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# Correlations for Direct Calculation of Vapor Pressures from Cubic Equations of State

Jean-Marie Ledanois,\* Erich A. Müller, Coray M. Colina,  
Dosinda González-Mendizabal, Jorge W. Santos, and Claudio Olivera-Fuentes

Thermodynamics (TADiP) Group, Universidad Simón Bolívar, Apartado Postal 89000,  
Caracas 1080, Venezuela

Vapor pressures computed from nine cubic equations of state (EOS's) of the van der Waals form are correlated in corresponding states form using the linear Pitzer principle and a simple temperature function anchored at the critical point. The results strongly suggest that cubic equations of state do not conform to the usually assumed linear dependence of fluid properties on acentric factor. The failure of three-parameter cubic equations of state to predict the exact vapor pressure consistent with a specified acentric factor is analyzed, and new correlations are presented for the characteristic parameter in Soave's cohesion function that minimize this intrinsic error over a wider range of acentric factors. Soave's direct procedure for calculation of vapor pressures from EOS is found to be more accurate than all other approximate methods by at least 1 order of magnitude. However, the leading coefficient in Soave's equations is shown to be inconsistent with the limiting slope of the vapor pressure curve predicted by the equations of state. New direct expressions are developed that eliminate this inconsistency and give good representation of vapor pressures with fewer adjustable coefficients.

## 1. Introduction

The calculation of vapor pressures of pure fluids from pressure-explicit equations of state (EOS's) is an iterative process in which the Maxwell equal area criterion, or equivalently the isofugacity criterion of phase equilibrium, is solved together with the EOS itself to yield the saturation pressure and phase volumes (see, for example, Walas (1985)). These fairly straightforward computations nevertheless take up valuable time, especially when performed repeatedly as in the course of separation process simulations. For a generic cubic EOS of the Schmidt-Wenzel type with only one temperature-dependent parameter,

$$P = \frac{RT}{v - b} - \frac{a_c \alpha(T_r)}{v^2 + ubv + wb^2} \quad (1)$$

Soave (1986) showed that  $P_r^{\text{sat}}/T_r$  is a unique function of  $\alpha/T_r$ , which he approximated by the empirical formula

$$\ln\left(\frac{P_r}{T_r}\right) = \sum_{k=1}^4 C_k \left(\frac{\alpha}{T_r} - 1\right)^{(k+1)/2} + \sum_{k=5}^{10} C_k \left(\frac{\alpha}{T_r} - 1\right)^{k-2} \quad (2)$$

and presented values of the 10 coefficients  $C_k$  for the van der Waals (1873), Redlich–Kwong (1949), and Peng–Robinson (1976) cubic EOS's.

Soave's direct procedure was extended by Adachi (1987) to all other cubic EOS's of the same general form, by generalizing the coefficients as polynomial functions of  $\Omega_a$

$$C_k = \sum_{n=0}^4 c_{k,n} \Omega_a^n \quad (3)$$

It is our purpose in the present work to further simplify the practical computation of vapor pressures from selected cubic EOS's. While a large number of EOS models have been proposed in the literature, only a handful of these have found widespread use in engineering application, notably the original Redlich–Kwong (1949) EOS, its modification by Soave (1972), and the Peng–Robinson (1976) EOS. These equations may be expressed in reduced form; thus, if any of them is chosen, saturated pressures can be calculated uniquely for the class of fluids it represents. The results can be put in the form of corresponding states correlations,

$$\ln P_r^{\text{sat}} = f(T_r; \omega) \quad (4)$$

The present study covers the nine cubic EOS's summarized in Table 1. For each equation we compute the saturation pressure curve, from the lowest practicable reduced temperature (typically 0.30) up to the critical point and over a wide range of values of acentric factor (typically from –0.5 to +2.1). We then correlate the results in the manner of eq 4 and, finally, compare the resulting formulas with eq 2 in terms of computational accuracy and convenience. It must be made clear that this work is not concerned with comparing EOS-predicted and experimental vapor pressures of actual fluids but only with developing computational alternatives to the iterative Maxwell procedure for the idealized fluids defined by each cubic EOS.

## 2. Two-Parameter Cubic Equations of State

The original van der Waals (1873), Berthelot (Malanowski and Anderko, 1992), and Redlich–Kwong (1949) EOS's employ universal cohesion functions that

\* To whom correspondence should be addressed. Phone: (+58 2) 906.3740. Fax: (+58 2) 906.3743. E-mail: jean@usb.ve.

**Table 1. Cubic Equations of State Studied in This Work**

| EOS                 | $u$ | $w$ | cohesion function | parametrization | ref                           |
|---------------------|-----|-----|-------------------|-----------------|-------------------------------|
| two-parameter       |     |     |                   |                 |                               |
| van der Waals       | 0   | 0   | 1                 | none            | van der Waals (1873)          |
| Berthelot           | 0   | 0   | $T_r^{-1}$        | none            | Malanowski and Anderko (1992) |
| Redlich–Kwong       | 1   | 0   | $T_r^{-1/2}$      | none            | Redlich and Kwong (1949)      |
| three-parameter     |     |     |                   |                 |                               |
| Soave–Redlich–Kwong | 1   | 0   | eq 6              | S72             | Soave (1972)                  |
|                     |     |     | eq 6              | GD78            | Graboski and Daubert (1978)   |
|                     |     |     | eq 6              | this work       |                               |
| Peng–Robinson       | 2   | -1  | eq 6              | PR76            | Peng and Robinson (1976)      |
|                     |     |     | eq 6              | RP78            | Robinson and Peng (1978)      |
|                     |     |     | eq 6              | this work       |                               |

**Table 2. Coefficients of Equation 5 for Two-Parameter Cubic EOS's<sup>a</sup>**

| EOS           | $T_r$     | $D_0$                              | $D_1$                             | $D_2$                              | $D_3$                             |
|---------------|-----------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|
| van der Waals | 0.19–0.99 | -3.408 602 857<br>(0.000 609 969)  | 0.299 232 702<br>(0.004 918 592)  | -1.715 876 838<br>(0.012 037 213)  | 0.842 558 717<br>(0.009 000 090)  |
| Berthelot     | 0.44–0.99 | -26.434 630 471<br>(0.116 163 218) | 60.310 960 495<br>(0.575 805 460) | -65.856 140 772<br>(0.931 707 549) | 25.177 049 177<br>(0.492 082 676) |
| Redlich–Kwong | 0.31–0.99 | -11.545 351 810<br>(0.035 488 297) | 21.212 460 166<br>(0.215 953 053) | -26.153 517 848<br>(0.419 100 841) | 11.121 438 485<br>(0.259 589 792) |

<sup>a</sup> Values given in parentheses are standard errors of parameter estimates.

can be written in modern notation as  $\alpha(T_r) = 1$ ,  $T_r^{-1}$ , and  $T_r^{-1/2}$ , respectively. Although these equations cannot be expected to predict vapor pressures accurately, they are included here because of their historical importance and also for illustration of the form of the correlations. The corresponding predicted acentric factors are -0.3020 (van der Waals), +0.0583 (Redlich–Kwong), and +0.4612 (Berthelot).

We have correlated the vapor pressure curves of two-parameter cubic EOS's using the function

$$\ln P_r^{\text{sat.}} = \left( \frac{1}{T_r} - 1 \right) \sum_{k=0}^3 D_k T_r^k \quad (5)$$

with coefficients given in Table 2. Regression statistics from calculated values are summarized in Table 3. Equation 5 belongs to the general class of vapor pressure expressions constructed on characteristic points, recently proposed by Ledanois et al. (1997) and shown by them to be at least as accurate as the traditional Riedel and Wagner vapor pressure formulas. The function is "anchored" at the critical point; i.e., it implicitly satisfies the boundary condition  $P_r^{\text{sat.}} = 1$  at  $T_r = 1$ .

### 3. Three-Parameter Cubic Equations of State

It is convenient to introduce a distinction between the volume and temperature dependencies of a cubic EOS. In the generalized eq 1, the van der Waals "repulsion" term  $RT/(v - b)$  is fixed, but the "attraction" term can take many different forms, depending on the choice of the volume function  $a_c/(v^2 + ubv + wb^2)$  and the temperature or "cohesion" function  $\alpha(T_r)$ . One may refer to a particular choice of parameters  $u$  and  $w$  as defining the EOS model; e.g.,  $u = w = 0$  for a van der Waals model,  $u = 1$ ,  $w = 0$  for a Redlich–Kwong model, and  $u = 2$ ,  $w = -1$  for a Peng–Robinson model. Specifying the cohesion function then defines a form or modification of the basic model; e.g., the Redlich–Kwong model with  $\alpha(T_r) = 1/T_r^{0.5}$  is the original form of this EOS but with

$$\alpha(T_r) = [1 + m(1 - T_r^{0.5})]^2 \quad (6)$$

becomes its Soave (1972) modification. Finally, different correlations or parametrizations may be available for obtaining characteristic constants such as  $m$ , required by a given form of an EOS.

The use of a fluid-specific cohesion function to improve the representation of vapor–liquid equilibria was first suggested by Wilson (1964) but did not become a standard feature of cubic EOS development until the introduction of eq 6 by Soave (1972). Both the Soave modification of the Redlich–Kwong EOS and the original Peng–Robinson EOS are based on this cohesion function, but different correlations  $m(\omega)$  are available, as shown in Table 4. None of these parametrizations is completely consistent; i.e., if an "input" acentric factor is specified and the appropriate EOS is used, it will predict a different "output" acentric factor, possibly by a substantial amount. This is largely a consequence of the form in which the characteristic parameter  $m$  has been computed (either from a single datum at the "omega temperature"  $T_r = 0.7$  or from a best fit over a range of temperatures), but there are in all cases the additional effects of the approximate nature of the polynomial function employed and of the limited range of acentric factors used in developing the correlation. Figure 1 illustrates the relative difference between calculated  $[P_{r,\text{cal}}^{\text{sat.}}]$  and defined  $[P_{r,\text{def}}^{\text{sat.}} = 10^{(-1-\omega)}]$  vapor pressures at  $T_r = 0.7$  over a wide range of acentric factors found, e.g., in the DIPPR compilation (Daubert and Danner, 1992). Larger deviations can be observed at negative acentric factors, which are seldom included in the development of the parametrizations, and also at large acentric factors that exceed the maximum value accounted for by the correlation. This result should be taken into account in practical applications of these EOS's or in comparisons of their ability to predict vapor pressures.

In this work, we have developed new expressions for  $m$  for use with the Soave cohesion function and the Redlich–Kwong and Peng–Robinson EOS models. The proposed formulas are also included in Table 4. It is interesting to point out that the PR/S/PR76 correlation has a maximum at  $\omega_{\text{in}} = 2.8569$ , where  $dm/d\omega = 0$ . This corresponds to  $m = 2.5777$  and gives  $\omega_{\text{out}} = 1.7626$  as the maximum acentric factor predicted by the original

**Table 3. Statistical Comparison of Correlations for Direct Calculation of Vapor Pressures**

| EOS <sup>a</sup> | $T_r^b$   | $\omega$ | mean <sup>c</sup> | min <sup>c</sup> | max <sup>c</sup> | RMSE <sup>c</sup> | SDEV <sup>c</sup> |
|------------------|-----------|----------|-------------------|------------------|------------------|-------------------|-------------------|
| VW/original      | 0.19      |          |                   |                  |                  |                   |                   |
| eq 2             |           |          | 7.15E-07          | -1.65E-06        | 1.39E-05         | 2.98E-06          | 2.92E-06          |
| eq 3             |           |          | -8.15E-05         | -4.46E-04        | 1.23E-05         | 1.53E-04          | 1.30E-04          |
| eq 5             |           |          | 3.30E-05          | -1.35E-03        | 8.39E-04         | 4.20E-04          | 4.21E-04          |
| eq 11            |           |          | -2.99E-03         | -9.04E-03        | 5.78E-03         | 5.25E-03          | 4.34E-03          |
| VW/Berthelot     | 0.44      |          |                   |                  |                  |                   |                   |
| eq 2             |           |          | 4.56E-07          | -1.61E-06        | 1.39E-05         | 2.48E-06          | 2.46E-06          |
| eq 3             |           |          | -1.09E-04         | -4.46E-04        | 1.23E-05         | 1.81E-04          | 1.46E-04          |
| eq 5             |           |          | 3.52E-04          | -5.26E-03        | 9.79E-03         | 3.19E-03          | 3.20E-03          |
| eq 11            |           |          | -2.69E-03         | -9.03E-03        | 5.79E-03         | 5.22E-03          | 4.51E-03          |
| RK/original      | 0.31      |          |                   |                  |                  |                   |                   |
| eq 2             |           |          | 6.73E-07          | -1.71E-06        | 1.69E-05         | 3.22E-06          | 3.18E-06          |
| eq 3             |           |          | -8.86E-05         | -4.18E-04        | 9.00E-05         | 1.60E-04          | 1.34E-04          |
| eq 5             |           |          | 5.41E-04          | -8.73E-03        | 1.73E-02         | 4.96E-03          | 4.97E-03          |
| eq 11            |           |          | -2.92E-03         | -1.01E-02        | 6.42E-03         | 5.82E-03          | 5.08E-03          |
| RK/S/S72         | 0.15/0.47 | -0.4-0.8 |                   |                  |                  |                   |                   |
| eq 2             |           |          | 7.70E-07          | -2.45E-06        | 1.71E-05         | 3.47E-06          | 3.39E-06          |
| eq 3             |           |          | -9.19E-05         | -4.19E-04        | 9.96E-05         | 1.64E-04          | 1.36E-04          |
| eq 7             |           |          | 5.04E-04          | -1.50E-01        | 3.81E-01         | 7.07E-02          | 7.08E-02          |
| eq 11            |           |          | -2.94E-03         | -1.01E-02        | 6.43E-03         | 5.84E-03          | 5.05E-03          |
| RK/S/GD78        | 0.27/0.49 | 0.0-1.0  |                   |                  |                  |                   |                   |
| eq 2             |           |          | 6.58E-07          | -1.73E-06        | 1.71E-05         | 3.28E-06          | 3.22E-06          |
| eq 3             |           |          | -1.04E-04         | -4.19E-04        | 9.97E-05         | 1.75E-04          | 1.41E-04          |
| eq 7             |           |          | -5.02E-04         | -5.47E-02        | 1.61E-01         | 2.56E-02          | 2.56E-02          |
| eq 11            |           |          | -2.77E-03         | -1.01E-02        | 6.43E-03         | 5.82E-03          | 5.13E-03          |
| RK/S/this work   | 0.15/0.57 | -0.8-2.4 |                   |                  |                  |                   |                   |
| eq 2             |           |          | 1.18E-06          | -5.54E-05        | 1.71E-05         | 4.99E-06          | 4.85E-06          |
| eq 3             |           |          | -9.03E-05         | -7.11E-04        | 9.85E-05         | 1.66E-04          | 1.40E-04          |
| eq 7             |           |          | 1.74E-02          | -3.89E-01        | 1.36E+00         | 2.17E-01          | 2.17E-01          |
| eq 11            |           |          | -2.68E-03         | -1.35E-02        | 6.43E-03         | 5.58E-03          | 4.90E-03          |
| PR/S/PR76        | 0.29/0.37 | 0.0-0.5  |                   |                  |                  |                   |                   |
| eq 2             |           |          | 1.07E-06          | -2.33E-06        | 2.52E-05         | 4.88E-06          | 4.77E-06          |
| eq 3             |           |          | -1.52E-04         | -8.69E-04        | 2.33E-05         | 2.31E-04          | 1.74E-04          |
| eq 7             |           |          | -3.53E-05         | -2.51E-02        | 3.73E-02         | 7.30E-03          | 7.32E-03          |
| eq 11            |           |          | -5.53E-03         | -1.80E-02        | 1.09E-02         | 1.04E-02          | 8.85E-03          |
| PR/S/RP78        | 0.33/0.57 | 0.0-2.0  |                   |                  |                  |                   |                   |
| eq 2             |           |          | 7.32E-07          | -4.57E-05        | 2.51E-05         | 5.22E-06          | 5.17E-06          |
| eq 3             |           |          | -1.72E-04         | -1.49E-03        | 2.33E-05         | 2.63E-04          | 1.99E-04          |
| eq 7             |           |          | -5.09E-04         | -8.62E-02        | 2.04E-01         | 4.04E-02          | 4.04E-02          |
| eq 11            |           |          | -5.04E-03         | -1.80E-02        | 1.09E-02         | 1.03E-02          | 8.95E-03          |
| PR/S/this work   | 0.07/0.57 | -0.6-2.4 |                   |                  |                  |                   |                   |
| eq 2             |           |          | 1.07E-06          | -1.75E-05        | 2.51E-05         | 4.96E-06          | 4.84E-06          |
| eq 3             |           |          | -1.59E-04         | -1.68E-03        | 2.33E-05         | 2.56E-04          | 2.01E-04          |
| eq 7             |           |          | 7.00E-03          | -2.67E-01        | 6.69E-01         | 1.35E-01          | 1.35E-01          |
| eq 11            |           |          | -5.21E-03         | -1.80E-02        | 1.09E-02         | 1.02E-02          | 8.77E-03          |

<sup>a</sup> Eq 2, Soave's original (1986); eq 3, Adachi's generalization (1987); eq 5 and eq 7, two- and three-parameter correlations, this work; eq 11, modified Soave's equation, this work. <sup>b</sup>  $T_r$  starting point depends on the value of  $\omega$  and ends at 0.99. <sup>c</sup> Where, for example, 7.15E-07 represents  $7.15 \times 10^{-7}$ .

**Table 4. Coefficients for Parameter  $m = a_0 + a_1\omega + a_2\omega^2 + a_3\omega^3$** 

| EOS           | $a_0$         | $a_1$         | $a_2$          | $a_3$         | range of<br>acentric factors | ref                         |
|---------------|---------------|---------------|----------------|---------------|------------------------------|-----------------------------|
| Redlich-Kwong |               |               |                |               |                              |                             |
| S/S72         | 0.48          | 1.574         | -0.176         | 0             | 0-0.5                        | Soave (1972)                |
| S/GD78        | 0.485 08      | 1.551 71      | -0.156 13      | 0             | ≤0.91                        | Graboski and Daubert (1978) |
| S/this work   | 0.478 972 559 | 1.576 809 191 | -0.187 219 516 | 0.020 424 946 | -0.8-2.4                     | this work                   |
| Peng-Robinson |               |               |                |               |                              |                             |
| S/PR76        | 0.374 64      | 1.542 26      | -0.269 92      | 0             | 0-0.5                        | Peng and Robinson (1976)    |
| S/RP78        | 0.379 642     | 1.485 03      | -0.164 423     | 0.016 666     | 0.2-2.0                      | Robinson and Peng (1978)    |
| S/this work   | 0.378 710 697 | 1.487 972 964 | -0.166 754 831 | 0.017 169 486 | -0.5-2.1                     | this work                   |

Peng-Robinson EOS. The RK/S/S72 and RK/S/GD78 correlations behave similarly but give values of  $\omega_{\text{out}} > 2.0$ . Cubic correlations such as PR/S/RP78 and those developed in this work are free from this problem and can be seen to give improved matching of input and output acentric factors over a much wider range.

Obviously a very large number of such functions can be derived, depending on the criterion and range of values employed. For a given EOS model and form of cohesion function, each parametrization gives rise to a different family of vapor pressure curves for the same

class of normal fluids. We have computed vapor pressures for the three versions each of the Redlich-Kwong-Soave (RK/S) and Peng-Robinson (PR/S) EOS's defined in Table 4 and correlated the results by a straightforward corresponding-states extension of eq 5:

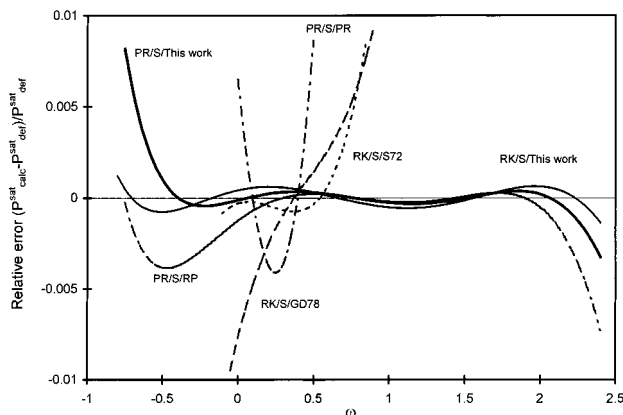
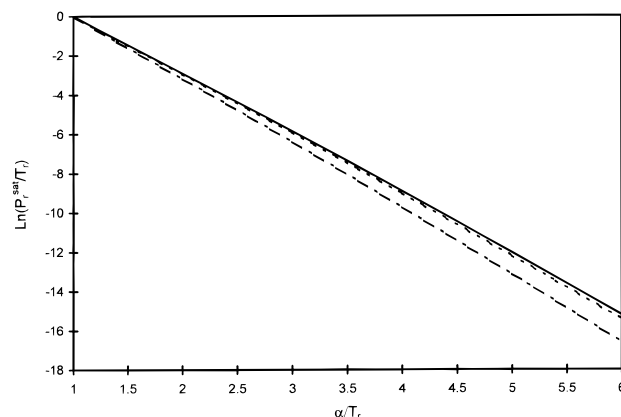
$$\ln P_r^{\text{sat.}} = \left( \frac{1}{T_r} - 1 \right) \left[ \sum_{k=0}^3 D_k T_r^k + \omega \sum_{k=0}^3 E_k T_r^k \right] \quad (7)$$

with coefficients given in Table 5.

**Table 5. Coefficients of Equation 7 for Three-Parameter Cubic EOS Forms<sup>a</sup>**

| EOS                     | $\omega$    | $T_r^b$   | coeff    | 0                                  | 1                                  | 2                                 | 3                                  |
|-------------------------|-------------|-----------|----------|------------------------------------|------------------------------------|-----------------------------------|------------------------------------|
| Redlich–Kwong<br>S/S72  | -0.4–0.8    | 0.15/0.47 | <i>D</i> | -4.989 846 436<br>(0.094 239 909)  | -5.481 877 166<br>(0.609 632 343)  | 13.426 980 467<br>(1.273 177 841) | -9.006 240 962<br>(0.851 741 679)  |
|                         |             |           | <i>E</i> | -5.991 830 710<br>(0.223 967 859)  | -11.949 311 024<br>(1.390 191 101) | 29.973 464 628<br>(2.849 407 730) | -16.627 870 452<br>(1.896 710 482) |
|                         | S/GD78      | 0.0–1.0   | <i>D</i> | -7.040 611 889<br>(0.102 589 783)  | 6.698 432 450<br>(0.659 876 459)   | -8.012 335 233<br>(1.338 240 549) | 2.634 567 379<br>(0.858 668 513)   |
|                         |             |           | <i>E</i> | -7.717 374 058<br>(0.366 696 485)  | -9.127 922 172<br>(1.958 238 714)  | 31.256 122 538<br>(3.459 911 016) | -19.058 897 066<br>(2.007 553 538) |
|                         | S/this work | -0.8–2.4  | <i>D</i> | -1.763 495 876<br>(0.151 941 588)  | -23.627 089 627<br>(1.013 430 304) | 44.099 174 375<br>(2.206 071 559) | -25.099 763 063<br>(1.554 031 832) |
|                         |             |           | <i>E</i> | -1.869 060 237<br>(0.243 173 727)  | -26.505 394 021<br>(1.560 106 443) | 44.143 103 412<br>(3.124 421 090) | -19.443 432 555<br>(1.992 252 769) |
| Peng–Robinson<br>S/PR76 | 0.0–0.5     | 0.29/0.37 | <i>D</i> | -6.496 149 241<br>(0.043 195 736)  | 5.233 802 465<br>(0.270 177 400)   | -7.218 653 452<br>(0.537 589 689) | 2.899 102 913<br>(0.340 352 437)   |
|                         |             |           | <i>E</i> | -11.151 271 123<br>(0.213 463 950) | 9.079 162 244<br>(1.231 470 625)   | 3.218 672 186<br>(2.297 786 661)  | -6.195 227 702<br>(1.383 337 573)  |
|                         | S/RP78      | 0.0–2.0   | <i>D</i> | -7.167 302 806<br>(0.333 059 578)  | 7.515 058 165<br>(1.923 711 281)   | -8.033 076 766<br>(3.557 473 969) | 1.476 550 028<br>(2.110 775 665)   |
|                         |             |           | <i>E</i> | -3.733 552 568<br>(0.591 018 477)  | -26.902 646 733<br>(2.922 013 432) | 55.363 253 700<br>(4.785 030 099) | -29.039 196 725<br>(2.583 893 702) |
|                         | S/this work | -0.6–2.4  | <i>D</i> | -2.886 107 033<br>(0.129 611 860)  | -16.965 064 675<br>(0.840 632 856) | 33.604 138 927<br>(1.789 559 493) | -20.428 493 143<br>(1.234 735 469) |
|                         |             |           | <i>E</i> | -3.473 515 102<br>(0.201 777 445)  | -19.280 876 319<br>(1.172 374 817) | 32.684 060 960<br>(2.204 245 969) | -13.226 640 851<br>(1.349 656 425) |

<sup>a</sup> Values given in parentheses are standard errors of parameter estimates. <sup>b</sup>  $T_r$  starting point depends on the value of  $\omega$  and ends at 0.99.

**Figure 1.** Discrepancy between calculated and defined  $[10^{(-1-\omega)}]$  vapor pressure for three-parameter cubic equations of state.**Figure 2.** Direct dependence of pressure and temperature parameters for cubic equation of state models: —, van der Waals; --, Redlich–Kwong; -·-, Peng–Robinson.

#### 4. Soave's Direct Procedure

The complexity of eq 2 was justified by Soave (1986) as being required by the highly nonlinear nature of the relation between the temperature and pressure parameters. In fact, this dependence is very close to linear, as discussed more recently by Zabaloy and Vera (1996) and illustrated in Figure 2 for the van der Waals, Redlich–Kwong, and Peng–Robinson models. The slope of this line at the critical temperature is a simple analytical function of the EOS parameters. This follows from the thermodynamic limit

$$\lim_{T \rightarrow T_c} \left( \frac{dP^{\text{sat}}}{dT} \right) = \lim_{\substack{T \rightarrow T_c \\ v \rightarrow v_c}} \left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{v_c - b} - \frac{a_c/T_c}{v_c^2 + ubv_c + wb^2} \lim_{T_r \rightarrow 1} \left( \frac{d\alpha}{dT_r} \right) \quad (8)$$

On combining this result with the EOS itself at the

critical point, a direct relation between the critical temperature derivatives of  $P^{\text{sat}}$  and  $\alpha$  ensues. We write the final result directly in reduced terms as

$$\left[ \frac{d \ln(P_r^{\text{sat}}/T_r)}{d(\alpha/T_r)} \right]_c = \frac{(dP_r^{\text{sat}}/dT_r)_{T_r=1} - 1}{(d\alpha/dT_r)_{T_r=1} - 1} = \frac{Z_c - \Omega_b - 1}{Z_c - \Omega_b} \equiv H_0 \quad (9)$$

where  $Z_c$  is the predicted critical compressibility factor. The differential coefficient  $H_0$  is exactly  $-3$  for the van der Waals,  $-3.053\,621\,57\dots$  for the Redlich–Kwong, and  $-3.355\,301\,397\dots$  for the Peng–Robinson models. By contrast, the leading coefficient  $C_1$  in eq 2 as given by Soave (1986) is  $-2.995\,9015$ ,  $-3.048\,6334$ , and  $-3.346\,6262$ , respectively, for the same models. Differentiation of eq 2 shows that both coefficients should



**Table 6. Coefficients of Equation 11 for Cubic EOS Models<sup>a</sup>**

| EOS           | $\alpha/T_r$ | $H_0$          | $H_1$                            | $H_2$                             | $H_3$                            | $H_4$                             |
|---------------|--------------|----------------|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|
| van der Waals | 1.0–6.0      | –3             | 0.204 848 074<br>(0.001 074 445) | –0.126 753 898<br>(0.000 979 746) | 0.026 607 789<br>(0.000 287 733) | –0.001 962 806<br>(0.000 027 239) |
| Redlich–Kwong | 1.0–6.0      | –3.053 621 576 | 0.222 851 409<br>(0.001 195 293) | –0.136 387 878<br>(0.001 089 943) | 0.028 690 101<br>(0.000 320 096) | –0.002 122 282<br>(0.000 030 302) |
| Peng–Robinson | 1.0–6.0      | –3.355 301 398 | 0.334 692 886<br>(0.002 163 024) | –0.195 124 450<br>(0.001 972 380) | 0.041 189 962<br>(0.000 579 251) | –0.003 063 572<br>(0.000 054 836) |

<sup>a</sup> Values given in parentheses are standard errors of parameter estimates.

coincide for thermodynamic consistency of the correlation; in fact, the homogeneous linear formula

$$\ln\left(\frac{P_r^{\text{sat.}}}{T_r}\right) \approx H_0\left(\frac{\alpha}{T_r} - 1\right) \quad (10)$$

works quite well as a first approximation, to the extent that we have found that regression statistics actually get worse in progressing from a linear to quadratic and cubic approximations, improving only from the fourth degree upward; Soave's remark on high nonlinearity was no doubt meant for the behavior of these residuals. We therefore propose the following correlation as the simplest alternative to eqs 2 and 10:

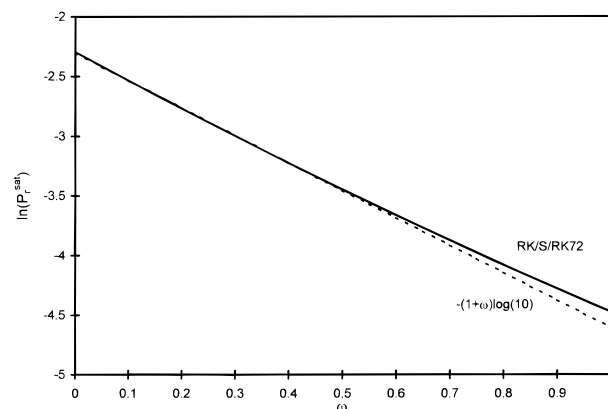
$$\ln\left(\frac{P_r^{\text{sat.}}}{T_r}\right) = \left(\frac{\alpha}{T_r} - 1\right) \left[ H_0 + \sum_{k=1}^4 H_k \left(\frac{\alpha}{T_r} - 1\right)^k \right] \quad (11)$$

with coefficients given in Table 6, for  $1.0 \leq \alpha/T_r \leq 6.0$  as recommended by Soave (1986).

## 5. Comparison of Correlations

Table 3 presents a summary of statistical parameters for the deviations in vapor pressures predicted by the five correlations mentioned or developed above: Soave's original direct method, eq 2; Adachi's generalization of the same, eq 3; the two-parameter universal correlations, eq 5; the three-parameter corresponding states correlations, eq 7; and the simplified direct method, eq 11. In all cases, deviations are measured in terms of relative errors in  $P_r^{\text{sat.}}$ , with reference to exact vapor pressures computed directly by the Maxwell procedure for each EOS model/form/parametrization. The limitations of each correlation have been duly taken into account; these include, in the case of three-parameter EOS's, the range of acentric factors over which the corresponding parametrizations give less than a 0.01 relative difference between calculated vapor pressure and defined vapor pressure from a given  $\omega$  and, in the case of the direct methods, the temperature restrictions imposed by the constraint  $\alpha/T_r < 6.0$  (e.g., comparisons for the "Berthelot fluid", a relatively heavy substance with  $\omega = 0.4612$  and  $\alpha/T_r = 1/T_r^2$ , are meaningful only for  $T_r > (1/6)^{0.5} = 0.408$ ).

It is evident from Table 3 that the original direct correlation by Soave (1986) is by far the most accurate predictor, as may of course be expected from its complex functional form with 10 carefully tuned coefficients for each EOS model. Even the presumably slight dispersion introduced by the Adachi (1987) generalization is sufficient to decrease the accuracy by more than 1 order of magnitude. However, the leading coefficient in these equations has been shown above to differ from the theoretical value so that this high accuracy is obtained at the expense of some thermodynamic consistency. The

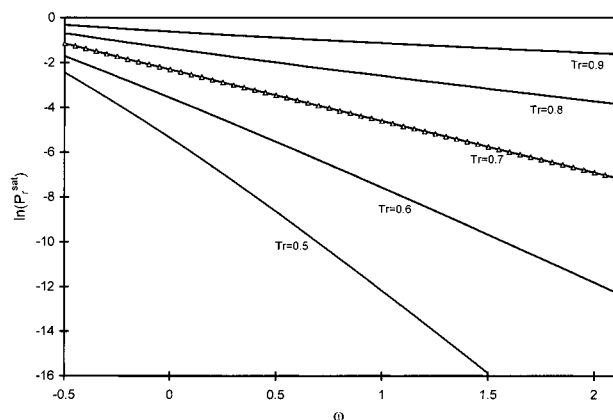


**Figure 3.** Dependence of saturation pressure on acentric factor for the original PR EOS at  $T_r = 0.7$ .

simpler direct formula proposed in the present work, eq 11, gives the correct slope at the critical temperature and predicts vapor pressures with root mean square errors (RMSE) ranging from 0.005 to 0.01 with only four adjusted coefficients. The direct method for computation of vapor pressures is in fact a two-step procedure in which a parametrized cohesion function (containing additional adjustable coefficients) must first be available for computation of  $\alpha(T_r; \omega)$ . Thus, even though the precision of eq 11 could no doubt be improved significantly by increasing the degree of the approximation, this added complexity is hard to justify, given the intrinsic inconsistency of the parametrizations employed with the usual cubic EOS's.

By contrast, eq 5 for two-parameter EOS's and eq 7 for three-parameter EOS's are truly direct. The temperature function used in these formulas has been discussed in greater detail by Ledanois et al. (1997). Its advantages are manifest in the case of eq 5, which outperforms the direct eq 11 with the same number of adjustable coefficients, giving RMSE from 0.0004 to 0.005.

Results are less clear for eq 7, which gives RMSE of 0.026 for the RK/S/GD78 and 0.007 for the PR/S/76 equations but becomes increasingly less adequate as the range of acentric factors covered by the EOS widens, i.e., in going from S/S72 to S/GD78 to S/this work for the RK model and from S/PR76 to S/RP78 to S/this work for the PR model. This is evidently a consequence of the linear dependence on the acentric factor assumed in eq 7, in keeping with the traditional Pitzer form of the corresponding states principle. Cubic EOS fluids do not conform to this principle, as made obvious by the correlations of Table 4 and illustrated in Figures 3 and 4. Figure 3 is a plot of reduced saturation pressures computed from the original Peng–Robinson EOS (PR/S/PR76) against the acentric factor at  $T_r = 0.7$ . The mismatch between input and output acentric factors can be appreciated from the fact that the predicted saturation pressures do not quite agree with the expected



**Figure 4.** Dependence of saturation pressure on acentric factor for the PR EOS with the parametrization of eq 17.

value shown as a broken line,  $\ln(P_r^{\text{sat}}) = -(1 + \omega) \ln(10)$ . Figure 4 is a similar plot for the Peng–Robinson EOS with the parametrization PR/S/this work. In the broader range of acentric factors made possible by this improved formula, it is clear that a linear dependence exists only by definition at  $T_r = 0.7$  and that deviations from linearity increase as the isotherms fan out from the  $\omega$  temperature, especially toward the lower temperatures.

## 6. Conclusions

Vapor pressures computed from several cubic EOS models have been correlated in corresponding states form using the linear Pitzer principle and a simple temperature function proposed in a previous paper. The correlations give vapor pressure directly as a function of temperature and acentric factor; i.e., no intermediate parameters need be calculated.

Soave's direct equations are very accurate and must be the method of choice if algebraic complexity is no obstacle. However, the leading coefficient in these approximations is inconsistent with the theoretical value of the limiting slope of the vapor pressure curve obtained in this paper for the specified cubic EOS models. Simpler correlations have been developed that give the correct limiting behavior and are sufficiently accurate for most practical purposes.

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## Nomenclature

$a_c$  = attraction parameter  
 $b$  = excluded volume parameter  
 $c$  = coefficients in Adachi method, eq 3  
 $C$  = coefficients in original Soave method, eq 2  
 $D, E$  = coefficients in corresponding states method, eqs 5 and 7  
 $f$  = generic function  
 $H$  = coefficients in simplified Soave method, eqs 9–11  
 $k$  = number of coefficients  
 $m$  = parameter in Soave cohesion function  
 $P$  = pressure  
 $R$  = gas constant  
 $T$  = temperature  
 $u$  = dimensionless parameter in generalized cubic EOS

$v$  = specific or molar volume

$w$  = dimensionless parameter in generalized cubic EOS

## Greek Symbols

$\alpha$  = cohesion parameter

$\omega$  = acentric factor

$\Omega_a$  = dimensionless EOS parameters,  $a_c P_c / (RT_c)^2$

## Subscripts and Superscripts

c = at critical point

r = reduced property

sat. = at saturation

## Abbreviations

PR = Peng–Robinson

RK = Redlich–Kwong

VW = van der Waals

/GD78 = Graboski–Daubert parametrization for RK/S EOS

/PR76 = Peng–Robinson parametrization for PR/S EOS

/RP78 = Robinson–Peng parametrization for PR/S EOS

/S = Soave form of cohesion function

/S72 = Soave parametrization for RK/S EOS

/this work = parametrizations proposed in this work

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