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RESEARCH ARTICLE

New Functionality for Energy Parameter of Redlich-Kwong Equation of State for Density Calculation of Pure Carbon Dioxide and Ethane in Liquid, Vapor and Supercritical Phases

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Abstract

A new equation of state has been proposed for calculating densities of pure carbon dioxide and ethane in the liquid, vapor, and supercritical phases. In this equation of state, a new function (β function) for energy parameter of Redlich-Kwong equation of state has been used versus temperature and pressure. The constants of the β function were calculated by minimizing of average absolute relative deviation percent (AARD%) between calculation results and experimental densities data reported in literature. The data points used for optimization were 2770 for carbon dioxide in the ranges of (220-1273) K for temperature and (8- 2000) bar for pressure and 2002 for ethane in the ranges of (95-625) K and (2-700) bar. The densities calculated by the proposed EoS (βRK-EoS) were in good agreement with experimental densities with AARD% of 1.68 and 0.49 for ethane and carbon dioxide, respectively.

Keywords

Density calculation, βRK-EoS, Ethane, Carbon dioxide

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1 Introduction

Density is a key fluid property that plays a significant role in many petroleum and gas engineering applications. For instance, the densities of fluids at high temperatures and pressures are very important in petroleum and gas engineering for investigating of enhance oil recovery processes like gas injection process. On the other hand, the simulation of fluid flow for the liquid hydrocarbons and gases in porous media and phase behavior of supercritical carbon dioxide need the accurate computation of density [1-4]. Applying accurate measurements is the most reliable method for measuring of gas properties like density; however, they are time-consuming, and costly. Therefore many researchers have attempted to develop reliable and accurate models for predicting of fluid density. In general, these models can be classified as equations of state [5-6] and empirically correlations [7-8]. For example, the HBT correlations of Chang et al. [9] are conventional method of describing the density of n-alkanes. The narrow ranges of pressure and temperature conditions in the application of empirical correlations and separate density correlations for liquid or vapor phases are two main limitations of empirical correlations. One way to overcome these limitations is using of equations of state as an accurate approach for predicting of fluid density.

Among different types of equations of state, the cubic equations of state are simple, flexible, and reliable. However, the cubic equations of state are inaccurate for the density calculation especially for the liquid densities under saturation and near critical densities. Heidaryan and Jarrahian [10] proposed a simple and explicit reduced temperature and reduced pressure expression to modify the density description of carbon dioxide, in the supercritical region by using the Redlich–Kwong equation of state. They fitted the parameters with the pure supercritical carbon dioxide density data. Lin and Duan [11] suggested an empirical temperature-dependent volume correction to improve the performance of Peng–Robinson equation of state (PR-EoS) for describing the densities of liquids in the saturated region. Lin et al. [12] presented a volume translation in terms of the critical properties and reduced temperature for improving the calculated densities of pure fluids and mixtures with the

Soave- Redlich-Kwong equation of state. Magoulas and Tassios [13] proposed volume translations for vdW and PR-EoSs for improving the density computations of C_1 to C_{20} n-Alkanes. For n-Alkanes, which were higher than C_{20}, they used extrapolated amounts of Tc, Pc and ω. Tsai and Chen [14] proposed a volume-translated Peng-Robinson (VTPR) equation of state to improve the density predictions for some polar and nonpolar fluids. Their equation of state was suitable for predicting the saturated vapor and liquid molar densities. Ahlers and Gmehling [15] utilized a volume translation for the PR-EoS for improving the liquid densities for pure components. They also compared their results with the PR and SRK equations of state.

In this work, a new expression for energy parameter of Redlich-Kwong EoS as a function of temperature and pressure similar to the modification of Heidaryan and Jarrahian [10] and similar to our previous work [16] but with new functionality was proposed to improve the density description of carbon dioxide and ethane for wide ranges of temperature and pressure in the liquid, vapor, and supercritical phases. In our previous work [16], the proposed Redlich-Kwong equation of state was used for calculating of solid solubility in supercritical carbon dioxide.

2 Description of suggested model

The Redlich-Kwong equation of state (RK-EoS) [17] is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a}{T_r^{0.5} v\left(v+b\right)} \tag{1}$$

The energy and volume parameter of RK-EoS, respectively a and b, are computed based on the critical properties of fluids. The critical properties for pure fluids have been shown in Table 1.

$$a = \mathbf{0.42747}\frac{\left(RT_c\right)^2}{P_c} \tag{2}$$

$$b = 0.0778\frac{RT_c}{P_c} \tag{3}$$

In this modeling study, in order to reproduce the densities of different phases including liquid, vapor, and supercritical phases, an expression for energy parameter of Redlich-Kwong equation of state has been suggested. This form of proposed equation for density computation can be written as follows:

$$P = \frac{RT}{v-b} - \frac{\beta a}{v\left(v+b\right)} \tag{4}$$

In Eq. (4), β is a function of temperature and pressure. In this study this form of β has been proposed for improving density calculation:

$$\beta = \frac{\beta_1 + \beta_2 T_r + \beta_3 P_r^{0.45}}{1 + \beta_4 T_r + \beta_5 P_r + \beta_6 P_r^{0.45}} \tag{5}$$

where β1-β6 represent the constant parameters of β function. These constant parameters of β function can be determined based on minimization of average absolute relative deviation percent (AARD%) between calculation results and experimental data for densities. AARD% is expressed by the following equation:

$$AARD\% = \frac{100}{N}\sum_i \frac{\left|\rho_{i,\exp} - \rho_{i,calc}\right|}{\rho_{i,\exp}} \tag{6}$$

where ρi,cal , ρi,exp and N are calculated density, experimental density data and number of data, respectively. In order to optimize the model parameters, non-linear optimization technique based on the Nelder–Mead simplex algorithm was used.

3 Results and discussion

In this work, a new EoS has been proposed to improve the performance of Redlich-Kwong equation of state (RK-EoS) for describing the densities of carbon dioxide and ethane over wide ranges of thermodynamic conditions, covering the liquid, vapor and supercritical phases (Tables 1 and 2). The thermodynamic conditions considered for modeling of carbon dioxide density were in the ranges of (220-1273) K for temperature and (8- 2000) bar for pressure. The temperature and pressure ranges were (95-625) K and (2-700) bar for ethane, respectively.

Table 1 The applied density data and thermodynamic conditions for carbon dioxide

Reference	T_{min} (K)	T_{max} (K)	P_{min} (bar)	P_{max} (ba)	ND[a]
Kennedy [18]	293	1273	25	1400	2100
Mantilla et al. [19]	310	450	9.9	159	41
NISTdata base [20]	225	303	15	2000	410
Van der Gulik [21]	220	280	8	1000	120
Total	220	1273	8	2000	2770

[a] Number of data

Table 2 The applied density data and thermodynamic conditions for ethane

Reference	T_{min} (K)	T_{max} (K)	P_{min} (bar)	P_{max} (bar)	ND[a]
Diller and Saber [22]	150	320	2.9	290	73
Funke et al.[23]	120	340	2	120	110
NIST data base [21]	95	625	1.5	700	1749
Claus et al. [24]	300	520	11	300	68
Total	95	625	2	700	2002

[a] Number of data

The constant parameters of β function in Eq. (5) were determined based on minimization of average absolute relative deviation percent (AARD%) between calculation results and the experimental data (Tables 3 and 4).

Table 3 The obtained parameters of βRK for ethane and carbon dioxide

	β1	β2	β3	β4	β5	β6
C_2H_6	3.3057	-8.422	-0.998	2.237	-0.0778	0.9336
Co_2	2.4435	-4.05	0.6225	1.573	-0.0332	-0.147

In order to recognize the reliability of proposed EoS for calculating of the densities of carbon dioxide and ethane for wide ranges of thermodynamic conditions in the liquid, vapor, and supercritical phases, sum of absolute residual (SAR), the coefficient of determination (R2) and maximum absolute relative deviation have been reported. Sum of absolute residual (SAR) can be defined as follows:

$$SAR = \sum_i \left| \rho_{i,\exp} - \rho_{i,calc} \right| \tag{7}$$

Furthermore, the coefficient of determination (R2) is expressed by the following equation:

$$R^2 = 1 - \frac{\sum_i \left(\rho_{i,\exp} - \rho_{i,calc} \right)^2}{\sum_i \left(\rho_{mean} - \rho_{i,\exp} \right)^2} \tag{8}$$

where ρ_{mean} is the mean of the experimental data. The coefficient of determination (R Squared or R2) is the square of the deviation between the experimental density data and the calculated density values. R^2 value closer to 1 denotes a good fit model based on good data.

The results of the proposed model have been compared with the results of original RK-EoS, PR-EoS and SRK-EoS in Table 4 and in Figs. 1-4.

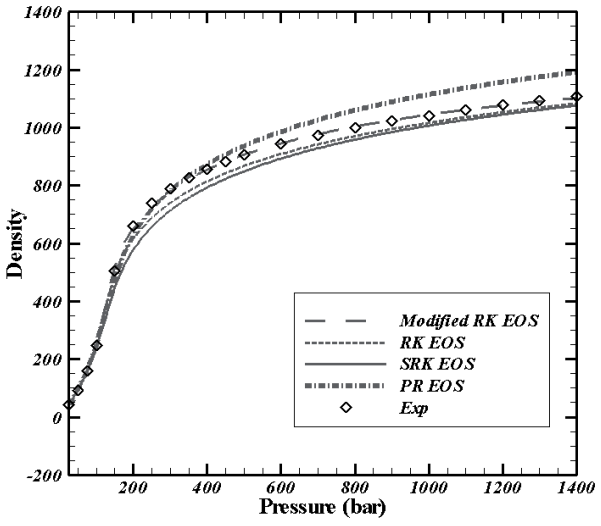

Fig. 1 Comparison of various models for densities of carbon dioxide at temperature of 343 K

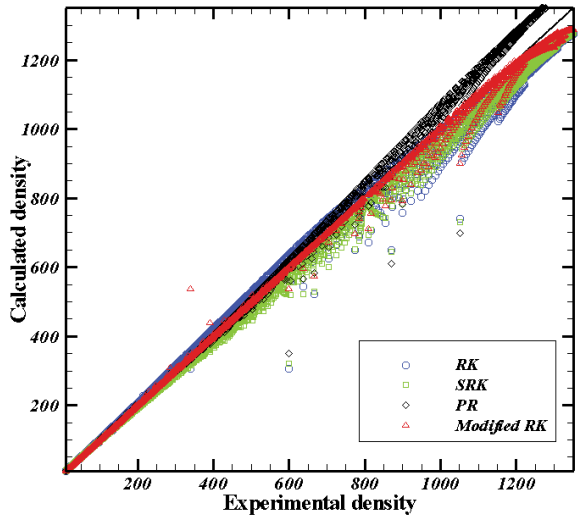

Fig. 2 Calculated densities versus experimental densities for carbon dioxide

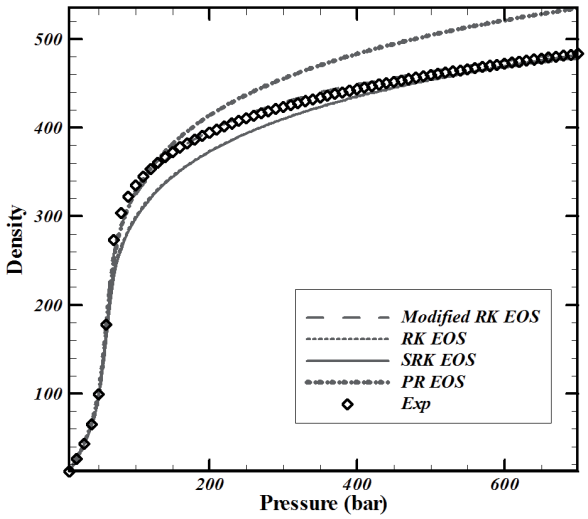

Fig. 3 Comparison of various models for densities of ethane at temperature of 308 K

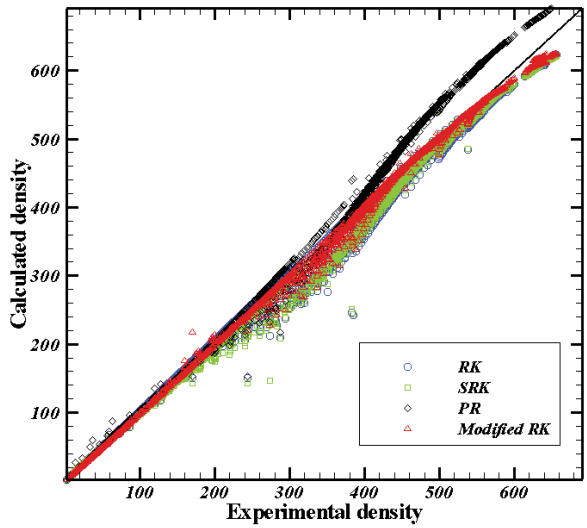

Fig.4 Calculated densities versus experimental densities for ethane

Table 4 Different obtained statistical parameters for the applied model

Compound	Model	AARD(%)	Maximum deviation(%)	SAR(Kg/m^3)	R^2
Ethane	RK	3.59	38.9	28117.5	0.987
	SRK	3.57	46.4	26298.4	0.989
	PR	5.12	51.3	57878.6	0.971
	Brk	1.68	21.1	11373.7	0.997
Carbon dioxide	RK	3.89	29.5	67248.2	0.991
	SRK	3.73	30.5	65133.85	0.995
	PR	3.1	41.7	59586.1	0.992
	βRK	0.49	9.9	17934.3	0.998

Table 5 The AARD% of densities of CO2 for this work and other investigations

Density model	Temperature (K)	Pressure (bar)	Phases	ND	AARD%.
Proposed model	229-1273	8-2000	Liquid-vapor-supercritical	2770	0.49
Jouyban et al. [8]	308-433	75-468	supercritical	1240	9.18
Bahadori et al. [8]	308-433	75-468	supercritical	1240	5.01
Haghbakhsh et al. [8]	308-523	75-468	supercritical	1240	1.94
Heidaryan and Jarrahian [10]	304.9-1273	73.8-4525	supercritical	3742	1.63

The AARD% between the calculation results and the experimental data for the proposed model were 1.68% and 0.49% for ethane and carbon dioxide, respectively. One can see in Table 4 that the coefficients of determination (R2) are very close to 1. The results showed that the proposed model performs more accurate than original RK-EoS, PR-EoS and SRK-EoS. Therefore, this model is suitable for density calculation of carbon dioxide and ethane over wide ranges of thermodynamic conditions and it successfully covers the liquid, vapor, and supercritical phases.

AARD% of the CO_2 densities obtained in this work was compared with AARD% reported in the works of Jouyban et al. [8], Bahadori et al. [8], Haghbakhsh et al.[8] and Heidaryan and Jarrahian [10] to indicate the validity and the advantages of the present model (in Table 5). This comparison shows that all previous models were done only for supercritical phase while the present model is applicable for liquid, vapor and supercritical phases. The AARDs% are in the range of (1.63-9.18) for other models while the AARD% of the present model is 0.49. The overall performance of the proposed model shows its excellent accuracy in comparison with other models.

4 Conclusions

The βRK-EoS has been proposed to reproduce the densities of carbon dioxide and ethane over wide ranges of pressures and temperatures in the liquid, vapor, and supercritical phases. The data points used for optimization were 2770 for carbon dioxide in the ranges of (220-1273) K and (8- 2000) bar and 2002 for ethane in the ranges of (95-625) K and (2-700) bar. The results showed that in spite of simplicity, this model has presented accurate results of density for carbon dioxide and ethane (AARD% of 1.68 and 0.49 for ethane and carbon dioxide, respectively). The comparison between reported results in literature and the results of the present model proves the accuracy and reliability of the present model.

Nomenclature

a	attraction parameter
AARD%	average absolute relative deviation (%)
b	repulsion parameter of the supercritical solution
EOS	equations of state
N	number of data
P	pressure
PR	Peng–Robinson
R	universal gas constant
RK	Redlich–Kwong EoS
SAR	Sum of absolute residual
SRK	Soave-Redlich-Kwong EoS
T	temperature
V	volume

Greek symbols

b	β function for energy parameter of proposed EoS
βRK	modified Redlich–Kwong
ρ	density

Subscripts

c	critical point
cal	calculated
exp	experimental

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