Evaluations on Compressibility Factor Calculation Methods for High-Pressure H_2S-Containing Natural Gases

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Abstract: The compressibility factor is an essential parameter for natural gas exploitation and processing. The method based on the equation of state (EoS) represents the most popular method for compressibility factor calculations. In this paper, the accuracy of compressibility factor calculations for two traditional cubic-EoSs (Soave-Redlich-Kwong (SRK) EoS, the Peng–Robinson(PR) EoS), the Benedict–Webb–Rubin-Starling (BWRs) EoS, and the Cubic-Plus-Association (CPA) EoS are evaluated based on experimental data for high-pressure H_2S-containing natural gases. A total of 234 sets of experimental compressibility factors are applied to validate the above four EoSs, which cover pressures from 70MPa to 131MPa. Results show that for the high-pressure and low H_2S content natural gas ($35MPa \le P < 70MPa$, $H_2S < 0.3\%$), the BWRS EoS yields the best results among the above four EoSs. The average relative deviation (ARD) between the experimental results and the calculated values is 1.07%. For high-pressure and high H_2S content natural gas ($35MPa \le P < 70MPa$, $H_2S \ge 0.3\%$), the CPA EoS yields the best results with an ARD of 1.01%. For ultra-high-pressure natural gas ($P \ge 70MPa$) without H_2S, the BWRS EoS gives the best results with an ARD of 0.32% and the maximum relative deviation is 1.50%.

Keywords: High-pressure natural gas, H_2S, Compressibility factor, Equation of state.

1. INTRODUCTION

The natural gas compressibility factor is an essential parameter for gas exploitation, metering, oil and gas pipeline transportation, and surface process design in the oil and gas industry (2014)[1]. Based on the compressibility factor, some other gas thermal physical properties such as natural gas volume, density, and fugacity can be further estimated. In recent years, some high-pressure H_2S-containing reservoirs have been developed in the northwestern area of the Sichuan Basin, China (2014) [2]. These H_2S-containing gas reservoirs usually have high pressures, i.e., over 70MPa. The accurate calculation of the compressibility factor is important for the development of gas reservoirs and processing.

The experimental measurements, empirical correlations, and equations of state (EoS) (2000) [3] are popular methods for computing gas compressibility factor. However, it is not easy to obtain the compressibility factor of high-pressure H_2S-containing natural gases based on the experimental methods due to the high toxicity of H_2S, which is also rarely in published literature. Some common empirical correlations have high accuracy within a certain pressure and temperature range with the absence of H_2S, including the Dranchuk-Purvis-Robinson method, the Brill-Beggs method, and the Hall-Yarborough method. Once the pressure and temperature ranges beyond the fitted pressure and temperature ranges, these correlations will deviate from the actual values (2007) [4]. Hence, these correlations are difficult to apply with high-pressure H_2S-containing natural gases.

The EoS method has high accuracy and wide application range, and is used in most commercial physical property calculation software. The well-known Soave-Redlich-Kwong(SRK) equation of state, Peng–Robinson(PR) equation of state, and Benedict–Webb–Rubin(BWR) equation of state have achieved good results in the calculation of the oil and gas phase, and physical properties. However, traditional cubic EoSs such as the SRK and PR EoSs are mainly developed for non-polar systems. The H_2S is a strongly polar molecule, especially at high pressures, the distance between molecules is smaller, which results in the force between polar molecules becoming stronger. As a result, the compressibility factor calculated by the traditional cubic EoSs deviates from the actual values.

The BWRS EoS reveals good accuracy in predicting the thermodynamic properties of hydrocarbon mixtures (1971) [5]. Besides, Kontogeorgis *et al*. (1996) [6] proposed the Cubic Plus Association(CPA) EoS based on the SRK EoS and the statistical association theory, which can describe the hydrogen bonding association between polar molecules (2009) [7]. Hence, using the BWRS EoS and the CPA EoS is expected to improve the accuracy in computing the compressibility factor of high-pressure H_2S-containing natural gases.

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In this paper, two traditional cubic EoSs (SRK EoS, PR EoS), BWRS EoS, and CPA EoS are evaluated based on experimental data for high-pressure H_2S-containing natural gases. A total of 234 sets of experimental compressibility factors are applied to validate the above four EoSs, which cover pressures from 70MPa to 131MPa.

2. EQUATIONS OF STATE

2.1. SRK EoS

Soave (1972) [8] proposed the SRK EoS in 1972. The SRK EoS is expressed by Eq.(1). The detailed equations can refer to Luo *et al*. (2007) [9].

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{1}$$

Where $A = \frac{aP}{R^2T^2}$ $B = \frac{bP}{RT}$, $a = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2}(1 - K_{ij})$. In this EoS, Soave introduced a binary interaction coefficient K_{ij} into the mixing rule of parameter *a*. The value of K_{ij} is generally fitted from the gas-liquid equilibrium data of the binary system.

2.2. PR EoS

The SRK EoS tends to underestimate the liquid densities and liquid phase fractions. Peng and Robinson (2016) [10] proposed the PR EoS in 1976 based on the SRK EoS to further improve the accuracy of predicting the thermodynamic properties and gas-liquid equilibrium data. The PR EoS is expressed by Eq.(2).

$$Z^3 - (1 - B)Z^2 + (A - 3B - 2B^2)Z - (AB - B^2 - B^3) = 0 \tag{2}$$

where, parameters A and B have the same form as those in the SRK EoS, but the parameters a and b are different from those in the SRK EoS. More details regarding the parameters a and b can refer to Luo *et al*. (2007) [11]

2.3. BWRS EoS

The Benedict–Webb–Rubin-Starling equation of state is proposed by Kenneth E. Starling (1971) [5].

$$Z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} + \frac{D_0}{RT^4} - \frac{E_0}{RT^4}\right)\rho + \left(b - \frac{a}{RT} - \frac{d}{RT^2}\right)\rho^2 + \frac{\alpha}{RT}\left(a + \frac{d}{T}\right)\rho^5 - \frac{c\rho^2}{RT^3}\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right) \tag{3}$$

where A_0, B_0, C_0, D_0, E_0, γ, a, b, c, d, α are eleven parameters of the EoS, which can be found from Starling (1973) [12].

2.4. CPA EoS

The SRK and PR EoSs are widely used in oil and gas industries, but they only consider the weak dispersion force and inducing forces between non-polar molecules, and do not consider the hydrogen-bond association between polar molecules such as the water molecules, and the H_2S molecules. Kontogeorgis *et al*. (1996) [6] proposed the CPA EoS by introducing an additional association term into the traditional cubic EoS, which considers the hydrogen bonding association between polar molecules, overcoming the traditional cubic EoS for poor applicability of systems containing polar substances. The basic form of the CPA EoS is expressed as follows:

$$P = \frac{RT}{v - b} - \frac{a}{v\left(v + b\right)} - \frac{1}{2}\frac{RT}{v}\left(1 - v\frac{\partial \ln g}{\partial v}\right)\sum_i x_i \sum_{A_i}\left(1 - X_{A_i}\right) \tag{4}$$

where *a* is the energy parameter; *b* is the volume parameter, $m^3 \cdot mol^{-1}$; *v* is the molar volume; *g* is the radius distribution function of the molecule, dimensionless; x_i is the mole fraction of component *i* in the mixture, dimensionless; A_i represents the active association point A on molecule *i*; X_A is the mole fraction of unassociated active site A in component *i*.

The parameters a and b in the mixture are calculated by the van der Waals mixing rule (2004) [13]; ε^{AiBj} and β^{AiBj} are calculated using the CR-1 mixing rule, as shown in the following formula:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij}\right) \qquad b = \sum_j x_i b_i \tag{5}$$

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \qquad \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \tag{6}$$

The CPA EoS uses five parameters, *a*, *b*, *k*, ε^{AiBj}, and β^{AiBj}, to characterize each component. For non-polar components (methane, ethane, etc.), ε^{AiBj} =0, β^{AiBj} =0, so the CPA EoS degenerates into the SRK EoS. For polar components, the above five parameters need to be obtained by fitting the density and saturation vapor pressure of the pure substance (2015) [14].

3. MEASUREMENTS OF COMPRESSIBILITY FACTORS

A total of 234 sets of experimental compressibility factor data (Table **1**) were collected to evaluate the accuracy of different EoSs for high-pressure H_2S-containing natural gas. The data in the pressure range from 20MPa to 100MPa are measured by Guo *et al*. (1999) [15]. The data in the pressure range from 8.5MPa to 50MPa with 14.99% H_2S content in terms of mole fraction are reported by Fang *et al*. (2011) [16]. The data in the pressure range from 15MPa to 43MPa with 0.675% H_2S content in terms of mole fraction are reported by Chen *et al*. (2010) [17]. The data in the pressure range from 10 to 40MPa with 8.36% H_2S content in terms of mole fraction are reported by Wang *et al*. (2004) [18]. The data in the pressure range from 7MPa to 49MPa are measured by Liang and Zuo *et al*. (2014) [19]. The data in the pressure range from 6.89 MPa to 37.13MPa with H_2S content in terms of mole fraction ranging from 6.8% to 70.03% were measured by Elsharkawy. (2002) [20]. More recently, Luo *et al*. [21] measured the compressibility factors of natural gas samples in the pressure range from 70MPa to 131MPa by the use of ST sulfur-resistant high-pressure PVT instrument (Figure **1**), in which the H_2S content is from 0.0001% to 0.8783% in terms of mole fraction. The ST sulfur-resistant high-pressure PVT instrument is mainly composed of a high-pressure metering pump, a sample storage container, a PVT gas cylinder, and a thermostat, which can accommodate the natural gas with H_2S content ≤20% and CO_2 content ≤50%. The above experimental data are classified according to the pressures and H_2S contents, as given by Table **2**.

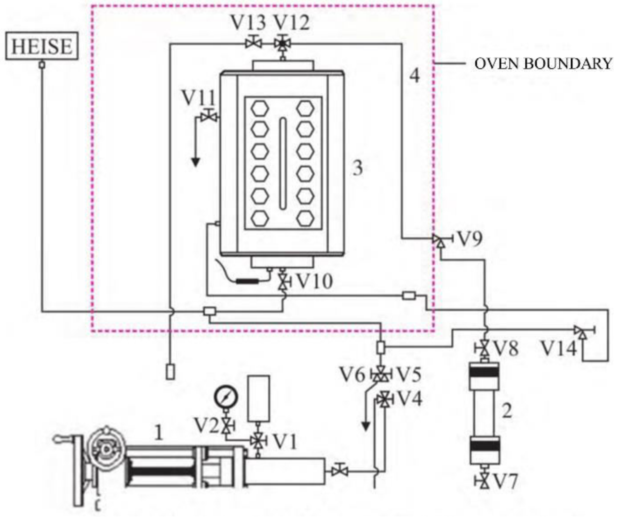

Figure 1: The flow diagram of ST PVT experimental instruments [21].

Table 1: **Experimental Compressibility Factor Data Source**

Source	Pressure Range (MPa)	H_2S Content Range (%)
Guo *et al*. (1999) [15]	20~100	0
Fang *et al*. (2011) [16]	8.5~50	14.99
Chen *et al*. (2010) [17]	15~43	0.675
Wang *et al*. (2004) [18]	10~40	8.36
Liang and Zuo (2014) [19]	7~49	0
Elsharkawy (2002) [20]	6.89~37.13	6.8~70.03
Luo *et al*. (2019) [21]	5~131	0~1.01

Table 2: **The Number of Experimental Data of High-Pressure and H_2S-Containing Natural Gas Compressibility Factors**

Gas Reservoir Type	Compressibility Factor Experiment Data Quantity /n
High-pressure and low H_2S content natural gas 35MPa≤P<70MPa, H_2S<0.3%	28
High-pressure, medium, and high H_2S content natural gas 35MPa≤P<70MPa, 0.3%≤H_2S<10%	54
High-pressure and ultra-high H_2S content natural gas 35MPa≤P<70MPa, H_2S≥10%	14
Ultra-high pressure H_2S-containing natural gas P≥70MPa	138

4. EVALUATION OF EOSs

In this section, the experimental compressibility factors are used to evaluate the accuracy of the above four EoSs. The average relative deviation between the calculated values and experimental data defined by Eq. (7), which was applied to evaluate these EoSs.

$$\theta=\frac{\left(Z_{\text{calc}}\text{-}Z_{\text{act}}\right)}{Z_{\text{act}}}\times 100\%,\quad \theta_{\text{average}}=\frac{\left|\sum_{i=1}^{n}\theta_i\right|}{n},\quad \theta_{\max}=\max\left(\left|\theta\right|\right) \tag{7}$$

where θ is the relative deviation; θ_{average} is the average relative deviation (ARD); $\theta_{\max}$ is the maximum relative deviation; Z_{calc} is the compressibility factor value calculated by each EoS; Z_{act} is the actual compressibility factor value; the subscript i is the relative deviation sequence number (*i*=1, 2, 3...n); *n* is the total number of experimental data.

The calculated values of the four EoSs are used to compare with the 234 sets of experimental compressibility factor data. The deviations between the experimental results and the calculated values are shown in Figures **2-5** below. The average relative deviation and maximum relative deviation of each EoS obtained from Figures **2-5** are depicted in Figures **6** and **7**.

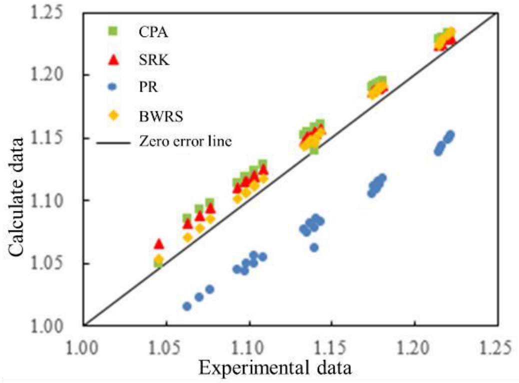

Figure 2: Comparisons of experimental compressibility factors against calculated values based on different EoSs for high-pressure and low H_2S content natural gases.

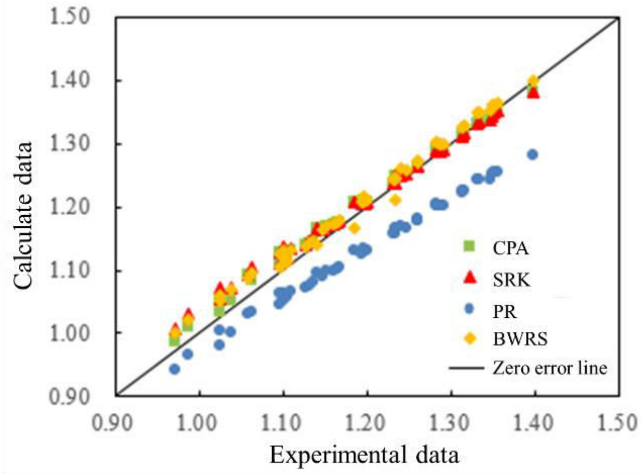

Figure 3: Comparisons of experimental compressibility factors against calculated values based on different EoSs for high-pressure, medium, and high H_2S content natural gases.

The above results demonstrate that:

1). For the high-pressure and low H_2S content natural gas, the ARDs of the BWRS EoS and the SRK EoS are equal to 0.83% and 0.74%, respectively. However, the maximum relative deviation of BWRS EoS is 1.07%, and that of the SRK EoS is 2.03%. Hence, the BWRS EoS is recommended for the high-pressure and low H_2S content natural gas (35MPa≤P<70MPa, H_2S<0.3%).

2). For ultra-high-pressure natural gas (P≥70MPa), the BWRS EoS has obvious advantages, with an ARD of 0.32% and a maximum relative deviation of 1.50%. The reason for this phenomenon is that the BWRS EoS is built based on the existing BWR EoS, and the mixture parameters (Equations 3) are improved to improve the accuracy of the compressibility factor calculations at high-pressures.

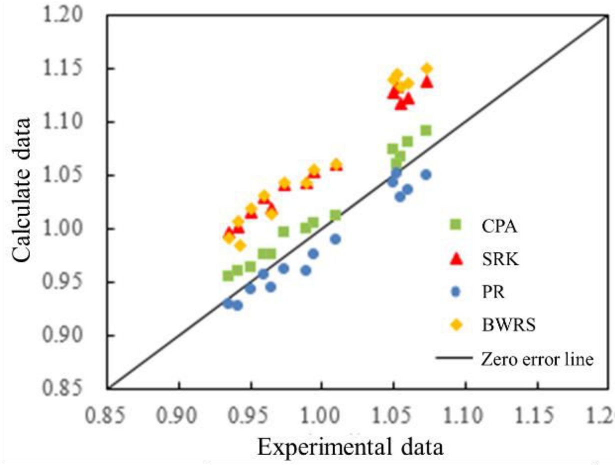

Figure 4: Comparisons of experimental compressibility factors against calculated values based on different EoSs for high-pressure and ultra-high H_2S content natural gases.

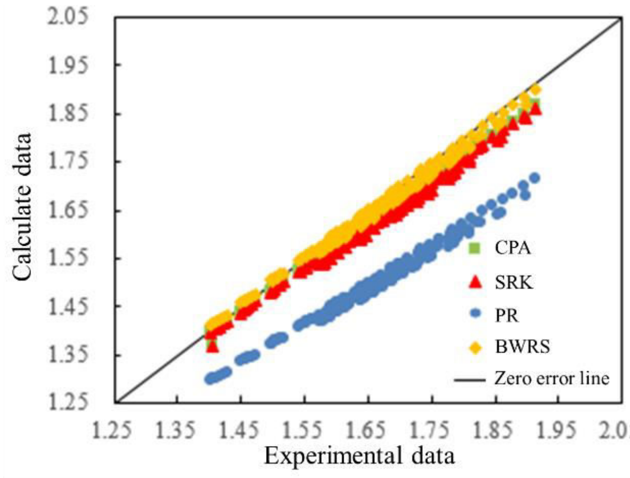

Figure 5: Comparisons of experimental compressibility factors against calculated values based on different EoSs for ultra-high pressure H_2S-containing natural gases.

3). For the high-pressure and medium-high H_2S content natural gas (35MPa≤P<70MPa, 0.3%≤H_2S <10%), and the high-pressure and ultra-high H_2S content natural gas (35MPa≤P<70MPa, 10%≤H_2S), the CPA EoS performs best in predicting the compressibility factors with an ARD of 1.01% and the maximum relative deviation of 3.36%. The reason for this phenomenon is that the spacing of such natural gas molecules is smaller, and the force between polar molecules such as H_2S is not negligible. The CPA EoS describes this polar effect well, so the prediction results are closer to the experimental value.

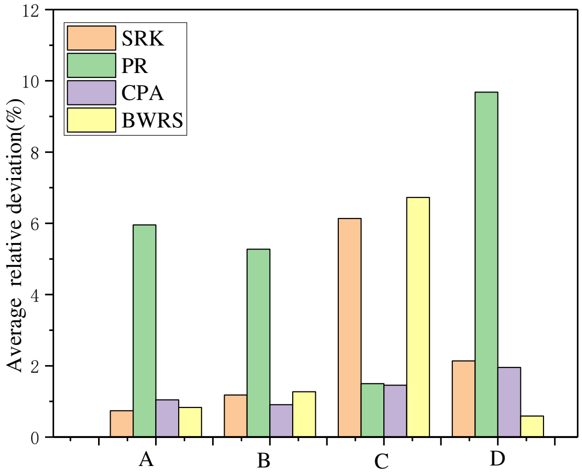

Figure 6: The average relative deviation of different types of natural gases calculated by each equation of state. A refers to high-pressure and low H_2S content natural gases; B refers to high-pressure, medium-high H_2S content natural gases; C refers to high-pressure and ultra-high H_2S content natural gases; D refers to ultra-high pressure H_2S-containing natural gas.

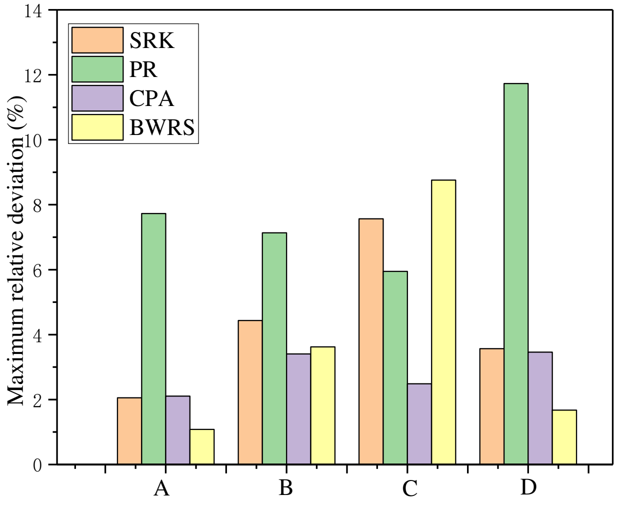

Figure 7: The maximum relative deviation of different types of natural gases calculated by each equation of state. A refers to high-pressure and low H_2S content natural gases; B refers to high-pressure, medium-high H_2S content natural gases; C refers to high-pressure and ultra-high H_2S content natural gases; D refers to ultra-high pressure H_2S-containing natural gas.

4). The SRK EoS and SRK EoS are not suitable for calculating the compressibility factor of high-pressure H_2S-containing natural gas. The reason for this phenomenon is that the SRK equation of state has improved the vapor pressure of hydrocarbons, and the PR equation of state has improved the calculation accuracy of liquid density and liquid fraction. However, these two EoSs do not consider the influence of high pressure and polar intermolecular forces on the calculation of natural gas compressibility factors.

5. CONCLUSIONS

In this paper, two traditional cubic-EoSs (SRK EoS, PR EoS), the BWRS EoS, and the CPA EoS are evaluated in terms of the accuracy on predicting the compressibility factors of high-pressure H_2S-containing natural gases, based on experimental data from 70MPa to 131MPa. The main conclusions are as follows:

1). For the high-pressure and low H_2S content natural gas ($35MPa \leq P < 70MPa$, $H_2S < 0.3\%$), the BWRS EoS yields the best results among the above four EoSs. The average relative deviation (ARD) between the experimental results and the calculated values is 1.07%.

2). For high-pressure and high H_2S content natural gas ($35MPa \leq P < 70MPa$, $0.3\% \geq H_2S$), the CPA EoS yields the best results with an ARD of 1.01%.

3). For ultra-high pressure natural gas ($P \geq 70MPa$) without H_2S , the BWRS EoS gives the best results with an ARD of 0.32% and the maximum relative deviation of 1.50%.

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