A Modified Alpha Function for Peng-Robinson Cubic Equation of State

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A piecewise alpha function was proposed for the Peng-Robinson equation of state (PR EoS) to predict the thermodynamic properties of pure compounds. The proposed alpha function and its derivations satisfied the requirement of consistency test. The new alpha function with PR EoS was used to predict the vapour pressure of 11 kinds of compounds, and the average relative deviation is 0.34 %. The average relative deviations of the new alpha function for the prediction of liquid volume, enthalpy of vaporization, and isobaric heat capacity of 7 kinds of compounds are 7.54 %, 1.37 %, and 6.90 %. The new alpha function is better than Soave and Stryjek-Vera alpha functions and is as accurate as of the other alpha functions for the prediction of the vapour pressure of pure compounds. The results of enthalpy of vaporization and isobaric heat capacity of the new alpha function are superior to that predicted with the other alpha functions, the deviations of liquid volume of the eight alpha functions are similar. The new alpha function with PR EoS can accurately predict the vapour pressure and enthalpy of vaporization of pure compounds but has great deviations for the prediction of liquid volume and isobaric heat capacity. It is a benefit to improve the predictive accuracy for liquid volume and isobaric heat capacity by modifying the form of PR EoS.

1. Introduction

Cubic equation of state (EoS) is one of the most important methods for the prediction of the thermodynamic properties of pure compounds and mixture (Rezakazemia et al., 2018). The first cubic equation of state was proposed by van der Waals in 1883 for the prediction of the vapour pressure of real gases. Redlich and Kwong modified the form of the attractive term of van der Waals EoS and introduced the variable $T_r^{0.5}$ to the energy parameter of the attractive term in 1949. Soave (Soave, 1972) adopts the form of Redlich-Kwong (RK) EoS and proposed an alpha function for the attractive term. Peng and Robinson (1976) modified the RK EoS and adopted Soave alpha function. Peng-Robinson (PR) EoS can accurately predict the vapour pressure of non-polar and weakly polar compounds but has great deviation for polar compounds.

An alpha function is an important variable in the attractive term of cubic EoS. The alpha function affects the predictive accuracy of PR EoS for the vapour pressure of pure compounds. Many alpha functions were modified to improve the prediction of vapour pressures for polar compounds. For example, Mathias and Copeman (1983) proposed an alpha function to extend the application of PR EoS to highly polar compounds, Stryjek and Vera (1986a, b) modified Soave alpha function to improve the prediction of vapour pressure at the low reduced tempreture range. Mahmoodi and Sedigh (2017) improved the predictive accuracy of the liquid density of pure compounds and the vapour pressure of heavy hydrocarbons with a proposed alpha function. Zhao et al. (2018) has concluded the polynomial and piecewise alpha functions based on the PR EoS and analyzed the functional forms fit for different kinds of compounds.

The alpha function as a variable of an attractive form of cubic EoS can weigh the attractive force intermolecular. The alpha function should not be negative, or else the alpha function is lack of physical meaning. Guennec et al. (2016) concluded and revised the constraints of consistency test of alpha function. Zhao et al. (2019) reviewed the development of constraints for alpha function. Among the alpha functions, many piecewise alpha function can accurate predict the vapour pressure of pure compounds. However, most cannot satisfy the requirement of consistency test.

Polynomial and piecewise alpha functions are important for the prediction of thermodynamic properties of pure compounds and mixtures. It is necessary to propose a new piecewise alpha function satisfying the requirement of consistency test. The predictive ability of the alpha function for the vapour pressure, liquid volume, isobaric heat capacity, and enthalpy of vaporization of pure compounds were also compared.

2. Equation of state

PR EoS is a common used method for the prediction of thermodynamic properties, such as vapour pressure. Based on PR EoS, the new alpha function was proposed and the parameters were fitted.

2.1 The PR EoS and representative alpha functions

Peng and Robinson modified the attractive term of RK EoS, adopted Soave alpha function and refitted the parameter k with vapour pressures of pure compounds. The PR EoS is presented as Eq(1) to Eq(4).

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

$$b = 0.07780 \frac{RT_c}{P_c} \tag{2}$$

$$a(T) = \left[0.45724 \frac{R^2 T_c^2}{P_c^2}\right] \alpha(T) \tag{3}$$

$$\alpha(T_r) = \left[1 + k\left(1 - \sqrt{T_r}\right)\right]^2 \tag{4}$$

Since the alpha function proposed by Soave in 1972, there are about 100 different alpha functions. According to the evaluation of 20 alpha functions by Young et al. (2016), seven representative alpha functions were chosen to be studied in this article.

Table 1: Seven representative alpha functions selected in this study

Functional name	Reference	Functional forms
Soave	(Peng and Robinson, 1976)	$\alpha(T_r) = \left[1 + k\left(1 - \sqrt{T_r}\right)\right]^2$ $k = 0.37464 + 1.54226\omega - 0.26992\omega^2$
Mathias-Copeman	(Mathias and Copeman, 1983)	$a(T_r) = \left[1 + c_1\left(1 - \sqrt{T_r}\right) + c_2\left(1 - \sqrt{T_r}\right)^2 + c_3\left(1 - \sqrt{T_r}\right)^3\right]^2 \quad T_r \leq 1$ $\alpha(T_r) = \left[1 + k\left(1 - \sqrt{T_r}\right)\right]^2 \quad T_r > 1$
Stryjek and Vera	(Stryjek and Vera, 1986a)	$\alpha(T_r) = \left[1 + k\left(1 - \sqrt{T_r}\right)\right]^2 \quad T_r \leq 0.7$ $\alpha(T_r) = \left[1 + k\left(1 - \sqrt{T_r}\right)\right]^2 \quad T_r > 0.7$
Androulakis-Kalospiros-Tassios	(Androulakis et al., 1989)	$a(T_r) = 1 + d_1\left(1 - T_r^{2/3}\right) + d_2\left(1 - T_r^{2/3}\right)^2 + d_3\left(1 - T_r^{2/3}\right)^3 \quad T_r \leq 1$ $a(T_r) = \exp\left[d_1\left(1 - T_r^{2/3}\right)\right] \quad T_r > 1$
Schwartzentruber-Renon-Watanasiri	(Schwartzentruber et al., 1990)	$a(T_r) = \left[1 + m\left(1 - \sqrt{T_r}\right) - \left(1 - \sqrt{T_r}\right)(n_1 + n_2 T_r + n_3 T_r^2)\right]^2 \quad T_r \leq 1$ $a(T_r) = \exp[1 + m(1 - T_r^n)] \quad T_r > 1$
Almeida-Aznar-Telles	(Almeida et al., 1991)	$\alpha(T_r) = \exp\left[m(1 - T_r)|1 - T_r|^{(\Gamma-1)} + n\left(\frac{1}{T_r} - 1\right)\right]$
	(Mahmoodi and Sedigh, 2017)	$\alpha(T_r) = \exp\left[2c_1\left(1 - \sqrt{T_r}\right) - \left(c_2\left(1 - \sqrt{T_r}\right)\right)^2 + \frac{2}{3}\left(c_3\left(1 - \sqrt{T_r}\right)\right)^3\right], \quad |c_3| \leq 1.25|c_1|$

2.2 A proposed alpha function

According to the characteristic of polynomial and piecewise alpha function, the parameter k of Soave alpha function was re-correlated with a quadratic function of the reduced temperature. To avoid the non-monotonous of Soave-type function, Heyen (1980) exponential alpha function was adopted in the supercritical regions. The form of the new alpha function was presented as Eq(5):

$$\alpha(T_r) = \begin{cases} \left[1 + (m_1 + m_2 T_r + m_3 T_r^2)\left(1 - \sqrt{T_r}\right)\right]^2 & T_r \leq 1 \\ \exp\left[n_1\left(1 - T_r^{n_2}\right)\right] & T_r > 1 \end{cases} \tag{5}$$

The adjusted empirical parameters m_1, m_2, and m_3 of the alpha function in the subcritical regions were fitted

with the experimental vapour pressures of 70 compounds (Zhao et al., 2020). The parameters n_1 and n_2 of the alpha function in supercritical regions were calculated according to the first- and second-order derivations of the piecewise function continuous at the critical point.

3. Results and discussion

The consistency of the proposed and the seven representative alpha functions was checked. The predictive accuracies of alpha functions for four kinds of thermodynamic properties were compared.

3.1 Consistency test of the proposed alpha function

The changing trends of the proposed and seven representative alpha functions and their derivations with increasing reduced temperature were determined with n-butanol in the reduced temperature range of 0.4 to 6. The Mathias-Copeman, Stryjek-Vera, Androulakis-Kalospiros-Tassios, and Schwartzentruber-Renon-Watanasiri piecewise alpha functions are continuous at the dividing point (Figure 1a). However, the first-order derivation of Stryjek-Vera and Schwartzentruber-Renon-Watanasiri function are not continuous at $T_r = 0.7$ and $T_r = 1$ (Figure 1b), the second-order derivation of Mathias-Copeman and Androulakis-Kalospiros-Tassios function are discontinuous at $T_r = 1$ (Figure 1c). Almeida-Aznar-Telles alpha function and its first-order derivation are continuous at the critical point. Because of the term $|1 - T_r|^{(\Gamma-1)}$ in the alpha function, the second- and third-order derivations does not exist at $T_r = 1$. Soave alpha function and its derivations are continuous but not monotonous in the full temperature range. The proposed piecewise alpha and its second-order derivation are positive and monotonically decreasing, the first-order derivation is negative and monotonically increasing, and the third-order derivation is negative (Figure 1d). The proposed and Mahmoodi-Sedigh alpha function can satisfy the requirement of consistency test.
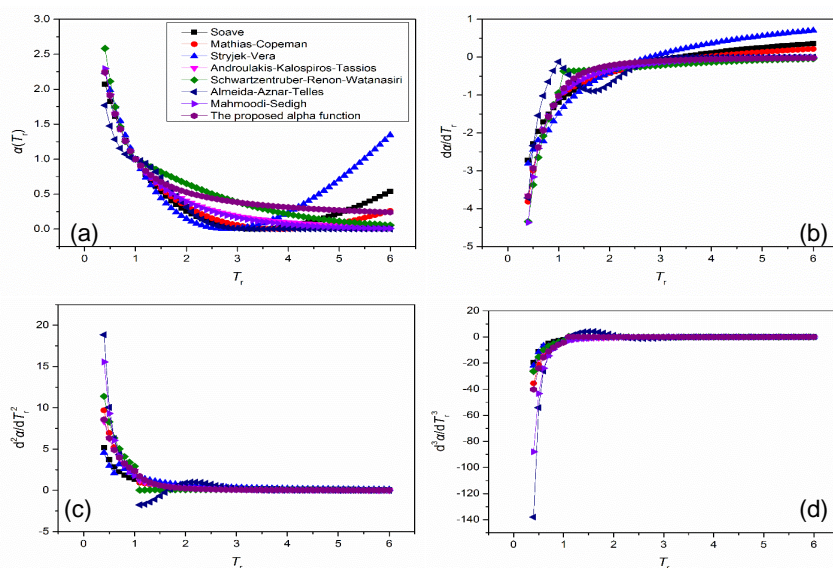

Figure 1: The representative and proposed alpha function and their derivatives for n-butanol in the reduced temperature region from 0.4 to 6. (a) alpha function; (b) the first-order derivation of alpha function; (c) the second-order derivation of alpha function; (d) the third-order derivation of alpha function.

3.2 The prediction of thermodynamic properties

The prediction of alpha functions for the vapor pressure, liquid volume, enthalpy of vaporization, and heat capacity were discussed in the following sections.

3.2.1 Vapour pressure

To compare the predictive ability of the alpha function in different forms, the parameters of alpha functions, except for Soave and Stryjek-Vera, are refitted with the vapour pressure of 70 compounds. The parameter k_0 of Stryjek-Vera alpha function was calculated with the correlation of acentric factor, and the parameter k_1 was also refitted. The parameter m of Soave (1976) in PR EoS was also calculated with the correlation of acentric factor. The average relative deviation (ARD) was calculated by the Eq (6).

$$ARD = \frac{1}{N}\sum_1^N \frac{|P_{cal}^{sat} - P_{exp}^{sat}|}{P_{exp}^{sat}} \times 100\ \% \tag{6}$$

Where P_{cal}^{sat} is the calculated value of saturated vapour pressure, and P_{exp}^{sat} is the experimental saturated vapour pressure. N is the number of experimental data.

Comparing the ARD of Stryjek-Vera and the proposed alpha function for the prediction of vapour pressure, it is shown that the proposed alpha function is more accurate than Stryjek-Vera alpha function in the reduced temperature range between 0.7 and 1.0. The ARDs of Stryjek-Vera is close to that of the proposed alpha function for the prediction of the vapour pressure of ketones, esters, hetercycles and water, but less accurate than the new alpha function for the other kinds of compounds. According to the mean ARD of 11 kinds of compounds (Table 2), the proposed alpha function (0.34 %) is more accurate than the generalized one-parameter Soave alpha function (4.50 %), especially for polar compounds and heavy hydrocarbons, such as normal alcohols, acids, and water. The mean ARD of semi-generalized two-parameter alpha function is 0.87 %. The mean ARDs of the Mathias-Copeman, Androulakis-Kalospiros-Tassios, Schwartzentruber-Renon-Watanasiri, Almeida-Aznar-Telles, and Mahmoodi-Sedigh alpha functions are 0.34 %, 0.33 %, 0.34 %, 0.33 %, and 0.38 %. The proposed alpha function is slightly more accurate than Mahmoodi-Sedigh alpha function and is as accurate as Mathias-Copeman, Androulakis-Kalospiros-Tassios, Schwartzentruber-Renon-Watanasiri, and Almeida-Aznar-Telles. The generalized and semi-generalized alpha functions with one or two parameters are not accurate as of the new alpha function for the prediction of vapour pressure, especially for the heavy hydrocarbons and polar compounds. The three-parameter alpha functions have similar predictive capability.

Table 2: The average relative deviation of eight alpha functions for vapour pressures of 11 kinds of compounds

Compounds type	Soave	Mathias-Copeman	Stryjek-Vera	Androulakis-Kalospiros-Tassios	Schwartzentruber-Renon-Watanasiri	Almeida-Aznar-Telles	Mahmoodi-Sedigh	The proposed alpha function
Normal alcohols	17.38	0.83	1.92	0.82	0.81	0.87	1.06	0.84
Normal alkanes	6.27	0.55	0.87	0.54	0.57	0.52	0.70	0.55
Aromatic hydrocarbons	2.11	0.33	0.91	0.30	0.34	0.36	0.38	0.34
Halogenated hydrocarbons	2.58	0.23	1.53	0.12	0.13	0.11	0.13	0.12
Gases	1.72	0.34	0.90	0.37	0.36	0.28	0.33	0.33
Acids	6.41	0.11	0.42	0.20	0.13	0.13	0.10	0.11
Ethers	2.22	0.14	0.76	0.16	0.14	0.10	0.14	0.13
Ketones	0.80	0.05	0.23	0.03	0.10	0.04	0.06	0.06
Esters	3.27	0.52	0.61	0.48	0.53	0.51	0.53	0.50
Heterocycles	2.21	0.60	0.85	0.60	0.60	0.65	0.61	0.64
Water	4.58	0.10	0.60	0.05	0.07	0.02	0.12	0.15
Average	4.50	0.34	0.87	0.33	0.34	0.33	0.38	0.34

3.2.2 Liquid volume

Because halogenated hydrocarbons and heterocycles are lack of the experimental data of liquid volume, enthalpy of vaporization, and isobaric heat capacity, and the strong associating compounds of acids and water were not suitable be predicted with PR EoS, the four kinds of compounds were not discussion in the following sections. The ARDs of eight alpha functions for the prediction of liquid volume, enthalpy of vaporization, and isobaric heat capacity of seven kinds of compounds were presented in Figure 2. The mean ARD of the proposed alpha function is 7.54 % for the liquid volume of seven kinds of comounds (Figure 2a). The ARDs of the new function for the liquid volume of normal alcohols, normal alkanes, aromatic hydrocarbons, ethers, and esters are 6.68 %, 8.56 %, 3.31 %, 3.30 %, and 4.69 %, and the ARDs for gases and ketones are 12.0 % and 14.2 %. The mean ARD of Soave is 7.84 %, the mean ARDs of Mathias-Copeman, Stryjek-Vera, Androulakis-Kalospiros-Tassios, Schwartzentruber-Renon-Watanasiri, Almeida-Aznar-Telles, and Mahmoodi-Sedigh are between 7.51 % and 7.56 %. The proposed alpha function is more accurate than Soave, and is slightly better than Mathias-Copeman, Androulakis-Kalospiros-Tassios, Mahmoodi-Sedigh. The PR EoS with eight alpha function has similar results for the prediction of liquid volume of seven kinds of compounds. According to the results of liquid volume, PR EoS is not suitable for the prediction of liquid volume of pure compounds.

3.2.3 Enthalpy of vaporization

The mean ARDs of the proposed alpha function is 1.37 % (Figure 2b) for enthalpy of vaporization of seven kinds of compounds. The new alpha function is more accurate than Soave (2.48 %) and Stryjek-Vera (1.80 %) alpha functions, is better than Mathias-Copeman (1.40 %), Androulakis-Kalospiros-Tassios (1.39 %), Almeida-Aznar-Telles (1.40 %), and Mahmoodi-Sedigh (1.46 %), and is as accurate as Schwartzentruber-Renon-Watanasiri (1.37 %). The ARDs of eight alpha functions, except Soave and Stryjek-Vera, for enthalpy of vaporization of normal alcohols, is between 2.5 % and 3 % and is less than 1.5 % for normal alkanes, aromatic hydrocarons, gases, ethers, ketones, esters. The prediction of PR EoS with an alpha function for enthalpy of vaporization is merely affected by the first-order derivation and the relative ratio of the compression factors of liquid and vapour. The form of PR EoS has little effect on the prediction of the enthalpy of vaporization. The predictions of enthalpy of vaporization are accurate.
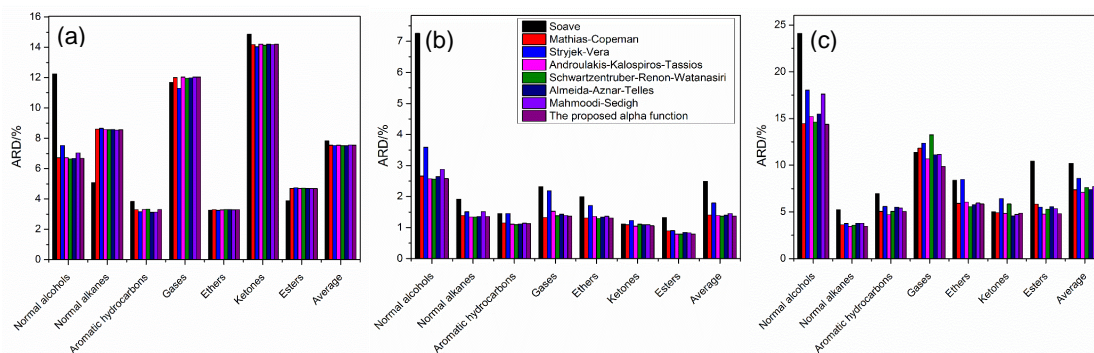

Figure 2: The ARDs of thermodynamic properties predicted with eight different alpha functions. (a) liquid volume; (b) enthalpy of vaporization; (c) isobaric heat capacity

3.2.4 Isobaric heat capacity

The mean ARD of the proposed alpha function is 6.90 % for the prediction of isobaric heat capacity (Figure 2c), the mean ARDs of Soave, Mathias-Copeman, Stryjek-Vera, Androulakis-Kalospiros-Tassios, Schwartzentruber-Renon-Watanasiri, Almeida-Aznar-Telles, and Mahmoodi-Sedigh are 10.21 %, 7.38 %, 8.59 %, 7.10 %, 7.60 %, 7.40 %, and 7.72 %. The new alpha function is better than the other seven alpha functions for the prediction of isobaric heat capacity. However, the ARDs of new alpha function for normal alcohols and gases are great, being 14.37 % and 9.86 %, and the ARDs for normal alkanes, aromatic hydrocarbons, ethers, ketones, esters are between 3 % and 6 %. The prediction of isobarc heat capacity is not only related to the second-order alpha function but also related to the functional form of the attractive and repulsive term of cubic EoS. Seeing from the perspective of molecular, the hydrogen bond forms between associating compounds, the strong induced force exists between the strong polar compounds, and the dispersion force mainly presents among the non-polar compounds. The intermolecular force is quite different between non-polar and polar compounds. PR EoS can accurately describe the intermolecular force among non-polar compounds, but it is difficult to describe that among polar compounds. The predicted deviation of isobaric heat capacity is great.

4. Conclusion

A piecewise alpha function for PR EoS was proposed for the prediction of the vapour pressure, liquid volume, enthalpy of vaporization, and isobaric heat capacity of non-polar, weakly polar, and polar compounds. The proposed alpha function and its first- and second-order derivations are monotonous and continuous in the full temperature range, and the value of third-order derivation is negative, which meets the requirement of consistency test. The proposed alpha function is superior to Soave, Stryjek-Vera, Mathias-Copeman, Androulakis-Kalospiros-Tassios, Schwartzentruber-Renon-Watanasiri, Almeida-Aznar-Telles alpha functions in the aspect of consistency test. The new proposed alpha function can accurately predict the vapour pressure and enthalpy of vaporization of pure compounds. The ARD of the new alpha function for vapour pressures of 11 kinds of compounds is 0.34 %, and the ARDs for enthalpy of vaporization, liquid volume, and isobaric heat capacity of seven kinds of compounds are 1.37 %, 7.54 %, and 6.90 %. The proposed alpha function for the prediction of vapour pressures is obviously better than Soave and Stryjek-Vera alpha function, is slightly more accurate than Mahmoodi-Sedigh alpha function and is as accurate as Mathias-Copeman, Androulakis-Kalospiros-Tassios, Schwartzentruber-Renon-Watanasiri, and Almeida-Aznar-Telles alpha functions. The new

alpha function are most accurate than the other seven alpha functions for the prediction of enthalpy of vaporization and isobaric heat capacity, but has similar precision with for the prediction of liquid volume. The proposed alpha improved the prediction of enthalpy of vaporization and isobaric heat capacity, and has good accuracy for the estimation of vapour pressures. To further improve the predictive accuracies of isobaric heat capacity and liquid volume of pure compounds, the form of PR EoS should be modified.

Acknowledgement

Nomenclature

ARD	average relative deviation	Superscripts/subscripts	
a	the parameter of attractive term	c	critical properties
b	volume of hard core	cal	calculated
c, d, k, m, n	parameters in alpha functions	exp	experimental
EoS	equation of state	sat	saturation
PR	Peng-Robinson	r	reduced state
P	vapour pressure, Pa	Greek letters	
R	universal gas constant, J/(mol·K)	α	temperature dependence of the attractive term in PR EoS
T	tempeture, K	Γ	a parameter in the alpha function
v	volume, m^3/mol	ω	acentric factor

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