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Reappraisal of the Vidal equation-of-state formulation for vapor/liquid equilibrium

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Abstract

In 1978 Jean Vidal outlined an equation-of-state formulation for vapor/liquid-equilibrium calculations based on direct fitting of the energy parameter. There soon followed a paper by Huron and Vidal devoted to mixing rules, which included a brief review of the Vidal formulation under the heading "polynomial mixing rule." Neither paper presented examples of Vidal's formulation in any detail. Subsequent work focusing on mixing-rule models – Huron/Vidal, its variations, and Wong/Sandler – are treated extensively in the 1998 monograph by Orbey and Sandler. However, no mention is made there of Vidal's formulation, and indeed it seems never to have been evaluated in any detail. The purpose of this paper is to revive and exploit the Vidal formulation for general application to vapor/liquid-equilibrium calculations. It is theoretically sound, and at least as convenient and accurate in application as the gamma/phi formulation.

Keywords: Equation of state; Mixing rules; Vapor/liquid equilibrium

1. Introduction

The equation-of-state (EOS) formulation for vapor/liquid-equilibrium (VLE) calculations dates from the work of van der Waals, published in 1873. A comprehensive review of subsequent publications is provided by Valderrama [1]. Many deal with the composition dependence of the EOS parameters, for which no general theory is known.

The van der Waals, Redlich/Kwong, Soave/Redlich/Kwong, and Peng/Robinson equations all contain two parameters, and are versions of a generic equation of state, cubic in molar volume V:

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

The pure numbers ϵ and σ are specific to the equation of state. For the special case of pure species i the parameters are a_i and b_i, and are substance dependent. Both are independent of pressure, but a_i is a function of temperature. Mixture parameters a and b are functions of composition, and the usual practice has been to relate them to the pure-species parameters by empirical *mixing rules*. As written for the liquid phase, denoted by superscript l and with x for mole fractions, the van der Waals prescriptions provide the simplest realistic expressions:

$$b^{\mathrm{l}} \equiv \sum_i x_i b_i \tag{2}$$

$$a^{\mathrm{l}} \equiv \sum_i \sum_j x_i x_j a_{ij} \tag{3}$$

with $a_{ji} = a_{ij}$. Like subscripts (*ii* and *jj*) signify pure-species parameters, equivalent to a_i or a_j, whereas unlike subscripts (*ij*) signify an *interaction* parameter, commonly evaluated from pure-species parameters by an empirical *combining rule*, e.g.,

$$a_{ij} \equiv (a_i a_j)^{1/2} \tag{4}$$

Analogous equations for the vapor phase (superscript v) replace x with y.

A new era began with the publications by Vidal [2] and Huron and Vidal [3] of a method to relate an EOS to an excess-Gibbs-energy model and so to provide more generally applicable

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mixing rules with a theoretical basis in solution behavior at the limit of infinite pressure. Subsequent publications of variations and elaborations on this theme are treated by Orbey and Sandler [4]. Prominent among the resulting mixing rules are those of Huron and Vidal [3] and of Wong and Sandler [5].

Vidal's formulation as presented in the original papers is in no way related to any excess-Gibbs-energy model, and is readily justified on an empirical basis. Despite its potential as a versatile and accurate formulation for VLE calculations, it has received scant attention.

2. Mathematical formalism

To provide a foundation for comparisons of EOS formulations we review the necessary mathematics, structuring it for simplicity and consistent notation.

Central to VLE calculations is the fugacity, related for species i in phase π to the fugacity coefficient:

$$\hat{f}_i^{\pi} = x_i \hat{\phi}_i^{\pi} P$$

For VLE, $\hat{f}_i^{l} = \hat{f}_i^{v}$, and combining this equation with the preceding definition yields:

$$x_i \hat{\phi}_i^{l} = y_i \hat{\phi}_i^{v} \quad (i = 1, 2, \ldots, N) \tag{5}$$

In combination with an equation for $\hat{\phi}_i^{\pi}$ (π = l,v), Eq. (5) provide N relations that may be solved for N equation-of-state variables.

Setting $V = ZRT/P$ introduces the compressibility factor Z. In addition, dimensionless alternative EOS parameters are provided by the definitions:

$$\beta \equiv \frac{bP}{RT} \tag{6}$$

$$q \equiv \frac{a}{bRT} \tag{7}$$

Substituting for ϵ, σ, V, a, and b in Eq. (1) leads to expression of the EOS as a cubic equation in Z. A suitable example is the Peng/Robinson equation, for which $\epsilon = 1 - \sqrt{2}$ and $\sigma = 1 + \sqrt{2}$. In standard form it becomes:

$$Z^3 + u_1 Z^2 + u_2 Z + u_3 = 0 \tag{8}$$

where $u_1 = \beta - 1$, $u_2 = (q - 3\beta - 2)\beta$ and $u_3 = (1 + \beta - q)\beta^2$.

For applications to VLE, all three roots are real and positive, with the largest root being Z^v, specific to the vapor phase, and the smallest Z^l, specific to the liquid phase. Analytic solution for these roots is simple and direct. For the special case of a pure species, EOS parameters in Eqs. (6)–(8) are written as a_i, b_i, q_i, and β_i.

For a given temperature EOS parameters q and β apply equally to liquid and vapor phases of the same composition, but for phases of different composition in equilibrium identifying superscripts are added. Thus, q^v and β^v denote values for a mixture with the vapor-phase composition and q^l and β^l, a mixture with the liquid-phase composition. For a pure species superscripts are meaningless, and only a species-identifying subscript is required.

As discussed by Van Ness and Abbott [6], mixture parameters a, b, and q may be associated with *partial* EOS parameters, $\bar{a}_i$, $\bar{b}_i$, and $\bar{q}_i$. They are interrelated by the equations:

$$\bar{p}_i \equiv \left[\frac{\partial(np)}{\partial n_i}\right]_{T,n_j} \tag{9}$$

$$p = \sum_i x_i \bar{p}_i \tag{10}$$

where p represents an EOS parameter. Eq. (9) defines a partial value. Because the parameters are independent of pressure, P does not appear as a variable. Eq. (10) is the *summability* relation. Application of Eq. (9) to Eq. (7) leads to:

$$\bar{q}_i = q\left(1 + \frac{\bar{a}_i}{a} - \frac{\bar{b}_i}{b}\right) \tag{11}$$

Fugacity coefficients for the constituent species of a mixture are implicit in an equation of state. They are given for both vapor (π = v) and liquid (π = l) phases by [7]:

$$\ln \hat{\phi}_i^{\pi} = \frac{\bar{b}_i^{\pi}}{b^{\pi}}(Z^{\pi} - 1) - \ln(Z^{\pi} - \beta^{\pi}) - \bar{q}_i^{\pi} I^{\pi} \tag{12}$$

Quantities b^{π}, Z^{π}, β^{π}, and I^{π}, without subscripts, are for the mixture. Application requires solution of Eq. (8) for Z^{π}; quantity I^{π} is given by [7]:

$$I^{\pi} = \frac{1}{\sigma - \epsilon} \ln\left(\frac{Z^{\pi} + \sigma\beta^{\pi}}{Z^{\pi} + \epsilon\beta^{\pi}}\right) \qquad (\epsilon \neq \sigma) \tag{13}$$

For the special case of a pure species, identifying subscript i is added.

3. Evaluation of pure-species parameters b_i and q_i

Pure-species parameters a_i and b_i are given by generalized expressions in relation to critical temperature T_{c_i}, critical pressure P_{c_i}, and acentric factor ω_i:

$$b_i = \Omega \frac{RT_{c_i}}{P_{c_i}} \tag{14}$$

$$a_i = \Psi \frac{\alpha(T_{r_i}; \omega_i) R^2 T_{c_i}^2}{P_{c_i}} \tag{15}$$

Combination of Eqs. (7), (14), and (15) yields:

$$q_i = \frac{\Psi \alpha(T_{r_i}; \omega_i)}{\Omega T_{r_i}} \tag{16}$$

For the Peng/Robinson EOS [8] constants Ω and Ψ and the function $\alpha(T_{r_i}; \omega_i)$ are

$$\Omega = 0.07780, \qquad \Psi = 0.45724$$

and $\alpha(T_{r_i}; \omega_i) = [1 + \kappa(1 - T_{r_i}^{1/2})]^2$

where $\kappa = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$