Using Vapor Pressure Information in a Cubic Equation of State

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Introduction

Different forms of cubic equations of state (EOS) have been used with various degrees of success for VLE calculations, provided a temperature-dependent attraction parameter law is stated, making the equation capable of reproducing pure-component vapor pressures. Even the original van der Waals equation is substantially improved when a temperature-dependent parameter is introduced (Soave, 1984).

Frequently, this attraction parameter is expressed as a generalized function of an arbitrary form. In particular, that proposed by Soave (1972) has been adapted to several EOS:

$$\alpha(Tr) = [1 + m(1 - \sqrt{Tr})]^2 \tag{1}$$

$$a(Tr) = a_c \cdot \alpha \tag{2}$$

where m is a function of the acentric factor.

Attempts at a better representation of the vapor pressure have used other forms for the attraction parameter, such as exponentials, polynomials, etc. (Adachi and Lu, 1984). If still more accuracy is required in VLE calculations, then specific-component parameters must be used; they are obtained by regression of the vapor pressure data (Soave, 1980).

Panagiotopoulos and Kumar (1985) proposed a general approach to obtain the pure-component parameters a and b from vapor pressure and liquid volume data. In their model, both parameters, expressed in a reduced form, are explicit functions of the liquid compressibility factor, which is needed as an input to the correlation.

For vapor-liquid equilibrium calculations, the molar volumes are used as dummy variables, and the problem of reproducing experimental vapor pressures can be separated from that of predicting liquid densities by using the translation approach, as shown by Peneloux and Rauzy (1982).

A variation of the technique of Panagiotopoulos is described in this note, whereby vapor pressure information is directly incorporated into the attraction parameter law, $a(T)$.

Procedure

The method proposed here, although general in principle, was developed using the van der Waals equation and the Soave modification of the Redlich-Kwong (SRK) equation. In both equations, it is convenient to define the following parameters:

$$A = a(T)\,P/(RT)^2 \tag{3}$$

$$B = bP/RT \tag{4}$$

$$Z = PV/RT \tag{5}$$

Next, the following parameter is defined, which does not include the pressure:

$$D = A/B = a(T)/bRT \tag{6}$$

Along the saturation envelope, the cubic equation of state is solved, together with the equal-fugacity criterion. This yields a single relationship between parameters B_s and D. As an example, the van der Waals equation written as

$$Z^3 - (B_s + 1)\,Z^2 + B_s DZ - B_s D = 0 \tag{7}$$

where

$$B_s = bP_s/RT \tag{8}$$

can be solved for the two roots Z_v and Z_L as functions of B_s and D.

If these two values are inserted into the equal-fugacity relation obtained from the same equation:

$$Z_v - Z_L - \ln (Z_v - B_s)/(Z_L - B_s) + B_s D(1/Z_L - 1/Z_v) = 0 \tag{9}$$

a single relation between D and B_s is obtained:

$$D = f_{vdw}(B_s) \tag{10}$$

A similar functional relation holds for the SRK equation. Since an explicit analytic solution for D is not possible, Eqs. 7 and 9 are solved numerically, and the results plotted on semilog graph paper. Figure 1 shows that almost straight lines are obtained. Then, as a first approximation

$$D = c_0 - c_1 \ln B_s \tag{11}$$

Also, at the critical point

$$(B_s)_c = \Omega_b; \quad D_c = \Omega_a/\Omega_b$$

If two new parameters are defined as

$$F = D/D_c = \alpha(Tr)/Tr \tag{12}$$

$$X = \ln\,[B_s/(B_s)_c] = \ln\,(Pr^s/Tr) \tag{13}$$

it follows that at the critical point, $F = 1$ and $X = 0$.

It must be observed that the righthand side of Eq. 13 is obtained if the covolume parameter b is set constant, equal to the value at the critical point.

Expanding F around the critical point, and taking into account Eq. 11:

$$F = 1 + X\,(dF/dX)_{x=0} + C_2 r(X) \tag{14}$$

Second- and higher order terms are lumped together in the residual term $r(X)$, which is important at low reduced temperatures. The following form was adopted for this residual:

$$r(X) = e^{x/3}\,X^2/(1 + e^{3x}) \tag{15}$$

The final results are:

$$\text{van der Waals}: (dF/dX)_{x=0} = -0.3333 \quad c_2 = 0.0115$$
$$\text{SRK}: (dF/dX)_{x=0} = -0.327 \quad c_2 = 0.0129$$

Other cubic EOS also can be used, although no values of these constants are reported here.

The first derivative $(dF/dX)_{x=0}$ is obtained analytically using the fact that the thermal pressure coefficient at the critical point becomes equal to the slope of the vapor pressure curve. The value of $\alpha(Tr)$ is calculated using Eqs. 12–15. For example, the van der Waals equation gives:

$$\alpha(Tr) = Tr[1 - 0.3333\,X + 0.0115\,r(X)] \tag{16}$$

P_r^s can be computed from any vapor pressure equation, or directly from experimental data. This value is inserted in the equation of state by means of Eq. 16, so that it will reproduce the given vapor pressure to within 0.2% for reduced temperatures ranging 0.5 to 1.0.

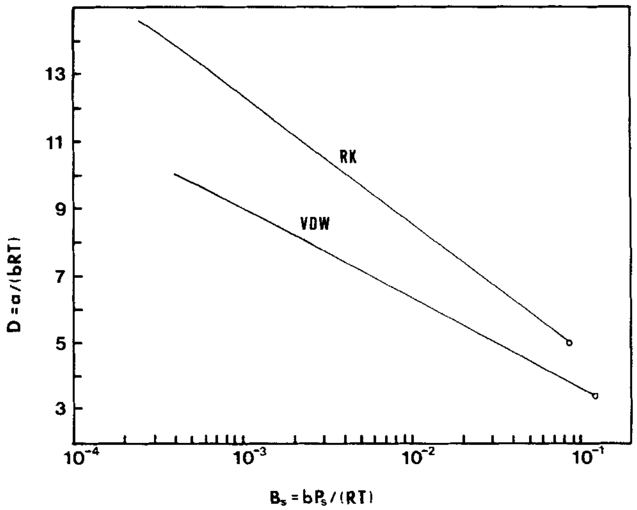

Figure 1. Relation between parameters D and B_s for van der Waals and Redlich-Kwong-Soave EOS.

Discussion

A comparison between Eq. 16 and the equations proposed by Panagiotopoulos is made for CO_2, from the triple point to the critical point, and is shown in Figure 2. Experimental vapor pressures were taken from Herington (1975) and used in both methods. Specific volumes needed for the Panagiotopoulos model were obtained from Panagiotopoulos and Kumar (1985). It should be noted that in the model proposed here, no attempt is made to fit the liquid volumes, so only the vapor pressure fit is compared.

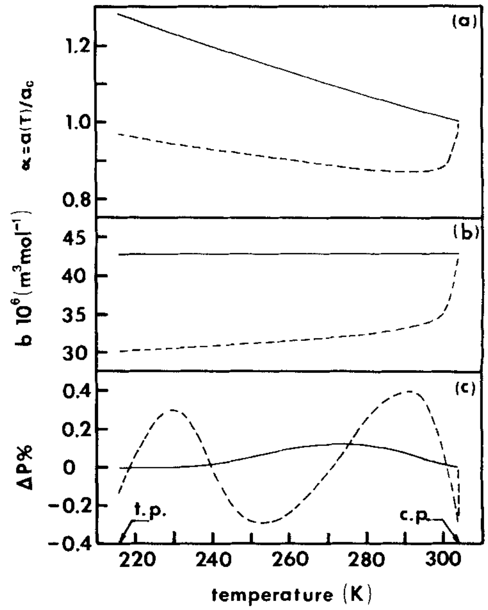

Figure 2. (a) Parameter α for CO_2 as a function of temperature.

(b) Parameter b, constant in this model.

(c) Percent relative errors for vapor pressure of CO_2

------- Panagiotopoulos, ——— this model.

Sixteen constants in two sets are used in the Panagiotopoulos model applicable to the van der Waals equation, compared with the two-constant equation, Eq. 16. Since both methods use the vapor pressure as an input, they are not predictive; Figure 2c shows the goodness of fit.

For VLE calculations, where the vapor pressures are of prime concern and where there is no need for accurate liquid volumes, the method proposed here is simpler.

Notation

A = parameter, Eq. 3
a, b = equation of state parameters
B = parameter, Eq. 4
$c_0 c_1$ = constants, Eq. 11
c_2 = parameter, Eq. 14
F = parameter, Eq. 12
P = pressure
R = gas constant
$r(X)$ = function, Eq. 15
T = absolute temperature
V = specific volume
X = parameter, Eq. 13
Z = compressibility factor
α = temperature function, Eq. 2
Ω_a = numerical constant, 0.42748 for SRK, 27/64 for VdW
Ω_b = numerical constant, 0.08664 for SRK, 1/8 for VdW

Subscripts

c = critical conditions
L = liquid phase
s = saturation condition
v = vapor phase

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