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Note

A Generalized Process for Phase Equilibrium Calculation with Cubic Equations of State

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This paper presents a general method for calculating the fugacity coefficient with a view to representing phase equilibria of fluids on the basis of cubic equations of state with two, three or four parameters. The basic formalism selected in this study is that of Schmidt and Wenzel.

KEY WORDS: equation of state; fugacity; phase equilibrium.

1. INTRODUCTION

A number of practical applications in industrial sectors with sometimes widely varying requirements (such as the food industry, petroleum engineering, pharmacology, fine chemistry, etc.) need knowledge, or at least prediction, of the pressure P and temperature T conditions of phase changes and of the compositions of the phases concerned. It is therefore essential to develop models able to characterize thermodynamic equilibria at pressures which can reach high levels. There are various ways of constructing models with this purpose, including models based on equations of state, models involving group contributions, statistical models, and a number of other approaches. If the equation-of-state type of model is chosen, then the search for equilibrium conditions will require calculation of the fugacity coefficients, and the complexity of this calculation will depend on the form of the equation of state selected.

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Among the wide range of equations of state proposed in the literature, those of a cubic form, essentially derived from modifications of the van der Waals equation, are very often selected by users for predicting phase equilibria. These equations have proved relatively successful for such calculations because of their structural simplicity. However, no single equation has been able to establish unrivalled supremacy and there are consequently a large number of versions (differing for example as regards to the number of parameters, mixing rules, etc.), and each having its own strengths and weaknesses. It is therefore often necessary in practice to use several cubic equations of state depending on (i.e., polar or apolar) of the components in the mixture.

This paper presents a simple methodology whereby all existing cubic equations, whether they involve two, three, or four parameters, can be encompassed within a general formalism. This unified formulation of fugacity calculations is clearly of interest, because it makes it possible to implement any cubic equation independently of the number of parameters and of the associated mixing rules.

2. GENERAL FORMALISM

All cubic equations of state share the power of three with respect to volume v and including the same repulsion term of the van der Waals equation. Because of this similarity, it is possible to move from one equation to another, adjusting the values of the parameters involved in the equations. This means that a single equation of state can be adopted to represent any of the equations of this family. The equation which we chose to use and which possesses this ability is the one proposed by Schmidt and Wenzel [1]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ubv + wb^2} \tag{1}$$

This general equation contains four parameters, a, b, u, and w, which we allow to depend on temperature as well as on the number of moles of the components in the mixture:

$$a = a(T, n_i), \qquad b = b(T, n_i), \qquad u = u(T, n_i), \qquad w = w(T, n_i) \tag{2}$$

In this form, cubic equations with two parameters (of the Redlich–Kwong [2] or Peng–Robinson [3] types, for example) are directly accessible through allocation of adequate numeric values to u and w, namely,

$$u = 1, \qquad w = 0 \qquad \text{for} \quad \text{R–K} \tag{3}$$

$$u = 2, \qquad w = -1 \qquad \text{for} \quad \text{P–R} \tag{4}$$

However, equations with three parameters (such as the Patel–Teja [4] equation) or four parameters (of the Adachi–Lu–Sugie [5] type) do not appear explicitly in the general form selected. For these equations, the correlations between the specific parameters of the primary equation and the coefficients u and w of the generalized form must be established in order to be able to determine the fugacity coefficient for example. Thus the identification leads to the following relationships:

$$u = 1 + \frac{c}{b}, \qquad w = -\frac{c}{b} \qquad \text{for the Patel–Teja equation} \tag{5}$$

and

$$u = \frac{d-c}{b}, \qquad w = -\frac{dc}{b^2} \qquad \text{for the Adachi–Lu–Sugie equation} \tag{6}$$

To represent a given cubic equation for mixtures by means of the selected generalized form, it is also necessary for the coefficients u and w to invoke mixing rules which are coherent with the mixing rules for the specific parameters of this cubic equation. Obtaining the required compatibility often involves complicated mixing rules for u and w. As an example, for the four-parameter Adachi–Lu–Sugie equation, for which the usual associated mixing rules are

$$c = \sum x_i c_i, \qquad d = \sum x_i d_i \tag{7}$$

the corresponding rules for the terms u and w of the general formalism are expressed as follows:

$$u = \frac{\sum x_i u_i b_i}{\sum x_i b_i}, \qquad w = \frac{\sum x_i b_i (u_i - \sqrt{u_i^2 - 4w_i}) * \sum x_i b_i (u_i + \sqrt{u_i^2 - 4w_i})}{4(\sum x_i b_i)^2} \tag{8}$$

The complicated form of the mixing rules for u and w means that a calculation of the fugacity on the basis of analytical expressions is awkward. Despite this difficulty, the possibility of implementing any cubic equation by means of a single procedure remains a very attractive one, particularly from an algorithmic point of view, for performing comparative assessments of the various cubic equations. Consequently, we develop a method for calculating the fugacity coefficient based on Eq. (1), which removes the need to convert the mixing rules and therefore gets around the difficulty emphasized above.

3. CALCULATION OF THE FUGACITY COEFFICIENT

The fugacity coefficient Φ_i of component i is calculated from the relationship

$$\ln \phi_i = \left(\frac{\partial n \, \Delta a^{r}}{\partial n_i} \right)_{T, V_T, n_{j \neq i}} - \ln Z \tag{9}$$

where

$$\Delta a^{r} = \frac{a - a^{r}}{RT} = \int_{\infty}^{v} \left(\frac{1}{v} - \frac{P}{RT} \right) dv \tag{10}$$

designates the residual Helmholtz free energy, which is expressed by means of the cubic equation of state (1) by

$$\Delta a^{r} = \ln \frac{v}{v-b} + \lambda, \qquad \text{with} \quad \lambda = \int_{\infty}^{v} \frac{a/RT}{v^2 + ubv + wb^2} \, dv \tag{11}$$

The analytical expressions for λ depend on the nature of the roots of the denominator:

$$\Delta > 0, \qquad \lambda = \frac{-a}{bRT\sqrt{\Delta}} \ln \left(\frac{2v + ub + b\sqrt{\Delta}}{2v + ub - b\sqrt{\Delta}} \right) \tag{12a}$$

$$\Delta < 0, \qquad \lambda = \frac{-2a}{bRT\sqrt{-\Delta}} \operatorname{Artan} \left(\frac{b\sqrt{-\Delta}}{2v + ub} \right) \tag{12b}$$

$$\Delta = 0, \qquad \lambda = \frac{-a}{RT} \frac{2}{2v + ub} \tag{12c}$$

with

$$\Delta = u^2 - 4w \tag{12d}$$

In practice, it is preferable to introduce reduced coefficients A and B and the compressibility factor Z defined by

$$A = \frac{aP}{(RT)^2}, \qquad B = \frac{bP}{RT}, \qquad Z = \frac{Pv}{RT} \tag{13}$$

The expression for the fugacity coefficient can be written in the reduced general form presented in Table I. The continuity of the fugacity coefficient between all three situations can easily be verified.

In this formulation the terms u and w are characteristic of the cubic form equation used, whereas the derivatives u^* and w^* depend on the mixing rules which must be used in the case of systems containing several components. It is at this level that conversion of mixing rules can be

Table I. Fugacity Coefficient

$$\ln \phi_i = -\ln(Z-B) + (Z-1)\, b^* + \lambda(a^* - b^*) + Ju^* + Kw^*$$

$\Delta \neq 0$

$$J = \frac{1}{\Delta}\left[-u\lambda - (uZ + 2wB)\left\{\frac{1}{Z-B} - 1\right\}\right]$$

$$K = \frac{1}{\Delta}\left[2\lambda + (2Z + uB)\left\{\frac{1}{Z-B} - 1\right\}\right]$$

$\Delta = 0$

$$J = \frac{2AB}{(2Z+uB)^2}$$

$$K = 0$$

$$a^* = \left(\frac{\partial n^2 a}{\partial n_i}\right)\Big/ na; \quad b^* = \left(\frac{\partial nb}{\partial n_i}\right)\Big/ b; \quad u^* = n\left(\frac{\partial u}{\partial n_i}\right); \quad w^* = n\left(\frac{\partial w}{\partial n_i}\right)$$

Table II. Two-Parameter Cubic Equations of State

Name	Year	Ref. No.	Equation	u	w	u^*	w^*
van der Waals	1873		$P = \frac{RT}{v-b} - \frac{a}{v^2}$	0	0	0	0
Redlich–Kwong	1949	2	$P = \frac{RT}{v-b} - \frac{a/\sqrt{T}}{v(v+b)}$	1	0	0	0
Wilson	1964	6	$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$	1	0	0	0
Soave	1972	7	$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$	1	0	0	0
Peng–Robinson	1976	3	$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$	2	−1	0	0
Harmens	1977	8	$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 3vb - 2b^2}$	3	−2	0	0
Peneloux et al.	1982	9	$P = \frac{RT}{\tilde{v}-b} - \frac{a(T)}{\tilde{v}(\tilde{v}+b)}; \quad v = \tilde{v} - c$	1	0	0	0
Adachi–Lu	1984	10	$P = \frac{RT}{v-b} - \frac{a(T)}{v^2}$	0	0	0	0
Watson et al.	1986	11	$P = \frac{RT}{\tilde{v}-b} - \frac{a(T)}{\tilde{v}^2}; \quad v = \tilde{v} - c(T)$	0	0	0	0

Table III. Three-Parameter Cubic Equations of State

Name	Year	Ref. No.	Equation	u	w	u^*	w^*
Clausius	1881		$P=\frac{RT}{v-b}-\frac{a}{(v+c)^2}$	$\frac{2c}{b}$	$\frac{u^2}{4}(\Delta=0)$	$u[c^*-b^*]$	—
Fuller	1976	12	$P=\frac{RT}{v-b(T)}-\frac{a(T)}{v(v+c(T)\,b(T))}$	c	0	$u[c^*-1]$	0
Schmidt–Wenzel	1980	1	$P=\frac{RT}{v-b}-\frac{a(T)}{v^2+(1+3c)v-3cb^2}$	$1+3c$	$-3c$	$-w[c^*-1]$	$w[c^*-1]$
Harmens–Knapp	1980	13	$P=\frac{RT}{v-b}-\frac{a(T)}{v^2+vcb-(c-1)\,b^2}$	c	$1-c$	$u[c^*-1]$	$-u[c^*-1]$
Heyen	1980	14	$P=\frac{RT}{v-b}-\frac{a(T)}{v^2+(b+c)v-bc}$	$1+\frac{c}{b}$	$-\frac{c}{b}$	$-w[c^*-b^*]$	$w[c^*-b^*]$
Kubic	1982	15	$P=\frac{RT}{v-b}-\frac{a(T)}{(v+c(T))^2}$	$\frac{2c}{b}$	$\frac{u^2}{4}(\Delta=0)$	$u[c^*-b^*]$	—
Patel–Teja	1982	4	$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)+c(v-b)}$	$1+\frac{c}{b}$	$-\frac{c}{b}$	$-w[c^*-b^*]$	$w[c^*-b^*]$
Yu–Lu	1987	16	$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+c)+b(3v+c)}$	$3+\frac{c}{b}$	$\frac{c}{b}$	$w[c^*-b^*]$	$w[c^*-b^*]$
Iwai–Margerum–Lu	1988	17	$P=\frac{RT}{v-b}-\frac{a(T)}{v^2+cb(v-b)}$	c	$-c$	$u[c^*-1]$	$-u[c^*-1]$
Guo–Du	1989	18	$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+c)+c(v-b)}$	$\frac{2c}{b}$	$-\frac{c}{b}$	$u[c^*-b^*]$	$w[c^*-b^*]$

Table IV. Four-Parameter Cubic Equations of State[a]

Name	Year	Ref. No.	Equation	u	w	u^*	w^*
Adachi–Lu–Sugie	1983	5	$P=\frac{RT}{v-b}-\frac{a(T)}{(v-c)(v+d)}$	$-\frac{c}{b}+\frac{d}{b}$	$-\frac{c}{b}\cdot\frac{d}{b}$	$-\frac{c}{b}[c^*-b^*]+\frac{d}{b}[d^*-b^*]$	$w[c^*+d^*-2b^*]$
Trebble–Bishnoi	1987	19	$P=\frac{RT}{v-b}-\frac{a(T)}{v^2+(b+c)-bc-d^2}$	$1+\frac{c}{b}$	$-\frac{c}{b}-\frac{d^2}{b^2}$	$\frac{c}{b}[c^*-b^*]$	$-\frac{c}{b}[c^*-b^*]-\frac{2d^2}{b^2}[d^*-b^*]$

[a] $a^*=(\partial n^2a/\partial n_i)/na$; $b^*=(\partial nb/\partial n_i)/b$; $c^*=(\partial nc/\partial n_i)/c$; $d^*=(\partial nd/\partial n_i)/d$; $u^*=n(\partial u/\partial n_i)$; $w^*=n(\partial w/\partial n_i)$.

avoided and the procedure simplified by expressing the derivatives u^* and w^* directly as a function of the derivatives of the parameters of the equation of state we wish to represent.

In Tables II, III, and IV we list the cubic equations of state frequently cited in the literature; for each of them we have expressed as a function of its parameters the terms u and w, as well as u^* and w^*, so as to encompass all the equations within the general formalism.

4. CONCLUSION

Research into the prediction of thermodynamic equilibria on the basis of cubic equations of state often requires comparison of their respective performances. The objective pursued here is to provide potential users with a unified tool for implementing any of these equations whatever the number of parameters and whatever the associated mixing rules.

The expression of the fugacity coefficient (Table I) in connection with the relationships presented in Tables II, III, and IV therefore allows cubic equations of state to be used for phase equilibrium calculation using a single procedure, whatever the sign of Δ (the most common situation in practice is $\Delta > 0$). Similar developments could be envisaged for other thermodynamic properties of liquids and gases such as thermal capacities, residual entropy, etc.

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