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A new generalized alpha function for a cubic equation of state Part 2. Redlich–Kwong equation

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Abstract

The approach described in the previous paper (Twu, C.H., Coon, J.E. and Cunningham, J.R., 1994a. A new generalized alpha function for a cubic equation of state. Part 1. Peng–Robinson equation. Fluid Phase Equilibria, 105: 49–59) is applied to the Redlich–Kwong cubic equation of state (RK CEOS) to develop a new generalized alpha function for this equation. The new generalized alpha function for the RK CEOS reproduces the vapor pressure for hydrocarbons from the triple point to the critical point with almost identical accuracy to the generalized alpha function used for the Peng–Robinson CEOS in the previous paper.

This indicates that the approach developed should be a general one, applicable to any cubic equation of state. The alpha function has been generalized in terms of the reduced temperature and acentric factor, so it can be used for any hydrocarbons and petroleum fractions, with no additional characterization to the standard methods required (Twu, 1984). The new alpha function is more appropriate for the RK CEOS than Soave's alpha function, which has been widely used in phase behavior calculations in the petroleum production and refinery industries over the last twenty years.

Keywords: Theory; Equations of state; Methods of calculation

1. Introduction

From the various cubic equations of state and associated procedures for parameter evaluation, two have acquired wide popularity: the Soave–Redlich–Kwong (Soave, 1972) and the Peng–Robinson (Peng and Robinson, 1976) procedures. Although they employ different two-parameter equations of state, the treatment of the parameters is identical in both cases. The

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Peng–Robinson equation of state was modified in the previous paper. The modified Redlich–Kwong equation of state is discussed below.

The first cubic equation of state (CEOS) to be successfully applied to the calculation of thermodynamic properties in the vapor phase was proposed by Redlich and Kwong (RK) (1949), and is given below:

$$P = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)} \tag{1}$$

The success of the RK CEOS has stimulated numerous researchers to propose various methods for improving the equation by changing the alpha function or the volume function, or by improving the mixing rule (Soave, 1972; Peng and Robinson, 1976; Twu et al., 1991; Twu et al., 1992).

As indicated by Twu et al. (1991), a proper temperature-dependent alpha function is essential for the reproduction of vapor pressures. Wilson (1964) was the first to introduce a general form of the temperature dependence of the "a" parameter in the RK CEOS:

$$a(T) = \alpha(T)a(T_c) \tag{2}$$

where $a(T_c)$ is the value of a at the critical point. Wilson (1966) expressed $\alpha(T)$ as a function of the reduced temperature, $T_r = T/T_c$, and the acentric factor, ω, as follows:

$$\alpha = [T_r + (1.57 + 1.62\omega)(1 - T_r)] \tag{3}$$

The temperature dependent $\alpha(T)$ function expressed in Eq. (3) is not suitable for the reproduction of vapor pressures. Therefore, Wilson's function never became popular in CEOS applications. A function that gained widespread popularity was proposed by Soave (1972) as an equation of the form

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 \tag{4}$$

The m parameter is obtained by forcing the equation to reproduce the vapor pressure for non-polar compounds at $T_r = 0.7$ and is correlated as a function of ω:

$$m = 0.480 + 1.574\omega - 0.175\omega^2 \tag{5}$$

Owing to its reasonable accuracy and simplicity, Soave's type of alpha function has since been used by many investigators, the application of Peng and Robinson (1976) being one of the most well known examples.

Soave's development of Eqs. (4) and (5) represents significant progress in the application of a CEOS. The resulting $\alpha(T)$ of Soave (1972), as a function of the reduced temperature and the acentric factor, adequately correlates the vapor pressures of hydrocarbons at high reduced temperatures. To improve the temperature dependence of $\alpha(T)$ at low reduced temperatures, Harmens and Knapp (1980) added one more term to Eq. (4):

$$\alpha = \left[1 + A(1 - T_r^{0.5}) - B\left(1 - \frac{1}{T_r}\right)\right]^2 \tag{6}$$

However, Harmens and Knapp were unable to generalize their alpha function using one unique set of parameters. Several sets of parameters were given as functions of different ranges of the

acentric factor and reduced temperature. As a result, a CEOS using the $\alpha(T)$ function of Harmens and Knapp has discontinuity problems in the temperature derivative thermodynamic properties.

Because the Soave modification of the Redlich–Kwong equation of state has been very successful in correlating the phase behavior of multicomponent systems containing non-polar and slightly polar compounds, the API Technical Data Book Procedure 8D1.1 (1987) adopted it for hydrocarbon–non-hydrocarbon vapor–liquid equilibria calculations, and Procedure 3C1.1 adopted it for calculating the vapor–liquid equilibria of petroleum fractions. However, separate sets of $\alpha(T)$ parameters as functions of the acentric factor and reduced temperature, instead of one unique set of parameters, are assigned to different types of petroleum fractions. The calculated vapor pressures tend to diverge from the experimental ones at lower reduced temperatures (Soave, 1993), so Soave made another attempt at improving the treatment of heavy hydrocarbons by the original Soave–Redlich–Kwong (Soave, 1972) CEOS. Soave (1993) rewrote Eq. (4), after some manipulation, as

$$\alpha = 1 + m(1 - T_r) + n(1 - T_r^{0.5})^2 \tag{7}$$

where m and n are obtained by correlating the vapor pressure values generated by the Lee–Kesler (Lee and Kesler, 1975) equation evenly in the T_r and ω ranges, and are given as

$$m = 0.484 + 1.515\omega - 0.44\omega^2 \tag{8}$$

$$n = 2.756m - 0.700 \tag{9}$$

As pointed out by Twu et al. (1994), the Lee–Kesler form of the Pitzer equation generally predicts accurate vapor pressures between the normal boiling point and the critical point, but its error increases rapidly at low reduced temperatures. The methodology of using vapor pressure values predicted by the Lee–Kesler equation to generate the alpha function actually defeated Soave's purpose of improving the vapor pressure predictions for heavy hydrocarbons. Because of this, the accuracy in predicting vapor pressures using Eqs. (7)–(9) in the RK CEOS is actually worse than that using Eqs. (4) and (5).

Although Soave's original alpha function was found to be incorrect at supercritical reduced temperatures as it does not always decrease monotonically, it will not predict negative alpha values as does Soave's new alpha function (Eqs. (7)–(9)). The Soave (1993) version is worse in the supercritical region than the original Soave (1972) version.

Numerous investigators have tried to improve Soave's alpha function by either altering the numbers or adding extra terms. As long as the same type of alpha function and the same approach are applied, the inherent weakness of the approach will not be overcome and the results from the CEOS will be either equivalent to or worse than those from Soave's original generalized alpha function. To improve the application of the CEOS to hydrocarbons and petroleum fractions, a new approach must be developed to derive the generalized alpha function for the proper representation of hydrocarbon vapor pressures from the triple point to the critical point. This investigation concerns the generalization of the temperature-dependent alpha function for the Redlich–Kwong equation of state, as applied to both light and heavy hydrocarbons.

2. A modified Redlich–Kwong cubic equation of state

The new equation of state has the same form as that proposed by Redlich and Kwong (1949), except that the term $a/T^{0.5}$ has been replaced with a generalized temperature-dependent function, $a(T)$, as pioneered by Wilson (1964):

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{10}$$

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

$$a(T_c) = 0.42748023354 R^2 T_c^2 / P_c \tag{11}$$

$$b = 0.086640349965 R T_c / P_c \tag{12}$$

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 is calculated from

$$a(T) = \alpha(T) a(T_c) \tag{13}$$

As shown in the previous paper, the generalized alpha function can be expressed as a function of two variables, the reduced temperature and acentric factor:

$$\alpha = \alpha(T_r, \omega) \tag{14}$$

The alpha function is generalized as

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \tag{15}$$

The same procedures used in the previous paper are applied to derive the values of $\alpha^{(0)}$ and $\alpha^{(1)}$ in Eq. (15) for the Redlich–Kwong equation of state. A brief description of the steps is given below.

(1) Derive alpha as a function of the temperature for each individual compound using the following alpha function:

$$\alpha = T_r^{N(M-1)} e^{L(1 - T_r^{NM})} \tag{16}$$

All the critical constants and vapor pressure data correlations from the triple point to the critical point are from DIPPR (Daubert and Danner, 1990). The values of L, M, and N obtained for the individual components are listed in Table 1.

(2) The α value of 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. The acentric factors used were computed from the DIPPR vapor pressure equation for internal consistency. The dependence of α on ω for a number of reduced isotherms is illustrated in Fig. 1. Straight lines derived from the RK CEOS are observed for α vs. ω plots in all regions. Similar results were achieved for the PR CEOS. This gives further verification that the approach developed here is general for any CEOS.

(3) 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 shows the dependence of $\alpha^{(0)}$ and $\alpha^{(1)}$ on T_r.

Table 1
The alpha parameters, L, M, and N, used in Eq. (16) for individual components

Component	T_c (K)	P_c (bar)	L	M	N
Argon	150.86	48.98	0.066152	0.929755	4.00972
Methane	190.58	46.04	0.106750	0.920161	3.09674
Ethane	305.42	48.80	0.261408	0.880773	1.89101
Propane	369.82	42.49	0.299207	0.870280	1.91998
n-Butane	425.17	37.97	0.308201	0.859571	2.00890
n-Pentane	469.65	33.69	0.305259	0.835681	2.08969
n-Hexane	507.85	30.31	0.128223	0.893666	4.88241
n-Heptane	540.26	27.36	0.206521	0.852664	3.32097
n-Octane	568.83	24.86	0.363345	0.825314	2.31282
n-Nonane	595.65	23.06	1.207950	1.013030	0.93111
n-Decane	618.45	21.23	0.316547	0.828468	2.90395
n-Undecane	638.76	19.66	0.275253	0.832595	3.40495
n-Dodecane	658.20	18.24	0.388200	0.818512	2.76409
n-Tridecane	675.80	17.23	0.473713	0.831460	2.58227
n-Tetradecane	692.40	16.21	0.271252	0.829926	3.92592
n-Pentadecane	706.80	15.20	0.265497	0.830649	4.16388
n-Hexadecane	720.60	14.19	0.360272	0.821583	3.50659
n-Heptdecane	733.37	13.17	0.174453	0.867959	6.57737
n-Octadecane	745.26	12.14	0.454677	0.800025	2.98071
n-Nonadecane	755.93	11.17	0.497353	0.789706	2.78549
Eicosane	767.04	10.40	1.949590	1.180080	0.78281
Cyclohexane	553.58	40.73	0.151079	0.865944	3.17613
Benzene	562.16	48.98	0.106109	0.890646	4.31730

(4) The final step is to correlate the tabulated data of (T_r, $\alpha^{(0)}$) and (T_r, $\alpha^{(1)}$) using Eq. (16) as follows:

$$\alpha^{(0)} = T_r^{-0.201158} e^{0.141599(1 - T_r^{2.29528})} \tag{17}$$

$$\alpha^{(1)} = T_r^{-0.660145} e^{0.500315(1 - T_r^{2.63165})} \tag{18}$$

The constants in Eqs. (17) and (18) are computed from the values of the L, M, and N parameters, which are listed in Table 2, according to Eq. (16). $\alpha^{(0)}$ and $\alpha^{(1)}$ in Eqs. (17) and (18)

Table 2
The values of the L, M, and N parameters used in the generalized alpha correlations, Eqs. (17) and (18) for subcritical conditions and Eqs. (19) and (20) for supercritical conditions, according to Eq. (16)

Alpha parameter	$T_r \leq 1$		$T_r > 1$	
	$\alpha^{(0)}$	$\alpha^{(1)}$	$\alpha^{(0)}$	$\alpha^{(1)}$
L	0.141599	0.500315	0.441411	0.032580
M	0.919422	0.799457	6.500018	1.289098
N	2.496441	3.291790	−0.200000	−8.000000

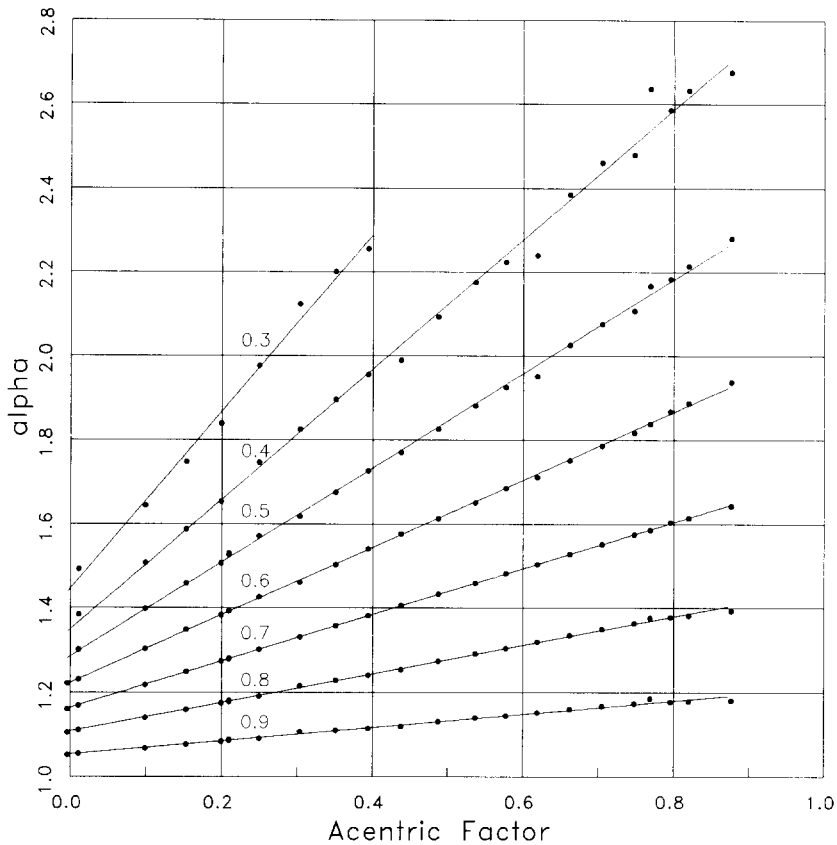

Fig. 1. Dependence of α on the acentric factor at several reduced temperatures: 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9.

are made consistent with the definition of the acentric factor at $\omega = 0$ and $\omega = 1$, respectively. The solid lines in Fig. 2 are from Eqs. (17) and (18), and fit the data points almost exactly.

For the supercritical regions, Eqs. (19) and (20) are recommended. The same methodology as in our previous work was applied. We used the modified RK CEOS to fit the alpha functions of hydrogen and methane in the supercritical region to reproduce the Henry's constants for these solutes in hydrocarbon liquids. We modified the $\alpha^{(0)}$ and $\alpha^{(1)}$ constants given by Eqs. (17) and (18) to approximate these values in the supercritical regions when $\omega = -0.218$ (hydrogen) and $\omega = 0.001$ (methane) are used:

$$\alpha^{(0)} = T_r^{-1.10000} e^{0.441411(1 - T_r^{-1.30000})} \tag{19}$$

$$\alpha^{(1)} = T_r^{-2.31278} e^{0.032580(1 - T_r^{-10.3128})} \tag{20}$$

The continuity of the prediction of the properties at the critical point is maintained by making sure that the departure from the derived enthalpy and heat capacity properties (first and second derivatives with respect to temperature) are both smooth at the critical point.

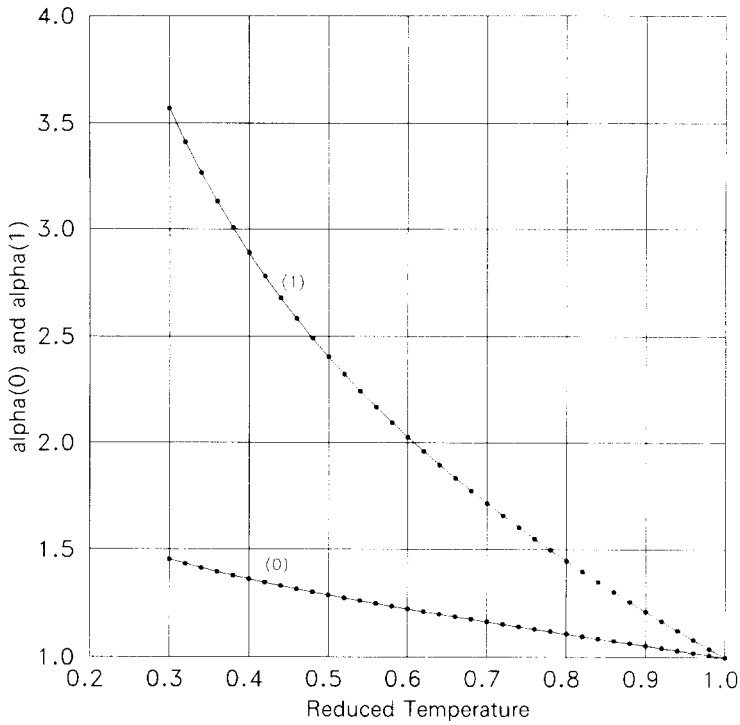

Fig. 2. Dependence of $\alpha^{(0)}$ and $\alpha^{(1)}$ on the reduced temperature: points are derived from DIPPR data and solid lines are from this work.

3. Results and conclusion

Generalized alpha functions in the subcritical and supercritical regions have been obtained for the Redlich–Kwong equation of state in terms of the reduced temperature and acentric factor. The deviations in the vapor pressure predictions for hydrocarbons from the triple point to the critical point resulting from the new generalized alpha function used with the RK CEOS are essentially identical to that obtained with the generalized alpha function used with the PR CEOS in the previous paper. The average absolute percentage deviation (AAD%) over all the vapor pressure points from the triple point to the critical point is 3.37% from the modified RK CEOS in this work, compared with 3.28% from the modified PR CEOS in our previous work. These results indicate that the prediction of the temperature-dependent pure component properties from a CEOS is primarily controlled by the functional form of alpha, and not by the CEOS itself. Similar to the results obtained from the modified Peng–Robinson (PR) CEOS in the previous work, the modified RK CEOS predicts an AAD% of the vapor pressure of less than 1% for reduced temperatures between 0.6 and 1.0, and of about 1.2% for reduced temperatures between 0.5 and 1.0. The results indicate that both the modified equations of state should predict the vapor pressures equally well. Because the correct representation of the vapor pressure is the primary requirement for vapor–liquid equilibrium calculations, the modified Redlich–Kwong and Peng–Robinson cubic equations of state are expected to be equally effective in correlating the phase equilibrium of systems containing hydrocarbons.

List of symbols

a, b	Redlich–Kwong 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. (2)
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 ($\omega = 1.0$)

References

API Technical Data Book — Petroleum Refining., 1987. Daubert, T.E. and Danner, R.P (Eds.), 4th edn. American Petroleum Institute, Washington, DC.

Daubert, T.E. and Danner, R.P., 1990. Data Compilation — Physical and Thermodynamic Properties of Pure Compounds. Taylor and Francis (extant).

Harmens, A. and Knapp, K., 1980. Three-parameter cubic equation of state for normal substances. Ind. Eng. Chem., Fundam., 19(3): 291–292.

Lee, B.I. and Kesler, M.G., 1975. A generalized thermodynamic correlation based on three-parameter corresponding states. AIChE J., 21(3): 510–527.

Peng, D.Y. and Robinson, D.B., 1976. A new two-constant equation of state. Ind. Eng. Chem., Fundam., 15: 58–64.

Redlich, O. and Kwong, N.S., 1949. On the thermodynamics of solutions. V: An equation of state. Fugacities of gaseous solutions. Chem. Rev., 44: 233–244.

Soave, G., 1972. Equilibrium constants from a modified Redlich–Kwong equation of state. Chem. Eng. Sci., 27: 1197–1203.

Soave, G., 1993. Improving the treatment of heavy hydrocarbons by the SRK EOS. Fluid Phase Equilibria, 84: 339–342.

Twu, C.H., 1984. An internally consistent correlation for predicting the critical properties and molecular weights of petroleum and coal-tar liquids. Fluid Phase Equilibria, 16: 137–150.

Twu, C.H., Bluck, D., Cunningham, J.R. and Coon, J.E., 1991. A cubic equation of state with a new alpha function and a new mixing rule. Fluid Phase Equilibria, 69: 33–50.

Twu, C.H., Coon, J.E. and Cunningham, J.R., 1992. A new cubic equation of state. Fluid Phase Equilibria, 75: 65–79.

Twu, C.H., Coon, J.E. and Cunningham, J.R., 1994. A generalized vapor pressure equation for heavy hydrocarbons. Fluid Phase Equilibria, 96: 19–31.

Wilson, G.M., 1964. Vapor–liquid equilibria correlated by means of a modified Redlich–Kwong equation of state. Adv. Cryog. Eng., 9: 168–176.

Wilson, G.M., 1966. Calculation of enthalpy data from a modified Redlich–Kwong equation of state. Adv. Cryog. Eng., 11: 392–400.