



A new generalized alpha function for a cubic equation of state Part I. Peng–Robinson equation

Chorng H. Twu*, John E. Coon, John R. Cunningham

Simulation Sciences, Inc., 601 South Valencia Avenue, Brea, CA 92621, USA

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Abstract

A generalized temperature and acentric factor dependent function of the attractive term, called the alpha function, of the Peng–Robinson cubic equation of state (PR EOS) is developed. The approach in this work allows the alpha function to become a linear function of the acentric factor at a constant reduced temperature, not a fourth or sixth order function as suggested by Soave and other researchers. The advantage of a linear function in the acentric factor is obvious in the extrapolation of the alpha function to heavy hydrocarbons, petroleum fractions, and gas condensates. The new generalized alpha function, when used with the PR EOS, allows the accurate reproduction of the vapor pressure data from the triple point to the critical point for hydrocarbons. The new EOS provides much more reliable and accurate vapor pressure predictions for light as well as heavy hydrocarbons than the original PR equation.

Keywords: Theory; Equations of state; Methods of calculation

1. Introduction

Since van der Waals (1873) proposed his well known cubic equation of state over a century ago, numerous equations of state have been proposed to correlate the thermodynamic properties of both pure components and mixtures in vapor and liquid phases. The ability of a EOS to correlate the phase equilibria of mixtures depends not only on the mixing rule, but also on the alpha function. Remarkable success in the development of a generalized alpha function was

* Corresponding author.

shown by Soave (1972). He recognized that a pre-requisite for the correlation of the phase equilibria of mixtures is the correlation of the vapor pressures of the pure components. The Soave modification of the Redlich and Kwong (1949) equation has been a major success in correlating the phase behavior of multicomponent systems containing non-polar and slightly polar components. The Soave approach was subsequently used in the work by Peng and Robinson (1976). This also helped the PR equation to become one of the most widely used equations of state in industry for correlating the vapor–liquid equilibria (VLE) of systems containing non-polar and slightly polar components.

Recently, many advanced alpha functions have been proposed to improve the accuracy in the prediction of vapor pressures from a CEOS for non-polar as well as polar molecules (Twu et al., 1991). Each different alpha function typically contains two or three parameters. Using these component-dependent adjustable parameters, the accuracy in reproducing the vapor pressure of non-polar or polar components from the triple point to the critical point is generally within experimental error. Owing to the empirical nature of these component-dependent parameters, however, no generalized correlation has been developed for these parameters in terms of pure component properties.

Although the vapor pressures of pure polar or non-polar compounds can be accurately reproduced using the component-dependent alpha function, a generalized alpha correlation with the acentric factor being the only parameter needed in addition to the critical temperature and pressure, for estimating the vapor pressures of pure hydrocarbons and petroleum fractions would be extremely valuable in the simulation of phase equilibrium calculations in the petroleum production and refining industries. The PR CEOS, using an alpha function of the Soave type, gives acceptable vapor pressure predictions at reduced temperatures of the order of 0.7 and above for non-polar components, but fails to reproduce the vapor pressures of pure components at low reduced temperatures. Using the PR CEOS for the extrapolation of vapor pressures to heavy hydrocarbons is also unreliable because the alpha function in the PR CEOS is not a linear function in the acentric factor, and the valid range is up to a value of the acentric factor equal to 0.5 (Peng and Robinson, 1976). In this paper, a new approach to developing a generalized alpha function using the Peng–Robinson equation of state will be presented. The new equation significantly improves the accuracy of the vapor pressure predictions for light as well as heavy hydrocarbons compared to the original Peng–Robinson equation or other versions of the PR CEOS.

2. A modified Peng–Robinson cubic equation of state

The new equation of state has the same form as that proposed by Peng and Robinson (1976), but with a different generalized alpha function.

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \quad (1)$$

In order to satisfy the critical constraints, the constants a and b are given by

$$a(T_c) = 0.457235528921R^2T_c^2/P_c \quad (2)$$

$$b = 0.0777960739039RT_c/P_c \quad (3)$$

where the subscript c denotes the critical point, b is kept constant and a is a function of temperature. The value of $a(T)$ at other temperatures can be calculated from

$$a(T) = \alpha(T)a(T_c) \quad (4)$$

where $\alpha(T)$ is a temperature-dependent function which takes into account the attractive forces between the molecules. For the real gas behavior to approach that of an ideal gas at high temperatures, α must approach a finite value as the temperature tends to infinity. Soave (1972) expresses α as an equation of the form

$$\alpha = [1 + m(1 - T_r^5)]^2 \quad (5)$$

where T_r is the reduced temperature, T/T_c , and m is a function of the acentric factor, ω , only. Following Soave, Peng and Robinson (1976) generalized m in terms of the acentric factor, ω , to

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (6)$$

Eqs. (5) and (6) indicate that α is a fourth order function of the acentric factor. On careful examination of Eq. (6), it becomes apparent that a questionable assumption is being made in the application of a fourth order polynomial equation in ω to heavy hydrocarbons or petroleum fractions. Since the numerical values in Eq. (6) are derived from the vapor pressures of a limited number of hydrocarbons up to an acentric factor of 0.5, it is unlikely that Eq. (6) will suffice for higher acentric factor petroleum fractions. While the equation performs well for light hydrocarbons at reduced temperatures between 0.7 and 1.0, there are significant errors at all temperatures for components with large acentric factors; these errors increase rapidly at low reduced temperatures for all compounds. To improve the results, Stryjek and Vera (1986) re-correlated m as a function of the acentric factor using the same form, but up to third order.

$$m = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (7)$$

Eq. (7) makes α become a sixth order function of the acentric factor. The use of a higher order of the acentric factor in Eq. (7) improves the vapor pressure prediction in the reduced temperature range from 0.7 to 1.0. However, Eqs. (6) and (7) give the same values of α when $\omega = 0.1$ and $\omega = 0.4$; because Eq. (7) uses a higher order polynomial in the acentric factor, this presents a problem in the extrapolation of the alpha function to heavy hydrocarbons having high values of the acentric factor. As a consequence, Eq. (7) produces the same large vapor pressure deviations as Eq. (6) at low reduced temperatures and high acentric factors. In order to reproduce the vapor pressures at low reduced temperatures, Stryjek and Vera (1986) had to introduce a temperature-dependent adjustable parameter for each component. Using component-dependent adjustable parameters in the alpha function is contrary to our goal in this work. Many advanced component-dependent alpha functions have been proposed (Twu et al., 1991) that predict more accurate vapor pressures than that of Stryjek and Vera (1986).

In this work we abandon Soave's type of alpha function and present a new approach. Since the principle of corresponding states is very useful for the prediction of the properties of a large class of substances from the knowledge of a few compounds, the aim is to find a way in which the principle of corresponding states can be applied to the alpha function. The problem then is in determining which compounds and how many different types of hydrocarbons should be selected in the development. It is best to fit a group of compounds which cover a wide range of

acentric factors. Since the normal paraffin hydrocarbons provide the most consistent variation of physical properties with acentric factor and the theory requires that any other types of hydrocarbons with equal values of the acentric factor should conform amongst themselves to the principle of corresponding states, the generalized alpha function is developed mostly from the properties of normal paraffin hydrocarbons with the inclusion of some other types of hydrocarbons for checking the generality.

3. Development of a generalized alpha function

The generalized alpha function can be expressed as a function of two variables, reduced temperature and acentric factor:

$$\alpha = \alpha(T_r, \omega) \quad (8)$$

The functional dependence on temperature and acentric factor is very complicated. Indeed, this complexity retarded advances in the field for almost a century after van der Waals (1873) developed the equation, until Soave (1972) generalized the alpha function (Eqs. 5 and 6). We will take a different approach to Soave and expand the alpha function as a power series in the acentric factor:

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \quad (9)$$

Note that if the same functional form is applied to $\alpha^{(0)}$ and $\alpha^{(1)}$, and if the parameters in these functions are linear, then $\alpha^{(0)}$ and $\alpha^{(1)}$ can be combined to give a single function. When α is expressed as in Eq. (9), the deviation term is obviously equivalent to $(\alpha^{(1)} - \alpha^{(0)})$. This expression is convenient because the same alpha function can be applied to $\alpha^{(0)}$ and $\alpha^{(1)}$. As explained in the next few paragraphs, α is a linear function of ω and higher order terms are not needed in Eq. (9). $\alpha^{(0)}$ and $\alpha^{(1)}$ correspond to $\omega = 0$ and $\omega = 1$, respectively, and are functions of reduced temperature only. Eq. (1) with Eqs. (4) and (9) gives the new cubic equation of state.

The first step in generalizing the alpha function is to derive alpha as a function of temperature for each individual compound. In this work, an appropriate alpha function proposed by Twu et al. (1991) is used for correlating the vapor pressure data of pure components:

$$\alpha = T_r^{N(M-1)} \exp(T_r^{M-1} - T_r^{N(M)}) \quad (10)$$

where the parameters L , M , and N are unique to each component and have been determined from the regression of pure component vapor pressure. All critical constants and vapor pressure data correlations from the triple point to the critical point are from DIPPR (Daubert and Danner, 1990). The obtained values of L , M , and N for individual components are listed in Table 1. The value of α for each compound is then computed at T_r increments of 0.02 from $T_r = 0.3$ to 1.0. The computed values of α at 36 different constant reduced temperatures are plotted as a function of the acentric factor. Since the acentric factors often differ from reference to reference, they were computed from the DIPPR vapor pressure equation to maintain internal consistency in this work. The dependence of α on ω for a number of reduced isotherms is illustrated in Fig. 1. Note that points below the triple point are obtained by extrapolation of the α function. In all regions, α vs. ω plots give good straight lines even at temperatures well

Table 1

Alpha parameters, L , M , and N , used in Eq. (10) for individual components

Component	T_c (K)	P_c (bar)	L	M	N
Argon	150.86	48.98	0.036512	0.935460	3.97643
Methane	190.58	46.04	0.081043	0.915696	2.61622
Ethane	305.42	48.80	0.311041	0.866279	1.29869
Propane	369.82	42.49	0.283800	0.858285	1.59420
<i>n</i> -Butane	425.17	37.97	0.351718	0.843261	1.47039
<i>n</i> -Pentane	469.65	33.69	0.343038	0.810237	1.55034
<i>n</i> -Hexane	507.85	30.31	0.088790	0.901528	5.08963
<i>n</i> -Heptane	540.26	27.36	0.169318	0.844860	3.03151
<i>n</i> -Octane	568.83	24.86	0.428179	0.805321	1.71898
<i>n</i> -Nonane	595.65	23.06	1.971720	1.628290	0.37765
<i>n</i> -Decane	618.45	21.23	0.315303	0.811589	2.42062
<i>n</i> -Undecane	638.76	19.66	0.246874	0.821219	3.03978
<i>n</i> -Dodecane	658.20	18.24	0.411574	0.802000	2.25086
<i>n</i> -Tridecane	675.80	17.23	0.509689	0.822738	2.10994
<i>n</i> -Tetradecane	692.40	16.21	0.236127	0.821870	3.61671
<i>n</i> -Pentadecane	706.80	15.20	0.229708	0.823364	3.85809
<i>n</i> -Hexadecane	720.60	14.19	0.340390	0.810309	3.11841
<i>n</i> -Heptadecane	733.37	13.17	0.134135	0.874867	6.76784
<i>n</i> -Octadecane	745.26	12.14	0.480721	0.783810	2.47646
<i>n</i> -Nonadecane	755.93	11.17	0.543018	0.772678	2.27430
Eicosane	767.04	10.40	2.731330	2.209970	0.30780
Cyclohexane	553.58	40.73	0.076117	0.882790	3.80751
Benzene	562.16	48.98	0.141223	0.844404	2.47802

removed from 0.7, at which ω is defined. Although all the vapor pressure data essentially conformed into straight lines, the vapor pressure data at reduced temperatures below 0.5, as shown in Fig. 1, are scattered slightly about the straight lines. This indicates that the low-temperature points are not as consistent as the high-temperature points. A plot like Fig. 1 can be very useful in testing the consistency of experimental data between compounds. The linear nature of the present alpha correlation as a function of the acentric factor is clearly an advantage over that of Soave for extrapolation to heavy hydrocarbons (higher values of ω). A least-squares linear fit of α vs. ω yields the intercept $\alpha^{(0)}$ and the slope $(\alpha^{(1)} - \alpha^{(0)})$ at each reduced temperature. A table of data of $(T_r, \alpha^{(0)})$ and $(T_r, \alpha^{(1)})$ are obtained for values of T_r from 0.3 to 1.0. Fig. 2 presents the dependence of $\alpha^{(0)}$ and $\alpha^{(1)}$ upon T_r .

The final step is to correlate the tabulated data of $(T_r, \alpha^{(0)})$ and $(T_r, \alpha^{(1)})$. Since $\alpha^{(0)}$ and $\alpha^{(1)}$ are functions of T_r only and Eq. (10) is a powerful tool for correlating the vapor pressure of pure compounds (Twu et al., 1991), this equation is used to correlate $\alpha^{(0)}$ and $\alpha^{(1)}$ in terms of T_r as follows:

$$\alpha^{(0)} = T_r^{-0.171813} e^{0.125283(1 - T_r^{1.72634})} \quad (11)$$

$$\alpha^{(1)} = T_r^{-0.607352} e^{0.511614(1 - T_r^{2.20517})} \quad (12)$$

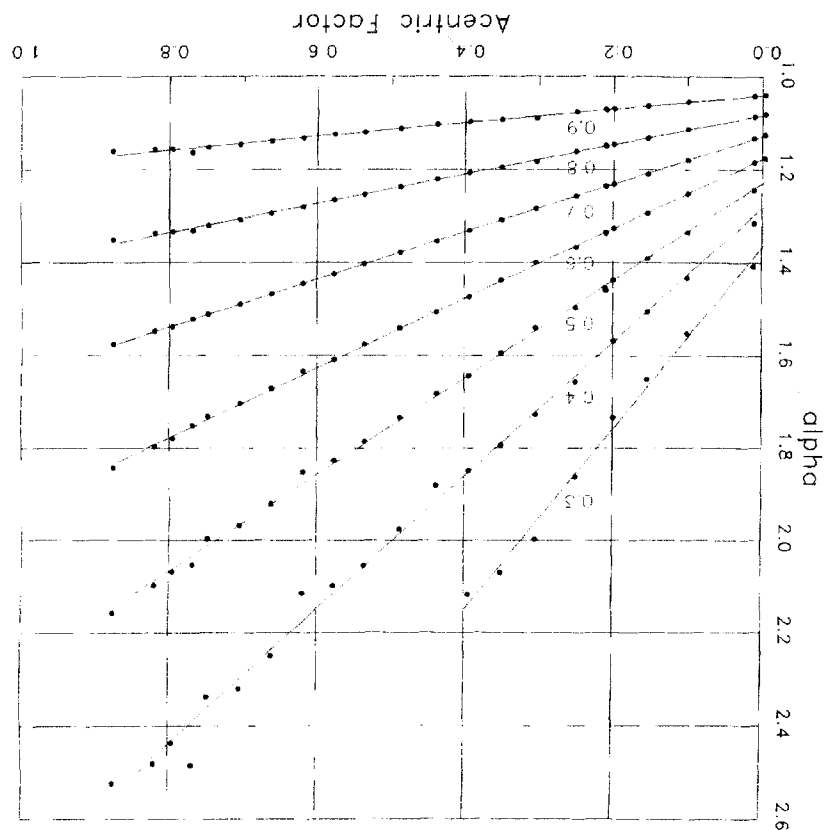


Fig. 1. Dependence of α on the acentric factor at several reduced temperatures: 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9.

The constants in Eqs. (11) and (12) are computed from the values of the L , M , and N parameters, which are listed in Table 2, according to Eq. (10). $\alpha^{(0)}$ and $\alpha^{(1)}$ in Eqs. (11) and (12) are consistent with the definition of the acentric factor at $\omega = 0$ and $\omega = 1$, respectively, i.e. these two alpha functions are forced to pass through the saturated vapor pressure at $T_r = 0.7$ for $\omega = 0$ and $\omega = 1$, respectively. The solid lines in Fig. 2 are from Eqs. (11) and (12), and fit the data points almost exactly.

The defined component data of this study were compared with the generalized correlation in this work, as well as the correlations proposed by Peng and Robinson (1976) and Stryjek and Vera (1986). The results are given in Table 3. While the correlation was developed primarily using the data for n -paraffins, it gives relatively high accuracy for various other hydrocarbons as expected from the corresponding states principle. The average absolute percentage deviation (AAD%) over all the vapor pressure points from the triple point to the critical point is only 3.28% from this work, compared with 12.08% from Peng and Robinson and 8.21% from Stryjek and Vera. This result indicates that the new generalized α function enables the new equation to

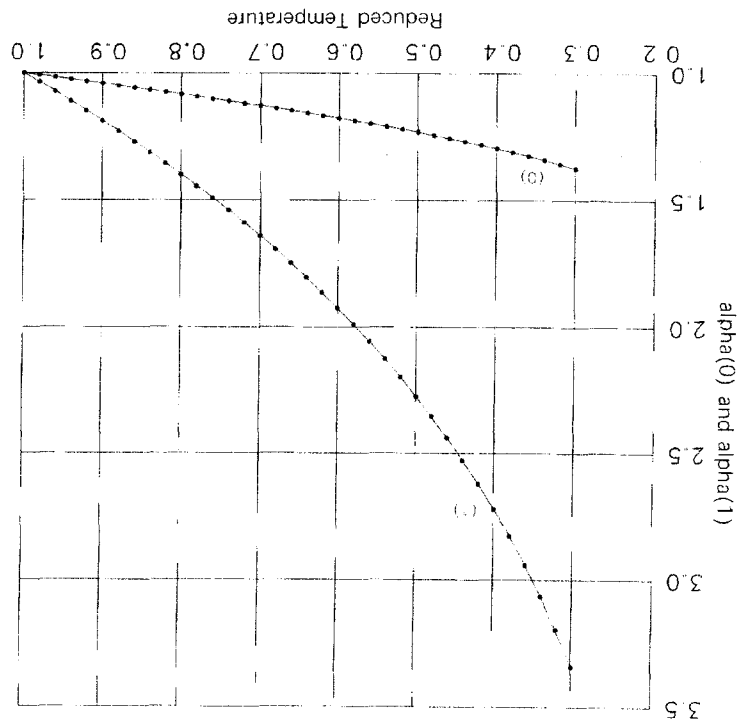


Fig. 2. Dependence of $\alpha^{(0)}$ and $\alpha^{(1)}$ on the reduced temperature: points are derived from DIPPR data and solid lines are from this work.

Table 2
The values of the L , M , and N parameters used in the generalized alpha correlations, Eqs. (11) and (12) for subcritical conditions and Eqs. (13) and (14) for supercritical conditions, according to Eq. (10)

Alpha parameter	$T_r \leq 1$		$T_r > 1$	
	$\alpha^{(0)}$	$\alpha^{(1)}$	$\alpha^{(0)}$	$\alpha^{(1)}$
L	0.125283	0.511614	0.401219	0.024955
M	0.911807	0.784054	4.963070	1.248089
N	1.948150	2.812520	-0.200000	-8.000000

predict vapor pressures much more accurately than the alpha functions of Peng and Robinson (1976) and Stryjek and Vera (1986). Owing to the definition of the acentric factor, any acentric factor based alpha function would be expected to give excellent accuracy in describing the vapor pressure curve in the range of $T_r = 0.7$ to 1.0 because the curve is predicted with the aid of two data points: at the critical point where $P_r = 1.0$ and at $T_r = 0.7$ where $P_r = 10^{-(1+\omega)}$. Therefore,

Table 3
Average absolute percentage (AAD%) in the prediction of the hydrocarbon vapor pressures from the triple point to the critical point from this work

PR ^a	SV ^b	This work	Temperature range
12.08	8.21	3.28	Triple to critical point
^a Peng–Robinson, ^b Stryjek–Vera			

similar accuracy in vapor pressure predictions is expected from this work, and the work of Peng and Robinson, and Stryjek and Vera in the temperature range $T_r = 0.7$ to 1.0. Within this temperature range, all the methods predict vapor pressures within the experimental error. The new equation generally predicts vapor pressures of less than 1% between reduced temperatures of 0.6 and 1.0, and of about 1.2% for reduced temperatures between 0.5 and 1.0 (note that the reduced temperature value of 0.5 is close to the reduced triple points of argon and methane, being 0.5553 and 0.4758, respectively). The new equation is most reliable for reduced temperatures greater than 0.5 for both light and heavy hydrocarbons, while the PR and PRSV equations are most reliable for reduced temperatures greater than 0.7 and 0.6, respectively, for light hydrocarbons only.

Since the α expression is derived from the vapor pressure data, using the same expression beyond the critical temperature represents extrapolation into an unknown region. In a parallel work (Twu et al., 1994b), we fitted the alpha values of hydrogen and methane in the supercritical region to reproduce the Henry's constants for these solutes in hydrocarbon liquids. In this work, we have modified the $\alpha^{(0)}$ and $\alpha^{(1)}$ constants given by Eqs. (11) and (12) to approximate these values in the supercritical regions when $\omega = -0.218$ (hydrogen) and $\omega = 0.001$ (methane) are used:

$$\alpha^{(0)} = T_r^{-0.792615} e^{0.401219(1 - T_r - 0.992615)} \quad (13)$$

$$\alpha^{(1)} = T_r^{-1.98471} e^{0.024953(1 - T_r - 0.98471)} \quad (14)$$

In addition to approximating the hydrogen and methane alpha values, maintaining the continuity of the prediction of the properties at the critical point is important. Eqs. (11) and (13) and Eqs. (12) and (14) are matching fits which are smooth in slope (first derivative) and curvature (second derivative) at the critical point, to ensure that the derived enthalpy departure and heat capacity properties are both smooth at the critical point. This choice of $\alpha^{(0)}$ and $\alpha^{(1)}$ in the supercritical region has the added benefit of preventing α from approaching a negative value for any reasonable acentric factor at any supercritical temperature.

4. Estimation of the acentric factor

Most oil and gas processing operations require the estimation of phase equilibria. Proper characterization of heavy petroleum fractions is a major problem. Cubic equations of state are

often applied to high molecular weight petroleum fractions. The key issue in the characterization of heavy petroleum fractions for the application of an equation of state is the selection of an internally consistent method to represent the vapor pressure.

When a CEOS is applied to either defined components or pseudo-petroleum fractions, the acentric factor is often input as the third parameter for predicting the phase behavior. While DIPPR (Dabert and Danner, 1990) lists values of the acentric factor, ω , for more than 1000 defined components, the values of ω for petroleum fractions are not available. Even for defined compounds, there are many instances when experimentally determined acentric factor values are not available. For example, the vapor pressure may not have been measured at $T_r = 0.7$ or the critical constants may simply not be available. In such circumstances, the acentric factor cannot be calculated and, consequently, estimation methods for the acentric factor must be used. While many estimation methods have been proposed, there are two practical ways to estimate ω from a single vapor pressure point.

One method is to use a generalized vapor pressure equation to derive ω (Twu et al., 1994a). The equation of state will be unable to predict the vapor pressure to any greater accuracy than the selected generalized correlation. The other method is to solve a CEOS for α , using an α form that depends only on ω . Although estimation of ω from a generalized vapor pressure equation is relatively simple and can give good accuracy, it is recommended that a CEOS method be used to compute ω for internal consistency if it is to be used in CEOS calculations. Using a CEOS to obtain ω requires not only the calculation of vapor and liquid fugacities at the relevant temperature, but also the choice of a proper temperature-dependent alpha function. Therefore, if Soave's widely used alpha function is used in the CEOS, higher accuracy can generally be achieved using the vapor pressure correlation method to estimate ω , since Soave's alpha function does not have the correct temperature-dependence at low temperatures. The conventional characterization parameters used for many years in the petroleum refining industry are the normal boiling point (NBP) and the specific gravity (SG); therefore, most literature methods for estimating the acentric factor of a petroleum fraction use NBP and SG. A simple and practical way to estimate ω is to first estimate the critical temperature and critical pressure by using NBP and SG from this type of correlation. The estimated critical temperature and pressure, which are crucial to the phase behavior calculations, depend on the correlation chosen. The correlation proposed by Twu (1984), which is currently widely used in refining industries, is recommended by Vougaris et al. (1991) for estimating the critical temperature and pressure of pure compounds, petroleum fractions, and coal liquid fractions. Using the Twu correlation for calculation of the critical temperature and pressure to determine T_r and P_r , ω can then be determined from the NBP point using the new CEOS, Eqs. (1), (4), (9), (11), and (12). This will provide a consistent accurate approach for predicting the vapor pressure of heavy hydrocarbons using an equation of state.

5. Conclusion

A modified Peng–Robinson equation of state is developed. The use of a new generalized alpha function has allowed the extension of a cubic equation of state to lower reduced temperatures and heavy hydrocarbons. This paper describes a method of analytically represent-

ing the alpha function. The new CEOS accurately represents the vapor pressure as a linear function of the acentric factor over the entire range of temperatures for light as well as heavy hydrocarbons. We believe that the improvement in the reproduction of the pure component vapor pressure should result in smaller and less temperature-dependent binary interaction parameters for hydrocarbon systems.

List of symbols

a, b	Peng–Robinson equation of state parameters
L, M, N	parameters in the α function
P	pressure
R	gas constant
T	temperature
v	molar volume

Greek letters

α	alpha function defined in Eq. (4)
ω	acentric factor defined at $T_r = 0.7$

Subscripts

c	critical property
r	reduced property

Superscripts

(0)	reference fluid property ($\omega = 0.0$)
(1)	reference fluid property ($\omega = 1.0$)

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