Article

New Alpha Functions for the Peng−Robinson Cubic Equation of State

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ABSTRACT: The alpha function is an important part of the attractive term of cubic equation of state (EoS), which affected the predictive accuracy of thermodynamic properties. In this paper, four new alpha functions (Alpha Function-1 to Alpha Function-4) were proposed for the Peng−Robinson (PR) EoS. The proposed alpha functions and their derivatives satisfied the requirements of the thermodynamic consistency test. The four alpha functions with PR EoS were used to predict the thermodynamic properties of 11 kinds of compounds, the average relative deviation (ARD) of Alpha Function-1 and Alpha Function-2 for the prediction of vapor pressures was 0.57%, and the ARDs of Alpha Function-3 and Alpha Function-4 were 0.44 and 0.38%, respectively. The ARDs of Alpha Function-4 for the estimation of enthalpy of vaporization, liquid volume, and liquid isobaric heat capacity of seven kinds of compounds were 1.46, 7.54, and 7.59%, respectively. The proposed three-parameter alpha functions were more accurate than the two-parameter function for the prediction the vapor pressure and enthalpy of vaporization of pure compounds. However, any alpha function used in the attractive term of PR EoS had great deviations for the estimation of liquid volume and isobaric heat capacity.
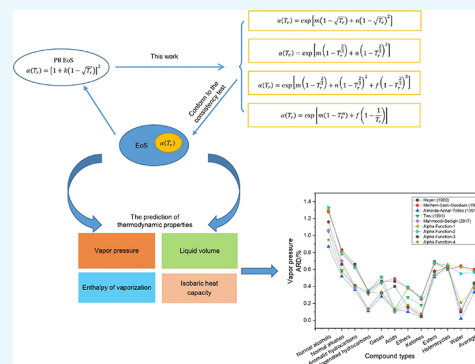
1. INTRODUCTION

A cubic equation of state (EoS) has a wide application range for the prediction of thermodynamic properties of various fluids, especially for the petroleum fluid. The first cubic EoS was proposed by van der Waals in 1873.[1] After that, the attractive term and alpha function of the van der Waals equation were modified by many researchers. Redlich and Kwong[2] improved the attractive term form of VDW EoS and changed the attractive term parameter a into the product of the attraction parameter at the critical point a_c and temperature function $1/T^{0.5}$, and the predictive accuracies of RK EoS for nonpolar as well as weakly polar compounds were much better than those of VDW EoS. Soave[3] modified the temperature function $1/T^{0.5}$ of RK EoS to a temperature correlation $\alpha(T)$. The predictions of vapor pressure of most nonpolar and weakly polar substances with SRK EoS were accurate. However, it had great deviation for some polar substances.[4] Peng and Robinson[5] modified the attractive term form of RK EoS. The PR EoS improved the calculation accuracy of liquid density and expanded the application range of the cubic equation. PR EoS became one of the most common methods for the chemical engineering calculations.

The alpha function of cubic EoS was an important factor, which affected the predictive accuracy of thermodynamic properties. Based on the Soave (1972) alpha function, many alpha functions were proposed. Graboski and Daubert[6,7] refitted the parameters of the Soave alpha function to calculate the phase equilibrium of hydrogen-containing systems. Heyen[8]

proposed an exponential alpha function with two parameters and adopted the similar form $(1 − T_r^n)$ of the Soave function. The accuracy of Heyen (1980) alpha function for the prediction of vapor pressures of hydrocarbons and polar compounds was similar to that of the Soave alpha function,[9] but it was not suitable for the calculation of the heavy hydrocarbon systems with more than 12 carbons. Hence, the Heyen (1980) alpha function started the development of the exponential alpha function. Twu[10] derived an alpha function from a probability distribution function, and it gave better accuracy for vapor pressure prediction than that predicted by the Soave alpha function. Melhem et al.[11] used $(1 − T_r)$ and $(1 − T_r^{0.5})$ as variables and two adjustable parameters m and n as coefficients, and a new two-parameter temperature dependency equation was proposed. By adding the second variation term, the prediction accuracy of vapor pressures can be improved for highly polar compounds. To increase the flexibility, Twu et al.[12] modified the Twu (1988) alpha function to be a three-parameter exponential alpha function instead of the constant 2 with the parameter N. The Twu (1991) alpha function can
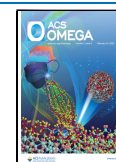
accurately predict the vapor pressure and liquid heat capacity for numerous components from a lower to higher boiling point. Gasem et al.[13] proposed a new exponential alpha function to improve the accuracy of predicting the vapor pressure of heavy hydrocarbons. Coquelet et al.[14] proposed a three-parameter exponential alpha function that combined the advantages of Trebble and Bishnoi[15] and Mathias and Copeman[16] alpha functions. A new alpha function in cubic EoS was proposed by Kud et al.[17] for the prediction of the mixtures containing polar compounds, and the parameters were fitted with the saturated vapor pressures. Li and Yang[18] revised the alpha function of the PR EoS and improved the prediction of vapor pressure for nonhydrocarbon and hydrocarbon compounds. Le Guennec et al.[19] proposed a tc-PR three-parameter EoS using the Twu (1988) and Twu (1991) alpha functions to predict the volumetric, energetic, and saturation properties of pure compounds in the subcritical and supercritical domains. Mahmoodi and Sedigh[20] proposed two new exponential alpha functions with the Taylor expansion, and the prediction of the vapor pressure was more accurate than that of the original Soave alpha function.[21] Yang et al.[22] modified the Soave (1972) and Twu (1991) alpha functions. The revised Yang alpha function was prior to the original Twu and Soave alpha functions. Huang and Yang[23] also modified an exponential alpha function to predict the ideal gas heat capacity and enthalpy of normal alkanes and alkenes in a wide range of temperature and pressure.

With the development of the alpha function for more than 40 years, the ability was significantly improved for the prediction of thermodynamic properties of nonpolar and polar substances. Forero and Velásquez[24] evaluated the prediction accuracy of Soave (1972) and the other five exponential alpha functions for thermodynamic properties of hydrocarbons, halogenated hydrocarbons, and polar substances. Hong et al.[25] compared the applicability of SRK EoS combined with Soave (1972), Twu (1991), and the other five alpha functions to calculate the vapor−liquid equilibrium (VLE), liquid−liquid equilibrium (LLE), and vapor−liquid− liquid equilibrium (VLLE) of the water−alcohol−ester system. Young et al.[26] evaluated the predictive accuracy of PR EoS combined with 20 alpha functions for 56 compounds vapor pressures below the critical temperature and found that the Almeida et al.[27] alpha function was the most accurate alpha function. Lopez-Echeverry et al. described the development history of PR EoS of about 40 years.[28] Zhao et al.[29] reviewed the alpha functions of cubic EoS for different research systems.

The alpha function should satisfy the thermodynamic consistency test. Le Guennec et al. concluded the constraints proposed by the researchers, which added a constraint of the third-order derivative.[30,31] The Heyen (1980) alpha function was monotonously decreasing and positive in the whole temperature range, which can satisfy the requirements of the consistency test of the alpha function. Thus, the Heyen alpha function avoided the shortcomings of the Soave alpha function.

The exponential function has the characteristic of monotonous decrease with the increase in x axis. Therefore, the exponential alpha function easily satisfies the thermodynamic consistency test. In this paper, new exponential alpha functions will be proposed. The predictive capability for the vapor pressure, liquid volume, isobaric heat capacity, and evaporation enthalpy will be evaluated.

2. IMPROVEMENT OF THE ALPHA FUNCTION

Due to PR EoS having a simple form and wide application ranges in the simulation and design of chemical engineering,[32] we selected PR EoS for the research of alpha functions in this paper.

2.1. PR EoS. Based on RK EoS, Peng and Robinson (1976) introduced the term $b(v - b)$ to the denominator of the attractive term of RK EoS. The predictive capability of the equation for the saturated vapor pressure and saturated liquid density was improved. The coefficient of the Soave (1972) alpha function was refitted to be suitable for the PR EoS. The PR EoS and its correlation are given below

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

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

$$a(T) = a_c \alpha(T_r) \tag{3}$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \tag{4}$$

$$\alpha(T_r) = [1 + k(1 - \sqrt{T_r})]^2 \tag{5}$$

where T_r is the reduced temperature, T/T_c, and k is generalized with the acentric factor, ω, to

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{6}$$

2.2. New Proposed Alpha Functions. According to the evaluation of 20 alpha functions by Young et al. (2016), the Almeida−Aznar−Telles (1991) alpha function was the most accurate for the vapor pressure prediction. However, Almeida−Aznar−Telles (1991) contains the term $|1 - T_r|^{(\Gamma - 1)}$, which caused the first derivative to increase, decrease, and then increase with increasing temperature, and the second derivative is discontinuous at the critical point. Therefore, the Almeida−Aznar−Telles (1991) alpha function cannot satisfy the consistency test, which affects the prediction of thermodynamic properties.

In this paper, four new alpha functions are proposed by combining the advantage of the Almeida−Aznar−Telles (1991) alpha function and the idea of Heyen, Melhem, and Mahmoodi. The four alpha functions are presented in Table 1.

Table 1. Proposed Four Alpha Functions for PR EoS

functional names	functional forms
Alpha Function-1	$\alpha(T_r) = \exp[m(1 - \sqrt{T_r}) + n(1 - \sqrt{T_r})^2]$
Alpha Function-2	$\alpha(T_r) = \exp[m(1 - T_r^{2/3}) + n(1 - T_r^{2/3})^2]$
Alpha Function-3	$\alpha(T_r) = \exp[m(1 - T_r^{2/3}) + n(1 - T_r^{2/3})^2 + f(1 - T_r^{2/3})^3]$
Alpha Function-4	$\alpha(T_r) = \exp\left[m(1 - T_r^n) + f\left(1 - \frac{1}{T_r}\right)\right]$

To evaluate the four new alpha functions, five exponential alpha functions are chosen to calculate the thermodynamic properties in this paper (Table 2).

2.3. Evaluation Method of the Alpha Function. There are about 4400 experimental vapor pressure data of 70 substances for alpha function evaluation.[33] The 70 substances are divided into 11 groups, including normal alkanols, normal alkanes, aromatic hydrocarbons, halogenated hydrocarbons,

Table 2. Five Alpha Functions for PR EoS

years	functional names	functional forms
1980	Heyen	$\alpha(T_r) = \exp\left[m(1 - T_r^n)\right]$
1989	Melhem−Saini−Goodwin	$\alpha(T_r) = \exp[m(1 - T_r) + n(1 - \sqrt{T_r})^2]$
1991	Almeida−Aznar−Telles	$\alpha(T_r) = \exp\left[m(1 - T_r)\lvert 1 - T_r\rvert^{(\Gamma-1)} + n\left(\frac{1}{T_r} - 1\right)\right]$
1991	Twu	$\alpha(T_r) = T_r^{N(M-1)}\exp[L(1 - T_r^{NM})]$
2017	Mahmoodi−Sedigh	$\alpha(T_r) = \exp\left[2c_1(1 - \sqrt{T_r}) - (c_2(1 - \sqrt{T_r}))^2 + \frac{2}{3}(c_3(1 - \sqrt{T_r}))^3\right]$, $\lvert c_3\rvert \leq 1.25\lvert c_1\rvert$

ethers, ketones, acids, esters, gases, heterocycles, and water. The pseudo-experiment data of liquid volumes, enthalpies of vaporization, and heat capacities are from *Perry's Chemical Engineering Handbook*.[34]

The alpha function parameters are fitted with the experimental vapor pressures of 70 compounds by minimizing an objective function accounting for the deviations between calculated and experimental vapor pressures (eq 7). To compare the different alpha functions with the same criterion, the parameters of the old five alpha functions in Table 2 are also refitted with the vapor pressure of 70 substances. The fitting parameters of the new and old alpha functions are shown in Tables S1 and S2 in the Supporting Information, respectively.

The calculation formula of average absolute relative deviation and maximum relative deviation are displayed as eqs 7 and 8. The vapor pressures are calculated with PR EoS combining different alpha functions according to the equal fugacity of the vapor phase and the liquid phase. The fitted parameters and calculated vapor pressures are solved by Matlab software.

$$\text{ARD} = \frac{1}{N}\sum_1^N \frac{\lvert P_{cal}^{sat} - P_{exp}^{sat}\rvert}{P_{exp}^{sat}} \times 100\% \tag{7}$$

$$\text{MARD} = \max\left(\frac{\lvert P_{cal}^{sat} - P_{exp}^{sat}\rvert}{P_{exp}^{sat}}\right) \tag{8}$$

where N is the number of saturated vapor pressure data points.

3. RESULTS AND DISCUSSION

The consistency test of the four new alpha functions is checked. The new alpha functions are used to predict the vapor pressure, liquid volume, enthalpy of vaporization, and isobaric heat capacity of 70 substances, and the predictive accuracies are compared.

3.1. A Consistency Test for New Alpha Functions. The empirical parameters m, n, and f of the proposed new alpha functions are fitted with the experimental vapor pressures of 70 compounds. *n*-Butanol is set as an example, and the fitting results of the four alpha function parameters are presented in Table 3.

Table 3. Parameters of Alpha Functions of *n*-Butanol

functional names	m	n	f
Alpha Function-1	2.1543	0.2600	
Alpha Function-2	1.6083	0.4143	
Alpha Function-3	0.8292	0.1393	1.1018
Alpha Function-4	2.4246	0.4397	0.01599

The derivative formulas of the four new alpha functions are presented in Appendix A. The parameters of alpha functions for *n*-butanol are taken into Alpha Function-1, Alpha Function-2, Alpha Function-3, and Alpha Function-4. The trends of the proposed alpha functions and their derivatives are determined in the reduced temperature range of 0.4 to 6.0 (Figure 1). The proposed four alpha functions and their second-order derivatives are positive and monotonically decreasing, the first-order derivations are negative and monotonically increasing, and the third-order derivations are negative. Therefore, all the proposed new alpha functions satisfy the requirement of the consistency test.

3.2. The Prediction of Thermodynamic Properties. The vapor pressure, liquid volume, enthalpy of vaporization, and isobaric heat capacity are predicted by PR EoS combined with the four new alpha functions and the other alpha functions. The evaluation results are discussed in the following sections.

3.2.1. Vapor Pressure. The predictive ability of the four new alpha functions is compared with the other alpha functions for the prediction of vapor pressure of 11 kinds of compounds. The results in Table 4 show that the proposed Alpha Function-1 and Alpha Function-2 with two parameters are more accurate than Heyen (1980) (0.6%) and Melhem−Saini−Goodwin (1989) (0.6%), the mean ARD is 0.57%, and the mean MARDs are 2.62 and 2.57%. The mean ARDs of the new Alpha Function-3 and Alpha Function-4 with three-parameter alpha functions are 0.44 and 0.38%, and the mean MARDs are 2.33 and 2.24%, respectively. The mean ARD of Alpha Function-4 for vapor pressures is the same as that of the Mahmoodi−Sedigh (0.38%) alpha function, but it is slightly higher than that of Almeida−Aznar−Telles (0.33%). The ARDs of nine alpha functions for the prediction of vapor pressures of hydrocarbons, gases, acids, esters, ethers, and water are less than 1%. However, the ARDs of the alpha functions for the vapor pressure of alcohols are greater than 1% except for Alpha Function-4 (0.95%) and the Almeida−Aznar−Telles (0.87%) alpha function.

Observing the predictions of vapor pressures, two reasons can illustrate this result. First, Alpha Function-4 and the Almeida−Aznar−Telles function have a similar functional form. In the alpha function, the $1/T_r$ term gives more flexibility for the vapor pressure prediction at the low temperature range. Therefore, these two alpha functions presented more accurate results than the other functions. Second, the more parameters are in the functional form, the more accurate is the alpha function for the prediction of vapor pressures. However, if there are too many parameters in the alpha function, it will be difficult to fit the parameters with vapor pressures because the parameters will inhibit each other in the fitting process. The multiparameter alpha function has a research value, but it lacks a practical value. It can be concluded that Alpha Function-4
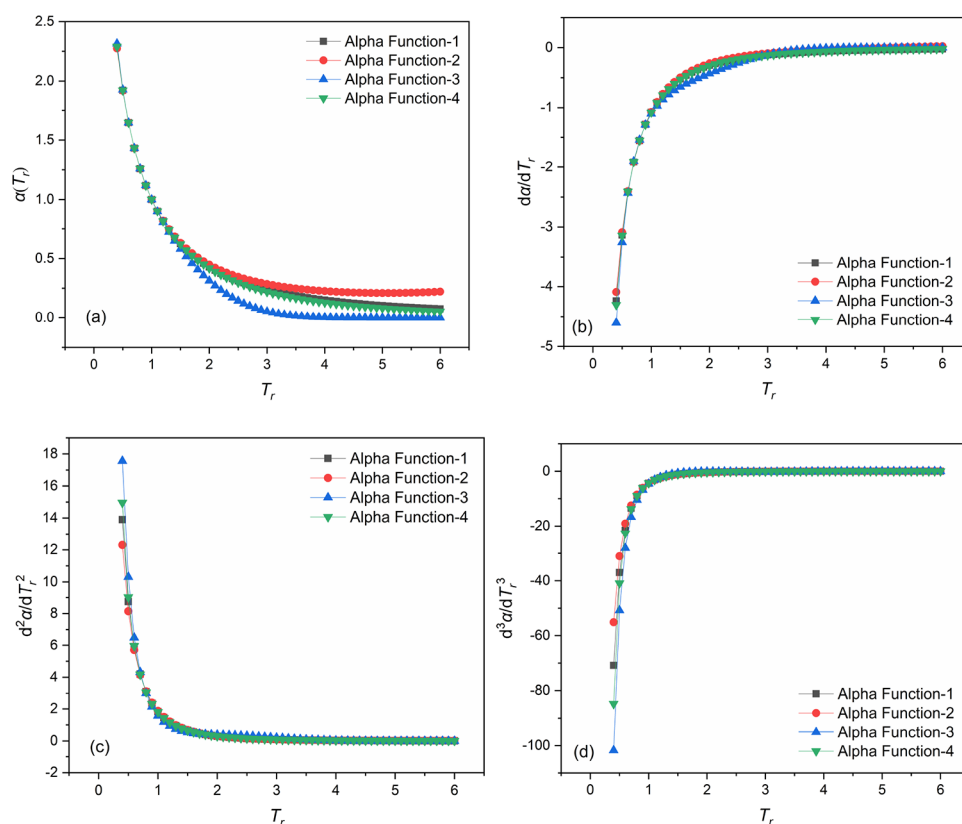
Figure 1. Proposed alpha functions and their derivatives for *n*-butanol in the reduced temperature range from 0.4 to 6.0: (a) alpha function, (b) first-order derivative of alpha function, (c) second-order derivative of alpha function, and (d) third-order derivative of alpha function.

Table 4. ARDs and MARDs of Alpha Function for the Vapor Pressure Predictions of 11 Kinds of Compounds

compound type	Heyen (1980)	Melhem−Saini−Goodwin (1989)	Almeida−Aznar−Telles (1991)	Twu (1991)	Mahmoodi−Sedigh (2017)	Alpha Function-1	Alpha Function-2	Alpha Function-3	Alpha Function-4
normal alcohols	1.29	1.28	0.87	1.05	1.06	1.30	1.33	1.16	0.95
	(5.44)	(5.59)	(4.35)	(4.99)	(4.91)	(5.52)	(5.56)	(5.18)	(4.49)
normal alkanes	0.83	0.82	0.52	0.59	0.70	0.80	0.78	0.66	0.57
	(3.85)	(3.81)	(3.93)	(3.82)	(3.85)	(3.71)	(3.73)	(3.89)	(3.74)
aromatic hydrocarbons	0.66	0.63	0.36	0.40	0.38	0.62	0.63	0.41	0.40
	(2.94)	(2.88)	(2.82)	(2.57)	(2.88)	(2.88)	(2.93)	(2.47)	(3.06)
halogenated hydrocarbons	0.35	0.34	0.11	0.31	0.13	0.34	0.35	0.33	0.14
	(3.06)	(3.04)	(1.94)	(2.99)	(2.50)	(3.04)	(3.04)	(3.01)	(2.57)
gases	0.46	0.45	0.28	0.44	0.33	0.51	0.51	0.32	0.33
	(1.83)	(1.77)	(1.74)	(1.75)	(2.09)	(2.20)	(2.20)	(1.79)	(1.77)
acids	0.46	0.49	0.13	0.11	0.10	0.13	0.12	0.40	0.12
	(2.10)	(2.18)	(1.35)	(1.33)	(1.34)	(0.91)	(0.98)	(1.94)	(1.41)
ethers	0.39	0.38	0.10	0.27	0.14	0.38	0.39	0.16	0.18
	(1.19)	(1.16)	(0.38)	(0.86)	(0.57)	(1.15)	(1.15)	(0.68)	(0.71)
ketones	0.26	0.25	0.04	0.18	0.06	0.27	0.27	0.05	0.08
	(0.99)	(0.95)	(0.29)	(0.72)	(0.35)	(0.95)	(0.88)	(0.37)	(0.34)
esters	0.69	0.67	0.51	0.56	0.53	0.67	0.68	0.58	0.53
	(2.87)	(2.84)	(2.61)	(2.71)	(2.55)	(2.83)	(2.84)	(2.37)	(2.57)
heterocycles	0.60	0.61	0.65	0.64	0.61	0.65	0.64	0.62	0.63
	(2.91)	(2.89)	(2.89)	(2.89)	(2.90)	(2.90)	(2.91)	(2.88)	(2.90)
water	0.64	0.63	0.02	0.13	0.12	0.63	0.55	0.10	0.21
	(2.63)	(2.54)	(1.07)	(1.02)	(1.02)	(2.74)	(2.08)	(1.03)	(1.12)
average	0.60	0.60	0.33	0.42	0.38	0.57	0.57	0.44	0.38
	(2.71)	(2.69)	(2.12)	(2.33)	(2.27)	(2.62)	(2.57)	(2.33)	(2.24)

can satisfy the accuracy of the alpha function and has good accuracy for the prediction of vapor pressures of nonpolar, weakly polar, and polar compounds.

3.2.2. Liquid Volume. An appropriate alpha function of a cubic EoS can accurately predict the vapor pressure and vapor−liquid equilibrium data, while the accuracy of the
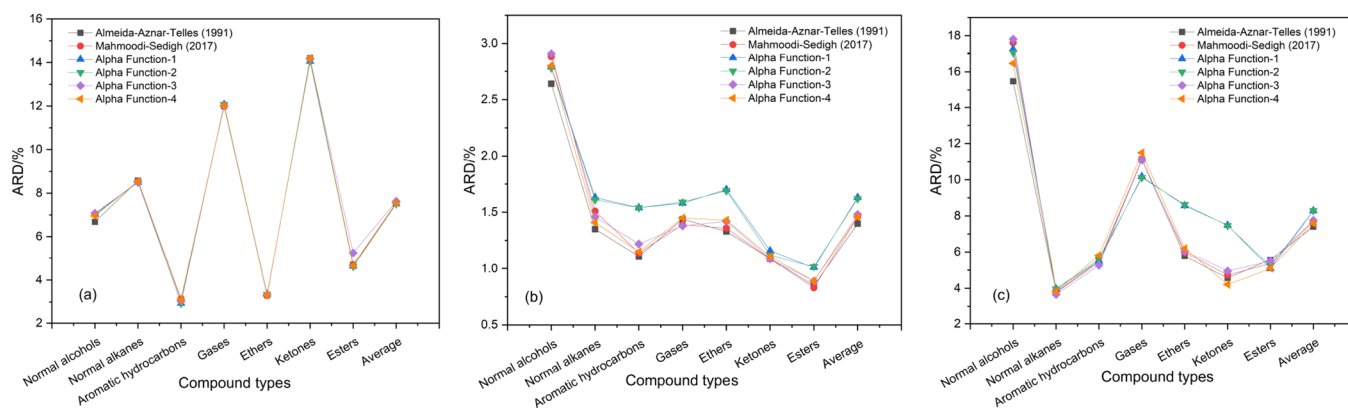
Figure 2. ARDs of alpha functions for the thermodynamic properties of seven kinds of compounds: (a) liquid volume, (b) enthalpy of vaporization, and (c) isobaric heat capacity.

predicted volumetric properties is governed by the volume. Alpha functions have a negligible influence on the correlation of liquid molar volumes.[35] The pseudo-experiment data of the liquid volume, enthalpy of evaporation, and liquid isobaric heat capacity of 56 components were used to evaluate the four new alpha functions and the other two functions with PR EoS (Figure 2).

For the liquid volume (Figure 2a), the mean ARDs of both Alpha Function-1 and Alpha Function-2 are 7.51%, which are the same as the predictions of the Almeida−Aznar−Telles (1991) alpha function. The mean ARD of the Alpha Function-4 results is 7.54%, which is better than those of Alpha Function-3 (7.63%) and the Mahmoodi−Sedigh (7.56%) alpha function. The six alpha functions have little differences for the prediction of the liquid volume of seven kinds of compounds. Therefore, the functional form of alpha functions has little effect on the prediction of liquid volume. To improve the predictive accuracy of liquid volume, there is an effective method by modifying the second-order polynomial $[(v + b) + b(v − b)]$ of the attractive term of cubic EoS. Privat et al. and Jaubert et al. applied a Péneloux-type volume translation to cubic EoS to predict the liquid volumes and heat capacities.[36,37]

3.2.3. Enthalpy of Vaporization. Combined with PR EoS, the six alpha functions are used to predict the enthalpy of vaporization of seven kinds of compounds, and the results are shown in Figure 2b. The mean ARD of Alpha Function-4 is as accurate as that of the Mahmoodi−Sedigh (2017) alpha function, being 1.46%, which is greater than that of the Almeida−Aznar−Telles (1991) alpha function (1.40%). The mean ARDs of Alpha Function-1, Alpha Function-2, and Alpha Function-3 are 1.63, 1.62, and 1.48%, respectively. Alpha Function-4 is more accurate than the other new alpha functions for the prediction of enthalpy of vaporization. The ARDs of the six alpha functions for the enthalpy of vaporization of *n*-alkanols are between 2.64 and 2.91%, and for *n*-alkanes, those of aromatic hydrocarbons, gases, ethers, ketones, and esters are less than 2%.

3.2.4. Isobaric Heat Capacity. The six alpha functions are used to predict the isobaric heat capacity of seven kinds of compounds (Figure 2c). Alpha Function-4 has a large deviation for the estimation of the isobaric heat capacity and the mean ARD is 7.59%, which is more accurate than the predictions of Alpha Function-1 (8.29%) and Alpha Function-2 (8.29%) and slightly better than that of Alpha Function-3 (7.76%) and the Mahmoodi−Sedigh function (2017) (7.71%).

The most accurate alpha function is the Almeida−Aznar−Telles (1991) alpha function, with the mean ARD being 7.40%. Observing from each kind of compound, the ARDs of *n*-alkanols and gases are more than 10%. The ARDs of alkanes and aromatics are between 4 and 6%. The predicted deviations of Alpha Function-1 and Alpha Function-2 for ethers and ketones are large, ranging from 7.46 to 8.63%, and the deviations of the predictions of Alpha Function-3 and Alpha Function-4 are between 4.21 and 6.20%. The predicted results of esters by the six alpha functions are more accurate, ranging from 0.83 to 1.02%.

4. CONCLUSIONS

Based on PR EoS, four new alpha functions (Alpha Function-1 to Alpha Function-4) are proposed for the prediction of thermodynamic properties, such as vapor pressure and enthalpy of vaporization. All the proposed alpha functions can satisfy the requirement of the consistency test.

Alpha Function-4 is the most accurate one among the proposed alpha functions. The predictions of the three-parameter Alpha Function-3 and Alpha Function-4 for vapor pressures are better than that of the two-parameter Alpha Function-1 and Alpha Function-2, and the ARDs of Alpha Function-3, Alpha Function-4, Alpha Function-1, and Alpha Function-2 are 0.44, 0.38, 0.57, and 0.57%, respectively. All the new alpha functions are more accurate than the Heyen (1980) (0.60%) alpha function. Alpha Function-4 is slightly less accurate than the Almeida−Aznar−Telles (1991) (0.33%) alpha function. The four proposed alpha functions, Almeida−Aznar−Telles (1991), and Mahmoodi−Sedigh (2017) functions can accurately predict the enthalpy of evaporation of the seven kinds of compounds. The ARD of Alpha Function-4 is 1.46%, which is more accurate than the other five alpha functions. The ARD of Alpha Function-4 for the prediction of the liquid volume of seven kinds of substances is 7.54%. The difference of the ARDs among different alpha functions is less than 0.05%. The ARD of Alpha Function-4 for isobaric heat capacity is 7.59%. Also, the ARDs of the predicted results for *n*-alkanols and gases are more than 10%. The ARDs of the predicted results for nonpolar alkanes and aromatic hydrocarbons are relatively small, between 4 and 6%.

According to the predictions of vapor pressures, it can be found that the three-parameter alpha function is more accurate than the two-parameter alpha function. The proposed Alpha Function-4 with three parameters can accurately predict the

vapor pressure and enthalpy of vaporization. However, the predictions of liquid volume and isobaric heat capacity have large deviations. To improve the predictive accuracy of liquid volume and isobaric heat capacity, it is necessary to modify the functional form of the PR cubic equation of state.

■ APPENDIX

A. Derivatives of Four New Alpha Functions

A.1. Alpha Function-1. A.1.1. First Derivative.

$$a1 = -\exp(n(\sqrt{T_r} - 1)^2 - m(\sqrt{T_r} - 1))$$
$$\left(\left(\frac{m}{2\sqrt{T_r}}\right) - n\frac{\sqrt{T_r} - 1}{\sqrt{T_r}}\right)$$

A.1.2. Second Derivative.

$$a2 = \exp(n(\sqrt{T_r} - 1)^2 - m(\sqrt{T_r} - 1))$$
$$\left(\left(\frac{m}{2\sqrt{T_r}}\right) - n\frac{\sqrt{T_r} - 1}{\sqrt{T_r}}\right)^2 + \exp(n(\sqrt{T_r} - 1)^2$$
$$- m(\sqrt{T_r} - 1))\left(\frac{m}{4T_r^{3/2}} + \frac{n}{2T_r} - \left(\frac{n(\sqrt{T_r} - 1)}{2T_r^{3/2}}\right)\right)$$

A.1.3. Third Derivative.

$$a3 = -\exp(n(\sqrt{T_r} - 1)^2 - m(\sqrt{T_r} - 1))$$
$$\left(\left(\frac{m}{2\sqrt{T_r}}\right) - n\frac{\sqrt{T_r} - 1}{\sqrt{T_r}}\right)^3 - \exp(n(\sqrt{T_r} - 1)^2$$
$$- m(\sqrt{T_r} - 1))\left(\frac{3m}{8T_r^{5/2}} + \frac{3n}{4T_r^2} - \frac{3n(\sqrt{T_r} - 1)}{4T_r^{5/2}}\right)$$
$$- 3\exp(n(\sqrt{T_r} - 1)^2 - m(\sqrt{T_r} - 1))$$
$$\left(\left(\frac{m}{2\sqrt{T_r}}\right) - n\frac{\sqrt{T_r} - 1}{\sqrt{T_r}}\right)\left(\frac{m}{4T_r^{3/2}} + \frac{n}{2T_r}\right.$$
$$\left. - \left(\frac{n(\sqrt{T_r} - 1)}{2T_r^{3/2}}\right)\right)$$

A.2. Alpha Function-2. A.2.1. First Derivative.

$$a1 = -\exp(n(T_r^{2/3} - 1)^2 - m(T_r^{2/3} - 1))$$
$$\left(\frac{2m}{3T_r^{1/3}} - \frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}}\right)$$

A.2.2. Second Derivative.

$$a2 = \exp(n(T_r^{2/3} - 1)^2 - m(T_r^{2/3} - 1))$$
$$\left(\frac{2m}{3T_r^{1/3}} - \frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}}\right)^2 + \exp(n(T_r^{2/3} - 1)^2$$
$$- m(T_r^{2/3} - 1))\left(\frac{2m}{9T_r^{4/3}} + \frac{8n}{9T_r^{2/3}} - \frac{4n(T_r^{2/3} - 1)}{9T_r^{4/3}}\right)$$

A.2.3. Third Derivative.

$$a3 = -\exp(n(T_r^{2/3} - 1)^2 - m(T_r^{2/3} - 1))$$
$$\left(\frac{2m}{3T_r^{1/3}} - \frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}}\right)^3 - \exp(n(T_r^{2/3} - 1)^2$$
$$- m(T_r^{2/3} - 1))\left(\frac{8m}{27T_r^{7/3}} + \frac{8n}{9T_r^{5/3}}\right.$$
$$\left. - \frac{16n(T_r^{2/3} - 1)}{27T_r^{7/3}}\right) - 3\exp(n(T_r^{2/3} - 1)^2$$
$$- m(T_r^{2/3} - 1))\left(\frac{2m}{3T_r^{1/3}} - \frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}}\right)$$
$$\left(\frac{2m}{9T_r^{4/3}} + \frac{8n}{9T_r^{2/3}} - \frac{4n(T_r^{2/3} - 1)}{9T_r^{4/3}}\right)$$

A.3. Alpha Function-3. A.3.1. First Derivative.

$$a1 = -\exp(n(T_r^{2/3} - 1)^2 - f(T_r^{2/3} - 1)^3$$
$$- m(T_r^{2/3} - 1))\left(-\frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}} + \frac{2f(T_r^{2/3} - 1)^2}{T_r^{1/3}}\right.$$
$$\left. + \frac{2m}{3T_r^{1/3}}\right)$$

A.3.2. Second Derivative.

$$a2 = \exp(n(T_r^{2/3} - 1)^2 - f(T_r^{2/3} - 1)^3 - m(T_r^{2/3} - 1))$$
$$\left(-\frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}} + \frac{2f(T_r^{2/3} - 1)^2}{T_r^{1/3}} + \frac{2m}{3T_r^{1/3}}\right)^2$$
$$+ \exp(n(T_r^{2/3} - 1)^2 - f(T_r^{2/3} - 1)^3$$
$$- m(T_r^{2/3} - 1))\left(\frac{2m}{9T_r^{4/3}} + \frac{8n}{9T_r^{2/3}} - \frac{4n(T_r^{2/3} - 1)}{9T_r^{4/3}}\right.$$
$$\left. - \frac{8f(T_r^{2/3} - 1)}{3T_r^{2/3}} + \frac{2f(T_r^{2/3} - 1)^2}{3T_r^{4/3}}\right)$$

A.3.3. Third Derivative.

$$a3 = -\exp(n(T_r^{2/3} - 1)^2 - f(T_r^{2/3} - 1)^3$$
$$- m(T_r^{2/3} - 1))$$
$$\left(-\frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}} + \frac{2f(T_r^{2/3} - 1)^2}{T_r^{1/3}} + \frac{2m}{3T_r^{1/3}}\right)^3$$
$$- \exp(n(T_r^{2/3} - 1)^2 - f(T_r^{2/3} - 1)^3$$
$$- m(T_r^{2/3} - 1))\left(\frac{16f}{9T_r} + \frac{8m}{27T_r^{7/3}} + \frac{8n}{9T_r^{5/3}}\right.$$
$$- \frac{16n(T_r^{2/3} - 1)}{27T_r^{7/3}} - \frac{8f(T_r^{2/3} - 1)}{3T_r^{5/3}}$$
$$\left. + \frac{8f(T_r^{2/3} - 1)^2}{9T_r^{7/3}}\right) - 3\exp(n(T_r^{2/3} - 1)^2$$
$$- f(T_r^{2/3} - 1)^3 - m(T_r^{2/3} - 1))$$
$$\left(-\frac{4n(T_r^{2/3} - 1)}{3T_r^{1/3}} + \frac{2f(T_r^{2/3} - 1)^2}{T_r^{1/3}} + \frac{2m}{3T_r^{1/3}}\right)$$
$$\left(\frac{2m}{9T_r^{4/3}} + \frac{8n}{9T_r^{2/3}} - \frac{4n(T_r^{2/3} - 1)}{9T_r^{4/3}} - \frac{8f(T_r^{2/3} - 1)}{3T_r^{2/3}}\right.$$
$$\left. + \frac{2f(T_r^{2/3} - 1)^2}{3T_r^{4/3}}\right)$$

A.4. Alpha Function-4. A.4.1. First Derivative.

$$a1 = \exp\left(-m(T_r^n - 1) - f\left(\frac{1}{T_r} - 1\right)\right)\left(\frac{f}{T_r^2} - mnT_r^{(n-1)}\right)$$

A.4.2. Second Derivative.

$$a2 = \exp\left(-m(T_r^n - 1) - f\left(\frac{1}{T_r} - 1\right)\right)\left(\frac{f}{T_r^2} - mnT_r^{(n-1)}\right)^2$$
$$- \exp\left(-m(T_r^n - 1) - f\left(\frac{1}{T_r} - 1\right)\right)$$
$$\left(\frac{(2f)}{T_r^3} + mn(n - 1)T_r^{(n-2)}\right)$$

A.4.3. Third Derivative.

$$a3 = \exp\left(-m(T_r^n - 1) - f\left(\frac{1}{T_r} - 1\right)\right)\left(\frac{f}{T_r^2} - mnT_r^{(n-1)}\right)^3$$
$$+ \exp\left(-m(T_r^n - 1) - f\left(\frac{1}{T_r} - 1\right)\right)$$
$$\left(\frac{6f}{T_r^4} - mn(n - 1)(n - 2)T_r^{(n-3)}\right) - 3$$
$$\exp\left(-m(T_r^n - 1) - f\left(\frac{1}{T_r} - 1\right)\right)$$
$$\left(\frac{2f}{T_r^3} + mn(n - 1)T_r^{(n-2)}\right)\left(\frac{f}{T_r^2} - mnT_r^{(n-1)}\right)$$

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06519.

Table S1: adjustable parameters of new exponential alpha functions and reduced temperature range of 70 pure compounds; Table S2: adjustable parameters of five old exponential alpha functions of 70 pure compounds (PDF)

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Notes

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■ GLOSSARY

a	attraction parameter
a_c	value of attraction parameter at the critical point
b	covolume parameter in a cubic EoS
ARD	average absolute relative deviation
EoS	equation of state
m, n, f, k, M, N, L, c₁, c₂, c₃, and Γ	parameters of alpha functions
PR	Peng−Robinson
P	vapor pressure (MPa)
RK	Redlich−Kwong
R	universal gas constant (8.314462 J·mol⁻¹·K⁻¹)
SRK	Soave−Redlich−Kwong
T	temperature (K)
VDW	van der Waals
v	molar volume (m³·mol⁻¹)

Greek Symbols

α alpha function

ω acentric factor

Superscripts and Subscripts

c   critical
cal   calculated
exp   experimental
r   reduced state
sat   saturation

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