ H ₁₂	nC ₅ H ₁₂	nC ₆ H ₁₄	nC ₇ H ₁₆
CO ₂	—	−0.0199970	0.1000000	0.1298000	0.1350000	0.1298000	0.1298000	0.1250000	0.1250000	0.1250000	0.1199000
N ₂	−0.0199970	—	0.0359990	0.0500000	0.0799980	0.0949990	0.0900000	0.0949990	0.1000000	0.1490000	0.1439000
CH ₄	0.1000000	0.0359990	—	0.0022413	0.0068288	0.0131134	0.0123047	0.0176275	0.0179254	0.0234741	0.0288643
C ₂ H ₆	0.1298000	0.0500000	0.0022413	—	0.0012579	0.0045736	0.0040964	0.0074133	0.0076095	0.0114138	0.0153243
C ₃ H ₈	0.1350000	0.0799980	0.0068288	0.0012579	—	0.0010406	0.0008189	0.0025834	0.0027005	0.0051420	0.0078874
iC ₄ H ₁₀	0.1298000	0.0949990	0.0131134	0.0045736	0.0010406	—	0.0000133	0.0003462	0.0003900	0.0015653	0.0032212
nC ₄ H ₁₀	0.1298000	0.0900000	0.0123047	0.0040964	0.0008189	0.0000133	—	0.0004951	0.0005472	0.0018663	0.0036464
iC ₅ H ₁₂	0.1250000	0.0949990	0.0176275	0.0074133	0.0025834	0.0003462	0.0004951	—	0.0000013	0.0004400	0.0014592
nC ₅ H ₁₂	0.1250000	0.1000000	0.0179254	0.0076095	0.0027005	0.0003900	0.0005472	0.0000013	—	0.0003934	0.0013733
nC ₆ H ₁₄	0.1250000	0.1490000	0.0234741	0.0114138	0.0051420	0.0015653	0.0018663	0.0004400	0.0003934	—	0.0002972
nC ₇ H ₁₆	0.1199000	0.1439000	0.0288643	0.0153243	0.0078874	0.0032212	0.0036464	0.0014592	0.0013733	0.0002972	—

$$1 - k_{ij} = C + D \left(\frac{v_{ci}}{v_{cj}} \right) + E \left(\frac{v_{ci}}{v_{cj}} \right)^2 \quad (11)$$

$$C = c_1 + c_2 |\omega_i - \omega_j| \quad (12)$$

$$D = d_1 + d_2 |\omega_i - \omega_j| \quad (13)$$

Where, v_c is the critical specific volume, mol/m³; $c_1 = 1.041$; $c_2 = 0.110$; $d_1 = -0.0403$; $d_2 = -0.0367$; $E = 0$.

The comparisons between the calculated z factors and experimental values of gas sample 2 and sample 6 are depicted in Fig. 1 and Fig. 2. The results demonstrate that lots of results fall out of the $\pm 5\%$ regions, which proves that the accuracy of Z factor predictions cannot be enhanced significantly by only modifying the binary interaction parameters. In this work, we didn't change the default binary interaction parameters listed in Table 9 for the new modified PR EoS.

3.2. Compressibility factor deviation analysis

According to Eq. (8), all the compressibility factors can be quickly calculated under the pressure and temperature conditions in accordance with Table 2–7. The accuracy of the original PR EoS is evaluated by comparing the experimental data and calculated

values. Taking the sample 6 for an instance, the results are listed in Table 10.

Table 10 shows that the relative deviations (RD) for the gas sample 6 are larger than 5% when the pressures beyond over 11 MPa. More comparisons show that the RD s are higher than 54% if the mole fraction of CO₂ is equal to 70.98% (Mohsen-Nia et al., 1994). Based on the inaccurate compressibility factors, the heat capacity, density and other physical parameters would inevitably have greater deviations. In order to solve this problem, this paper researched the improvement method with regard to the original PR EoS.

4. Improved PR EoS

4.1. Improvement method for PR EoS

According to the experimental data, the PR EoS can be improved by using the least squares method (Miller, 2006). The method is a standard and widely used approach in regression analysis to the approximate solution of overdetermined systems. Its objective minimizes the sum of square residuals between the experimental and calculated values. Suppose there are M groups of experimental compressibility factors, take these experimental data Z_k into Eq. (8) and resulting Eq. (14). If the calculated compressibility factors are equal to the experimental values, Eq. (14) should be equal to zero. In other words, the value of function f is closer to 0, the PR EoS has higher accuracy.

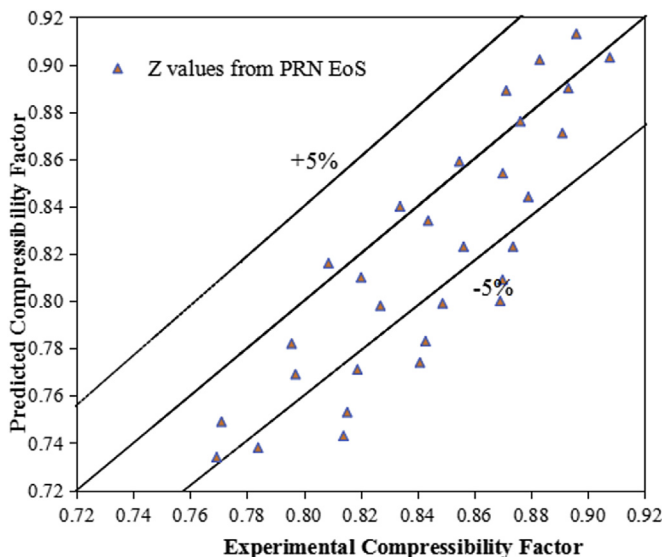


Fig. 1. Z factor comparisons for gas with $V_c = 9.84\%$.

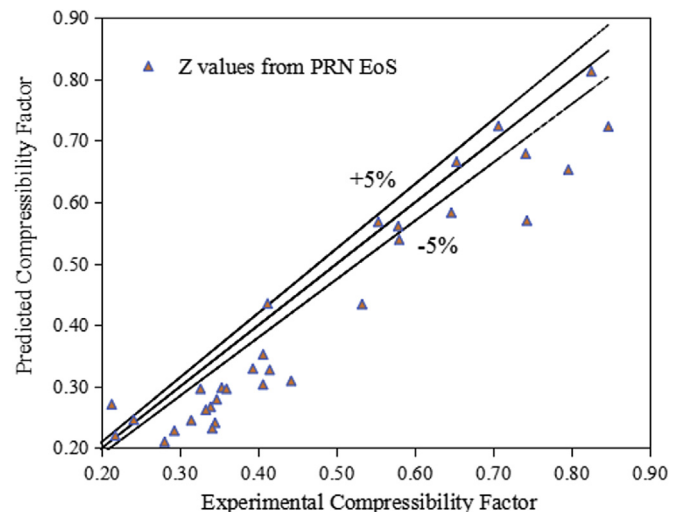


Fig. 2. Z factor comparisons for gas with $V_c = 91.77\%$.

Table 10Comparisons between calculated and experimental z factors for gas with $V_c = 9.84\%$.

Parameters	$T(^{\circ}\text{C})$	P (MPa)						
		15	13	11	9	7	5	3
Exp.	40	0.8692	0.8700	0.8737	0.8791	0.8911	0.9078	0.9323
Cal.		0.8064	0.8134	0.8272	0.8469	0.8726	0.9037	0.9395
RD		-7.22%	-6.50%	-5.32%	-3.66%	-2.08%	-0.45%	0.77%
Exp.	30	0.8409	0.8429	0.8489	0.8563	0.8701	0.8932	0.9237
Cal.		0.7805	0.7885	0.8036	0.8262	0.8557	0.8914	0.9321
RD		-7.18%	-6.45%	-5.33%	-3.52%	-1.65%	-0.20%	0.91%
Exp.	20	0.8140	0.8153	0.8189	0.8270	0.8438	0.8763	0.9122
Cal.		0.7512	0.7595	0.7763	0.8021	0.8362	0.8772	0.9236
RD		-7.71%	-6.84%	-5.20%	-3%	-0.90%	0.10%	1.25%
Exp.	10	0.7779	0.7774	0.7839	0.7971	0.8202	0.8548	0.8960
Cal.		0.7182	0.7260	0.7444	0.7738	0.8133	0.8607	0.9138
RD		-7.67%	-6.61%	-5.04%	-2.92%	-0.84%	0.69%	1.99%

$$f = \sum_{k=1}^M \left[Z_k^3 - (1 - B_k)Z_k^2 + (A'_k - 2B_k - 3B_k^2)Z_k - (A'_k B_k - B_k^2 - B_k^3) \right]^2 \quad (14)$$

$$B_k = \frac{bP_k}{RT_k} = \frac{P_k}{RT_k} \times 0.0778R \sum y_i \frac{T_{ci}}{P_{ci}} = 0.0778 \frac{P_k}{T_k} \sum y_i \frac{T_{ci}}{P_{ci}} \quad (15)$$

Where, Z_k is the k th group compressibility factor of the; P_k is k th group pressure; T_k is k th group temperature.

Although PR EOS contains many adjustable parameters, existing improvement methods mainly focus on the BIPs (PPR78 EoS), pseudocritical parameters and attractive term a (PRSV EoS). The BIPs and the pseudocritical parameters are fitted from the vapor pressures or the liquid density. The attractive term is a straight-forward parameter to influence the compressibility factor (Kontogeorgis and Folas, 2009). We thus assumed the deviations were mainly caused by the inaccurate attractive term a , and compared the calculated values of attractive term a and experimental values. Fig. 3 and Fig. 4 show the comparisons of the attractive term values a for gas samples 2 and 6. We can observe large deviations from calculated values and experimental data. This phenomenon proves the assumption proposed previously.

In order to improve the original PR EoS, a new correction coefficient x is introduced into the temperature dependent function α , and resulting a modified attractive term. It is expressed by Eq. (16).

$$x\alpha = x \left[1 + \left(1 - T_r^{0.5} \right) \left(\xi_1 + \xi_2 \omega + \xi_3 \omega^2 \right) \right]^2 \quad (16)$$

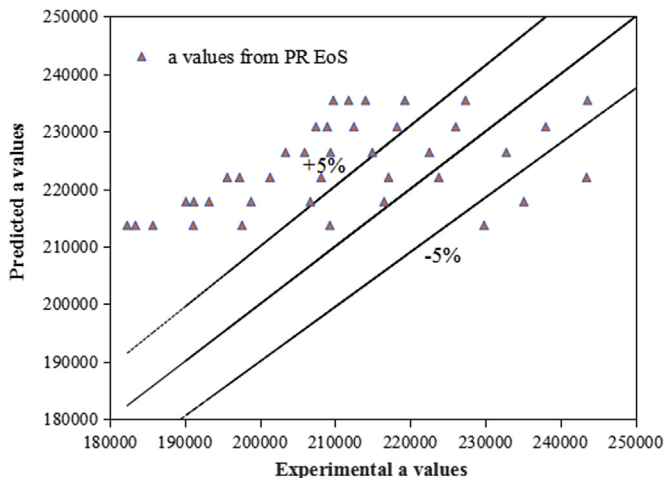
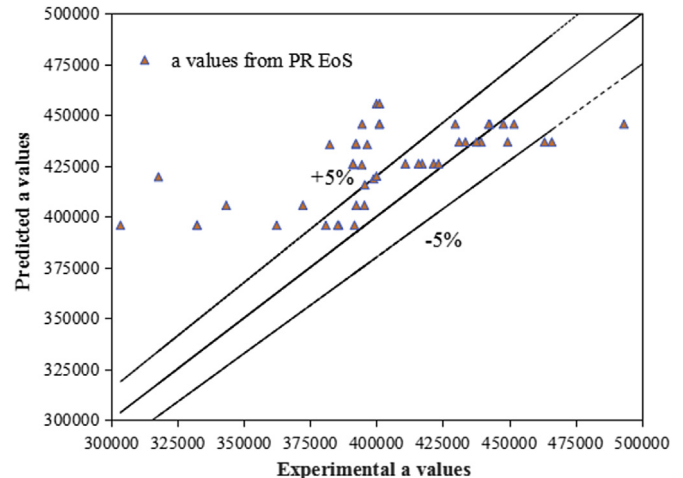
Introduce Eq. (16) into Eq. (9), and resulting Eqs.(17)–(20).

$$A'_k = \frac{a'_k P_k}{R^2 T_k^2} = \frac{P_k}{R^2 T_k^2} \left\{ 0.45724 R^2 \sum_i \sum_j y_i y_j \left[\frac{T_{ci}}{P_{ci}^{0.5}} \times \frac{T_{cj}}{P_{cj}^{0.5}} x \alpha_{ik}^{0.5} \alpha_{jk}^{0.5} (1 - K_{ij}) \right] \right\} \quad (17)$$

$$A'_k = 0.45724 x \frac{P_k}{T_k^2} \sum_i \sum_j y_i y_j \left[\frac{T_{ci}}{P_{ci}^{0.5}} \frac{T_{cj}}{P_{cj}^{0.5}} \alpha_{ik}^{0.5} \alpha_{jk}^{0.5} (1 - K_{ij}) \right] \quad (18)$$

$$A'_{k1} = x 0.45724 \frac{P_k}{T_k^2} \sum_i \sum_j y_i y_j \left\{ \frac{T_{ci}}{P_{ci}^{0.5}} \frac{T_{cj}}{P_{cj}^{0.5}} (1 - K_{ij}) \left[1 + \left(1 - \frac{T_k^{0.5}}{T_{ci}^{0.5}} \right) \left(\xi_1 + \xi_2 \omega_i + \xi_3 \omega_i^2 \right) \right] \right\} \quad (19)$$

$$A'_k = A'_{k1} \times \left[1 + \left(1 - \frac{T_k^{0.5}}{T_{cj}^{0.5}} \right) \left(\xi_1 + \xi_2 \omega_j + \xi_3 \omega_j^2 \right) \right] = x A_k \quad (20)$$

Fig. 3. a values comparisons for gas with $V_c = 9.84\%$.Fig. 4. a values comparisons for gas with $V_c = 91.77\%$.

Where ξ_{1-3} are the coefficients in term α , the values are equal to 0.37464, 1.54226, -0.26992, respectively.

Take partial derivative of Eq. (14) with respect to x , and set it to zero, the Eq. (21) can be obtained:

$$\frac{\partial f}{\partial x} = 2 \sum_{k=1}^M [Z_k^3 - (1 - B_k)Z_k^2 + (A_k x - 2B_k - 3B_k^2)Z_k - (xA_k B_k - B_k^2 - B_k^3)](Z_k - B_k) \frac{\partial A'_k}{\partial x} = 0 \quad (21)$$

There are two sub-terms in Eq. (21), which are expressed by Eqs. (22) and (23).

$$(Z_k - B_k) \neq 0 \quad (22)$$

$$\frac{\partial A'_k}{\partial x} = A_k \neq 0 \quad (23)$$

Due to both of above equations are not equal to zero, Eq. (21) is simplified into Eqs. (24) and (25).

$$x \sum_{k=1}^M (A_k Z_k - A_k B_k) = - \sum_{k=1}^M [Z_k^3 - (1 - B_k)Z_k^2 - (2B_k + 3B_k^2)Z_k + (B_k^2 + B_k^3)] \quad (24)$$

$$x = - \frac{\sum_{k=1}^M [Z_k^3 - (1 - B_k)Z_k^2 - (2B_k + 3B_k^2)Z_k + (B_k^2 + B_k^3)]}{\sum_{k=1}^M (A_k Z_k - A_k B_k)} \quad (25)$$

Take each group of pressure, temperature, acentric factor and experimental z factor into Eq. (25), the correction factor x for each gas sample at a specific pressure and temperature can be calculated. If the calculated x value is less than the experimental data, the value of x is less than one. Otherwise, the value of x is greater than one. However, if we introduce all the experimental data into the Eq. (25) at one time, only one correction factor x can be obtained. As a result, the improved PR EoS may have not enough accuracy.

In order to solve this problem, the variable M in Eq. (25) is set to the value of the unity, so that we can get one correction parameter x by using each group of experimental compressibility factor, temperature, pressures and composition. Thus, 267 x values also can be calculated, based on the 267 groups of experimental data. If we can build a function to depict the relationship between the variable x and temperature, pressure and CO_2 mole fraction of the gas, the PR EoS can be modified to predict the compressibility factor of CO_2 -content gases with satisfactory accuracy (Hall and Yarborough, 1973). However, it's difficult to find a simple and reliable correlation to depict such a relationship by simply using mathematical fitting method.

Stryjek and Vera modified the temperature function in the attractive term in original PR EoS and resulting the PRSV I EoS [26], which adopts a similar improvement idea as this work. Thus, we referenced the improvement method of the temperature function of PRSV I EoS. The temperature function in PRSV I EoS are expressed by Eqs.(26)–(28)

$$\alpha = [1 + f_\omega(1 - T_r^{0.5})]^2 \quad (26)$$

$$f_\omega = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (27)$$

$$k_0 = 0.37889 + 1.48972\omega - 0.17132\omega^2 + 0.01966\omega^3 \quad (28)$$

Eq. (29) is the derivative of temperature function Eq. (26) in PRSV EoS. Many researchers study the derivative of temperature function in cubic EoS to observe thermodynamic properties of pure components and mixtures.

$$T \left(\frac{d\alpha}{dT} \right) = - [1 + f_\omega(1 - T_r^{0.5})] [f_\omega T_r^{0.5} + k_1(1.4T_r - 4T_r^2)] \quad (29)$$

Taking the square on both sides of Eq. (29), we can get Eq. (30). Compare the Eq. (30) and Eq. (31), the new expression form of parameter x is obtained as expressed by Eq. (32).

$$\left[T \left(\frac{d\alpha}{dT} \right) \right]^2 = [1 + f_\omega(1 - T_r^{0.5})]^2 [-f_\omega T_r^{0.5} + k_1(-1.4T_r + 4T_r^2)]^2 \quad (30)$$

$$x\alpha = [1 + f_\omega(1 - T_r^{0.5})]^2 x \quad (31)$$

$$x = [-f_\omega T_r^{0.5} + k_1(-1.4T_r + 4T_r^2)]^2 \quad (32)$$

In order to simplify the form of parameter x , the square of Eq. (32) is removed and resulting Eq. (33):

$$x = -[f_\omega T_r^{0.5} + k_1(1.4T_r - 4T_r^2)] \quad (33)$$

In Eqs. (33) and (34), the acentric-related term f_ω and T_r keep the same values as the original PR EoS. The correction coefficient x is calculated from the deviation between the experimental compressibility factors and calculated values. Thus, a totally of 267 groups of k_1 values can be obtained by using Eq. (34) and all the experimental data. If all the k_1 data points can be depicted by a specific function, we can finally present the improved expression of the temperature function.

$$k_1 = \frac{x + f_\omega T_r^{0.5}}{4T_r^2 - 1.4T_r} \quad (34)$$

4.2. Expression of parameter k_1

Natural gas compressibility factor is mainly related with the gas composition, pressure and temperature. The corresponding state theory point out if gases have the same reduced temperature and reduced pressure, they have similar compressibility factors (Li et al., 2012). Thus, this paper correlates the reduced temperature and reduced pressure to the parameter k_1 . The reduced temperature is defined by Eq. (5), and reduced pressure is defined as Eq. (35).

$$P_r = \frac{P}{P_c} \quad (35)$$

According to the experimental data listed in Table 2, all the experimental z factors, reduced pressures, reduced temperatures and calculated x values are listed in Table 11. However, we cannot found significant correlations between the k_1 values and the other parameters from Table 11. We have to use the non-linear data fitting method to construct the general expression of the parameter k_1 .

Suppose parameter k_1 is dependent on CO_2 volume content, reduced temperature, and reduced pressure, we need a ternary function to construct the mathematical relationship among them. However, it's difficult to determine the appropriate form of such a target ternary function by using the non-linear fitting method.

Table 11
Correction factors for gas with $V_c = 9.84\%$.

z	P_r	T_r	x	k_1	z	P_r	T_r	x	k_1
0.8700	2.71	1.54	0.8596	0.1794	0.8438	1.46	1.39	0.9803	0.2221
0.8737	2.30	1.54	0.8695	0.1807	0.8763	1.04	1.39	1.0240	0.2285
0.8791	1.88	1.54	0.8936	0.1838	0.9122	0.63	1.39	1.1270	0.2626
0.8911	1.46	1.54	0.9229	0.1875	0.7779	3.13	1.34	0.9006	0.2265
0.9078	1.04	1.54	0.9764	0.1943	0.7774	2.71	1.34	0.906	0.2274
0.9323	0.63	1.54	1.0710	0.2064	0.7839	2.30	1.34	0.9202	0.2296
0.8409	3.13	1.49	0.8749	0.1925	0.7971	1.88	1.34	0.9439	0.2334
0.8429	2.71	1.49	0.8788	0.1930	0.8202	1.46	1.34	0.9764	0.2386
0.8489	2.30	1.49	0.8872	0.1942	0.8548	1.04	1.34	1.0270	0.2467
0.8563	1.88	1.49	0.9118	0.1975	0.8960	0.63	1.34	1.1240	0.2834
0.8701	1.46	1.49	0.9468	0.2023	0.7471	3.13	1.30	0.8932	0.2434
0.8932	1.04	1.49	0.9906	0.2082	0.7484	2.71	1.30	0.9006	0.2447
0.9237	0.63	1.49	1.0740	0.2196	0.7548	2.30	1.30	0.9089	0.2461
0.8140	3.13	1.44	0.8830	0.2078	0.7693	1.88	1.30	0.9299	0.2498
0.8153	2.71	1.44	0.8894	0.2087	0.7957	1.46	1.30	0.9628	0.2555
0.8189	2.30	1.44	0.9066	0.2113	0.8339	1.04	1.30	1.0300	0.2671
0.8270	1.88	1.44	0.9361	0.2156	0.8831	0.63	1.30	1.1020	0.2732

Thus, we have to set the mole fraction of CO_2 as constant, and find a binary function that depicts the relationship among k_1 , reduced temperature and reduced pressure. By screening a large number of binary functions, Eq. (36) is selected as the best one to fit the parameter k_1 . Besides, this function gives a unified description of k_1 with the CO_2 volume content of 9.84%, 28.86%, 50.99%, 70.98%, 91.77% and 100%.

$$k_1 = p_1 + p_2 \frac{\ln P_r}{P_r} + \frac{p_3}{T_r^2} \quad (36)$$

Although Eq. (36) fits the k_1 values at six specific CO_2 volume contents with satisfactory accuracy, it doesn't contain the CO_2 volume content term. It cannot be extended to the mixtures with different CO_2 volume contents. Thus, an additional exponent term with regard to the CO_2 volume content is added to Eq. (36), as expressed by Eq. (37). As the values of reduced pressures and reduced temperatures are significantly larger than the CO_2 volume contents, the exponent value is determined to be 0.3.

$$k_1 = p_1 + p_2 \frac{\ln P_r}{P_r} + \frac{p_3}{T_r^2} + p_4 V^{0.3} \quad (37)$$

There are four parameters p_1 – p_4 in Eq. (37). The non-linear fitting method should be applied once again to calculate their values. The final fitting results are listed in Table 12. The degree of correlation in Table 12 shows Eq. (37) is able to give unified, accurate descriptions for parameter k_1 at different reduced temperatures, reduced pressures and CO_2 volume contents.

4.3. Validation of the attractive term

Actually, above achievements modify the temperature function α in the attractive term of the original PR EoS, which has a considerable influence on vapor pressure of gas mixtures (Sandoval

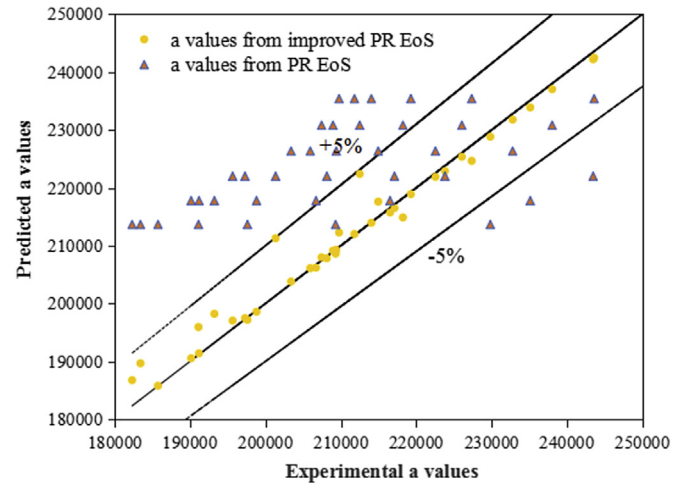


Fig. 5. a values comparisons for gas with $V_c = 9.84\%$.

et al., 1989). In order to avoid the incorrect vapor pressures, the attractive term should be validated by the experimental a values. Figs. 5 and 6 show the comparisons of a values for gas sample 2 and sample 6. These results demonstrate that a values calculated by the improved PR EoS are much more closer to the experimental data than those of the original PR EoS. Thus, better vapor pressures of gas mixtures can be obtained by using the improved PR EoS.

5. Results and discussions

5.1. Comparisons between the original PR and improved PR EoSs

The experimental compressibility factors and calculated values are compared to verify the accuracy of the improved PR EoS. The results are depicted in Figs. 7–12. The average absolute deviation (AAE) is defined to evaluate the accuracy quantitatively, as expressed by Eq. (38).

$$AAE = \frac{1}{N} \sum_{i=1}^N \frac{|Z_{cali} - Z_{exp i}|}{Z_{exp i}} \quad (38)$$

Where, N is the total number of data points; Z_{cali} is the calculated compressibility factor; $Z_{exp i}$ is the experimental compressibility factor.

Figs. 7–12 present the degree of agreements between the experimental compressibility factors and calculated values. If the agreement is perfect, the correlation points lie on the 45° line on the plot. Therefore, it can be concluded that the scattered data points obtained by improved PR EoS are closer to the experimental data. Table 13 lists the AAE analysis.

Table 13 Reveals that the AAEs of the original PR EoS range from 4.150% to 33.679%, and the overall AAE is 11.688%. The AAEs of the

Table 12
 p_1 – p_4 values in Eq. (37).

parameters	$V_c, \%$					
	9.84–28.86	28.86–50.99	50.99–70.98	70.98–91.77	91.77–100	100
p_1	−0.1882	−0.1363	−0.2327	−0.0142	−5.1958	−0.4720
p_2	−0.0162	0.0682	0.0349	0.0057	0.0325	0.1198
p_3	0.5299	0.6952	0.7073	0.8930	1.1666	1.7284
p_4	0.2889	0.0564	0.1708	−0.2348	4.7989	−0.4853
degree of correlation	0.9792	0.9934	0.9854	0.9873	0.9673	0.9886

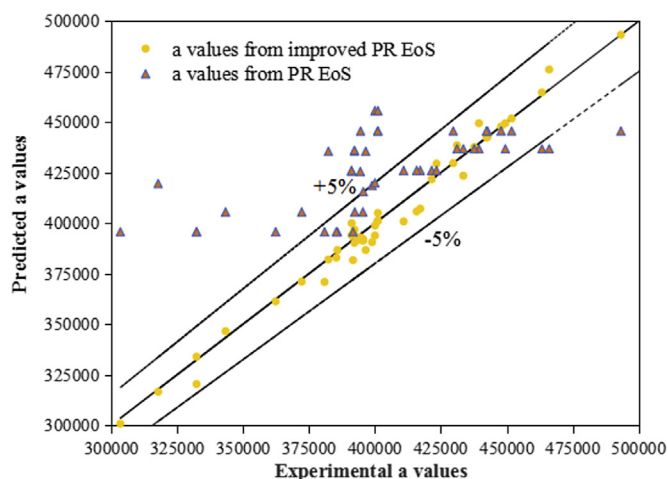


Fig. 6. a values comparisons for gas with $V_c = 91.77\%$.

improved PR EoS range from 0.276% to 7.163%, and the overall AAE is 2.708%. By using the improved PR EoS, the AAE of the calculated compressibility factor is reduced by 8.98% when compared with that of the original PR EoS.

5.2. Comparisons among the improved PR, PRSV, PRTwu, BWRS, PC-SAFT EoSs

In order to validate the merits of the improve PR EoS, more comparisons between the improved PR EoS and PR, PRSV, PRTwu, BWRS, PC-SAFT EoSs are demonstrated in this section (Poling et al., 2001).

Both of the PRSV and PRTwu EoSs are cubic EoS, and have different temperature functions α with the improved PR EoS. All of them have simply form and easily to be solved. BWRS EoS is an eleven-parameter, which has been applied to the non-hydrocarbon systems but difficult to be solved. The PC-SAFT EoS is theoretically derived model based on the perturbation theory (Kontogeorgis and Folas, 2009). The association term in the PC-SAFT EoS takes into account the polarity of self-association of gas molecules (Privat et al., 2010), so that it can be applied to the highly non-ideal mixtures (Diamantonis et al., 2013). But, PC-SAFT EoS has a very

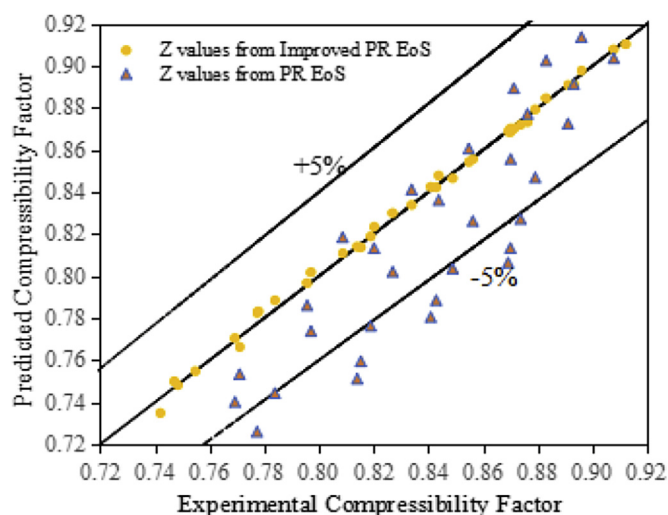


Fig. 7. Compressibility factor comparisons for gas with $V_c = 9.84\%$.

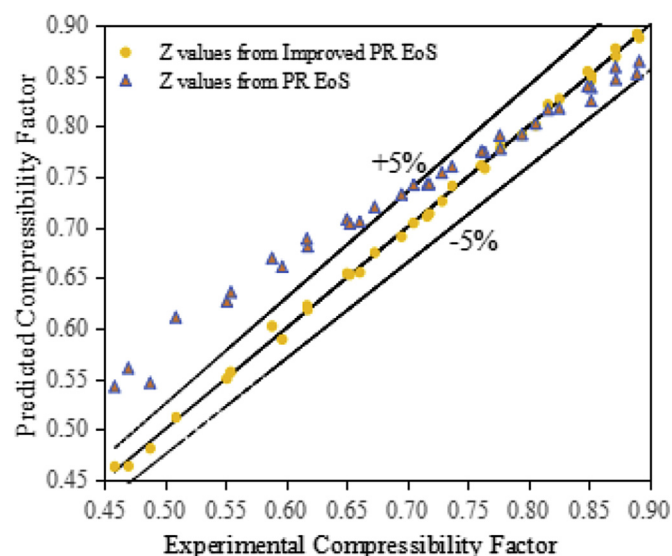


Fig. 8. Compressibility factor comparisons for gas with $V_c = 28.86\%$.

complicated form, whose solution process it also not easy (Jia et al., 2016). The comparisons between the results calculated by the improved PR EoS, other EoSs and PC-SAFT model are depicted in Figs. 13–20.

Table 14 shows the AAEs of the PRSV, PRTwu, BWRS and PC-SAFT EoSs are from 3.850% to 13.365%, from 3.150% to 10.469%, from 2.750% to 10.143% and from 0.457% to 5.354%, respectively. The overall AAEs are equal to 8.608%, 6.810%, 6.810% and 2.906%, respectively.

5.3. Discussions

The previous work proves that the improved PR EoS has significant better performance on the compressibility factor predictions of high CO_2 -content natural gases when compared with the original PR, PRSV, PRTwu and BWRS EoSs. It is essentially comparable in predictability to PC-SAFT EoS.

In order to build the improved PR EoS, we just need to replace

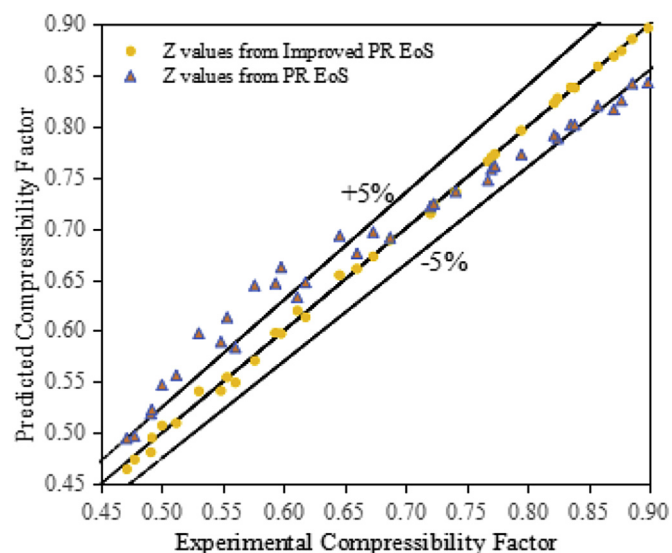


Fig. 9. Compressibility factor comparisons for gas with $V_c = 50.99\%$.

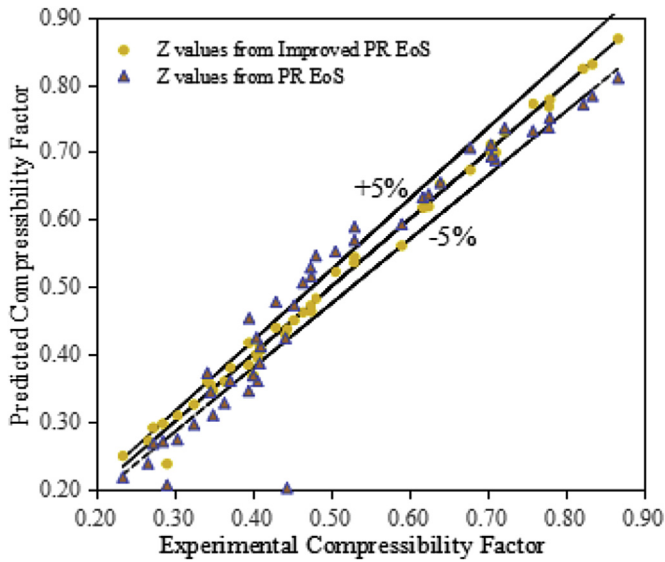


Fig. 10. Compressibility factor comparisons for gas with $V_c = 70.98\%$.

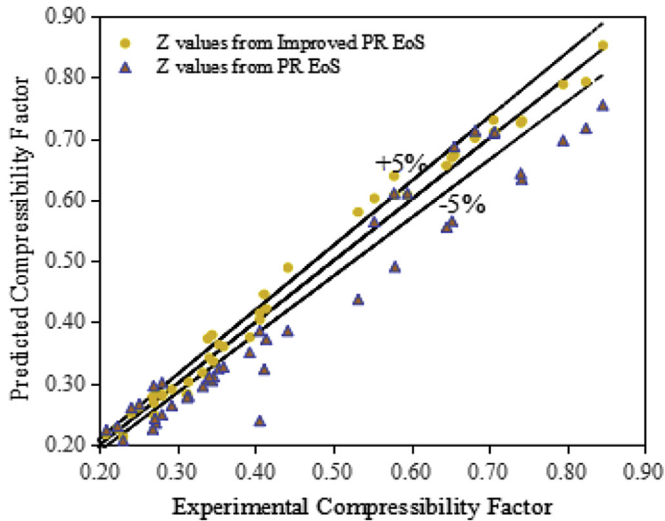


Fig. 11. Compressibility factor comparisons for gas with $V_c = 91.77\%$.

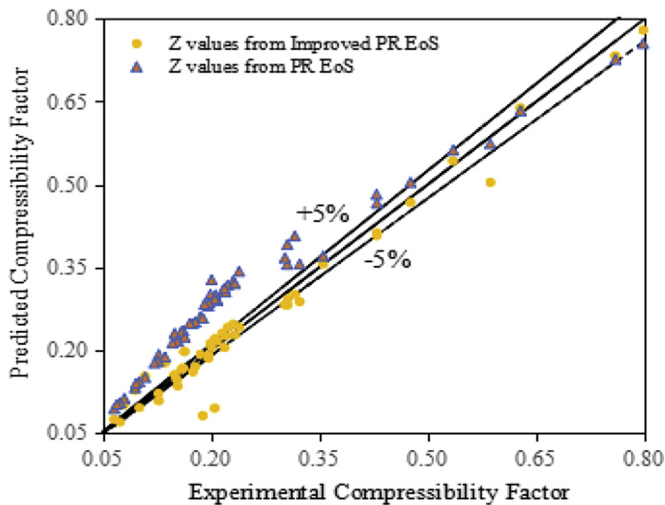


Fig. 12. Compressibility factor comparisons for gas with $V_c = 100\%$.

Table 13
AAEs comparisons of compressibility factors.

$V_c\%$	Data points	AAE of improved PR EOS	AAE of PR EOS
9.84	42	0.276%	4.150%
28.86%	38	0.598%	6.289%
50.99%	40	0.624%	5.201%
70.98%	45	2.464%	7.938%
91.77%	55	7.163%	12.869%
100%	47	5.120%	33.679%
Overall	267	2.708%	11.688%

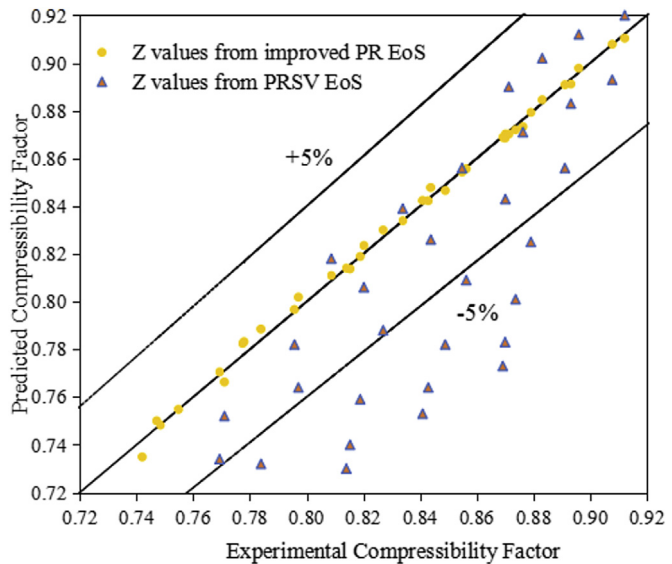


Fig. 13. Compressibility factor comparisons for gas with $V_c = 9.84\%$.

the temperature function α in Eq. (4) with the new α presented by Eqs. (26)–(28) and Eq. (34). Accordingly, the improved EoS keeps the simply form as the original PR EoS, and thus it is easily to be solved. The models of other properties, such as the density, heat capacity, enthalpy and entropy also keep the same forms as those deduced from the original PR EoS. This improved EoS not only provides an effective way to calculate the compressibility factors of high CO_2 -content natural gas, but also is a promising way to

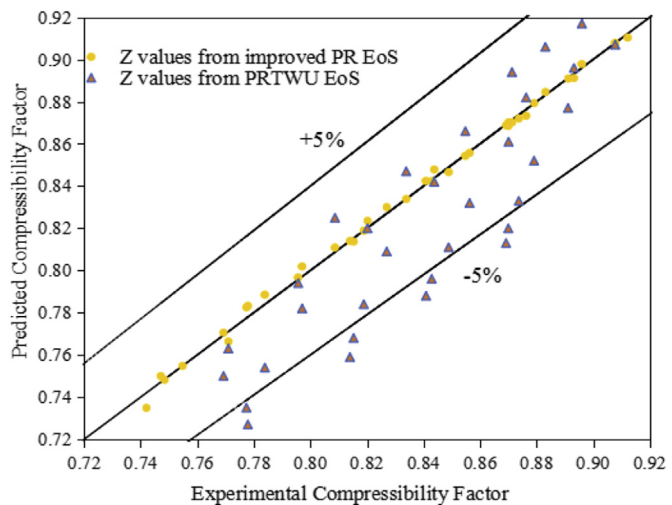


Fig. 14. Compressibility factor comparisons for gas with $V_c = 9.84\%$.

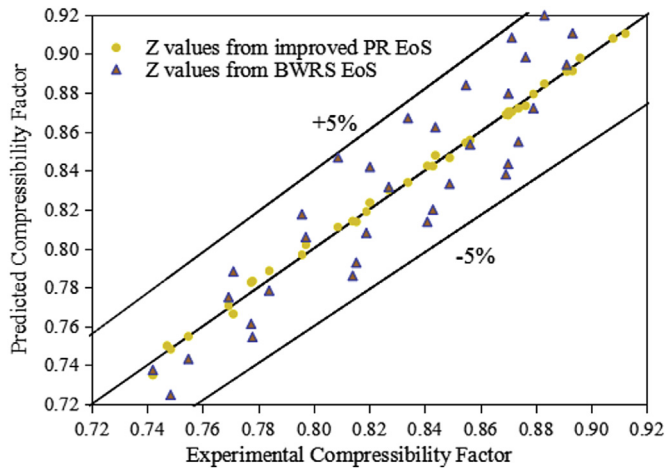


Fig. 15. Compressibility factor comparisons for gas with $V_c = 9.84\%$.

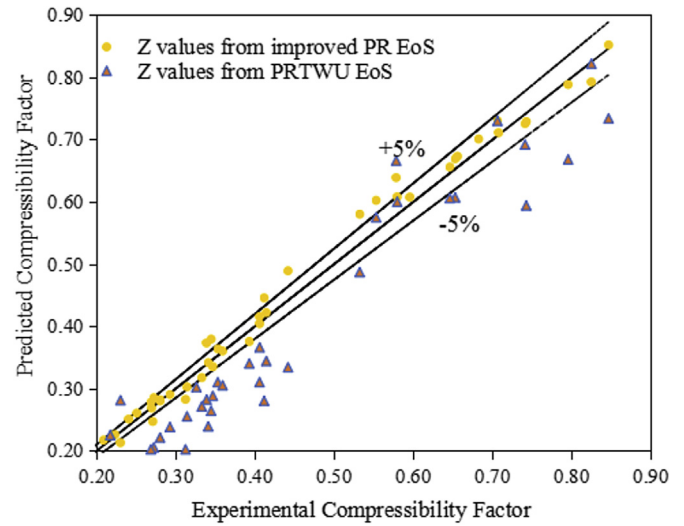


Fig. 18. Compressibility factor comparisons for gas with $V_c = 91.77\%$.

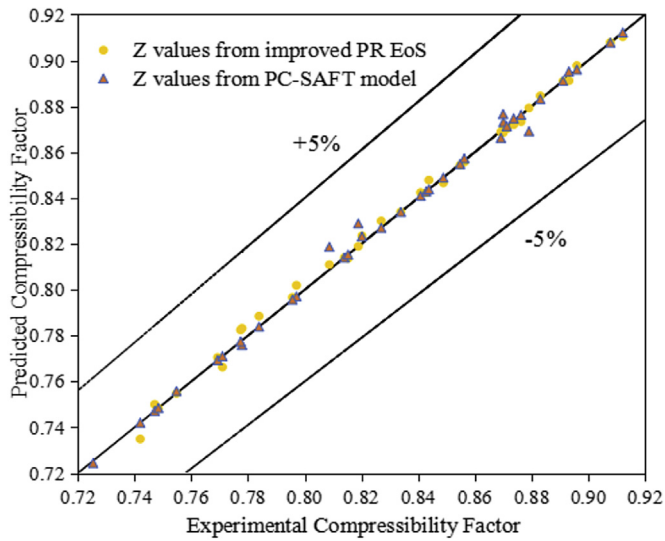


Fig. 16. Compressibility factor comparisons for gas with $V_c = 9.84\%$.

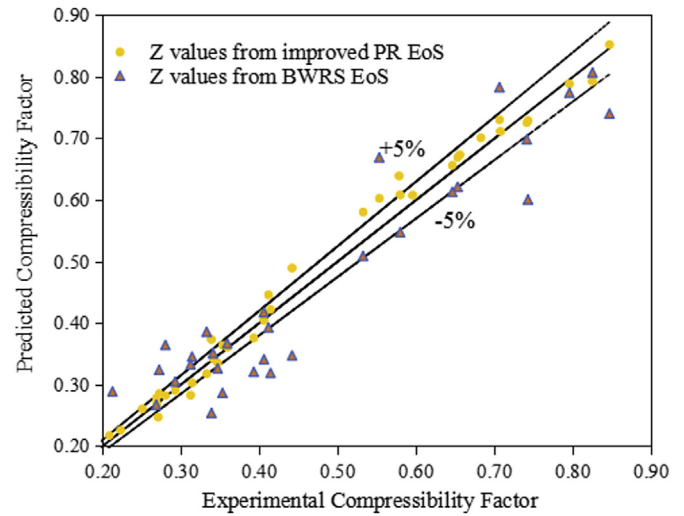


Fig. 19. Compressibility factor comparisons for gas with $V_c = 91.77\%$.

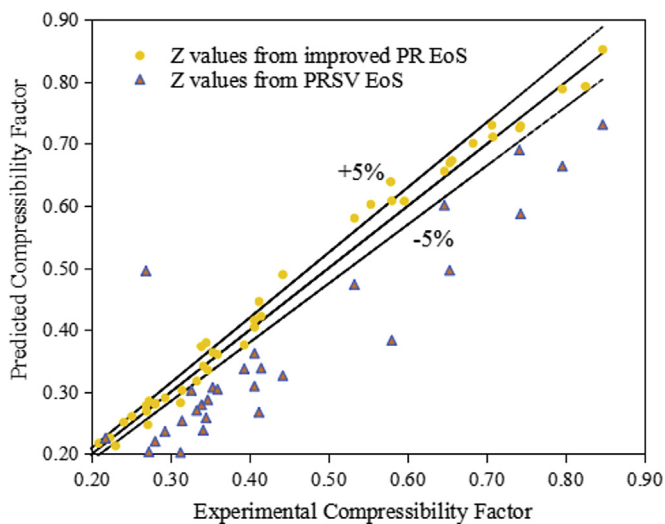


Fig. 17. Compressibility factor comparisons for gas with $V_c = 91.77\%$.

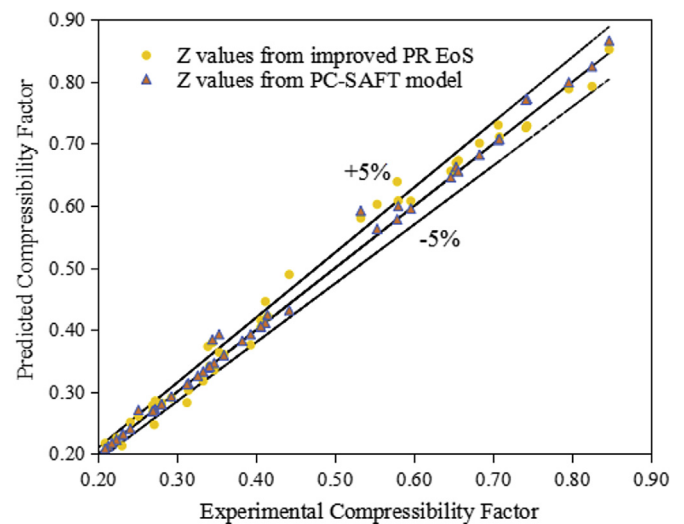


Fig. 20. Compressibility factor comparisons for gas with $V_c = 91.77\%$.

Table 14

AAEs comparisons of compressibility factors.

V_c , %	Data points	AAE of PRSV EOS	AAE of PRTWU EOS	AAE of BWRS EOS	AAE of PC-SAFT model
9.84	42	3.850%	3.150%	2.750%	0.457%
91.77	55	13.365%	10.469%	10.143%	5.354%
Overall	267	8.608%	6.810%	6.447%	2.906%

calculate other thermodynamic properties.

The accuracy of the improved PR EoS is just verified in the pressures ranging from 3 MPa to 15 MPa, and temperatures from 263.15 K to 313.15 K. The accuracy in extended pressure and temperature ranges should be researched in the future work. Beside the compressibility factor model, the models of other properties based on the imported EoS also should be verified.

7. Conclusions

In order to enhance the accuracy of applying PR EoS to calculate the compressibility factors of high CO₂-content natural gases, a new correction parameter associated with three-parameters (the reduced temperature T_r , reduced pressure P_r and CO₂ volume content) is introduced into the attractive term of original PR EoS by fitting the deviations between 267 groups of experimental compressibility factors and corresponding calculation values. The experimental data contain six gas samples with CO₂ volume content of 9.84%, 28.86%, 50.99%, 70.98%, 91.77% and 100%, and cover pressures from 3 MPa to 15 MPa, and temperatures from 263.15 K to 313.15 K.

The comparisons between the experimental data and the calculated compressibility factors show that average absolute deviation of the improved PR EoS is 2.708%, whereas that of the original PR EoS 11.688%. It has better performance than PRSV, PRTWU BWRS EoSs when it is applied to compute the compressibility factors of high CO₂-content natural gases, and is essentially comparable in predictability to PC-SAFT EoS. Achievements of this paper not only enhance the compressibility factor prediction accuracy for high CO₂ volume content gases, but also provide a new way to construct mathematical models for enthalpy, entropy, heat capacity and other basic physical parameters.

Acknowledgment

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