A Modified Redlich-Kwong Equation for Phase Equilibrium and Enthalpy Calculations

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The great success of the Soave (1972) equation of state (EOS) or the Peng-Robinson (1976) EOS in vapor-liquid-phase equilibria is generally attributed to its ability to predict the vapor pressures of pure fluids with good accuracy. The Soave form chosen for the temperature and acentric factor dependence of the parameter a is credited with this success. Peng and Robinson retained the same form in their EOS, but redetermined the constants. These two EOSs have become the hydrocarbon industry's favorites for calculating phase equilibria and thermal properties, because of their simplicity and accuracy. They have been also used, though with less frequency, for estimating vapor-phase compressibility factors.

The Soave EOS is generally better than the Peng-Robinson for representing the density of simple fluids, while the latter is markedly better than the former for heavier hydrocarbon gases. In this work, a simplified version of the Fuller EOS (1976) was chosen as a compromise after investigating several other possibilities, as shown in the Appendix.

$$P=\frac{RT}{V-b}-\frac{a}{V(V+1.5b)} \tag{1}$$

where

$$a=0.43164\,\frac{(RT_c)^2}{P_c}\,\alpha \tag{2}$$

$$b=0.076349\,\frac{RT_c}{P_c} \tag{3}$$

As shown in Table 1, this EOS gives the density within a few percent of the Peng-Robinson result for the liquid and the critical isotherm, and about a half-way between the Soave and Peng-Robinson predictions for the vapor density.

α Function

The α functions in literature agree well for $T_r < 1$, but vary significantly above $T_r = 1$; while some become negative, others go through a minimum or asymptotically approach zero. Our primary goal here is to represent α as a monotonic function of T_r as well as a linear function of ω, as was done by Wilson (1966), as opposed to the 4th-order polynomials in the original Soave function. The linear relationship of α with ω should, once established, provide a better means of extrapolating this function to heavy hydrocarbons and petroleum fractions. The following dual α functions were chosen for this purpose.

$$\alpha=1+(1-\sqrt{T_r})\left(c_1+c_2\omega+\frac{c_3+c_4\omega}{\sqrt{T_r}}\right)\quad \text{for } T_r\le 1 \tag{4}$$

and

$$\alpha'=\exp\left[(1-\sqrt{T_r})\left(c_1'+c_2'\omega+\frac{c_3'+c_4'\omega}{\sqrt{T_r}}\right)\right]\text{for } T_r>1 \tag{5}$$

In Eq. 5, α' is not linear with ω, but this does not pose a serious problem because an extrapolation to high ω is mostly needed for Eq. 4, as heavy (high ω) components remain in subcritical state in most hydrocarbon processing. The partial derivatives of Eqs. 4 and 5 with respect to T_r are:

$$\left(\frac{\partial\alpha}{\partial T_r}\right)_\omega=\frac{1}{2}\,[c_1+c_3+\omega(c_2+c_4)]\quad \text{at } T_r=1 \tag{6}$$

$$\left(\frac{\partial\alpha'}{\partial T_r}\right)_\omega=-\frac{1}{2}\,[c_1'+c_3'+\omega(c_2'+c_4')]\quad \text{at } T_r=1 \tag{7}$$

Table 1. Compressibility Factor Comparison

				Compressibility Factor		
Phase	Tr	Pr	ω	SRK	P-R	Eq. 1
Liquid	0.7	0.2	0	0.034	0.031	0.032
	0.7	1.0	0	0.171	0.152	0.155
	0.7	10	0	1.533	1.371	1.381
	0.7	0.2	0.3	0.033	0.029	0.030
	0.7	1.0	0.3	0.162	0.144	0.147
	0.7	10.	0.3	1.500	1.339	1.372
Vapor	0.95	0.5	0	0.764	0.745	0.756
	1.0	0.2	0	0.929	0.921	0.926
	1.0	10.0	0	1.250	1.120	1.140

Table 2. Vapor Pressure Comparison

Hydrocarbon	Temp.	No. of Pts.	Avg. Abs. % Dev. SRK	P-R	Eq. 1
C_1 – C_{10}	$T>$BP	314	1.80	0.71	0.93
	$T<$BP	270	3.08	3.59	1.13
	All T	584	2.39	2.04	1.09
C_{11} – C_{18}	$T>$BP	110	3.28	3.89	2.06
	$T<$BP	410	3.15	4.55	2.33
	All T	520	3.18	4.41	2.27
Octacosane	All T	37	2.64	31.96	2.04

These two equations are identical for all values of the acentric factor, that is, Eqs. 4 and 5 are continuous at $T_r = 1$, as long as $(c_1 + c_3) = (c_1' + c_3')$ and $(c_2 + c_4) = (c_2' + c_4')$. This means that the four constants in Eq. 4 may be determined solely from vapor pressure data, and two of the constants in Eq. 5 may be optimized from binary mixture vapor-liquid equilibrium data above the critical temperature of the light component, with no loss of the continuity at $T_r = 1$. This gives an important additional degree of freedom for improving the K-value predictions for supercritical components.

The constants in Eq. 4 were determined from the vapor pressure data methane through octadecane taken from McGarry (1983) and Daubert (1990a) using the critical constants from Reid et al. (1987) as follows:

$$\alpha = 1 + \beta(1 - \sqrt{T_r}) \quad \text{for } T_r \leq 1 \tag{8}$$

where

$$\beta = 0.965 + \omega\left(1.45 + \frac{1.6}{\sqrt{T_r}}\right)$$

To determine the optimal constants for Eq. 5, one would need experimental VLE data in the supercritical region for a series of supercritical components in all possible binary mixtures and the binary interaction coefficients, k_{ij}, obtained from the subcritical VLE data using only Eq. 4. To explore possible improvement of the K-value prediction for the supercritical components, we used a limited number of strategically selected binary mixtures with methane through n-pentane as the light component for which all k_{ij}'s were obtained from the subcritical VLE data alone, to optimize only c_1' by floating c_3' and keeping c_2' and c_4' the same as c_2 and c_4, respectively. This exercise alone improved both the bubble pressure and K-value predictions, but the tentatively determined values of c_1' and c_3' are not reported here. Instead, it is suggested that the same β be used for Eq. 9 as well, until a full set of optimized values of c_1' and c_2' are determined.

Table 3. Enthalpy Deviation Comparison

Hydrocarbon	Temp.	No. of Pts.	Avg. Abs. Dev., J/g SRK	P-R	Eq. 1
Pure	$T>$BP	1,315	5.6	5.1	5.1
	$T<$BP	126	5.6	8.4	5.1
Mixture	$T>$BP	5,896	5.6	5.9	5.6
	$T<$BP	597	7.2	8.8	6.3

$$\alpha' = \exp[\beta(1 - \sqrt{T_r})] \quad \text{for } T_r > 1 \tag{9}$$

The Soave and Peng-Robinson EOSs and Eq. 1 were first compared in Table 2 for vapor pressures and in Table 3 for enthalpies.

Conclusions

The linear representation of α function with ω appears to be well justified; the use of 4th-order polynomials appears to be superfluous. The dual α functions give the flexibility to fit the K values in the supercritical region with improved accuracy. Equations 4 and 5 may be easily extended to nonhydrocarbons.

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Notation

a, b = equation of state parameters
c, c' = equation constants
P = pressure
R = gas constant
T = temperature
V = molar volume
Z = compressibility factor

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Appendix

The following EOS is a generic form for a group of cubic EOS such as van der Waals, Redlich-Kwong, Peng-Robinson, Eq. 1, and so on. But it is not as generic as the Abbott's expression.

$$P = \frac{RT}{V - b} - \frac{a}{(V + mb)(V + nb)} \tag{A1}$$

The parameters a and b may be determined by comparing the cubic form of this equation with the expanded form of $(V - V_c)^3 = 0$ to obtain the following expressions.

$$Z_c = 1/[3 + (m + n - 1)h]$$

$$h = 1/[1 + (s-q)^{1/3} + (-s-q)^{1/3}]$$

$$s = (p^3 + q^2)^{1/2}$$

where

$$p = -(m + n + mn + 1)$$

and

$$q = p[1 + 0.5(m+n)]$$

$$\Omega_a = 3Z_c^2 + (m+n)\Omega_b + (m+n-mn)\Omega_b^2$$

where

$$\Omega_b = hZ_c$$

For example:

	m	n	Ω_a	Ω_b	Z_c
vdW EOS	0	0	0.42188	0.125	0.375
R-K EOS	0	1	0.42748	0.086640	0.33333
EQN 1	0	1.5	0.43164	0.076349	0.32061
P-R EOS	$1-2^{1/2}$	$1+2^{1/2}$	0.45724	0.077796	0.30740
	−0.5	2.5	0.46468	0.080917	0.30636

Thermodynamic functions derived from Eq. 1

$$Z^3 - (1-0.5B)Z^2 + [A - 1.5B(1+B)]Z - AB = 0$$

$$A = \frac{aP}{(RT)^2}; \quad B = \frac{bP}{RT}$$

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}(1-k_{ij}); \quad b = \sum_{i=1}^{n} x_i b_i$$

$$a_i = a_{ci}\alpha; \quad b_i = 0.07635\,\frac{RT_{ci}}{P_{ci}}$$

$$a_{ci} = 0.43164\,\frac{(RT_{ci})^2}{p_{ci}}$$

$$\alpha_i = 1 + \beta_i(1-\sqrt{T_{ri}}) \quad \text{for } T_{ri} \le 1$$

$$\alpha_i = \alpha_i' = \exp(\beta_i(1-\sqrt{T_{ri}})) \quad \text{for } T_{ri} > 1$$

$$\beta_i = 0.965 + \omega\left(1.45 + \frac{1.6}{\sqrt{T_{ri}}}\right)$$

$$\frac{H-H^*}{RT} = Z - 1 - \left(1 - \frac{T}{a}\frac{\partial a}{\partial T}\right) Q$$

$$T\frac{\partial a}{\partial T} = 2T\sum_{i=1}^{n}\sum_{1=j}^{n} x_i x_j \sqrt{a_i}\,\frac{\partial\sqrt{a_j}}{\partial T}(1-k_{ij})$$

$$2T\frac{\partial\sqrt{a_i}}{\partial T} = -\sqrt{a_{ci}}\,\frac{\beta_i'}{\sqrt{\alpha_i}} \quad \text{for } T_{ri} \le 1$$

$$2T\frac{\partial\sqrt{a_i}}{\partial T} = -\sqrt{a_{ci}}\beta_i'\sqrt{\alpha_i'} \quad \text{for } T_{ri} > 1$$

$$\beta_i' = 0.5(\beta - 0.965(1-\sqrt{T_{ri}}))$$

$$Q = \frac{A}{1.5B}\ln\left(1 + \frac{1.5B}{Z}\right)$$

$$\ln\phi_i = -\ln(Z-B) + (Z-1)B_i - (2A_i' - B_i')\,Q$$

$$A_i' = \frac{\sqrt{a_i}}{a}\sum_{j=1}^{n} x_j\sqrt{a_j}(1-k_{ij}); \quad B_i' = \frac{b_i}{b}$$

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