Explicit Phase Equilibrium Calculations from Cubic Equations of State

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Introduction

Equations of state may be used to calculate pure component vapor-liquid equilibrium properties such as vapor pressure, heat of vaporization, liquid density, and vapor density. The standard approach requires coupling the EOS with a phase equilibrium criterion such as free energy, chemical potential, or fugacity. The resulting equations are nonlinear and must be solved by numerical methods.

An alternative approach is applicable to cubic EOS such as the commonly used Soave-Redlich-Kwong and Peng-Robinson equations. Equilibrium properties may be explicitly expressed as power series in reduced temperature or related functions. These results are more convenient than numerical calculations, but are subject to truncation error in many practical situations.

Modifications or alternatives to these power series methods were developed. These included simplified versions of the power series which minimized truncation error, a generalized version of the Antoine equation for vapor pressure, and a new expression for vapor pressure which showed reasonable accuracy over the temperature range from the triple point to the critical point. All results were expressed as universal functions of temperature and the acentric factor. Deviations between these results and the exact equilibrium property predictions from the EOS were illustrated by generalized graphs.

VLE from Cubic Equations of State

Cubic equations of state of the Van der Waals type are widely used in chemical engineering practice because they provide a reasonable balance between accuracy and simplicity. Two common examples are the Soave-Redlich-Kwong [1] and Peng-Robinson [2] equations, shown below as Eqs. (1) and (2),

$$P=\frac{RT}{V-b_{SRK}}-\frac{a_{SRK}(T)}{V(V+b_{SRK})} \qquad (1)$$

$$P=\frac{RT}{V-b_{PR}}-\frac{a_{PR}(T)}{V(V+b_{PR})+b_{PR}(V-b_{PR})} \qquad (2)$$

In these equations, the attractive function $a_{EQ}(T)$ has the form

$$a_{EQ}(T)=a_{c,EQ}[1+f_{EQ}(\omega)(1-T_r^{1/2})]^2 \qquad (3)$$

with the critical value of

$$a_{c,EQ} = \frac{a_{0,EQ} R^2 T_c^2}{P_c} \tag{4}$$

and the acentric factor functions given by

$$f_{SRK}(\omega) = 0.480 + 1.574\omega - 0.176\omega^2 \tag{5}$$

$$f_{PR}(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{6}$$

The occupied volume parameter b is given by

$$b_{EQ} = \frac{b_{0,EQ} R T_c}{P_c} \tag{7}$$

Values of the dimensionless numerical constants in Eqs. (4) and (7) are $a_{0,SRK}$ = 0.42748, $a_{0,PR}$ = 0.45724, $b_{0,SRK}$ = 0.08664, and $b_{0,PR}$ = 0.07780.

Like many equations of state, SRK and PR may be used to calculate vapor pressure and other pure component vapor-liquid equilibrium properties. Doing this requires coupling the EOS with a phase equilibrium criterion such as free energy, chemical potential, or fugacity. Eqs. (8) and (9) give expressions for the pure component fugacity coefficient for SRK and PR.

$$\ln \phi_{SRK} = z - 1 - \ln z - \ln(1-h) - \frac{a_{SRK}}{b_{SRK} RT} \ln(1+h) \tag{8}$$

$$\ln \phi_{PR} = z - 1 - \ln z - \ln(1-h) - \frac{a_{PR}}{2\sqrt{2} b_{PR} RT} \ln \frac{1 + h(1+\sqrt{2})}{1 + h(1-\sqrt{2})} \tag{9}$$

$$z = \frac{PV}{RT} \tag{10}$$

$$h = \frac{b_{EQ}}{V} \tag{11}$$

When an equilibrium state exists, Eq. (1) gives three real roots for volume from SRK. The smallest and largest of these are liquid and vapor volumes, respectively. The fugacity coefficients calculated by Eq. (8) will be equal when the liquid volume is substituted and when the vapor volume is substituted. For PR, Eqs. (2) and (9) are used. A numerical algorithm is required to solve either of these sets of nonlinear equations.

Power Series Methods for Cubic Equation VLE

A formal procedure [3] is available to express results for phase densities and vapor pressure of coexisting liquid and vapor phases as analytic power series in temperature. The approach begins by writing reduced deviation variables for phase densities ($\Delta\rho^L$ and $\Delta\rho^V$) and temperature (ΔT) about the critical point. These variables are defined as

$$\Delta M = M_r - 1 = \frac{M - M_c}{M_c} \tag{12}$$

with M representing either ρ^L, ρ^V, or T. The resulting formal power series are

$$P_r = \sum_{j=0}^{\infty} A_j (\Delta T)^j \tag{13}$$

$$\Delta\rho^L = \sum_{i=1}^{\infty} B_i (-\Delta T)^{i/2} \tag{14}$$

$$\Delta\rho^V = \sum_{i=1}^{\infty} (-1)^i B_i (-\Delta T)^{i/2} \tag{15}$$

After equilibrium constraints are applied to these series, the coefficients A_j and B_i are observed to be functions of the acentric factor function $f_{EQ}(\omega)$ which depend upon the cubic EOS being applied. They are substance-dependent since they contain the acentric factor function. For SRK and PR, A_j is given by a polynomial of degree j in the acentric factor function, B_i is given by a polynomial of degree (i-1) in the acentric factor function for even i, and by a similar polynomial multiplied by the square root of $(1+ f_{EQ}(\omega))$ for odd i. Expressions for these polynomials have been tabulated. [4,5]

The utility of this method stems from the convenience of direct computation of coexisting phase properties without need for auxiliary equilibrium criteria such as fugacities. The weaknesses of the method arise from being based upon a series expansion about the critical point. In practice, the infinite series given by Eqs. (13) to (15) must be truncated. Few terms are required near the critical point, but this is the situation where cubic EOS are least accurate. At moderately high or moderate temperatures, where the equations have reasonable accuracy, many series terms are needed to prevent truncation error. The magnitude of truncation error also depends upon the property (phase density or vapor pressure) and varies with acentric factor. In general, truncation errors are largest for vapor density and smallest for liquid density, they are larger for the PR equation as compared to SRK, and they increase with increasing acentric factor.

Modifications and Alternatives to the Existing Power Series Method for Vapor Pressure

Three approaches were attempted to make the existing method more useful for practical vapor pressure calculations. These were an algebraic rearrangement of the series centered away from the critical point, an alternative series approach based upon a low temperature limit, and a derivation of generalized Antoine vapor pressure functions.

The algebraic approach was designed to minimize truncation error at moderate to moderately high temperatures, where the underlying EOS are reasonably accurate. The strategy was applied to the SRK equation and proceeded in two stages. In the first (recentering) stage, the formal power series of Eq. (13) about the critical point was replaced with a power series expanded about some moderate reduced temperature below the critical point, denoted by the variable T_E for expansion temperature.

$$P_r = \sum_{j=0}^{\infty} A'_j (\Delta T')^j = \sum_{j=0}^{\infty} A'_j (T_r - T_E)^j \qquad (16)$$

In practice, only a finite number of terms were available for Eq. (13). Equating the expressions in Eqs. (13) and (16), using terms up to j = 13, gave a set of algebraic equations which were solved for the new coefficients A_j' in Eq. (16). Since Eq. (16) represented a power series about the temperature T_E, rather than T_c, truncation error for this new series was minimized in the vicinity of T_E. Hence, it was possible to use significantly fewer terms in the new series of Eq. (16) without introducing large truncation errors.

Figure 1 shows truncation error contours at the one percent level for a typical situation with the SRK equation. Terms up to j = 8 were used in the new series, and the expansion temperature T_E was chosen as 0.7. In general, expansion temperatures near T_E = 0.7 resulted in a good balance between errors near the critical temperature and at low temperatures when the new series was truncated. In the example, only for extremely high acentric factors are there noticeable (greater than one percent) truncation errors at high temperatures.

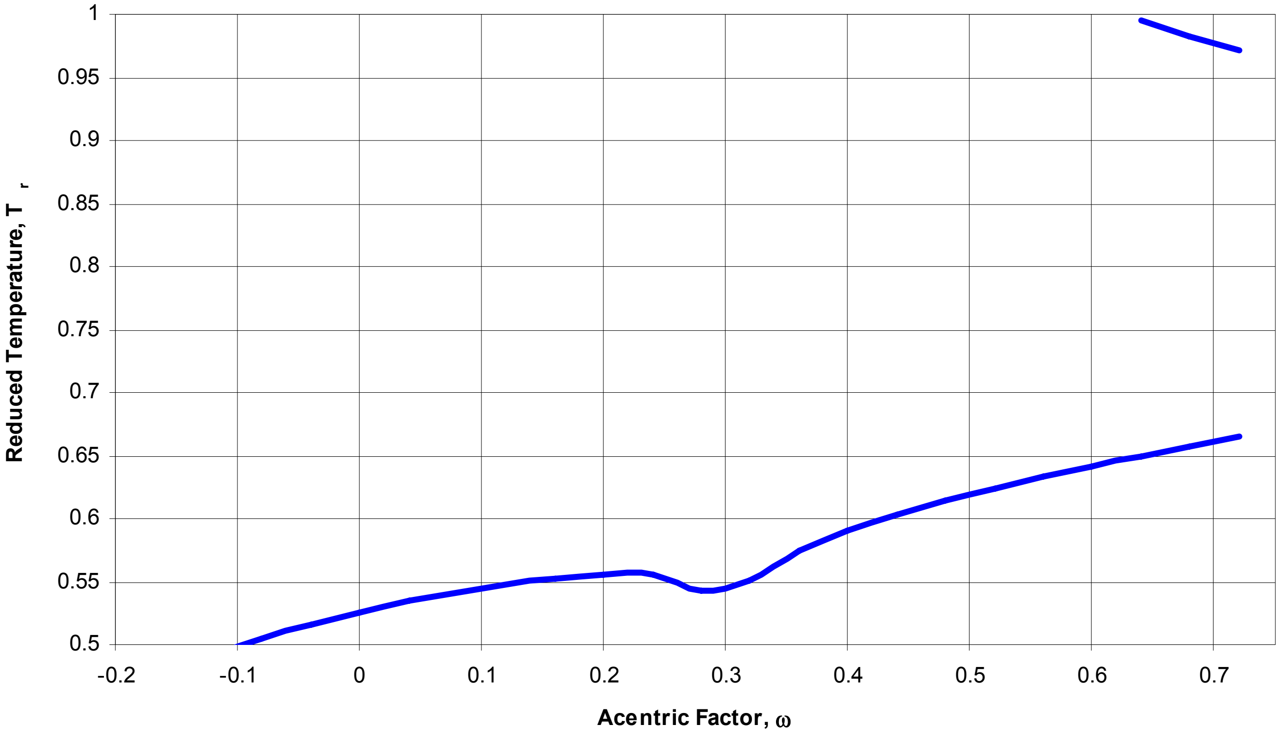

Figure 1. Truncation error contours (1 Percent) for 8 Term Truncated Series, T_E = 0.7.

In the second (error-correcting) stage of the algebraic method, the truncation error near the critical point was minimized by adding one additional term to the series expansion. Theory suggests that the truncation error in a Taylor-type power series is proportional to the next term in the series. For example, in a series truncated at j = 5, the error is expected to be proportional to $(T_r-T_E)^6$. Since the correct result is known at the critical point, the truncation error was easily characterized there using the expression $A'_{j+1}(1-T_E)^{j+1}$.

An example is shown in Figure 2. Here the truncation error for an error-corrected new series, Eq. (16) with j = 5, was compared to the original series with j =13 and also with j = 5. The expansion temperature 0.64 was used, and results were generated for an acentric factor of 0.36. The figure shows that the truncation error for the new series stayed below one percent for all reduced temperatures between 0.58 and 1.0, and never exceeded 0.1 percent above reduced temperature of 0.62. As long as 0.1 percent truncation error is acceptable, this was nearly as good as the original series with j = 13, and a large improvement on the original series with j = 5, for which truncation error exceeded one percent for all reduced temperatures below 0.77.

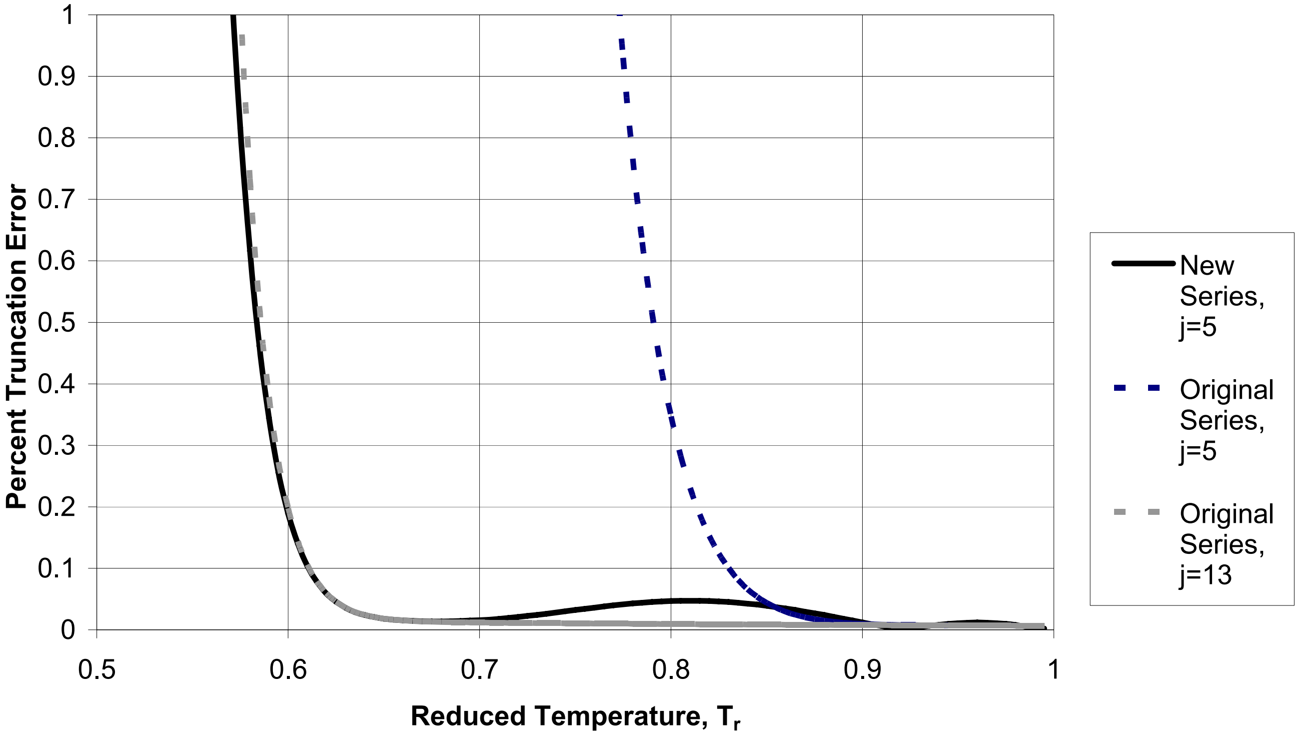

Figure 2. Comparison of Truncation Errors for T_E = 0.64 and ω = 0.36

Work continues on tuning the expansion temperature, number of terms, and error correction procedure for this method.

A second approach worked with the EOS and fugacity relationships in the low temperature limit, as T approached zero. This is an unphysical limit from the standpoint of VLE, as liquid behavior does not persist below the triple point which typically falls near a reduced temperature of 0.3 to 0.4. The strategy was to derive a limiting expression for low temperatures that extrapolated reasonably well to moderate temperatures where physical behavior is represented. In the best case, the existing series about the critical point did not extrapolate accurately below a reduced temperature of approximately 0.58, and even that accuracy required j = 13 in the series expansion for SRK.

For the SRK equation, a relationship between reduced vapor pressure and reduced temperature was found in the mathematical (unphysical) zero temperature limit as follows.

$$\ln P_r = \frac{C_1}{T_r} + \frac{C_2}{T_r^{1/2}} + C_3 + C_4 T_r^{1/2} + C_5 T_r \tag{17}$$

$$C_1 = -\frac{a_{0,SRK}(1+f_{SRK}(\omega))^2 \ln 2}{b_{0,SRK}} \tag{18}$$

$$C_2 = \frac{2a_{0,SRK} f_{SRK}(\omega)(1+f_{SRK}(\omega))\ln 2}{b_{0,SRK}} \tag{19}$$

$$C_3 = \ln\frac{a_{0,SRK}(1+f_{SRK}(\omega))^2}{2b_{0,SRK}} - \frac{a_{0,SRK}(f_{SRK}(\omega))^2 \ln 2}{b_{0,SRK}} - \ln b_{0,SRK} \tag{20}$$

$$C_4 = -\frac{4 f_{SRK}(\omega)}{1+f_{SRK}(\omega)} \tag{21}$$

$$C_5 = -\frac{2b_{0,SRK}}{a_{0,SRK}(1+f_{SRK}(\omega))^2} + \frac{3(f_{SRK}(\omega))^2}{(1+f_{SRK}(\omega))^2} \tag{22}$$

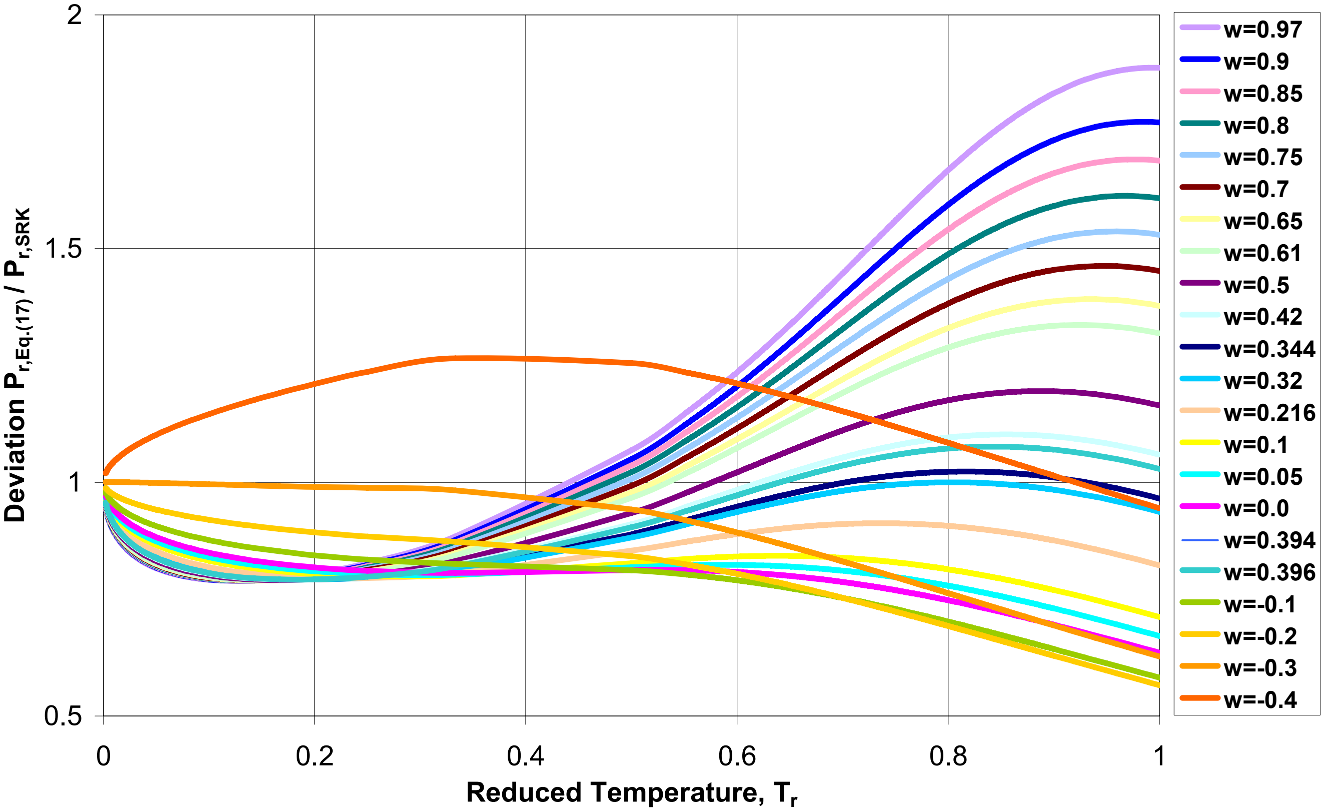

Figure 3. Deviation Ratio between Eq. (17) and Exact SRK Vapor Pressure.

Figure 3 shows results when vapor pressure predicted by Eq. (17) is compared to the exact result from the SRK equation. The curves plotted in Figure 3 represent various acentric factors. Since the coefficients in Eq. (17) were fit in the low temperature limit, the deviation between the predictions and the exact SRK result went to zero in that limit. Behavior at increasing temperatures was interesting. Although no additional corrections were made to the fit of the equation, the zero temperature limit equation was capable of tracking the exact vapor pressure from the SRK equation within an order of magnitude; in fact, within a factor of two, over the entire temperature range from zero to the critical point. This was unlike the behavior observed with the truncated critical point series of Eqs. (13) and (16), where the deviation caused by truncation error increased by polynomial or exponential order away from the critical point.

Work continues on verifying the method and adapting it to use at practical temperatures where VLE is observed.

In the third and final approach for improving the utility of the series method, a generalized form of the Antoine vapor pressure equation was developed. In the traditional Antoine equation, dimensional constants are used to fit vapor pressure data over a temperature range.

$$\ln P = A - \frac{B}{T + C} \tag{23}$$

For the new approach, the Antoine equation was written in reduced variables and the constants were taken as functions of the acentric factor.

$$\ln P_r = A^* - \frac{B^*}{T_r + C^*} \tag{24}$$

Complete results for the functions A^*, B^*, and C^* will be available in a future publication. [6] The method used to determine these functions was a continuous version of least squares regression in which the difference between Eq. (24) and a variation of Eq. (13) was minimized by adjusting parameters within the functions A^*, B^*, and C^*. After an initial regression fit was completed, the results were compared to the exact vapor pressure predictions of the EOS, and the functional parameters were further adjusted by an algebraic and statistical technique.

Table 1. Antoine Constant Functions for the SRK Equation for $0.70 < T_r < 0.84$.

$A^* = 4.4401 + 2.2128f_{SRK}(\omega) - 0.53518f_{SRK}(\omega)^2 + 0.17368f_{SRK}(\omega)^3 - 0.018512f_{SRK}(\omega)^4$
$B^* = 5.0075 + 1.2494f_{SRK}(\omega) - 0.78155f_{SRK}(\omega)^2 + 0.32010f_{SRK}(\omega)^3 - 0.047601f_{SRK}(\omega)^4$
$C^* = 0.124652 - 0.273702f_{SRK}(\omega) + 0.0750076f_{SRK}(\omega)^2 - 0.0137818f_{SRK}(\omega)^3 + 0.00145038f_{SRK}(\omega)^4$

Typical results for the method are shown in Table 1. As is the case with the traditional Antoine equation, the range of accuracy was limited -- in this example to reduced temperatures between 0.70 and 0.84. Figure 4 illustrates the accuracy of the method. Each curve in Figure 4 represents a different acentric factor. Within the specified temperature range ($0.70 < T_r < 0.84$) the vapor pressures predicted by Eq. (24) matched the exact SRK vapor pressures to within less than 0.1 percent deviation.

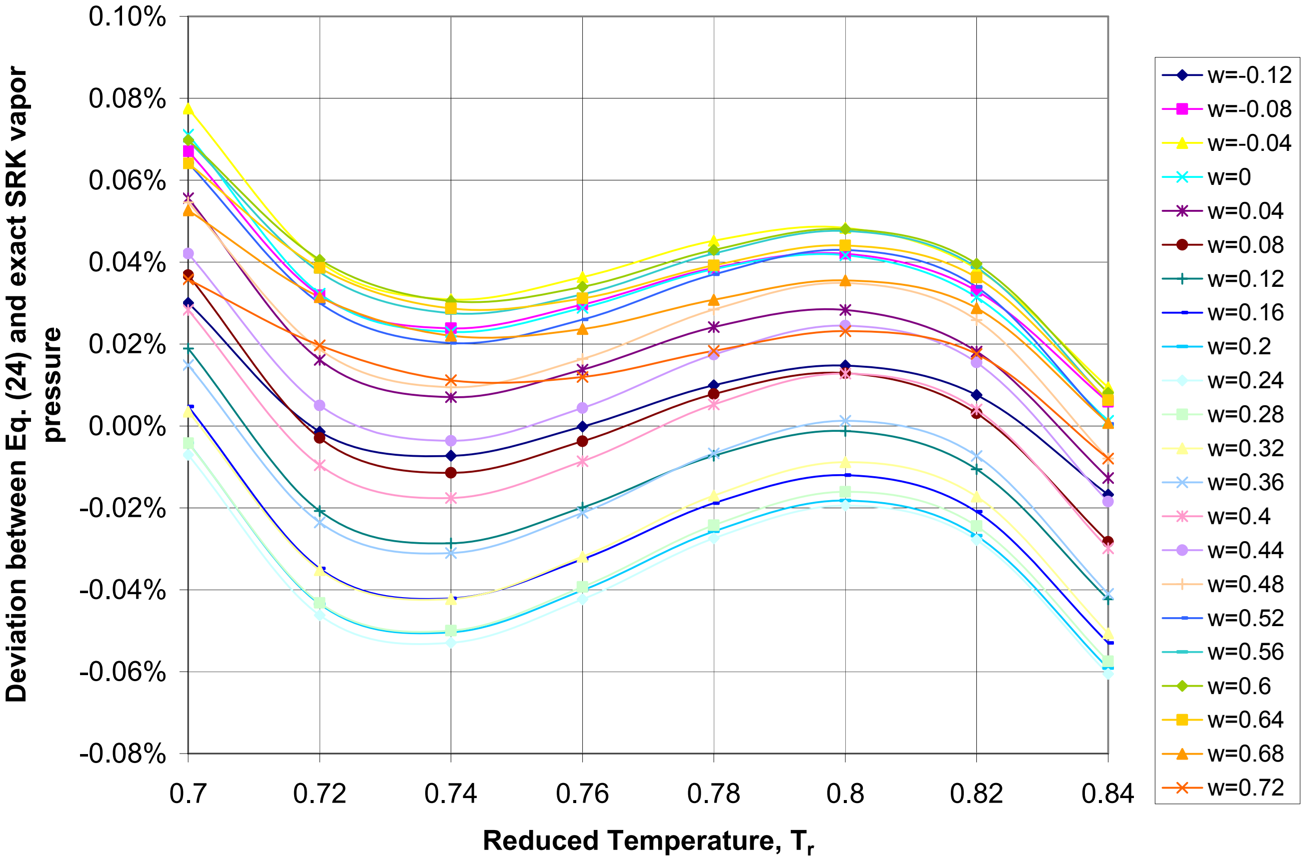

Figure 4. Percentage Deviation between Vapor Pressure Predicted by Generalized Antoine Equation, Eq. (24), and Exact SRK Vapor Pressure for Various Acentric Factors.

Conclusions

Three methods for explicit estimation of vapor pressure from cubic EOS were presented. These approaches were shown to reproduce, with reasonable accuracy, the vapor pressure determined by combining the EOS with a phase equilibrium constraint such as fugacity. These methods also alleviated some of the truncation error problems inherent in previous explicit vapor pressure methods which relied upon power series about the critical point.

Acknowledgements

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Nomenclature

A	Constant in Eq. (23), Antoine vapor pressure equation
A^*	Function of acentric factor in Eq. (24), generalized Antoine vapor pressure equation
A_j	temperature coefficients in Eq. (13) for reduced pressure
A_j'	temperature coefficients in Eq. (16), recentered series for reduced pressure
$a_{EQ}(T)$	energy parameter in attractive term
$a_{c,EQ}$	energy parameter in attractive term at the critical point
$a_{0,EQ}$	dimensionless numerical coefficient of energy parameter
B	Constant in Eq. (23), Antoine vapor pressure equation
B^*	Function of acentric factor in Eq. (24), generalized Antoine vapor pressure equation
B_i	temperature coefficients in Eqs. (14) and (15) for reduced density deviation variables
b_{EQ}	excluded volume parameter in equation of state
$b_{0,EQ}$	dimensionless numerical coefficient of excluded volume parameter
C	Constant in Eq. (23), Antoine vapor pressure equation
C^*	Function of acentric factor in Eq. (24), generalized Antoine vapor pressure equation
C_i	coefficients in Eq. (17), vapor pressure equation at low temperature limit
$f_{EQ}(\omega)$	quadratic function of acentric factor
h	ratio of excluded volume parameter to molar volume
M	general thermodynamic state property (T, ρ^L or ρ^V) in Eq. (12)
P	absolute pressure
R	gas constant
T	absolute temperature
T_E	reduced temperature used for recentered series expansion in Eq. (16)
V	molar volume
z	compressibility

Greek letters

ΔM	reduced deviation variable of state property M (T, ρ^L or ρ^V) defined by $M_r - 1$
$\Delta T'$	reduced temperature deviation variable in Eq. (16), defined by $T_r - T_E$
ρ	molar density
φ_{EQ}	fugacity coefficient for equation of state
ω	acentric factor

Subscripts

c	critical (temperature, pressure, or molar density)
EQ	parameter or coefficient applying to equation of state EQ (SRK or PR)
r	reduced (temperature, pressure, or molar density)

Superscripts

L	liquid (molar density or molar volume)
V	vapor (molar density or molar volume)

References

[1] D.-Y. Peng, D.B. Robinson, Ind. Eng. Chem. Fundam. 15 (1976) 59-64.
[2] G. Soave, Chem. Engng. Sci. 27 (1972) 1197-1203.
[3] J.V. Sengers, J.M.H. Levelt Sengers in: C.A. Croxton (Ed.), Progress in Liquid Physics, Wiley, New York, 1978, pp. 103-174.
[4] C.D. Singley, I.P. Burns, M.J. Misovich, Fluid Phase Equilib. 137 (1997) 99-109.
[5] D.A. Schaich, S.A. Gangloff, M.J. Misovich, manuscript in preparation for Computers and Chemical Engineering. (2005)
[6] A.J. DeDoes, M.D. Goetz, M.J. Misovich, accepted for publication in Chem. Eng. Progr. (2005)