

REVIEWS

The State of the Cubic Equations of State

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The development of van der Waals cubic equations of state and their application to the correlation and prediction of phase equilibrium properties is presented and analyzed. The discussion starts with a brief account of the contributions to equation of state development during the years before van der Waals. Then, the original equation proposed in the celebrated thesis of van der Waals in 1873 and its tremendous importance in describing fluid behavior are analyzed. A chronological critical walk through the most important contributions during the first part of the 1900s is made, to arrive at the proposal that I consider to be the most outstanding since van der Waals: the equation proposed by Redlich and Kwong in 1949. The contributions after Redlich and Kwong to the modern development of equations of state and the most recent equations proposed in the literature are analyzed. The application of cubic equations of state to mixtures and the development of mixing rules is put in a proper perspective, and the main applications of cubic equations of state to binary and multicomponent mixtures, to high-pressure phase equilibria, to supercritical fluids, to reservoir fluids, and to polymer mixtures are summarized. Finally, recommendations on which equations of state and which mixing rules to use for given applications are presented.

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Introduction

Since van der Waals proposed the first version of his celebrated equation of state (EoS) more than a century

ago,¹ many modifications have been proposed in the literature to improve the predictions of volumetric, thermodynamic, and phase equilibrium properties. Although the van der Waals (vdW) equation is not accurate for most applications, it can be considered the major contribution to this field since the first attempts to represent *PVT* behavior made by Boyle in the 17th century.² The vdW equation and the many modifications that are now available are special cases of a generic cubic equation, which can be written as

$$P = \frac{RT}{V - b} - P_{\text{att}}(T, V) \quad (1)$$

$$P_{\text{att}}(T, V) = \frac{a}{V(V + d) + c(V - d)} \quad (2)$$

Here, *a*, *b*, *c*, and *d* can be constants or functions of temperature and some fluid properties (acentric factor, critical compressibility factor, normal boiling point, etc.). These parameters cannot be chosen arbitrarily, as certain theoretical and empirical restrictions must be imposed.^{3,4}

Many complex and more accurate EoS have been proposed through the years and several theories have been devised to better represent *PVT* properties and vapor–liquid equilibrium. Complex molecular-based equations of state have received special attention, and the power and usefulness of this type of model have been noted many times. However, not many articles questioning the results and conclusions obtained from these equations have been published. Recently, Nezbeda⁵ analyzed this type of EoS and summarized some basic rules that should be observed for developing molecular-based EoS that can be considered as truly molecular-based. The papers by Anderko⁶ and Wei and Sadus⁷

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Table 1. Advantages and Disadvantages of van der Waals Cubic EoS

advantages		disadvantages	
a	third degree in volume, which makes calculations relatively simple to perform	a	actual <i>PVT</i> data tend to follow a fourth-degree equation instead of a cubic equation
b	present correct limiting behavior: as $V \rightarrow b$, $P \rightarrow \infty$ in all van der Waals type equations	b	both the repulsive and attractive terms are inaccurate, as shown by molecular simulations
c	known inaccuracies of both the repulsive and attractive terms are canceled when the EoS are used to calculate fluid properties, in particular VLE	c	cubic equations cannot represent all properties of a fluid in all different ranges of P and T
d	for most applications, cubic EoS can be tuned to give accurate values for any volumetric or thermodynamic property	d	temperature dependency of the force constant a is not well established; co-volume b seems to be density-dependent, but the dependence is unknown
e	extension to mixtures is relatively easy using mixing and combining rules of any complexity	e	because interactions between unlike molecules are unknown, most mixing and combining rules are empirical, and interaction parameters are usually required
f	cubic equations are suitable for the application of modern mixing rules that include Gibbs free energy models or concentration-dependent parameters	f	in applications to complex mixtures, several interaction parameters might be required, even with the use of modern mixing rules

reviewed several of these complex EoS, although they also pay some attention to cubic vdW equations of state. Empirical multiparameter EoS, all of them of noncubic type and with 15–60 or more parameters, became available during the 1970s. The advantages and disadvantages of these equations and the development of such equations during the past 20 years are reviewed and analyzed in the book by Sengers et al.⁸ For pure substances, multiparameter EoS are divided into reference and technical EoS. For mixtures, the introduction of Helmholtz free energy based multifluid mixture models enabled highly accurate descriptions of thermodynamic properties for the first time. Multiparameter EoS have recently been reviewed by Span et al.⁹ According to these authors, the unsolved problems in this field offer a multitude of scientific challenges with regard to the actual development of EoS and mixture models.

Despite the many equations of different types and the several new applications, cubic equations similar to eq 1 are still used in semiquantitative predictions of equilibrium phenomena, in process design, and in

simulations. There are several reasons for this popularity but also several disadvantages of cubic equations, which have encouraged many researchers to look for different approaches such as those mentioned above. Table 1 summarizes some of these advantages and disadvantages of cubic EoS.

To clarify the limits and scope of this paper, a convenient classification is shown in Figure 1. This paper is limited to those aspects that the author finds relevant in the development of the group called “cubic empirical equations”. The paper starts with a short review of the history of cubic EoS, leading to an assessment of which EoS might be most useful for several applications. Because of the enormous amount of literature on the subject of EoS, one can always quarrel with which publications to include in a review like the present one. Thus, the publications included here represent what the author considers most relevant for the practitioners in the field of fluid properties and phase equilibria using cubic EoS.

A recent book published by IUPAC⁸ reviews the main advances of EoS for fluids and fluid mixtures. The

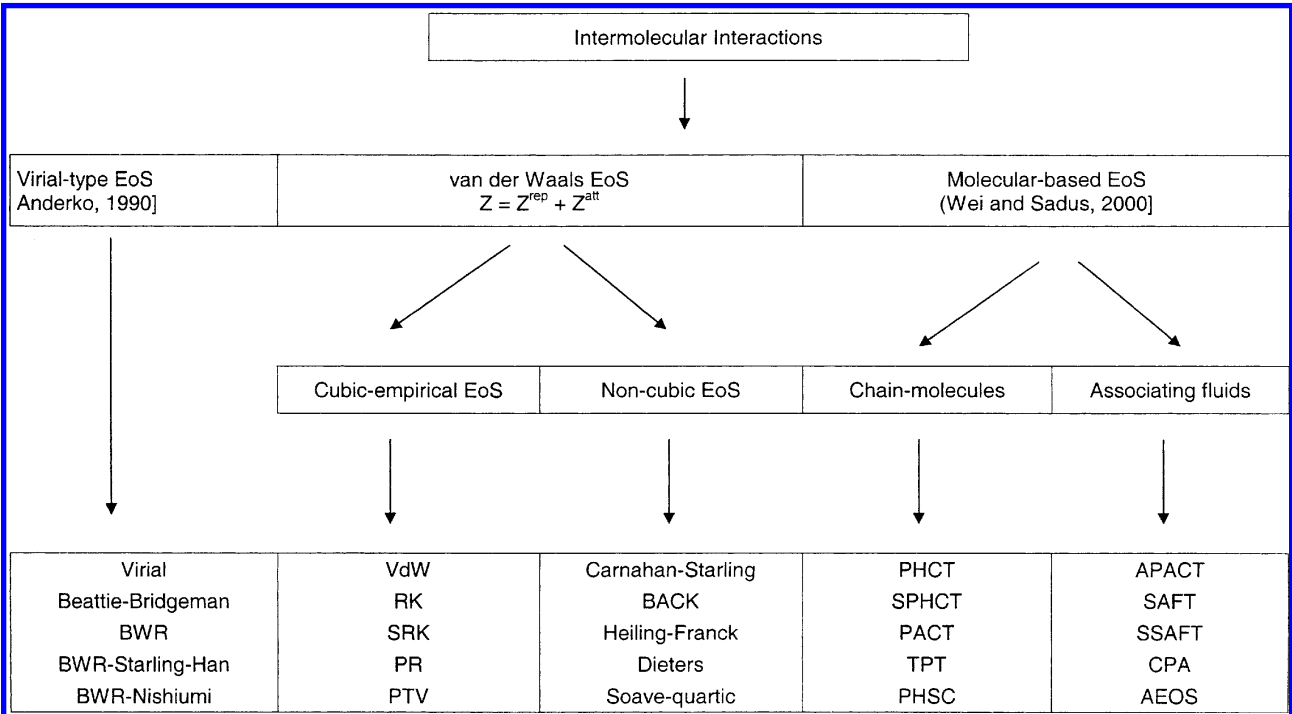


Figure 1. Classification of various type of equations of state, with a selection of equations for each group. In this classification, van der Waals EoS are those cubic and noncubic equations that consider the compressibility factor as $Z = Z^{\text{rep}} + Z^{\text{att}}$.

theoretical basis and practical use of each type of equation is discussed, and the strengths and weaknesses of each are analyzed. Topics addressed include the virial equation of state, cubic equations and generalized van der Waals equations, multiparameter EoS, perturbation theory, integral equations, corresponding states, and mixing rules. Special attention is also devoted to associating fluids, polydisperse fluids, polymer systems, self-assembled systems, ionic fluids, and fluids near critical points. For those interested in cubic EoS, the chapters by Anderko on cubic and generalized van der Waals equations and by Sandler and Orbey on mixing and combining rules, included in this IUPAC book, should be read. For those interested in more theoretical aspects of EoS, the review by Sarry¹⁰ and the recently published book by Eliezer et al.¹¹ present detailed pedagogical accounts of EoS and their applications in several important and fast-growing topics in theoretical physics, chemistry, and engineering.

van der Waals' Proposal

Before van der Waals, some attempts to represent the real behavior of gases were made. The main drawback of the proposals presented before van der Waals was that they did not consider the finite volume occupied by the molecules, which is also the case for the ideal gas model. The idea of including the volume of the molecules into the repulsive term was suggested by Bernoulli at the end of the 18th century,¹² but it was ignored for a long time. The works of Hirn¹³ and Dupre¹⁴ revived this idea. The volume V was replaced by $(V - b)$, where b represents the volume occupied by the molecules, which Dupre named the "covolume". However, none of these contributions were of general use, and none was able to answer the many questions related to fluid behavior remaining at that time. It was van der Waals with his celebrated doctoral thesis "The Continuity of the Liquid and Gaseous States" and other works derived from it who gave rise to what seems to be the most longed-for but still unattainable goal of many researchers: finding the most simple and generalized EoS. van der Waals¹ proposed in his thesis the following equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = R(1 + \alpha t) \quad (3)$$

In this equation, P is the external pressure, V is the molar volume, b is a multiple of the molecular volume, a is the "specific attraction", and α is a constant related to the kinetic energy of the molecules. This equation later became what is now known as the van der Waals equation of state

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \quad (4)$$

The parameters, or so-called "equation of state constants", a and b were first calculated using PVT data but were later related to critical properties by applying the condition of continuity of the critical isotherm at the critical point. This requirement allows the constants to be related to the critical pressure and temperature, P_c and T_c , respectively, and also gives a constant value for the critical compressibility factor ($z_c = 0.375$).

van der Waals' equation of state and his ideas on intermolecular forces have been the subjects of many

studies through the years. Andrews' discovery of the existence of the critical point helped van der Waals in formulating a theory that accounts for the behavior of fluids both above and below the critical point. van der Waals unified most of the experimental knowledge on fluid properties up to the 1870s in a single equation, which not only accounted for deviations from the ideal gas but also predicted the existence of a critical point. The equation also simultaneously considered the vapor and liquid phases, phase equilibrium below the critical point, and even the separation of phases above the critical point, a phenomenon that was experimentally verified several years later by Krichevskii.¹⁵ The concepts developed by van der Waals on the separation of repulsion forces caused by molecular size from cohesive forces caused by molecular attraction still remain as the basis of several theories concerning the prediction of fluid properties and of computer simulations based on statistical mechanics. Also, his ideas on the existence of a continuous equation connecting the liquid and vapor states, on the corresponding state principle, and on the extension of the pure-component equation of state to mixtures through the use of mixing rules have contributed greatly to the present developments in this area. A good study on the van der Waals equation is given in the book by Vukalovich and Novikov.¹⁶

Clausius,¹⁷ contrary to what van der Waals claimed in his thesis, recognized that the attractive term should be temperature-dependent. Clausius also modified the volume dependency of the attractive term. His proposal was²

$$P = \frac{RT}{(V - b)} - \frac{a/T}{(V + c)^2} \quad (5)$$

Clausius arrived at his equation by considering that molecules at low temperature do not move freely but form clusters of molecules in which stronger attractions occur (the van der Waals term a/V^2 is too small at low temperatures). This equation has been the subject of several studies through the years, and some contradictory arguments about its accuracy can be found in the literature.^{4,12,18} It can be seen that Clausius' equation allows for the use of an additional empirical parameter, because the critical compressibility factor is no longer constant, as occurs with the van der Waals equation. This fact has given rise to a group of important EoS known as "three-parameter equations". Modifications to the repulsive term were also considered soon after van der Waals' proposal. However, most modifications to the repulsive term give rise to noncubic equations.

The Redlich-Kwong (RK) Proposal

By the time of the proposal of Redlich and Kwong,¹⁹ there were about 200 equations of state. Otto²⁰ gave a list of 56 equations, most of them modifications to vdW equation. Also, the book by Vukalovich and Novikov¹⁶ contains a list of 150 EoS published by 1944, and the book by Walas²¹ gives a list of about 60 equations published before 1949. The renewed interest in van der Waals type equations came years after Redlich and Kwong's contribution, but these authors certainly showed the way on how to improve upon van der Waals' ideas. As Prausnitz²² wrote, "Redlich's great contribution was to revive the spirit of van der Waals."

Redlich and Kwong were very much concerned about the limiting behavior of the EoS. They wanted correct

representations at low density and at high density and proposed the following equation

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T)}{V(V+b)} \quad (6)$$

$$\alpha(T) = a/T^{0.5} \quad a_c = \Omega_a R^2 T_c^{2.5}/P_c \quad \Omega_a = 0.4278 \\ b = \Omega_b RT_c/P_c \quad \Omega_b = 0.0867$$

This equation did not have a strong theoretical background but proved to give good results for many gaseous systems. It should also be mentioned that, when Redlich and Kwong proposed their celebrated equation of state, they were interested in developing a good equation for gases only. Not a single application to liquids can be found in Redlich and Kwong's original paper.

During the period 1960–1980, the interest in Redlich–Kwong-type equations was so high that the RK equation can be considered the most modified EoS ever. A complete account of all such equations is not easy to provide; however, following some good review articles and our own findings, it is not adventurous to estimate that there must be about 150 RK-type equations and a total of 400 cubic EoS proposed to date in the literature. During the 15 years after Redlich and Kwong's proposal, the equation seemed to be one more of the already many modifications to the vdW equation, with the Chao–Seader correlation being the only major application of this EoS. The works of Wilson,²³ Barner et al.,²⁴ and Chueh and Prausnitz²⁵ attracted renewed interest in exploring Redlich and Kwong's equation.

From Redlich–Kwong to Soave

Wilson²³ made a major contribution to the attempts at generalizing the RK equation. He was able to consider the variations in behavior of different fluids at the same reduced pressure and reduced temperature by introducing Pitzer's acentric factor (ω) into the attractive term. Wilson's equation was largely ignored during the rest of the 1960s and until 1972, the time of Soave's proposal.

Soave²⁶ proposed a new improved version of Wilson's idea. He redefined the $\alpha(T_R, \omega)$ function and kept the RK volume functionality, giving what became, in a short period, one of the most popular EoS in the hydrocarbon industry. Computer simulation packages became popular during the late 1960s, and there was great need for a simple, generalized, and reasonably accurate EoS for the many repetitive calculations required in process simulations. Soave's EoS, commonly known as the SRK equation, satisfied the need at that time. Also, in the mid 1970s, optimization of industrial processes became extremely important, because of the so-called oil crisis, and Soave's equation was again of great help for the type of calculations required in optimization algorithms. The SRK equation can be summarized as follows

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_R, \omega)}{V(V+b)} \quad (7)$$

$$a_c = 0.42747 \frac{RT_c^{2.5}}{P_c} \quad \alpha(T_R, \omega) = [1 + m(1 - T_R^{0.5})]^2 \\ b = 0.08664 \frac{RT_c}{P_c} \quad m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (8)$$

After Soave's proposal, many modifications were presented in the literature for improving predictions of one or another property. These works were not limited to proposing new temperature models for $\alpha(T_R, \omega)$, but also considered modifications of the volume dependence of the attractive pressure term. The most popular of all of these modifications is the one proposed by Peng and Robinson.²⁷ Peng and Robinson improved upon Soave's equation by recalculating the $\alpha(T_R, \omega)$ function and by modifying the volume dependency of the attractive term. These changes allowed them to obtain better results for liquid volumes and better representations of vapor–liquid equilibrium (VLE) for many mixtures. Peng and Robinson's equation is

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_R, \omega)}{V(V+b) + b(V-b)} \quad (9)$$

$$a_c = 0.45724 \frac{RT_c^{2.5}}{P_c} \quad \alpha(T_R, \omega) = [1 + m(1 - T_R^{0.5})]^2 \quad (10)$$

$$b = 0.07780 \frac{RT_c}{P_c} \\ m = 0.37464 - 1.54226\omega - 0.26992\omega^2$$

The SRK and the PR equations are the most popular cubic equations used currently in research, simulations, and optimizations in which thermodynamic and VLE properties are required. These two equations have been considered for all types of calculations, from simple estimations of pure-fluid volumetric properties and vapor pressures to descriptions of complex multicomponent systems. New models for the equation of state parameters and for the mixing rules are the most common modifications. Overall, all of these modifications did not contribute to any major development until the early 1980s, with the so-called three-parameter EoS and the development of new mixing rules. Nevertheless, most modern computer process simulation packages (ChemCAD, AspenPlus, Hysim, PRO/II) include the SRK and PR equations among the thermodynamic options.

Modifications to the SRK and PR Equations

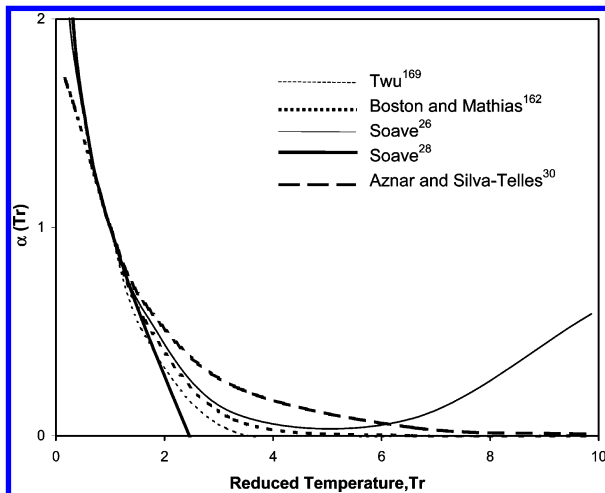
The trends in research on cubic EoS after Soave's and Peng and Robinson's contributions have followed three main routes: (i) modifications to $\alpha(T_R)$ in the SRK and PR equations, (ii) modifications of the volume dependence of the attractive pressure term, and (iii) use of a third substance-dependent parameter. The first approach has focused on looking for more accurate predictions of vapor pressure and vapor–liquid equilibrium. The second route has given rise to the “volume-translation” concept. The third line of development constitutes the so-called group of “three-parameter equations of state”, of which some promising generalized three-parameter equations have been proposed.

Modifications to $\alpha(T_R)$

Modifications of the temperature-dependent function $\alpha(T_R)$ in the attractive term of the SRK and PR equations have been mainly proposed to improve correlations and predictions of vapor pressure for polar fluids. Table 2 shows some selected expression proposed in the

Table 2. Selected Models for the Temperature Dependence of the Attractive Term $\alpha(T)$ in Cubic Equations of State

expression for $\alpha(T)$	ref
$1/\sqrt{T_r}$	Redlich and Kwong ¹⁹
$T_r(1 + mT_r^{-1})$	Wilson ²³
$m/T_r + n/T_r^2$	Barner et al. ²⁴
$[1 + m(1 - \sqrt{T_r})]^2$	Soave ²⁶
$1 + m(T_r - 1)^2(1 - \sqrt{T_r})^2$	Usdin and McAuliffe ⁵⁰
$\alpha(T_r) = 1 + (1 - T_r)(m + n/T_r)$	Soave ²⁸
$\exp[C(1 - T_r^m)]$	Heyen ⁵²
$[1 + m(1 - \sqrt{T_r}) + n\sqrt{1 - T_r/0.7}]^2$	Raimondi ¹⁶⁰
$m_1 + m_2/T_r + m_3/T_r^2$	Ishikawa et al. ¹⁶¹
$\exp[C(1 - T_r^q)]$	Boston and Mathias ¹⁶²
$[1 + m(1 - \sqrt{T_r}) - p(1 - T_r)(0.7 - T_r)]^2$	Mathias ¹⁶³
$1 + m_1(1 - \sqrt{T_r}) + m_2(1 - \sqrt{T_r})^2 + m_3(1 - \sqrt{T_r})^3$	Mathias and Copeman ⁸²
$[1 + m(1 - \sqrt{T_r})]^2/T_r$	Bazua ¹⁶⁴
$m_1 + m_2/T_r + m_3/T_r^2 + m_4/T_r^3$	Adachi and Lu ¹⁶⁵
$1 + m_1(T_r - 1) + m_2(\sqrt{T_r} - 1)$	Gibbons and Laughton ¹⁶⁶
$[1 + m(1 + T_r^q)]^2$	Kabadl and Danner ¹⁶⁷
$[1 + m(1 - \sqrt{T_r}) + n(1 - T_r)(0.7 - T_r)]^2$	Stryjek and Vera ⁶⁸
$[1 + m(1 - \sqrt{T_r})]^2 + n(T_r - 0.6)^2$	Adachi and Sugie ⁶⁹
$[1 + m(1 - \sqrt{T_r}) - p(1 - T_r)(q - T_r)]^2$	Du and Guo ¹⁶⁸
$\{[1 + n \exp(-k)]/[1 + n \exp(-k T_r^{2m})]\} T_r^{2m-1} \exp[(1 - T_r^{2m})^k]$	Twu ¹⁶⁹
$\exp[m(1 - T_r) + n(1 - \sqrt{T_r})^2]$	Melhem et al. ¹⁷⁰
$\exp[p(1 - T_r) 1 - T_r ^{\Gamma-1} + q(T_r^{-1} - 1)]$	Almeida et al. ²⁹
$[1 + m(1 - \sqrt{\theta_r})]^2, \theta = (T - T_{pt})/(T_c - T_{pt})$	Nasrifar and Moshfeghian ¹⁷¹

**Figure 2.** Selected temperature functions in the attractive term of cubic EoS for carbon dioxide.

literature for the $\alpha(T_r)$ function. The most popular of all of the generalized models is that of Soave.²⁶ Of the models containing component-dependent parameters, those of Soave²⁸ and Almeida et al.²⁹ have been extensively studied; these expressions are

$$\alpha(T_r) = 1 + (1 - T_r)(m + n/T_r)$$

and

$$\alpha(T_r) = \exp[p(1 - T_r)|1 - T_r|^{\Gamma-1} + q(T_r^{-1} - 1)] \quad (11)$$

respectively. The parameters m and n for the Soave model and p , q , and Γ for the Almeida et al. model are available for about 500 substances for the SRK, PR, and Patel–Teja–Valderrama (PTV) equations.^{30–32}

Figure 2 shows how some of these functions behave at low and high temperature. The main conclusions from all of these works is that, indeed, two-parameter cubic EoS can be adjusted to give good representations of PVT properties of pure polar fluids by modifying the temperature functionality of the attractive term. Benmekki

and Mansoori³³ have mentioned that when, EoS are applied to mixtures, the classical vdW mixing rules are for constants of an equation of state and not for any thermodynamic state function that might appear in the equation of state. Therefore, they parametrized the PR equation by introducing an additional parameter, resulting in an EoS with three temperature-independent constants. This point is further discussed later in this paper in the section on mixtures.

Volume-Translated Equations

The volume-translation concept first suggested by Martin⁴ and developed by Peneloux et al.³⁴ has received some attention.^{35–40} Peneloux et al.³⁴ proposed a consistent volume correction in the SRK equation of state, which improves volume predictions without changing the VLE conditions. The method consists of using a corrected volume $V^* = V + t$, where t is a small component-dependent molar volume correction factor. Thus, for the vdW equation the following expression is obtained

$$P = \frac{RT}{V + t - b} - \frac{a}{(V + t)^2} \quad (12)$$

Peneloux et al.³⁴ pointed out that other volume corrections such as the correction factor of Lin and Daubert⁴¹ do not preserve this characteristic of improving a given property while keeping others unchanged. The method has been highly recommended for calculating phase and volumetric behavior of hydrocarbon mixtures and reservoir fluids. An extension of the volume-translation concept has been proposed by Mathias et al.,⁴² consisting of adding another term to the corrected volume ($V + s$) proposed by Peneloux et al.³⁴

Other works on translated equations include applications to the calculation of saturated densities of binary mixtures,⁴³ to the modeling of solid phases,⁴⁴ and to phase equilibrium in mixtures containing supercritical components.⁴⁵ Tsai and Chen³⁸ developed a volume-translated Peng–Robinson (VTPR) equation in which the temperature dependence of the EoS energy param-

Table 3. PTV Equation of State and Fugacity Coefficients^a

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + c(V-b)}$$

$$\begin{aligned} a &= a_c \alpha(T_R) \\ a &= \Omega_a (R^2 T_c^2 / P_c^2) \\ \alpha(T_R) &= [1 + F(1 - \sqrt{T_R})]^2 \\ b &= \Omega_b (RT_c / P_c) \\ c &= \Omega_c (RT_c / P_c) \end{aligned}$$

$$\begin{aligned} \Omega_a &= 0.661\,21 - 0.761\,057z_c \\ \Omega_b &= 0.022\,07 - 0.208\,68z_c \\ \Omega_c &= 0.577\,65 - 1.870\,80z_c \\ F &= 0.462\,83 + 3.582\,30\omega z_c + 8.194\,17(\omega z_c)^2 \end{aligned}$$

$$Z^3 + (C-1)Z^2 + [A - 2BC - B^2 - (B+C)Z + (B^2C + BC - AB)]Z + (B^2C + BC - AB) = 0$$

$$Z = \frac{PV}{RT} \quad A_i = \frac{a_i P}{R^2 T^2}, \quad B_i = \frac{b_i P}{RT}, \quad C_i = \frac{c_i P}{RT} \quad A = \frac{aP}{R^2 T^2}, \quad B = \frac{bP}{RT}, \quad C = \frac{cP}{RT}$$

$$\ln \phi_i = -\ln(Z - B) + \frac{A/2}{\sqrt{BC + \left(\frac{B+C}{2}\right)^2}} \left[\frac{\bar{A}_i}{A} + 1 - \frac{\alpha''/4}{BC + \left(\frac{B+C}{2}\right)^2} \right] \ln \left[\frac{Z + \left(\frac{B+C}{2}\right) - \sqrt{BC + \left(\frac{B+C}{2}\right)^2}}{Z + \left(\frac{B+C}{2}\right) + \sqrt{BC + \left(\frac{B+C}{2}\right)^2}} \right] +$$

$$\frac{1}{4} \left[\frac{Z\alpha'' + \beta''}{BC + \left(\frac{B+C}{2}\right)^2} \right] \left(1 - \frac{1}{Z-B} \right) + \frac{\bar{B}_i}{Z-B}$$

$$\bar{A}_i = \left(\frac{\partial nA}{\partial n_i} \right)_{T,V,n_j}, \quad \bar{B}_i = \left(\frac{\partial nB}{\partial n_i} \right)_{T,V,n_j}, \quad \bar{C}_i = \left(\frac{\partial nC}{\partial n_i} \right)_{T,V,n_j}$$

$$\alpha'' = 3B\bar{C}_i + 3C\bar{B}_i + C\bar{C}_i + B\bar{B}_i \quad \beta'' = (-B + C)(C\bar{B}_i - B\bar{C}_i)$$

^a Expressions for the partial derivatives included in the above equations are obtained for each mixing rule to be employed.

eter was regressed by an improved expression that yields better correlations of pure-fluid vapor pressures. The VTPR equation is comparable to other EoS in VLE calculations with various mixing rules, but it yields better predictions for the molar volumes of liquid mixtures. De Sant'Ana et al.³⁹ evaluated an improved volume-translated EoS for the prediction of volumetric properties of fluids. According to these authors, the proposed equation does not present some inconsistencies found by several authors for this type of EoS, an argument that has been refuted in the literature.⁴⁶ More recently, Cabral et al.⁴⁰ used molecular simulation results to study the performance of a translated Peng–Robinson EoS. The authors emphasized the special effects of the combining rules for better predicting vapor–liquid equilibrium and excess properties using the proposed translated PR–Lennard-Jones EoS. Despite the progress made on this type of modification, translated cubic EoS have not become popular for practical users.

Three-Parameter Equations of State

It has been mentioned several times that one of the major drawbacks of vdW-type equations, is that the critical compressibility factor z_c takes on fixed values, regardless of the substance ($z_c = 0.375$ for vdW, 0.333 for RK and SRK, and 0.307 for PR). To overcome this deficiency, it has been suggested that the fixed value of z_c should be replaced by a substance-dependent adjustable critical parameter.³ This approach has been mainly applied by introducing a third parameter into the equation of state. Many three-parameter equations have been proposed during the past 25 years, although the idea is not new and can be traced back to the end of the 19th century. As mentioned earlier here, Clausius¹⁷ proposed a three-parameter equation that allowed for variations of the critical compressibility factor, although the concept of z_c was not well established at that time. Himpan⁴⁷ provided a major contribution in this direction, but the idea did not gain popularity, especially because of the success of other simpler equations. The studies of Elshayal and Lu,⁴⁸ Fuller,⁴⁹ and Usdin and

McAuliffe⁵⁰ revived the interest in this approach. Patel and Teja⁵¹ reworked the equation previously proposed by Heyen⁵² to obtain

$$P = RT/(V-b) - a_c \alpha(T)/[V(V+b) + c(V-b)]$$

The constants a_c , b , and c are determined as functions of two substance-dependent parameters, ζ_c and F . Valderrama⁵³ generalized this equation using the acentric factor (ω) and the critical compressibility factor (z_c) as generalizing parameters. In another work, the author had justified the use of these two properties, ω and z_c , for generalizing the parameters of a cubic EoS.⁵⁴ The generalized Patel–Teja EoS, known as the PTV equation, has been successfully applied to correlate vapor–liquid equilibrium in mixtures.^{55–58} Valderrama and Alfaro⁵⁹ evaluated the PTV and other generalized EoS equations for the prediction of saturated liquid densities, concluding that, for this type of calculation, cubic EoS should be used with care. Xu et al.⁵⁵ found that the PTV equation was the best equation for predicting VLE in CO₂ reservoir fluids without using interaction parameters. Table 3 summarizes the PTV equation of state.

Application to Mixtures

Until recent years, most of the applications of EoS to mixtures considered the use of the classical mixing rules. An interaction parameter has been introduced into the force parameter a in vdW-type equations to improve predictions of mixture properties.⁶⁰ It has been recognized, however, that, even with the use of interaction parameters, the classical vdW one-fluid mixing rules do not provide accurate results for complex systems.^{61–63} During the past 20 years, efforts have been made to extend the applicability of cubic EoS to obtain accurate representations of phase equilibria in highly polar mixtures, associated mixtures, and other very complex systems. The different approaches presented in the literature include the use of multiple interaction parameters in the quadratic mixing rules,^{64,65} the introduction of the local-composition concept,⁵² the connection between excess Gibbs free energy models and

EoS,⁶⁶ and the use of nonquadratic mixing rules.^{67–79} Solorzano et al.⁷⁰ presented a comparative study of mixing rules for cubic EoS in the prediction of multi-component vapor–liquid equilibria. They concluded that a true evaluation of the accuracy of mixing rules is their application to multicomponent mixtures.

Classical Mixing Rules

In the past, simple, classical mixing rules of the van der Waals type were used in most applications

$$\begin{aligned}a &= \sum_i \sum_j x_i x_j a_{ij} \\b &= \sum_i \sum_j x_i x_j b_{ij} \\c &= \sum_i \sum_j x_i x_j c_{ij}\end{aligned}\quad (13)$$

Customarily, the geometric mean was used for the force parameter a_{ij} , and the arithmetic mean was used for the volume parameters b_{ij} and c_{ij} . Concentration-independent interaction parameters have been introduced into a_{ij} , b_{ij} , and c_{ij} to improve the correlation of phase equilibrium. This has been done as follows

$$\begin{aligned}a_{ij} &= \sqrt{a_i a_j} (1 - k_{ij}) \\b_{ij} &= \frac{1}{2}(b_i + b_j)(1 - \beta_{ij}) \\c_{ij} &= \frac{1}{2}(c_i + c_j)(1 - \delta_{ij})\end{aligned}\quad (14)$$

These modifications retain the quadratic concentration dependence of the EoS parameters and the quadratic concentration dependence of the second virial coefficient. However, the introduction of such parameters does not improve correlations in some complex cases such as those found in supercritical fluid processes and wine distillation processes, among others.

Interaction parameters such as k_{ij} , β_{ij} , or δ_{ij} in eq 14 are usually calculated by regression analysis of experimental phase equilibrium data, although some predictive correlations have been proposed for some mixtures. The basic idea in this regression analysis is to apply the EoS to the calculation of a particular property and then minimize the differences between predicted and experimental values. The values of the interaction parameters that minimize these differences correspond to the optimum interaction parameters. The differences between calculated and experimental values are expressed through an objective function that is arbitrarily but conveniently defined. Several objective functions have been presented in the literature,^{60,71–73} with the most popular being those that include deviations in the bubble pressure.

Some authors have attempted to obtain binary interaction parameters from pure-component property data. Chueh and Prausnitz²⁵ related the binary interaction parameter in the RK equation to the critical volumes of the pure components. Graboski and Daubert⁷² correlated the binary interaction parameter in the SRK equation in terms of the solubility parameter difference between the hydrocarbon and non-hydrocarbon components. Arai and Nishiumi⁷⁴ developed a semiempirical

correlation for the interaction parameter in the PR equation in terms of the critical volumes and acentric factors of the pure components. Gao et al.⁷⁵ correlated the interaction parameters in the PR equation as functions of the critical temperatures and critical compressibility factors of the pure components. Coutinho et al.⁷⁶ used combining rules for molecular parameters to propose correlations for the interaction parameters in the SRK equation as functions of the pure-component parameters (critical properties and ionization potentials). None of these proposals, however, have proven to be of general applicability, and at present, an accurate predictive or correlating method for evaluating the interaction parameters does not exist. The available correlations and estimation methods are not always suitable for extrapolation and, in many cases, are only applicable to particular mixtures.^{58,75,76} Therefore, regression analysis of experimental phase equilibrium data is the preferred way to obtain the required interaction parameters. Care must be taken, however, in complex systems in which multiple optimum interaction parameters could be obtained.

Also, combining rules for intermolecular parameters such as the energy (ϵ) and size (σ) parameters in the Lennard-Jones potential have been used in connection with cubic EoS. Several combining rules have been proposed in the literature and different expressions for the EoS parameters (for instance, a and b in the SRK equation) have been derived from the combining rules for ϵ and σ .^{33,64,77–79} The results obtained using this type of combining rule are not very impressive. If accurate results are required, one cannot avoid introducing binary interaction parameters into the mixing rules.

Volume-Dependent Mixing Rules

Volume-dependent mixing rules have also been proposed in the literature. The local-composition concept²³ has been used in this approach,^{80,81} and applications of cubic EoS to highly nonideal mixtures have been made with relative success. Mathias and Copeman⁸² introduced some modifications to the original ideas of Mollerup, extended the Peng–Robinson EoS to complex mixtures, and evaluated various forms of the local-composition concept. Zheng et al.⁸³ developed a unified density-dependent local-composition model combined with an EoS to be applied to strongly polar and asymmetric mixtures. Conventional quadratic mixing rules (vdW one-fluid rules) were used, and the approach was successfully extended to ternary mixtures. The model failed to give accurate representations of polar–polar systems such as methanol–water and acetone–water. Inaccuracies were also found in the critical region.

Sandler⁸⁴ presented a theoretical analysis of the van der Waals partition function to conclude that several models based on the local-composition concept, including those of Mollerup⁸⁰ and of Whiting and Prausnitz,⁸¹ do not satisfy necessary boundary conditions required by statistical mechanical analysis. Sandler recognized, however, the importance of Mollerup's works in the development of better mixing rules for EoS. The main contribution was to recognize that the application of EoS to mixture is not restricted to the use of quadratic mixing rules.

Nonquadratic Mixing Rules

Quadratic mixing rules are usually sufficient for the correlation of phase equilibrium in simple systems. To

Table 4. Selected Mixing Rules and Combining Rules Used in Two-Constant Cubic Equations of State

mixing/combining rule	formulas	
van der Waals one parameter: k_{ij} two parameters: k_{ij}, l_{ij}	$a = \sum_i \sum_j x_i x_j a_{ij}$ $a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$	$b = \sum_i \sum_j x_i x_j b_{ij}$ $b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij})$
Panagiotopoulos–Reid (PR) two parameters: k_{ij}, k_{ji} three parameters: k_{ij}, k_{ji}, l_j	$a_{ij} = \sqrt{a_i a_j} [1 - k_{ij} + (k_{ij} - k_{ji}) x_i]$ $b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij})$	
general nonquadratic (GNQ) two parameters: δ_i, δ_j three parameters: $\delta_i, \delta_j, \beta_i$	$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$ $b_{ij} = 0.5[b_i(1 - \beta_i) + b_j(1 - \beta_j)]$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents	$k_{ij} = \delta_i x_i + \delta_j x_j$
Kwak–Mansoori (KM) three parameters: $k_{ij}, \beta_{ij}, l_{ij}$	$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$ $d_{ij} = 0.5(d_i^{1/3} + d_j^{1/3})^3 (1 - l_{ij})$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents	$b_{ij} = 0.5(b_i^{1/3} + b_j^{1/3})^3 (1 - \beta_{ij})$
Kwak–Mansoori modification 1 (KM-1) three parameters: k_{ij}, l_{ij}, β_i (one solute)	$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$ $d_{ij} = 0.5(d_i^{1/3} + d_j^{1/3})^3 (1 - l_{ij})$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents	$b_{ij} = 0.5[b_i(1 - \beta_i) + b_j(1 - \beta_j)]$
Kwak–Mansoori modification 2 (KM-2) three parameters: $\delta_i, \delta_j, \beta_i$ (one solute)	$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$ $k_{ij} = \delta_i x_i + \delta_j x_j$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents	$d_{ij} = 0.5(d_i^{1/3} + d_j^{1/3})^3$ $b_{ij} = 0.5[b_i(1 - \beta_i) + b_j(1 - \beta_j)]$
Kurihara et al. (KTK) three parameters: η_1, η_2, η_3	$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} - (\tau - \phi) g_{\text{RES}}^E / \ln[(b - \phi)/(b - \tau)]$ $b = \sum_i \sum_j x_i x_j b_{ij}$ $b_{ij} = \frac{1}{2}(b_i + b_j)$ $g_{\text{RES}}^E = RT x_1 x_2 [\eta_1 + \eta_2(x_1 - x_2) + \eta_3(x_1 - x_2)^2]$	
Wong–Sandler one parameter: k_{ij} two parameters: k_{ij}, l_i (one solute)	$b = \sum_i \sum_j x_i x_j (b - a/RT)_{ij} / [1 - \sum_i x_i a_i / b_i RT - A_{\infty}^E(x) / \Omega RT]$ $a = b [\sum_i x_i a_i / b_i - A_{\infty}^E(x) / \Omega]$ $(b - a/RT)_{ij} = 0.5[b_i(1 - l_i) + b_j] - (a_i a_j)^{0.5} (1 - k_{ij}) / RT$ $l_i \neq 0$ for all solutes and $l_j = 0$ for all solvents	

treat more complex systems, Panagiotopoulos and Reid⁶⁷ introduced a second interaction parameter by making the k_{ij} parameter concentration-dependent, thus transforming the mixing rule in a nonquadratic form

$$a_{ij} = \sqrt{a_i a_j} [1 - k_{ij} + (k_{ij} - k_{ji}) x_i] \quad \text{with } k_{ij} \neq k_{ji} \quad (15)$$

Expressions similar to that of Panagiotopoulos and Reid have been presented by Adachi and Sugie⁶⁹ and by Sandoval et al.⁸⁵ The classical and nonquadratic mixing rules can be summarized in one general form, called the “general nonquadratic mixing rule”,⁸⁶ in terms of two parameters δ_i and δ_j . That is, $k_{ij} = \delta_i x_i + \delta_j x_j$. This mixing rule, although it suffers from the so-called Michelsen–Kistenmacher syndrome, has been successfully applied to binary mixtures containing a supercritical component.⁸⁶

EoS + Gibbs Free Energy Models

Among the modern approaches presented in the literature to describe phase equilibria in mixtures, methods of the type “EoS + Gibbs free energy” seem to be the most appropriate for modeling mixtures with highly asymmetric components. The basic concepts related to this type of model can be found in Orbey and Sandler⁸⁷ and Sengers et al.⁸ Since the first proposals of Vidal⁸⁸ and Huron and Vidal,⁶⁶ these models have been extensively used and applied to low- and high-pressure vapor–liquid mixtures, to liquid–liquid equilibria, and gas–solid equilibria. Important contributions to this area are those of Møllerup,⁸⁰ Kurihara et al.,⁸⁹ Michelsen,⁹⁰ Heidemann and Kokal,⁹¹ Dahl and Michelsen,⁹² Holderbaum and Gmehling,⁹³ Soave,⁹⁴ and Wong and Sandler.⁹⁵

Wong and Sandler (WS)⁹⁵ proposed a mixing rule for two-parameter cubic EoS consistent with statistical mechanical requirements. In particular, the model gives the quadratic concentration dependence of the second virial coefficient. The WS mixing rule is

$$b_m = \sum_i \sum_j x_i x_j (b - a/RT)_{ij} / [1 - \sum_i x_i a_i / b_i RT - A_{\infty}^E(x) / \Omega RT] \quad (16)$$

$$a_m = b_m [\sum_i x_i a_i / b_i + A_{\infty}^E(x) / \Omega]$$

$$(b - a/RT)_{ij} = (b_i + b_j)/2 - (a_i a_j)^{0.5} (1 - k_{ij}) / RT$$

This mixing rule has been the focus of several studies during the past several years.^{87,96–99} Verotti and Costa⁸⁷ presented an extensive study on the use of the WS mixing rule to correlate liquid–liquid equilibrium in 47 polar binary liquid mixtures. The authors also considered the mixing rules of Huron and Vidal,⁶⁶ Heidemann and Kokal,⁹¹ and Dahl and Michelsen⁹² and the NRTL and UNIQUAC models for the excess Gibbs free energy. The study shows that, for strongly polar–nonpolar mixtures, the combination WS + NRTL gives the best results and, for strongly polar + strongly polar mixtures, the combination WS + UNIQUAC gives the best results.

Yang et al.¹⁰⁰ extended the application of the WS mixing rule to three-parameter equations. They used the Patel–Teja equation of state and tested the model using VLE data for binary and ternary mixtures. A comparison with results obtained using classical vdW mixing rules showed much better results for highly asymmetric mixtures and for conditions near the critical regions of the mixtures.

Table 5. Mean Deviations in Vapor Mole Fraction for EoS + Wong–Sandler Mixing Rule (WS) and Three Equations of State^{a,b}

			y_2 (%)			
no.	system	T (K)	SRK	PR	PTV	PTV
			WS/KTK	WS/KTK	WS/KTK	MRS
1	naphthalene	308	1.3/1.1	1.1/2.3	1.0/3.9	1.2
		313	1.5/1.2	1.3/2.4	1.1/4.1	2.1
		318	2.4/2.6	1.9/5.3	1.5/5.3	2.6
2	phenanthrene	318	7.9/7.6	7.3/5.7	6.3/7.1	5.7
		328	8.3/7.3	5.5/7.0	3.4/7.8	2.4
		338	8.3/8.4	7.1/6.5	6.3/8.4	6.4
3	anthracene	303	6.6/10.7	5.9/19.3	5.2/8.1	2.6
		323	15.7/7.2	16.2/18.6	19.1/9.5	6.4
		343	9.2/9.9	8.4/21.3	7.1/11.2	9.5
4	2,3-dimethyl-naphthalene	308	2.5/2.5	2.3/11.8	2.4/5.2	3.3
		318	7.1/2.6	5.3/8.8	4.3/4.5	2.8
		328	2.7/4.3	4.3/6.7	3.7/1.8	5.2
5	2,6-dimethyl-naphthalene	308	6.6/4.9	5.5/2.4	5.4/6.4	4.2
		318	6.4/5.1	4.0/3.5	3.1/7.2	2.8
		328	15.7/5.5	5.6/5.2	4.2/8.8	5.0
6	caffeine	313	4.4/15.3	2.2/15.6	2.0/15.5	2.4
		333	4.3/22.8	2.5/24.2	2.8/22.9	2.3
		353	6.3/20.1	4.1/20.9	4.1/19.9	7.7
		% average deviation		6.5/7.7	5.0/10.4	4.6/8.7

^a Results obtained using a modified regular solution (MRS) model are also included. ^b In the mixing rule the UNIQUAC model for A_{∞}^E was used.

Kurihara, Tochigi, and Kojima⁸⁹ proposed a mixing rule (KTK) based on a convenient separation of the excess Gibbs free energy as

$$g^E = g_{RS}^E + g_{RES}^E \quad (17)$$

where g_{RS}^E is the excess Gibbs free energy for a regular solution and g_{RES}^E is the residual excess Gibbs free energy. Kurihara et al.⁸⁹ derived an expression for the regular solution contribution using a general cubic equation of state, and for the residual contribution, they used a Redlich–Kister expansion. For the force parameter, the mixing rule is given by

$$a_m = \sum_i \sum_j x_i x_j (a_{ij})^{0.5} - (\tau - \phi) g_{RES}^E / \ln[(b - \phi)/(b - \tau)] \quad (18)$$

$$g_{RES}^E = RTx_1x_2[\eta_1 + \eta_2(x_1 - x_2) + \eta_3(x_1 - x_2)^2]$$

and the mixing rules for the other parameters are detailed in Table 4.

A recent paper by Wyczesany⁹⁸ presents a critical analysis of several EoS + excess Gibbs free energy models for the correlation of vapor–liquid equilibria of several mixtures at high pressures. The author indicates that, for mixtures containing a supercritical component, this type of model is not sufficiently accurate. In our group in La Serena, we have extensively explored both WS and KTK mixing rules for describing solid–gas and liquid–gas mixtures containing supercritical carbon dioxide. We have been successful in correlating phase equilibrium properties in liquid–gas and solid–gas binary systems by introducing an additional parameter (l_i) into the solute volume constant only. This modified mixing rule is shown in Table 4. For solubility calculations, this modified WS mixing rule has an acceptable physical meaning and does not suffer from the so-called Michelsen–Kistenmacher syndrome.

Table 5 gives some selected results for five solid–gas systems. It should be noted that deviations in the gas solute mole fraction, y_2 , are presented. The solvent concentration is correlated with deviations below 0.5% in all cases. Also, we have developed a new model using the PTV equation of state with a residual contribution determined by a modified regular solution model that considers the polar and hydrogen-bonding contributions. For the nonpolar part, the concepts of regular solutions (for which the excess volume and excess entropy are 0) are used to derive a mixing rule for the force parameter a in the equation of state.¹⁰¹ The last column in Table 5 (PTV–MRS) also reports the results obtained with this new model.

Mixing Rules of Mansoori and Co-workers

A new concept for the development of mixing rules for cubic EoS consistent with statistical mechanical theory of the van der Waals mixing rules was introduced by Benmekki and Mansoori.³³ This concept is based on statistical mechanical arguments and the fact that rules are for constants of an equation of state and not for any thermodynamic state function that might appear in an equation of state. For these mixing rules, the cubic EoS must be rewritten. For instance, the Peng–Robinson EoS is reformulated as

$$P = \frac{RT}{V - b_m} - \frac{a_m + RTd_m - 2\sqrt{a_m d_m RT}}{V(V + b_m) + b_m(V - b_m)} \quad (19)$$

This form suggests three independent EoS parameters (a_m , b_m , and d_m), which are expressed using the classical van der Waals mixing rules as

$$\begin{aligned} a_m &= \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} \\ b_m &= \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij} \\ d_m &= \sum_{i=1}^n \sum_{j=1}^n x_i x_j d_{ij} \end{aligned} \quad (20)$$

The combining rules for a_{ij} , b_{ij} , and d_{ij} given by Kwak and Mansoori (KM) are

$$\begin{aligned} a_{ij} &= \sqrt{a_i a_j} (1 - k_{ij}) \\ b_{ij} &= \left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3 (1 - \beta_{ij}) \\ d_{ij} &= \left(\frac{d_i^{1/3} + d_j^{1/3}}{2} \right)^3 (1 - \delta_{ij}) \end{aligned} \quad (21)$$

$$\begin{aligned} a_i &= a(Tc_i)(1 + m_i)^2 \\ b_i &= \frac{0.07780 RTc_i}{Pc_i} \\ d_i &= \frac{a(Tc_i)m_i^2}{RTc_i} \end{aligned} \quad (22)$$

Figure 3 shows results for the vapor-phase concentration for the system 2-methyl-1-pentanol + CO₂ at high pressure and 453 K using the PR equation with the

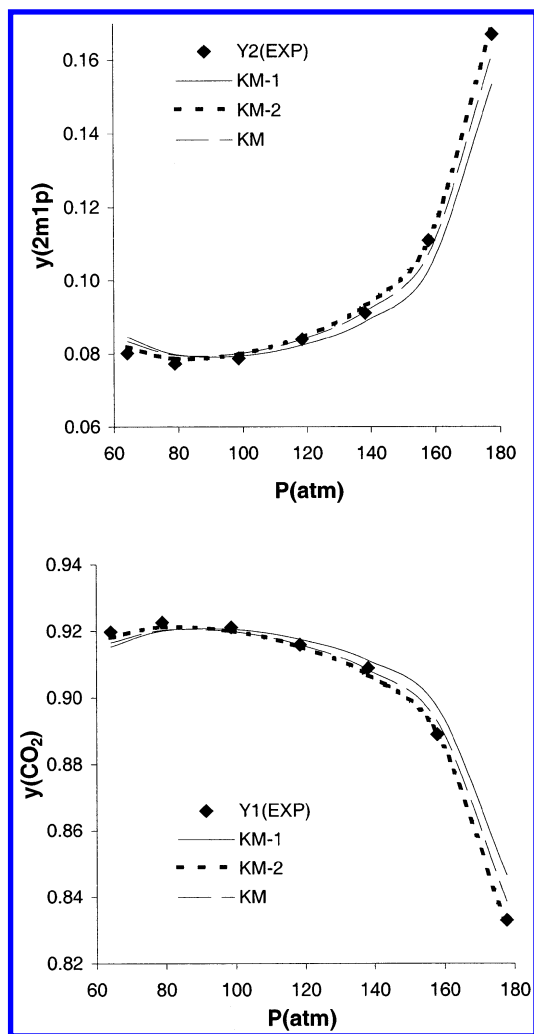


Figure 3. Gas-phase concentration vs pressure in the system 2-methyl-1-pentanol + CO₂ using the Peng–Robinson EoS and Kwak–Mansoori mixing rules and some modifications.

above mixing rules. Our results show that, as for other complex mixing rules, correlation of VLE is not improved as expected by the complexity and the alleged foundations of the mixing and combining rules. For complex systems, more than one interaction parameter must be used if accurate results for the solute concentration in the gas phase are needed. The clear advantage of the KM reformulation is that an EoS that includes temperature-independent parameters only is obtained.

Applications of Cubic EoS to Reservoir Fluids

The application of EoS to correlate VLE and properties of reservoir fluids has received special attention. Important contributions include those of Yarborough,¹⁰² Firoozabadi et al.,^{103,104} Vogel et al.,¹⁰⁵ Willman and Teja,^{106–108} Lira-Galeana et al.,¹⁰⁹ and Skjold-Jorgensen.¹¹⁰ Cubic equations of state have shown surprisingly good capabilities for correlating VLE and volumetric properties of complex reservoir fluids.^{103,111–115} Two approaches are usually used in these applications. One of these approaches is the use of pseudocomponents, that is, grouping the mixture into a limited number of fractions, with each fraction having specific critical properties and acentric factor. These properties are calculated using well-known standard correlations. The system then becomes a defined mixture of a given

number of pseudocomponents. The other approach is the representation of the properties of a naturally occurring reservoir mixture through a continuous distribution, using some characteristic property such as the molecular weight or the normal boiling temperature. This method is known as “continuous thermodynamics”, a concept that was already used by Bowman and Edmister more than 50 years ago^{116,117} and reformulated later by Ratzsch and Khelen¹¹⁸ and by Cotterman et al.¹¹⁹ using the equations of state. Other works on continuous thermodynamics include those by Cotterman and Prausnitz,¹²⁰ Du and Mansoori,¹²¹ Haynes and Mathews,¹²² Zuo and Zhang,¹²³ and Vakili-Nezhaad et al.¹²⁴

Xu et al.⁵⁵ and Danesh et al.⁵⁷ evaluated the performance of several cubic EoS for predicting phase behavior and volumetric properties of reservoir fluids. Saturation pressures, liquid and gas densities, and equilibrium ratios for several multicomponent mixtures were correlated using the selected EoS. The main conclusions obtained from these works are as follows: (i) the modified Patel–Teja equation (PTV)⁵³ and the Zudkevitch and Joffe modified Redlich–Kwong equation⁶⁰ are, overall, superior to all of the other EoS; (ii) the abilities of the SRK and the PR equations to predict liquid density were improved by the inclusion of the volume translation concept; (iii) the phase volumes obtained by flash calculations were unsatisfactory with all of the equations tested; and (iv) phase concentrations were reasonably well predicted by all of the equations at all conditions.

Mixtures Containing Supercritical Components

Equations of state are usually employed for high-pressure phase equilibria such as systems containing supercritical components. The first efforts to model the phase behavior in systems containing supercritical fluids were made using the virial EoS,¹²⁵ but these attempts were not successful. The best results have been obtained using cubic EoS such as SRK and PR.^{126,127} Several combinations between cubic EoS and mixing rules have been employed and have been presented in the literature. These included different applications and modifications of the PR and SRK equations with mixing rules such as van der Waals, Panagiotopoulos–Reid, Kwak–Mansoori, Huron–Vidal, Kurihara et al., and Wong–Sandler, among others.^{128–139} The book by Sados¹⁴⁰ includes a chapter dedicated to cubic equations applied to phase equilibria in multicomponent mixtures.

However, none of these works represents a thorough study on the problem of phase equilibrium in systems containing a supercritical fluid. Thus, the problem is not yet exhausted, and there is ample room for research on different aspects of phase equilibrium modeling. Literature information and our own research indicate that, with the present state of knowledge, it is necessary to include more than one interaction parameter, even in complex models such as the Kurihara et al. and Wong–Sandler mixing rules.

A common practice in several applications of cubic EoS to mixtures containing supercritical fluids has been to analyze the results in terms of the concentration of the supercritical solvent in the gas phase, y_1 . Some optimistic statements and conclusions found in the literature are usually drawn by analyzing the vapor-phase concentration of the solvent only (usually carbon dioxide) and not the concentration of the solute, y_2 , as should be done to accurately test the capabilities of an

Table 6. Best Combination of EoS + Mixing Rules for Several Gas–Liquid and Gas–Solid Systems Containing Supercritical Carbon Dioxide

system	<i>T</i> (K)	<i>P</i> (MPa)	EoS	mixing rule ^a	Δy_2 (%)
1-octanol	403	6.5–18.4	PTV	GNQ	5.2
	453	6.5–19.0	PTV	GNQ	8.1
1-decanol	348	7.0–19.0	PTV	GNQ	12.4
	403	6.0–19.0	PR	KM-2	10.5
	453	6.5–19.0	SRK	GNQ	3.4
2-methyl-1-pentanol	348	6.5–11.9	PR	GNQ	12.3
	403	6.5–15.4	PTV	KTK	7.3
	453	6.5–17.9	PTV	GNQ	1.1
lauric acid	423	9.1–5.1	PR	KM-2	15.5
	473	9.1–5.1	PR	KM-2	13.1
palmitic acid	423	9.1–5.1	PR	KM-2	14.3
	473	9.1–5.1	SRK	WS	17.8
oleic acid	313	7.2–28.2	PR	KM-1	15.1
	333	7.1–28.6	PTV	KTK	17.1
limonene	313	5.9–7.9	PTV	vdW-2	11.6
	323	4.9–10.3	PR	KM-2	19.3
α -pinene	313	3.3–7.9	PR	KM	6.1
	323	4.5–9.6	PTV	GNQ	9.6
	328	4.8–9.5	PR	KM-1	15.3
phenanthrene	318	11.9–27.7	PTV	GNQ	4.5
	328	11.9–27.7	PTV	GNQ	3.0
	338	11.9–27.7	PTV	GNQ	6.7
benzoic acid	318	11.9–27.7	SRK	KTK	7.1
	328	11.9–27.7	SRK	KTK	4.0
	338	11.9–27.7	PTV	MRS	0.9
caffeine	313	19.7–29.7	PTV	MRS	1.5
	333	19.7–29.6	PTV	MRS	2.7
	353	19.7–29.6	PR	vdW-2	3.5
anthracene	303	10.3–41.0	PTV	MRS	2.6
	323	9.0–41.0	SRK	MRS	6.4
	343	11.7–20.6	PTV	GNQ	7.8
naphthalene	308	10.4–29.7	PTV	KTK	1.1
	313	9.9–34.6	PTV	MRS	2.1
	318	10.1–31.1	PTV	MRS	2.6
2,6-dimethyl-naphthalene	308	9.6–27.7	PTV	MRS	4.2
	318	9.6–27.7	PTV	KTK	2.4
	328	9.5–27.7	PTV	WS	4.3
2,3-dimethyl-naphthalene	308	9.8–27.7	PTV	WS	2.4
	318	9.8–27.7	PTV	GNQ	3.2
	328	9.8–27.7	SRK	KTK	1.8
β -cholesterol	313	9.9–24.8	PR	KM	4.4
	323	9.9–24.8	PR	KM	4.5
	333	12.9–24.8	PR	vdW-2	5.5

^a Notation for mixing rules as indicated in Table 4.

EoS. In the studies presented in the literature, although the deviations in the calculated solvent concentration in the gas phase (which is usually on the order of 0.999) are lower than 1%, the deviations in the calculated solute concentration (which is close to 0) can be as high as 200% when expressed as percent deviations: Δy (%) = $100[(y_{\text{exp}} - y_{\text{cal}})/y_{\text{exp}}]$.^{45,141–144} These high deviations in the gas-phase solute concentration (y_2) are not usually reported and discussed in papers related to phase equilibrium modeling of mixtures containing a supercritical component using cubic EoS. Not reporting these high deviations is at least a misleading way of analyzing the accuracy of a proposed model.

Although an accurate general conclusion cannot be drawn at present, results indicate that, for mixtures including a supercritical component, the use of Gibbs free energy models in the EoS parameters and nonquadratic mixing rules with interaction parameters in the volume constants of the EoS give the best results. However, one cannot avoid including more than one interaction parameter in the mixing rules if accurate correlations of the solute concentration in the gas phase are needed. Table 6 summarizes the work we have done

in this area in our group in La Serena. For all of the cases shown in Table 6, the pressure is predicted with deviations below 10% and the solvent concentration with deviations below 1%. The solute concentration in the gas phase is predicted with variable deviations. However, these deviations are below those reported in the literature for similar systems.

Cubic EoS Applied to Polymer Solutions

For polymer–solvent and polymer–polymer mixtures, several polymer-specific EoS have been proposed that can be classified into two broad groups: lattice models and continuum models.¹⁴⁵ Applications of cubic EoS to describe VLE in this type of mixture have been undertaken with some success.^{147–153}

Sako, Wu, and Prausnitz¹⁴⁶ (SWP) used the van der Waals theory to propose a cubic EoS applicable to large molecules and polymers and extended it to mixtures using simple mixing rules. The main advantage of the proposed equation is that it can be applied to polymer–solvent systems with a minimum of experimental information. The SWP equation has been used with relative success by Tork et al.^{154,155} Using a different approach, Orbey and Sandler¹⁴⁷ combined the SRK equation with the Flory–Huggins activity coefficient model in a Huron–Vidal EoS + G^{ex} mixing rule. They analyzed binary polystyrene–hydrocarbon solvent mixtures, obtaining acceptable results. The authors concluded that, unless extensive VLE data for accurately correlating the data and determining the model parameters are available, the use of multiparameter phase equilibrium models for the moderately polar polymer–solvent mixtures studied is not justifiable. Orbey et al.¹⁴⁵ used a polymer SRK equation to correlate polyethylene–ethylene mixtures and compared the results with the Sanchez–Lacombe and SAFT calculations. Other EoS + G^{ex} models have been used with some success.¹⁴⁹ Kalospiros and Tassios¹⁴⁹ found satisfactory results with the use of a simplified Wong–Sandler mixing rule proposed by Zhong and Masuoka (ZM).¹⁵⁰

Louli and Tassios¹⁵⁶ applied the PR equation to polymers including a single set of energy and co-volume parameters per polymer (*a* and *b*) fitted to experimental volume data. Excellent results for the volumetric behavior of the polymer up to very high pressures were obtained. Correlations of VLE data for a variety of nonpolar and polar polymer solutions, including hydrogen-bonding ones, were carried out by using three mixing rules. The best results were found with the ZM mixing rule.¹⁵⁰ Kang et al.¹⁵⁷ used the PR equation with the Wong–Sandler mixing rule to calculate bubble-point pressures and vapor-phase mole fractions for several polymer mixtures. This model was found to give generally good results away from critical regions and except for nonpolar polymers in polar, nonassociating solvents. These studies show that mixing rules for polymer–solvent mixtures need to be further investigated.

Future developments of EoS for polymer mixtures are not clear, and some contradictory statements can be found in the literature. Some authors indicate that cubic equations can be extended to accurately correlate and predict VLE in polymer mixtures.^{147,152,153} Other authors state that, considering the complexity of this type of mixture, it seems that simplicity is not a necessary requirement for an EoS, with the calculation of parameters for the mixture components being more important.¹⁵⁸ There is agreement, however, on the fact that

Table 7. Recommendations on Generalized Equations of State to Use for Several Pure-Fluid Properties

property	comments	recommendations
gas volume at moderate/high pressure	most cubic EoS with two or three parameters	SRK, PR, PTV
gas volume at low temperature, moderate/high pressure	most cubic EoS with two or three parameters adjusted using low-temperature data	SRK, PR
saturated vapor volume	most cubic equations	SRK, PR, PT
saturated liquid volume for nonpolar fluids	three-parameter equations seem to be better	PTV, PT, but empirical correlations should be preferred
saturated liquid volume for polar fluids	two- or three-parameter equations with parameters adjusted for polar fluids	PT, but empirical correlations should be preferred
compressed liquid volume	none of the cubic equations	empirical correlations or specific equations for a given fluid should be used
volume near the critical point	most cubic EoS fail in this region, but three-parameter equations should be preferred	PTV or other three-parameter EoS with parameters adjusted using near-critical data
vapor pressure for nonpolar fluids	most cubic EoS, although those that use more involved $a(T)$ functions give better results	SRK, PR, PTV, but prefer $\alpha(T)$ with specific parameters for polar fluids, such as Soave-polar ²⁸
vapor pressure for polar fluids	most cubic equations, although those that use specific parameters for polar fluids should be preferred	PR, PTV with complex $\alpha(T)$ function, such as that of Twu ¹⁶⁹
vapor pressure for associating fluids	none of the cubic equations	noncubic equations specially developed for this type of fluid should be preferred
enthalpy and entropy of liquids	none of the cubic equations give accurate results	specific equations, usually polynomial, should be preferred
enthalpy and entropy of gases at low pressure	most cubic equations, although those that use specific parameters for polar fluids should be preferred	SRK, PR, PTV, but prefer $\alpha(T)$ with specific parameters
enthalpy and entropy of gases at moderate/high pressure	most cubic equations, although those that use specific parameters for polar fluids should be preferred	PR and PTV with $\alpha(T)$ with specific parameters; noncubic equations are also good

Table 8. Recommendations on Generalized EoS and Mixing Rules for Different Types of Liquid–Vapor Mixtures^a

type of mixture	EoS	temp function	mixing rule
low pressure (<10 atm)			
nonpolar + nonpolar	SRK, PR, PTV	Soave ²⁶	P&R, WS
nonpolar + polar	SRK, PR, PTV	Soave-polar ²⁸	P&R, WS
polar + polar	SRK, PR, PTV	Soave-polar, ²⁸ Mathias ¹⁶³	WS
asymmetric mixtures	SRK, PR, PTV	Twu	P&R, MWS-1P
polymer solutions	SRK, PR, SWP	Soave, ²⁶ Mathias ¹⁶³	HV, MWS-1P, ZM
moderate and high pressures (>10 atm.)			
nonpolar + nonpolar	SRK, PR	Soave ²⁶	vdW-1 or -2
nonpolar + polar	SRK, PR, PTV	Soave-polar ²⁸	vdW-1 or -2
polar + polar	SRK, PR	Soave-polar, ²⁸ Mathias ¹⁶³	vdW-2, P&R
nonpolar + nonpolar	SRK, PR	Soave ²⁶	vdW-1 or -2
reservoir fluids	SRK, PR, PTV	Soave ²⁶	vdW-1 or -2
polymer solutions	SRK, PR, SWP	Soave, ²⁶ Mathias ¹⁶³	WS, ZM
one supercritical component	PR, PTV	Soave, ²⁶ Twu ¹⁶⁹	P&R, WS-2P, WS-3P

^a Notation for mixing rules as indicated in Table 4. Also ZM is Zhong–Masuoka, HV is Huron–Vidal, and SWP is Sako–Wu–Prausnitz.

future developments of EoS for polymer mixtures must emphasize the study of mixing rules and that the EoS input parameters should be related to common measured properties of the polymers.

Recommendations

On the basis of the abundant information available in the literature and our own findings, some general recommendations on which cubic EoS to use for different applications are summarized in Tables 7 and 8. The recommendations must be considered as general guideline, and they do not mean that other EoS or mixing rules could not be used for the applications listed in the tables. For instance, in several cases for pure fluids (Table 7), the SRK and PR equations are recommended, although other cubic equations could also be used. However, these two EoS are of common use, have been widely studied, and are incorporated in most commercial and academic software. Thus, for the practical user, there is no reason to use other equations. Also, in some cases in Table 7, empirical correlations are recommended, although some cubic EoS could give equally

good results. However, the good results found for some applications cannot be generalized. This is the case for liquid volume, for which empirical correlations and generalized models have been demonstrated to be accurate and of general applicability.^{59,159}

Similar comments can be made for the recommendations given in Table 8. Although several other mixing rules can be used in some applications, the list in this table includes those commonly used and frequently studied in the literature (classical vdW-2, P&R, Wong–Sandler) This fact does not mean that for some particular cases, models such as Kwak–Mansoori, Kurihara–Tochigi–Kojima, Zhong–Masuoka, or other mixing rules could not give similar or better results. The recommendations given in Table 8 mean that those rules give reasonable results for the wide group of substances indicated in the first column of that table.

Conclusions

Through the years, many researchers have discovered and taken advantage of the tremendous capabilities of cubic EoS. These equations have been modified and

applied to almost any situation in which they have been needed. When applied to pure components, the main modifications include changes in the EoS volume dependency and in the temperature dependency of the attractive term. For mixtures, several theories have been devised to propose new mixing and combining rules. One of the most successful to date has involved the use of Gibbs free energy models in the EoS parameters. Theoretical approaches have not been practically successful, and those that have been more accurate and useful employ noncubic EoS.

Also, we know that a single cubic EoS cannot provide reliable predictions for all volumetric, thermodynamic, and phase equilibrium properties, for all type of fluids and mixtures. Therefore, we cannot expect any major developments in EoS until we better understand how molecules interact. However, considering their overwhelming advantages, cubic EoS can be adjusted in many ways to find acceptable results for most practical applications. Thus, it is my impression that, for the time being and for the near future, cubic equations of state are here to stay.

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