MODIFICATION OF THE REDLICH-KWONG-AUNGIER EQUATION OF STATE TO DETERMINE THE MAIN THERMODYNAMIC PARAMETERS IN THE PURE LIQUID CO$_2$ REGION

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The most important parameters for determining the state of real gas and the thermodynamic properties of the working fluid in a pure liquid region are pressure, specific volume, enthalpy and entropy. The paper presents a modified Redlich-Kwong-Aungier equation of state for determining pressure, specific volume, enthalpy and entropy in the pure liquid phase of real gas. CO$_2$ was selected as the studied working fluid. When solving this problem, the author identified the main parameters of liquid carbon dioxide thermodynamics with the least error in comparison with experimental data in a wide range from 220 K to 300 K. It is possible to calculate pressure, specific volume, density, enthalpy and entropy of liquid CO$_2$ with the help of the proposed method, for which the initial data are temperature, density, critical properties, molar mass and acentric factor of the working fluid. In particular, a modified Redlich-Kwong-Aungier equation is used to calculate the pressure of the working fluid. The author proposes a correlation equation of the scale correction, which is used in the Redlich-Kwong-Aungier equation for CO$_2$ in the region of pure liquid phase. The results obtained for the pressure, enthalpy and entropy of liquid CO$_2$ showed good agreement with the basic values, which provides the application of the proposed method in the field of pure liquid CO$_2$ limited by the temperature range from 220 K to 300 K. The simplicity of the equation of state and the small number of empirical coefficients allows to use this method to solve practical problems of computational gas dynamics without spending a lot of time on calculations.

**Keywords:** pure liquid CO$_2$ region, Aungier-modified Redlich-Kwong Equation of State, pure liquid pressure, pure liquid enthalpy, pure liquid entropy.

Introduction

The first attempt to determine the liquid behavior belongs to van der Waals. This equation of state for the real liquids is based on taking into account molecular interactions. However, discrepancies between theoretical method of the van der Waals equation and the experiments data were significant. Modifications of the original van der Waals equation of state, such as the Redlich-Kwong [1], the Guggenheim [2], the Peng-Robinson [3] ones, give some positive quantitative results, but universal description of thermodynamic properties for the real gases in the pure liquid region has not been achieved. Another group of equations of state, which are based on Helmholtz energy [4–5] is more accurate in liquid region. Significant disadvantages of these equations are large number of specific coefficients, a complex form of the equations and the fact that they take a lot computational time. Scaling equations of state [6] and [7] have the same disadvantages. In paper [7], $P\rho T$ parametrization of SAFT equation of state, which gave fine agreement between the theoretical results and the experimental data for the liquid phase density, was proposed.

The main purpose of this article is to represent accurate equation of state, which contains simple form and small number of specific coefficients. A new modification of the Peng-Robinson cubic equation of state (The PR-Saali EoS) is able to reproduce the vapor pressure of different pure components, especially polar ones, and associate pure and mixture components with high accuracy. However, there is a limitation for this modification, which should be taken into account: this cubic equation of state is not able to predict liquid densities of heavy hydrocarbons and systems with hydrogen bonds [8]. Research work [9] presents a unique form of two-parameters cubic equation of state, which uses critical compressibility factor to address the issue of unreliable volumetric phase behavior predictions from conventional two-parameters cubic EoS. The method to determine the main thermodynamic properties in the two-phase region of the carbon dioxide was presented in paper [10]. This method is based on Aungier-modified Redlich-Kwong equation of state, which can predict fluid properties in the two-phase region with sufficient accuracy. It was decided to apply the methodology described in [10] for using in the pure liquid CO$_2$ region.

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Materials and methods

Determination of the thermodynamic parameters of the working fluid in carbon dioxide can be divided into three steps: finding the liquid pressure, finding the liquid enthalpy, finding the liquid entropy.

Step 1. The liquid pressure can be found with the RKA equation of state. The original form of the two-parameter Aungier-modified Redlich-Kwong equation of state is [11]:

\[ P = \frac{RT}{V - b + c} \cdot \left( \frac{V}{V + b} \right)^n, \]

where

\[ A(T) = a \left( \frac{T_c}{T} \right)^n, \]
\[ b = 0.08664 \cdot R \cdot \frac{T_c}{P_c}; \]
\[ c = \frac{R \cdot T_c}{P_c + V_c \cdot (V_c + b)}. \]

Where \( R \) is the gas constant for a particular working fluid; \( T \) is the current temperature value; \( P \) is the current pressure value; \( T_c \) is the critical temperature of the working fluid; \( P_c \) is the critical pressure of the working fluid; \( V_c \) is the critical volume of the working fluid. Constants \( a \) and \( b \) are related to the gas critical pressure and critical temperature. Constant \( c \) is a correction to eliminate a known weakness of the Redlich-Kwong model at the critical point, where it predicts a compressibility factor of 1/3. The optimum value for parameter \( n \) is correlated by R. H. Aungier:

\[ n = 0.4986 + 1.1735 \cdot \omega + 0.4754 \cdot \omega^2, \]

where \( \omega \) is the compressibility factor for the working fluid.

The method described below can be used for density-based solvers, when temperature and density of the working fluid are known values and pressure is found from equation of state.

In general, the Redlich-Kwong-Aungier equation of state has similar with experimental data tendency for isothersms distribution in each carbon dioxide phases. This fact gives ability to modify the RKA equation of state for accurate prediction of regions where difference between the theoretical results and the base data is increased. The data from the mini-REFPROP (Reference Fluid Thermodynamic and Transport Properties) program were selected as the base data required to verify the used method. Mini-REFPROP is a free and abbreviated sample of the full version of the NIST REFPROP software. The program was developed by the National Institute of Standards and Technology (NIST); it calculates the thermodynamic properties of only pure substances. The most accurate models close to the experimental data are used for the calculation. For CO\(_2\), mini REFPROP uses the Span-Wagner model, which describes the CO\(_2\) operating range with high accuracy. The Span-Wagner equation is successfully used in 1D modeling, for example, to calculate the flow in labyrinth seals [12]. However, the Span-Wagner model has drawbacks for practical application in computational fluid dynamics of 3D calculations: it requires a lot of time to calculate and determine thermodynamic relations. The technique based on the use of the two-parameter equation of state requires less calculation time and uses fewer auxiliary parameters and coefficients. The two-parameter form of equation of state is faster for the same processing and calculations.

Step 2. The liquid enthalpy can be found from the Redlich-Kwong-Aungier equation of state.

\[ H = H^0(T) + pV - RT - \frac{A(T)}{b_0} (1 + n) \ln \left( \frac{V + b_0}{V} \right), \]

where \( H^0 \) is the enthalpy function for a thermally perfect gas.

Superscript 0 refers to a reference state, where the ideal gas law is applicable.

Step 3. The liquid entropy can be found from the Redlich-Kwong-Aungier equation of state.

\[ S = S^0(T, p^0) + R \ln \left( \frac{V - b'}{V^0} \right) + \frac{(da(T))}{dT} \ln \left( \frac{V + b_0}{V} \right), \]

where \( S^0 \) is the entropy function for a thermally perfect gas.

Derivative \((da(T))/dT\) can be found as:

\[ \frac{da(T)}{dT} = -n \frac{A(T)}{T}. \]

Superscript 0 refers to a reference state, where the ideal gas law is applicable.
Results and discussions

The results of verification of the method from previous section are described below:

Results for step 1. Determination of the liquid pressure for carbon dioxide

The liquid isotherms tendencies comparison for temperature of 280 K is shown on Fig. 1. Calculation of "RKA" isotherm is based on Redlich-Kwong-Aungier equation of state. The "base data" isotherm is taken from mini-REFPROP database.

Fig. 1 shows similar tendencies for the Redlich-Kwong-Aungier equation of state and for the base data. To reduce difference between the isotherms, the Redlich-Kwong-Aungier equation of state is modified with scale factor $n_{\text{liquid}}$. Scale factor is included to $A(T)$ coefficient and gives opportunity to reduce difference between the RKA isotherm and the base data isotherm. Modified $A(T)_{\text{liquid}}$ coefficient can be found as:

$$A(T)_{\text{liquid}} = a \cdot \left( \frac{T_{cr}}{T} \right)^{\frac{n_{\text{liquid}}}{\alpha}}.$$

Scale factor $n_{\text{liquid}}$ values are defined in wide temperature range in the pure liquid region from the minimum carbon dioxide temperature of 216.59 K to the near critical temperature 300 K with step in 20 K. Scale factor $n_{\text{liquid}}$ distribution is shown on Fig. 2.

Parameter $A(T)_{\text{liquid}}$ after modification has similar tendency as in the original parameter $A(T)$ (Fig. 3).

The optimum value of scale factor $n_{\text{liquid}}$ can be defined for any temperature from 216.59K to 300K by the empirical function:

$$n_{\text{liquid}} = a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 + a_4 \cdot T^4 + a_5 \cdot T^5 + a_6 \cdot T^6,$$

where in Eq. (7) $a_0=-3.80666 \cdot 10^{-3}$; $a_1=6.59754 \cdot 10^{-1}$; $a_2=-3.92603 \cdot 10^{-1}$; $a_3=6.11597 \cdot 10^{-4}$; $a_4=2.74395 \cdot 10^{-6}$; $a_5=-1.18587 \cdot 10^{-8}$; $a_6=1.26942 \cdot 10^{-11}$.

The isotherms of the modified RKA equation of state are closer to the base data for temperature of 280 K, as shown on Fig. 4.

Next step of modification for the Redlich-Kwong-Aungier equation of state is implementation of the shift-parameter $\alpha$ for achieving the closest results for calculation of the liquid pressure to the base data. For this, the liquid pressure and the liquid volume, which were defined in the previous step of modification, are multiplied by shift parameter $\alpha$. Shift-parameter $\alpha$ here is an angle, which is used for turning isotherm of modified the RKA closer to the base isotherm. Angle distribution was found for wide temperature range from the minimum temperature of 216.59 K to the near critical 300 K with step in 20 K (Fig. 5).
Shift-parameter $\alpha$ can be found for any temperature from range of 216.59 K to 300 K, given by Eq. (8)

$$
\alpha = a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 + a_4 \cdot T^4,
$$

where in Eq. (8) $a_0 = 7.564 \cdot 10^4$; $a_1 = 1.1807 \cdot 10^3$; $a_2 = -6.8682$; $a_3 = 1.7656 \cdot 10^2$; $a_4 = -1.6927 \cdot 10^2$.

The liquid pressure after the second modification for the Redlich-Kwong-Aungier equation of state can be defined as:

$$
P = P_{\text{mod}} \cdot \cos(\alpha) + V \cdot \sin(\alpha),
$$

where

$$
P_{\text{mod}} = \frac{R \cdot T}{V - b + c} \cdot \frac{A(T)_{\text{liquid}}}{V \cdot (V + b)},
$$

where $P_{\text{mod}}$ – liquid pressure, which was defined after the first modification of RKA equation of state.

The original RKA equation isotherm, the first modification for isotherm of RKA equation (Modification 1), the second modification for isotherm of RKA equation (Modification 2) and the base data isotherm are shown on Fig. 6.

The second modification of the Redlich-Kwong-Aungier equation is validated with the base data for the temperature range from 220 K to 300 K for the liquid pressure. Results are shown below on Fig. 7.

The scale factor $n_{\text{liquid}}$ and the shift-parameter $\alpha$ are able to reduce difference between the modified RKA equation of state and the base data to satisfying tolerance for liquid pressure – around 3-25% as relative error for the pure liquid CO$_2$ region from 220 K to 300 K (Fig. 8).

The shift-parameter $\alpha$ is also implemented to achieve the results for calculated liquid enthalpy and entropy that are the closest to the base data. For this, enthalpy, entropy and volume, which were defined in previous step of modification, are multiplied by $\alpha$. The shift-parameter here is an angle, which is used for turning modified isotherm closer to base isotherm. $\alpha$-distribution was found for temperature range from temperature of 220 K to 300 K with step in 20 K (Fig. 9–10).
Equation remains the same for enthalpy and entropy.

$$\alpha = a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 + a_4 \cdot T^4 + a_5 \cdot T^5 + a_6 \cdot T^6,$$

where coefficients for enthalpy: $a_0 = -6653.908; a_1 = 82.5535; a_2 = -0.2864; a_3 = -7.7175 \cdot 10^{-5}; a_4 = 1.3095 \cdot 10^{-6}; a_5 = 1.92518 \cdot 10^{-9}; a_6 = -7.59698 \cdot 10^{-12}$. Coefficients for entropy: $a_0 = 45.5899; a_1 = -0.05667; a_2 = -0.0002944; a_3 = 8.678409 \cdot 10^{-7}; a_4 = -6.245244 \cdot 10^{-10}; a_5 = -1.945913 \cdot 10^{-12}; a_6 = 3.104539 \cdot 10^{-15}$.

The liquid enthalpy and the liquid entropy after modification of the RKA equation of state can be defined as:

$$I = I_{mod} \cdot \cos(\alpha) + V \cdot \sin(\alpha); \quad S = S_{mod} \cdot \cos(\alpha) + V \cdot \sin(\alpha);$$

$$H = H^0(T) + P_{mod} V - RT - \frac{A(T)_{liquid}}{b}(1 + n_{liquid}) \ln \left( \frac{V + b}{V} \right);$$

$$H^0(T) = C_1 \cdot T + \frac{1}{2} C_2 \cdot T^2 + \frac{1}{3} C_3 \cdot T^3 + \frac{1}{4} C_4 \cdot T^4 + \frac{1}{5} C_5 \cdot T^5 - H^0(T^0);$$

$$S_{liquid} = S^0(T, P^0) + R \ln \left( \frac{V - b}{V^0} \right) + \frac{\left( \frac{da(T)}{dT} \right)}{b} \ln \left( \frac{V + b}{V} \right);$$

$$S^0(T, P^0) = S(T^0, P^0) + C_1 \ln(T) + C_2 T + \frac{1}{2} C_3 T^2 + \frac{1}{3} C_4 T^3 + \frac{1}{4} C_5 T^4 - f(T^0);$$

$$\frac{da(T)}{dT} = -n_{liquid} \frac{A(T)_{liquid}}{T},$$

where $I_{mod}$ – liquid enthalpy, which defines from modified RKA equation; $S_{mod}$ – liquid entropy, which defines from modified RKA equation; $H^0, S^0$ – ideal gas enthalpy and entropy.

The liquid enthalpy and the liquid entropy from the original RKA equation, from the modified of RKA equation and from the base data are shown on Fig. 11–12.

The scale factor and the shift-parameter are able to reduce difference between the modified RKA equation of state and the base data with satisfying tolerance for the liquid enthalpy – around 1–2% and for the liquid entropy – around 1–1.5% (Fig. 13–16).
Conclusions

The modified Redlich-Kwong-Aungier equation of state presented here has better accuracy in prediction of liquid phase pressure, enthalpy and entropy, than original forms of cubic equation of state and, from the other side, modified equation has simpler form and fewer fitting parameters than scaling equations of state. The equation was verified for wide temperature range from 220 K to 300 K in pure liquid region of
carbon dioxide. Results were compared with Span and Wagner equation from mini-REFPROP, which were selected as the base data. Comparison analysis showed fine agreement, relative error had significant drop tendency from saturation line to high pressures region in comparison with original form of the Redlich-Kwong-Aungier equation of state.

The presented method requires two additional parameters in comparison with the original form of equation – the scale factor and the shift-parameter for pressure and individual shift-parameters for enthalpy and entropy respectively. Equations for each of these parameters are presented here in convenient form and described whole liquid region from 220 K to 300 K for isotherms from minimal to maximum liquid volumes for each corresponding temperature.

The modified equation of state has the original form of Redlich-Kwong-Aungier model and can be used without requiring excessive computational time. The shift-parameters and the scale factors can be selected not only for liquid region, but for near-critical regions for achieving accurate results near critical point.

Acknowledgement
This research was not funded by any grant.

References

Received 09 May 2022
Модифікація рівняння стану Редліха-Квонга-Ангьє для визначення основних термодинамічних параметрів в області чистого рідкого CO₂

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Найважливішими параметрами визначення стану реального газу і термодинамічних властивостей робочого тіла в чистій рідкій фазі є тиск, питомий об’єм, ентальпія й ентропія. У статті представлено модифікація рівняння стану Редліха-Квонга-Ангьє для визначення тиску, питомого об’єму, ентальпії та ентропії у чистій рідкій фазі реального газу. Досліджуваним робочим тілом обрано CO₂. Авторкою при вирішенні поставленого завдання визначені основні параметри термодинаміки рідкого двоокису вуглецю вузькою з найменшою хибкою в порівнянні з експериментальними даними в широкому діапазоні від 220 K до 300 K. Доведено, що за допомогою запропонованого методу, вихідними даними для якого виступають температура, густина, критична властивості, молярна маса й ацентричний фактор робочого тіла, обчислюються тиск, молярна маса й ацентричний фактор робочого тіла в чистій рідкій області.

Ключові слова: область чистого рідкого CO₂, модифікація Ангьє рівняння стану Редліха-Квонга, тиск рідкого CO₂, ентальпія рідкого CO₂, ентропія рідкого CO₂

Література