

Generalization of composition-dependent mixing rules for multicomponent systems: prediction of vapor–liquid and liquid–liquid equilibria

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Abstract

A consistent generalization to mixing rules depending on the composition proposed by Adachi and Sugie, Panagiotopoulos and Reid, and Stryjek and Vera for the two-parameter mixing rule and by Schwartzentruber and Renon for the three-parameter mixing rule is presented. The invariance problem and dilution effect shortcomings pointed out by Michelsen and Kistenmacher when the original mixing rules are applied to multicomponent mixtures, are avoided by the generalized mixing rules. The proposed mixing rules involving their respective excess function models associated with a cubic equation of state (PRSV or PRCRP), were used on the representation of binary vapor–liquid (hydrocarbon–hydrocarbon, acetone–alcohol, acetone–water, alcohol–water, and alcohol–hydrocarbon) and liquid–liquid (hydrocarbon–water) equilibrium data. The binary interaction parameters of the model were used to test the performance of the generalization on the prediction of ternary vapor–liquid (acetone–methanol–water, acetone–ethanol–water and hexane–ethanol–benzene) and liquid–liquid (water–methanol–benzene, water–ethanol–hexane and water–1-propanol–benzene) equilibria. In addition, it is shown that a more satisfactory prediction of the ternary vapor–liquid and liquid–liquid equilibria can be obtained by using a limit form of the generalized three-parameter excess function model. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vapor–liquid equilibria; Liquid–liquid equilibria; Equation of state; Excess function; Mixing rule

1. Introduction

It is well known that the representation of phase equilibria of mixtures is carried out, usually, by using equations of state with mixing rules. In general, satisfactory representations are obtained with classical one-parameter mixing rules when these are applied to simple mixtures. On the contrary, for complex mixtures it is necessary to consider mixing rules depending on the composition with two or three binary interaction parameters like those suggested by Panagiotopoulos and Reid [1], Adachi and Sugie [2], Stryjek and Vera [3], and Schwartzentruber and Renon [4]. However, Michelsen and Kistenmacher [5] have shown that these mixing rules are limited to the representation of binary systems, i.e., the extrapolation of these mixing rules to multicomponent mixtures is incoherent due to the invariance problem and the

dilution effect. In order to overcome these shortcomings, a generalization for the two-parameter mixing rules was proposed by Mathias et al. [6] and by Schwartzentruber and Renon [7] for, respectively, the Panagiotopoulos–Reid and Adachi–Sugie mixing rules. After applying their mixing rules on the prediction of ternary liquid–liquid equilibria, Mathias et al. concluded that their formulation does not provide a significantly improved correlative capability over the original mixing rules. On the other hand, Schwartzentruber and Renon applied their generalized Adachi–Sugie mixing rules only on binary and ternary vapor–liquid equilibria but not in systems showing liquid–liquid equilibria.

In this work, a simple generalization for both the two- and three-parameter mixing rules are presented. The application of this generalization was tested on the prediction of ternary vapor–liquid and liquid–liquid equilibria using their corresponding excess function models associated to two modified versions of the Peng–Robinson equation of state [8].

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2. Problem statement

2.1. General formalism of the model equation of state — excess function

In the formalism of equations of state associated with excess functions using the reference at constant packing fraction, $\eta = b/v$, the compressibility factor, $z = Pv/RT$, of a mixture at p components can be written as [9],

$$z = \frac{1}{1 - \eta} - \frac{a}{bRT} Q'(\eta) \quad (1)$$

with

$$\frac{a}{b} = \sum_{i=1}^p x_i \frac{a_i}{b_i} - E(T, x) \quad (2)$$

and

$$b = \sum_{i=1}^p x_i b_i \quad (3)$$

where $Q'(\eta)$ is a packing fraction function depending on the cubic equation of state considered and $E(T, x)$ is the excess free energy which can be expressed either from the classical forms of excess functions (e.g., van Laar, NRTL, UNIQUAC, UNIFAC) or derived from a given mixing rule.

By introducing the following function into Eq. (1)

$$Q'(\eta) = \frac{\eta}{(1 + c_1\eta)(1 + c_2\eta)} \quad (4)$$

we obtain different equations of state depending on the values of constants c_1 and c_2 . Thus, for instance, with $c_1 = 0$ and $c_2 = 1$, the Redlich–Kwong [10] equation of state is obtained.

In this work, the Peng–Robinson equation of state with $c_1 = 1 - \sqrt{2}$ and $c_2 = 1 + \sqrt{2}$, and that with $c_1 = 0$ and $c_2 = 2 + \sqrt{2}$, as suggested by Rauzy [11], were used in all phase equilibrium calculations. However, it is well known that an excellent correlation of the pure-component vapor pressures is a requirement for accurate prediction of the vapor–liquid equilibria of mixtures. Therefore, the temperature-dependent function of equation of state energy parameter a must be carefully chosen to reproduce pure-component vapor pressures. Toward this end, we have chosen both the Stryjek–Vera [12] and Carrier–Rogalski–Péneloux [13] correlations for function $a(T)$ in our calculations. We refer to these as the PRSV and PRCRP equations of state, and they are given in Appendices A and B, respectively.

In Eq. (2), the excess function is $E(T, x)$ postulated to be

$$E(T, x) = \frac{1}{2} \sum_{i=1}^p \sum_{j=1}^p x_i x_j \frac{b_i b_j}{b} E_{ij}, \quad E_{ji} = E_{ij}, \quad E_{ii} = 0 \quad (5)$$

when it is related to the classical van der Waals mixing rules linear in b , Eq. (3), and quadratic in a

$$a = \sum_{i=1}^p \sum_{j=1}^p x_i x_j \sqrt{a_i a_j} (1 - k_{ij}), \quad k_{ji} = k_{ij}, \quad k_{ii} = 0 \quad (6)$$

where k_{ij} is the interaction parameter of binary i and j . It is shown that Eq. (5) is strictly equivalent to these mixing rules if the binary energy parameter E_{ij} is defined as

$$E_{ij} = (\delta_i - \delta_j)^2 + 2\delta_i \delta_j k_{ij}, \quad \delta_i = \frac{\sqrt{a_i}}{b_i} \quad (7)$$

Hence, we can use in Eq. (7) composition-dependent interaction parameters k_{ij} , like those proposed by Panagiotopoulos and Reid [1], Adachi and Sugie [2], Stryjek and Vera [3] for the two-parameter mixing rules (hereafter referred as 2PCD mixing rule) or Schwartzentruber and Renon [4] for the three-parameter mixing rule (hereafter referred as 3PCD mixing rule). Although the three 2PCD mixing rules mentioned above are apparently different, Sandoval et al. [14] have shown that they have the same functional form.

2.2. Composition-dependence mixing rules

As pointed above, the expressions of the binary interaction parameters k_{ij} for the 2PCD and 3PCD mixing rules, are equivalent to those energy interaction parameters E_{ij} based on the excess function formalism. Thus, the interaction parameter k_{ij} for the 2PCD-mixing rule is given by

$$k_{ij} = k_{ij}^{(0)} + k_{ij}^{(1)}(x_i - x_j) \quad (8)$$

where

$$k_{ji}^{(0)} = k_{ij}^{(0)}, \quad k_{ji}^{(1)} = -k_{ij}^{(1)}, \quad k_{ii}^{(0)} = k_{ii}^{(1)} = 0 \quad (9)$$

while for the 3PCD mixing rule, the interaction parameter k_{ij} is expressed by

$$k_{ij} = k_{ij}^{(0)} + k_{ij}^{(1)} \frac{k_{ij}^{(2)} x_i - k_{ji}^{(2)} x_j}{k_{ij}^{(2)} x_i + k_{ji}^{(2)} x_j} (x_i + x_j) \quad (10)$$

where

$$k_{ji}^{(0)} = k_{ij}^{(0)}, \quad k_{ji}^{(1)} = -k_{ij}^{(1)}, \quad k_{ji}^{(2)} = 1 - k_{ij}^{(2)}, \\ k_{ii}^{(0)} = k_{ii}^{(1)} = 0, \quad 0 < k_{ij}^{(2)} < 1 \quad (11)$$

Notice that for binary systems, if $k_{ij}^{(2)} = 0.5$, Eq. (10) reduces to Eq. (8).

2.3. The “Michelsen–Kistenmacher syndrome” and the dilution effect

Michelsen and Kistenmacher [5] showed that mixing rule such as given by Eq. (6) with interaction parameters expressed by Eqs. (8) and (10), are not conservative when two components are made identical in a mixture. In other words,

these expressions do not yield the same value of a if we consider a mixture of three components with mole fractions x_1 , x_2 and x_3 ; 2 and 3 being identical components so that $k_{12}^{(0)} = k_{13}^{(0)}$, $k_{12}^{(1)} = k_{13}^{(1)}$, $k_{12}^{(2)} = k_{13}^{(2)}$ and $k_{23}^{(0)} = k_{23}^{(1)} = 0$, and an equivalent mixture of only two components with mole fractions x_1 and $\hat{x}_2 = x_2 + x_3$. Another shortcoming pointed out by these authors is the so-called dilution effect. That is, when the number of components in the mixture increases, the composition-dependent term in the mixing rule vanishes and the relation given by Eq. (8) in expression (6), reduces to the classical one-parameter mixing rule. However, it can be noted that Eq. (10) does not suffer of this effect. A thorough discussion concerning the different tests for checking the dilution effect and the invariance of composition-dependent mixing rules can be found in Zabaloy and Vera [15].

2.4. Previous generalized composition-dependent mixing rules

Mathias et al. [6] presented the following generalized two-parameter mixing rule, which was developed as a polynomial depending on the composition,

$$a = \sum_{i=1}^p x_i \left\{ \sum_{j=1}^p x_j a_{ji} (1 - k_{ji}^{(0)}) + \left[\sum_{k=1}^p x_k (a_{ki} k_{ki}^{(1)})^{1/3} \right]^3 \right\} \quad (12)$$

For binary mixtures, this expression is equal to the mixing rule suggested by Panagiotopoulos and Reid [1]. Calculations carried out by these authors using their proposed mixing rule and that of Panagiotopoulos and Reid for the prediction of vapor–liquid and liquid–liquid equilibria of ternary systems showed that the results obtained using both mixing rules were similar.

Alternatively, Schwartzenuber and Renon [7] proposed two modifications to the Adachi–Sugie mixing rule [2]. Firstly, to avoid the invariance problem, these authors include a ternary interaction parameter in the mixing rule,

$$a = \sum_{i=1}^p \sum_{j=1}^p x_i x_j \left[a_{ij} (1 - k_{ij}^{(0)}) + \sum_{k=1}^p \chi_{ijk} x_k \right] \quad (13)$$

with

$$3\chi_{ijk} = \delta_{ij} k_{ik}^{(1)} + \delta_{ik} k_{ij}^{(1)} + \delta_{ji} k_{jk}^{(1)} + \delta_{jk} k_{ji}^{(1)} + \delta_{ki} k_{kj}^{(1)} + \delta_{kj} k_{ki}^{(1)} \quad (14)$$

where δ_{ij} is a “physical” Kronecker delta that is the unity if the indexes i and j refer to the same component (not only if $i = j$) and equal to zero otherwise.

Secondly, to circumvent the problem of the dilution effect, these authors presented a “distance-parameter” expression based on the difference between critical properties, acentric

factors and dipole moments of molecules i and j ,

$$D_{ij}^2 = \frac{1}{4} \left[\left(\frac{a_{c_i} - a_{c_j}}{a_{c_i} + a_{c_j}} \right)^2 + \left(\frac{b_{c_i} - b_{c_j}}{b_{c_i} + b_{c_j}} \right)^2 + \left(\frac{\omega_i - \omega_j}{\omega_i + \omega_j} \right)^2 + \left(\frac{\mu_i - \mu_j}{\mu_i + \mu_j} \right)^2 \right] \quad (15)$$

so that δ_{ij} can be expressed as

$$\delta_{ij} = 1 - D_{ij}, \quad 0 \leq \delta_{ij} \leq 1 \quad (16)$$

δ_{ij} is considered as a binary parameter, which is correlated to a certain “distance” between molecules i and j , so that $\delta_{ij} = 1$ when molecules i and j are strictly identical, and decreases continuously to zero when these molecules become different. Nevertheless, it should be pointed out that Eq. (15) is highly empirical and its use is sometimes incoherent. For instance, we found that for molecules like pentane and dodecane or pentane and isopentane, the distance value in both cases is about 0.5. Since the dipole moments of pentane and dodecane are zero [16], then only the contribution of the first three terms in the right-hand side of this equation is taken into account. However, for molecules such as pentane and isopentane, which have a dipole moment slightly different to zero [16], the last term is the most important contribution in this expression.

3. Approach proposed

The simples but coherent generalizations to p component systems proposed in this work for the 2PCD, Eq. (8), and 3PCD, Eq. (10), mixing rules are

$$k_{ij} = k_{ij}^{(0)} \left[1 + \sum_{m=1}^p x_m (\hat{k}_{mi(ij)}^{(1)} + \hat{k}_{mj(ij)}^{(1)}) \right] \quad (17)$$

and

$$k_{ij} = k_{ij}^{(0)} \left[1 + \frac{\sum_{m=1}^p x_m (\hat{k}_{mi(ij)}^{(1)} k_{mi}^{(2)} + \hat{k}_{mj(ij)}^{(1)} k_{mj}^{(2)})}{\sum_{m=1}^p x_m (k_{mi}^{(2)} + k_{mj}^{(2)})} \right] \quad (18)$$

We refer Eqs. (17) and (18) as the G2PCD and G3PCD mixing rules, respectively.

For both generalized expressions, the interaction parameters satisfy the following conditions if molecules i and j are strictly identical ($i = j$ or i and j are the indexes referring to the same component as in the case of a binary mixture 1–2 developed as a pseudo-ternary 1–3):

$$k_{ij} = k_{ij}^{(0)} = 0, \quad \hat{k}_{ij(mi)}^{(1)} = 0, \quad k_{ij}^{(2)} = k_{ji}^{(2)} = 0 \quad (19)$$

otherwise $k_{ij}^{(0)}$ is different to zero, so that we can define the following relations:

$$\hat{k}_{mi(ij)}^{(1)} = \frac{k_{mi}^{(1)}}{k_{ij}^{(0)}}, \quad \hat{k}_{mj(ij)}^{(1)} = \frac{k_{mj}^{(1)}}{k_{ij}^{(0)}},$$

$$k_{ij}^{(2)} + k_{ji}^{(2)} = 1, \quad 0 < k_{ij}^{(2)} < 1 \quad (20)$$

where $\hat{k}_{mi(ij)}^{(1)}$ and $\hat{k}_{mj(ij)}^{(1)}$ are the interaction parameters of the binary $i - j$.

An inspection of the above expressions, shows that the interaction parameter $k_{ij}^{(0)}$ in Eq. (17) is the same to that given in Eq. (8) while the interaction parameters $k_{ij}^{(0)}$ and $k_{ij}^{(2)}$ of Eq. (18) are the same to those given in Eq. (10). Additionally, it is assumed in Eqs. (17) and (18) that interactions between molecules i and j depend not only on the interactions between them but also on the nature of the medium in which these molecules are found. That is, for a mixture with p components, the influence of the others components m of the mixture is translated mediating their mole fractions, x_m , and their physicochemical properties which are related to the parameters $\hat{k}_{mi(ij)}^{(1)}$ and $\hat{k}_{mj(ij)}^{(1)}$.

3.1. Limit form of the G3PCD mixing rule

For a binary mixture, Eqs. (17) and (18) are identical when the third interaction parameters $k_{ij}^{(2)}$ are $k_{ij}^{(2)} = k_{ji}^{(2)} = 0.5$. Therefore, it can be seen that Eq. (8) is a limit form of that given by Eq. (10).

On the contrary, for a mixture containing p components, if all the interaction parameters $k_{ij}^{(2)}$ are assumed to be $k_{ij}^{(2)} = 0.5$ when the components i and j are different, and $k_{ij}^{(2)} = k_{ji}^{(2)} = 0$ when the components are identical or the indexes i and j are referred to the same component, Eq. (18) becomes,

$$k_{ij} = k_{ij}^{(0)} \left[1 + \frac{0.5 \sum_{m=1}^p x_m (\hat{k}_{mi(ij)}^{(1)} + \hat{k}_{mj(ij)}^{(1)})}{1 - 0.5(x_i + x_j)} \right] \quad (21)$$

which is the limit form of the G3PCD mixing rule, and this is different to the G2PCD mixing rule, Eq. (17), when it is applied to p components. It can also be verified that in continuous thermodynamics, the summation term of $x_m (\hat{k}_{mi(ij)}^{(1)} + \hat{k}_{mj(ij)}^{(1)})$ in Eq. (21) is reduced by a factor of 0.5 with respect to the corresponding term in the G2PCD mixing rule.

3.2. Excess function models from mixing rules

To represent binary vapor–liquid and/or liquid–liquid equilibrium data as well as to predict the phase equilibria of multicomponent systems using the formalism “equation of state — excess function” at constant packing fraction [9], we have derived the corresponding expressions of the excess function models from the mixing rules described above. Thus, the interaction parameters E_{ij} derived from Eqs. (8) and (10) are

$$E_{ij} = E_{ij}^{(0)} + E_{ij}^{(1)}(x_i - x_j) \quad (22)$$

and

$$E_{ij} = E_{ij}^{(0)} + E_{ij}^{(1)} \frac{e_{ij}^{(2)} x_i - e_{ji}^{(2)} x_j}{e_{ij}^{(2)} x_i + e_{ji}^{(2)} x_j} (x_i + x_j) \quad (23)$$

where

$$E_{ji}^{(0)} = E_{ij}^{(0)}, \quad E_{ji}^{(1)} = -E_{ij}^{(1)}, \quad e_{ji}^{(2)} = 1 - e_{ij}^{(2)},$$

$$E_{ii}^{(0)} = E_{ii}^{(1)} = 0, \quad 0 < e_{ij}^{(2)} < 1 \quad (24)$$

while the corresponding interaction parameters E_{ij} derived from the proposed mixing rules, Eqs. (17), (18) and (21) are

$$E_{ij} = E_{ij}^{(0)} \left[1 + \sum_{m=1}^p x_m (e_{mi(ij)}^{(1)} + e_{mj(ij)}^{(1)}) \right] \quad (25)$$

$$E_{ij} = E_{ij}^{(0)} \left[1 + \frac{\sum_{m=1}^p x_m (e_{mi(ij)}^{(1)} e_{mi}^{(2)} + e_{mj(ij)}^{(1)} e_{mj}^{(2)})}{\sum_{m=1}^p x_m (e_{mi}^{(2)} + e_{mj}^{(2)})} \right] \quad (26)$$

and

$$E_{ij} = E_{ij}^{(0)} \left[1 + \frac{0.5 \sum_{m=1}^p x_m (e_{mi(ij)}^{(1)} + e_{mj(ij)}^{(1)})}{1 - 0.5(x_i + x_j)} \right] \quad (27)$$

Again, Eq. (27) is the limit form of the G3PCD excess function, Eq. (26), and it is obtained by setting $e_{ij}^{(2)} = e_{ji}^{(2)} = 0.5$ when components i and j are different, and $e_{ij}^{(2)} = e_{ji}^{(2)} = 0$ when the components are identical or the indexes i and j are referred to the same component.

In Eqs. (25)–(27), the common parameters satisfy the following conditions, if molecules i and j are strictly identical (i.e., if $i = j$ or i and j are the indexes referring to the same component as in the case of a binary mixture 1–2 developed as a pseudo-ternary 1–3).

$$E_{ij} = E_{ij}^{(0)} = 0, \quad e_{ij(mi)}^{(1)} = 0,$$

$$e_{ij}^{(2)} = e_{ji}^{(2)} = 0, \quad 0 < e_{ij}^{(2)} < 1 \quad (28)$$

while if $E_{ij}^{(0)}$ is different to zero, the following expressions can be defined:

$$e_{mi(ij)}^{(1)} = \frac{E_{mi}^{(1)}}{E_{ij}^{(0)}}, \quad e_{mj(ij)}^{(1)} = \frac{E_{mj}^{(1)}}{E_{ij}^{(0)}}, \quad e_{ij}^{(2)} + e_{ji}^{(2)} = 1 \quad (29)$$

where $e_{mi(ij)}^{(1)}$ and $e_{mj(ij)}^{(1)}$ are the interaction parameters for the binary $i - j$.

4. Application of the approach

The approach presented in this work was tested on the representation of binary vapor–liquid and liquid–liquid

Table 1

Estimated interaction parameters for the 2PCD and 3PCD excess function models associated with the PRCRP equation of state

System	Adachi–Sugie				Schwartzentruber–Renon			
	$A_{12}^{(0)}$ (J cm ⁻³)	$B_{12}^{(0)}$ (J cm ⁻³)	$A_{12}^{(1)}$ (J cm ⁻³)	$B_{12}^{(1)}$ (J cm ⁻³)	$A_{12}^{(0)}$ (J cm ⁻³)	$B_{12}^{(0)}$ (J cm ⁻³)	$A_{12}^{(1)}$ (J cm ⁻³)	$e_{12}^{(2)}$
<i>Vapor–liquid equilibria</i>								
Benzene–hexane	106.0	123.0	0.0	0.0	106.0	123.0	0.0	0.500
Methanol–benzene	546.0	–405.2	–204.2	0.0	657.8	–397.4	–266.2	0.712
Ethanol–hexane	458.7	–360.4	–214.2	0.0	581.0	–344.8	–268.3	0.737
Ethanol–benzene	386.6	–238.3	–128.1	0.0	470.4	–235.4	–174.7	0.751
1-Propanol–benzene	315.4	–114.6	–77.2	0.0	350.8	113.9	–98.1	0.707
Acetone–methanol	211.9	0.0	42.2	0.0	211.9	0.0	42.2	0.500
Acetone–ethanol	188.9	491.8	0.0	0.0	188.9	491.8	0.0	0.500
Acetone–water	1084.0	–1372.7	476.8	0.0	1084.0	–1372.7	476.8	0.500
Methanol–water	360.3	–1063.5	78.5	0.0	305.9	–1238.7	87.1	0.728
Ethanol–water	776.0	–1179.5	199.5	0.0	714.3	–1225.1	185.2	0.668
1-Propanol–water	1100.9	–1081.9	280.0	0.0	1100.9	–1081.9	280.0	0.500
<i>Liquid–liquid equilibria</i>								
Water–pentane	4006.0	–29.9	–2092.0	–2477.0				
Water–hexane	3809.0	1604.0	–1981.0	–3740.0				
Water–benzene	3026.0	–2041.0	–1428.0	–1588.0				
Water–heptane	3768.0	1096.0	–1944.0	–3330.0				
Water–octane	3720.0	1129.0	–1939.0	–3739.0				

equilibria using the PRSV [12] and PRCRP [13] equations of state associated with the 2PCD and 3PCD excess function models. Furthermore, the prediction of ternary vapor–liquid and liquid–liquid equilibria using this formalism was performed for the systems acetone–methanol–water, acetone–ethanol–water, and hexane–ethanol–benzene for vapor–liquid equilibria, and water–methanol–benzene, water–ethanol–hexane, and water–1-propanol–benzene for liquid–liquid equilibria.

4.1. Representation of binary vapor–liquid and liquid–liquid equilibria

It has been recognized that for obtaining accuracy representations of phase equilibria of mixtures in a wide range of temperatures, it is necessary to consider the model parameters as depending on temperature. Therefore, the following inverse temperature linear function was used for representing the variation on temperature of the interaction

Table 2

Estimated interaction parameters for the 2PCD and 3PCD excess function models associated with the PRSV equation of state

System	2PCD excess function model				3PCD excess function model			
	$A_{12}^{(0)}$ (J cm ⁻³)	$B_{12}^{(0)}$ (J cm ⁻³)	$A_{12}^{(1)}$ (J cm ⁻³)	$B_{12}^{(1)}$ (J cm ⁻³)	$A_{12}^{(0)}$ (J cm ⁻³)	$B_{12}^{(0)}$ (J cm ⁻³)	$A_{12}^{(1)}$ (J cm ⁻³)	$e_{12}^{(2)}$
<i>Vapor–liquid equilibria</i>								
Benzene–hexane	38.6	49.1	0.0	0.0	38.6	49.1	0.0	0.500
Methanol–benzene	187.9	–142.8	–70.3	0.0	229.1	–135.6	–93.7	0.721
Ethanol–hexane	157.9	–125.0	–75.3	0.0	204.2	–102.7	–95.4	0.744
Ethanol–benzene	133.6	–74.5	–44.8	0.0	162.0	–73.5	–60.3	0.747
1-Propanol–benzene	108.8	–32.5	–27.2	0.0	125.6	38.5	–36.3	0.742
Acetone–methanol	72.7	0.0	15.2	0.0	72.7	0.0	15.2	0.500
Acetone–ethanol	65.5	17.7	0.0	0.0	65.5	17.7	0.0	0.500
Acetone–water	373.1	–471.3	164.7	0.0	373.1	–471.3	164.7	0.500
Methanol–water	122.6	–384.7	27.1	0.0	104.1	–439.0	29.4	0.725
Ethanol–water	267.3	–394.2	68.8	0.0	244.4	–418.9	62.9	0.669
1-Propanol–water	385.1	–329.7	99.0	0.0	385.1	–329.7	99.0	0.500
<i>Liquid–liquid equilibria</i>								
Water–pentane	1368.0	73.5	–711.2	–933.7				
Water–hexane	1309.0	526.6	–681.7	–1254.0				
Water–benzene	1038.0	0.0	–490.2	–549.5				
Water–heptane	1293.0	379.2	–667.1	1140.0				
Water–octane	1276.0	474.5	–665.2	–1371.0				

parameters given in the above equations,

$$E_{ij}^{(k)} = A_{ij}^{(k)} + B_{ij}^{(k)} \left(\frac{T_0}{T} - 1 \right) \quad (30)$$

where T_0 is the reference temperature set equal to 298.15 K. For vapor–liquid equilibria, we consider only one temperature-dependent parameter ($k = 0$) while for liquid–liquid equilibria, two temperature-dependent parameters ($k = 0, 1$) were considered.

In general, the interaction parameters $A_{ij}^{(k)}$ and $B_{ij}^{(k)}$ for the excess function models considered were estimated by minimizing the deviations between experimental and calculated values of either vapor–liquid or liquid–liquid equilibrium data of binary mixtures. For the systems studied Tables 1 and 2 give the interaction parameters for the excess function models, Eqs. (22) and (23), associated to the PRCRP and PRSV equations of state, respectively, which were estimated by minimization of the following objective functions:

$$F_{LV} = \frac{\delta P}{P} + 100\delta y \quad (31)$$

and

$$F_{LL} = \frac{\delta x_1}{x_1} + \frac{\delta x_2}{x_2} \quad (32)$$

where

$$\frac{\delta P}{P} = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| \quad (33)$$

$$\delta y = \frac{1}{N_p} \sum_{i=1}^{N_p} |y_i^{\text{exp}} - y_i^{\text{calc}}| \quad (34)$$

$$\frac{\delta x_1}{x_1} = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{x_{1i}^{\text{exp}} - x_{1i}^{\text{calc}}}{x_{1i}^{\text{exp}}} \right| \quad (35)$$

and

$$\frac{\delta x_2}{x_2} = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{x_{2i}^{\text{exp}} - x_{2i}^{\text{calc}}}{x_{2i}^{\text{exp}}} \right| \quad (36)$$

In these equations ($P_i^{\text{exp}} - P_i^{\text{calc}}$), ($y_i^{\text{exp}} - y_i^{\text{calc}}$), ($x_{1i}^{\text{exp}} - x_{1i}^{\text{calc}}$), ($x_{2i}^{\text{exp}} - x_{2i}^{\text{calc}}$) are the residuals between the experimental and calculated values of, respectively, bubble-point pressure, vapor compositions, mole fractions of water solubilized in hydrocarbon, and mole fractions of hydrocarbon solubilized in water for an experiment i , and N_p is the total number of experiments.

The agreement between theory and experiment was established through the absolute percent relative deviation in pressure, $\delta P/P$, and absolute deviation in vapor compositions, δy , for vapor–liquid equilibria, and absolute percent relative deviation in mole fractions of water solubilized in hydrocarbon, $\delta x_1/x_1$, and mole fractions of hydrocarbon solubilized in water, $\delta x_2/x_2$, for liquid–liquid equilibria. These deviations were obtained from the 2PCD and 3PCD excess function models by using the optimal values of the interaction parameters and they are given in Tables 3 and 4 for, respectively, vapor–liquid and liquid–liquid equilibria. Experimental phase equilibrium data used on the representation were taken from vapor–liquid and liquid–liquid equilibrium data compilations [17–19]. On the whole, Tables 3 and 4 show that the quality of the fit to experimental values is good for most systems.

Table 3 indicates that a good representation was obtained for the system benzene–hexane using the 2PCD and 3PCD excess function models associated to the PRSV ($\delta P/P = 0.72\%$, $\delta y = 0.005$) and PRCRP ($\delta P/P = 0.55\%$, $\delta y = 0.004$) equations of state, but that for the systems alcohol–hydrocarbon, the best representation was obtained using the 3PCD excess function model. For the systems acetone–alcohol, acetone–water and water–alcohol both models gave similar results.

Table 3
Vapor–liquid equilibria using the PRCRP and PRSV equations of state associated with the 2PCD and 3PCD excess function models

System	N_p	Temperature range (K)	PRCRP EoS + 2PCD excess function model		PRCRP EoS + 3PCD excess function model		PRSV EoS + 2PCD excess function model		PRSV EoS + 3PCD excess function model	
			$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy
Benzene–hexane	286	293–403	0.55	0.004	0.55	0.004	0.72	0.005	0.72	0.005
Methanol–benzene	163	288–373	1.99	0.020	1.05	0.012	1.99	0.020	1.04	0.012
Ethanol–hexane	224	298–353	3.21	0.019	0.81	0.011	3.42	0.020	0.89	0.013
Ethanol–benzene	251	293–339	1.56	0.019	0.65	0.011	1.59	0.019	0.65	0.011
1-Propanol–benzene	294	273–348	2.46	0.013	2.22	0.012	2.77	0.014	2.36	0.014
Acetone–methanol	157	288–328	1.55	0.011	1.55	0.011	1.52	0.011	1.52	0.011
Acetone–ethanol	96	288–328	1.70	0.010	1.70	0.010	1.74	0.008	1.74	0.008
Acetone–water	132	288–373	1.67	0.008	1.67	0.008	1.65	0.008	1.65	0.008
Methanol–water	182	298–413	1.40	0.008	1.26	0.007	1.28	0.008	1.14	0.007
Ethanol–water	239	293–363	0.98	0.009	0.53	0.005	1.03	0.009	0.64	0.006
1-Propanol–water	189	298–363	1.46	0.012	1.46	0.012	1.62	0.014	1.62	0.014
Global	2213		1.68	0.012	1.17	0.009	1.76	0.013	1.23	0.010

Table 4
Liquid–liquid equilibria using the PRCRP and PRSV equations of state with the 2PCD excess function model

System	N_p	Temperature range (K)	$\delta x_1/x_1$ (%)	δx_1^a	$\delta x_2/x_2$ (%)	δx_2^b
<i>PRCRP equation of state</i>						
Water–pentane	4	273–298	3.22	0.125×10^{-4}	3.12	0.327×10^{-6}
Water–hexane	6	273–313	5.20	0.183×10^{-4}	1.32	0.390×10^{-7}
Water–benzene	11	293–343	0.66	0.559×10^{-4}	1.13	0.595×10^{-5}
Water–heptane	6	273–313	2.31	0.257×10^{-4}	5.39	0.282×10^{-7}
Water–octane	5	273–303	2.13	0.620×10^{-5}	6.52	0.820×10^{-8}
<i>PRSV equation of state</i>						
Water–pentane	4	273–298	1.62	0.468×10^{-5}	3.11	0.327×10^{-6}
Water–hexane	6	273–313	5.26	0.245×10^{-4}	1.23	0.349×10^{-7}
Water–benzene	11	293–343	0.66	0.503×10^{-4}	1.14	0.583×10^{-5}
Water–heptane	6	273–313	2.31	0.257×10^{-4}	5.48	0.283×10^{-7}
Water–octane	5	273–303	1.88	0.107×10^{-4}	6.50	0.800×10^{-8}

$$^a \delta x_1 = \frac{1}{N_p} \sum_{i=1}^{N_p} |x_{1i}^{\text{exp}} - x_{1i}^{\text{calc}}|.$$

$$^b \delta x_2 = \frac{1}{N_p} \sum_{i=1}^{N_p} |x_{2i}^{\text{exp}} - x_{2i}^{\text{calc}}|.$$

Table 4 shows the results obtained with the 2PCD excess function model associated to the PRCRP and PRSV equations of state on the representation of mutual solubilities for the systems water–pentane, water–hexane, water–benzene, water–heptane and water–octane. The same calculations were also carried out using the 3PCD excess function model but we have found no significant improvements in adjusting one more parameter. For this reason, we have not report the estimated three parameters of this model.

4.2. Prediction of ternary vapor–liquid and liquid–liquid equilibria

Isothermal and/or isobaric vapor–liquid equilibrium calculations were performed to predict the phase diagrams of the systems acetone–methanol–water, acetone–ethanol–water, and hexane–ethanol–benzene. Table 5 gives the results obtained from the predictions using the G3PCD excess function model, Eq. (26). In particular, for the limit form of the G3PCD excess function model, Eq. (27), the

Table 5
Predicted isothermal and isobaric vapor–liquid equilibria of ternary systems using the PRCRP and PRSV equations of state associated with the G3PCD excess function model

System	T or P	N_p	Method 1 ^a		Method 2 ^b	
			$\delta P/P$	δy	$\delta P/P$	δy
<i>PRCRP equation of state</i>						
Acetone–methanol–water	373.15 K	51	1.56	0.021	1.61	0.023
	523.15 K	57	1.89	0.006	1.33	0.007 ^c
	1.01 bar	58	7.11	0.053	6.80	0.051
	1.01 bar	54	3.34	0.016	3.56	0.016
Acetone–ethanol–water	323.15 K	60	7.18		7.61	
Hexane–ethanol–benzene	328.15 K	43	7.85	0.028	7.69	0.030
Global		323	4.79	0.024	5.00	0.026
<i>PRSV equation of state</i>						
Acetone–methanol–water	373.15 K	51	1.57	0.021	1.91	0.022
	523.15 K	57	1.31	0.006	1.55	0.007 ^c
	1.01 bar	58	7.09	0.053	7.20	0.053
	1.01 bar	54	3.29	0.016	3.59	0.016
Acetone–ethanol–water	323.15 K	60	7.76		7.69	
Hexane–ethanol–benzene	328.15 K	43	7.44	0.026	7.26	0.023
Global		323	4.73	0.024	4.86	0.025

^a Limit form of the G3PCD excess function model with $e_{ij}^{(2)} = 0.5$ and the interaction parameters of the 2PCD excess function model given in Tables 1 and 2.

^b G3PCD excess function model with interaction parameters given in Tables 1 and 2.

^c Experimental data taken from Griswold and Wong [20].

calculations were carried out by using $e_{ij}^{(2)} = 0.5$ together with parameters $E_{ij}^{(0)}$ and $E_{ij}^{(1)}$ of the 2PCD excess function model given in Tables 1 and 2.

An examination of Table 3 indicates that, with exception of the system ethanol–hexane, the representation of the vapor–liquid equilibria for the systems studied were very satisfactory when the 2PCD excess function models is used. Consequently, it is possible to understand why we did not find appreciable differences in the predictions reported in Table 5 using both methods for the systems acetone–methanol–water and acetone–ethanol–water. Conversely, for the system hexane–ethanol–benzene, where the influence of a third parameter in the excess function model is sensible on the representation of the system ethanol–hexane, the two methods lead to almost the same results when these are applied to the prediction of ternary systems. Hence, it can be said that the singularities detected on the representation of the thermodynamic properties of binary systems are not conserved as a system become multicomponent when it is formed from these binary systems.

Ternary liquid–liquid phase diagrams of the systems water–methanol–benzene, water–ethanol–hexane, and water–1-propanol–benzene, were predicted using the formalism “equation of state — excess function” in conjunction with the G2PCD and G3PCD excess function models.

Results of the predictions are presented in Figs. 1–3. In these figures, the filled circles with full lines are the experimental data [17] while the open circles with dashed lines are the calculated values. All calculations were performed using the PRSV and PRCRP equations of state; however, because the quality for predicting liquid–liquid equilibria was similar for both equations, then only the performance of one of them will be reported in all figures hereinafter.

The method of calculation for the ternary liquid systems was a two-phase flash calculation using equimolar global compositions obtained from experimental compositions of the coexisting phases. The predicted tie lines presented in Figs. 1–3, show how the slopes of these tie lines change with respect to the experimental ones.

Fig. 1 shows the prediction of the liquid–liquid equilibria for the system water–methanol–benzene at 303.15 K using the limit form of the G3PCD excess function model, Eq. (27) with $e_{ij}^{(2)} = 0.5$, and the interaction parameters $E_{ij}^{(0)}$ and $E_{ij}^{(1)}$ of the 2PCD excess function model. An inspection of this figure shows that most of the predicted mutual solubilities are in good accordance with the experimental data.

In order to study the behavior of the G3PCD excess function model with parameters, $E_{ij}^{(0)}$, $E_{ij}^{(1)}$, and $e_{ij}^{(2)}$ for this ternary system, we have analyzed the deviations obtained from the regression of phase equilibrium data for the systems

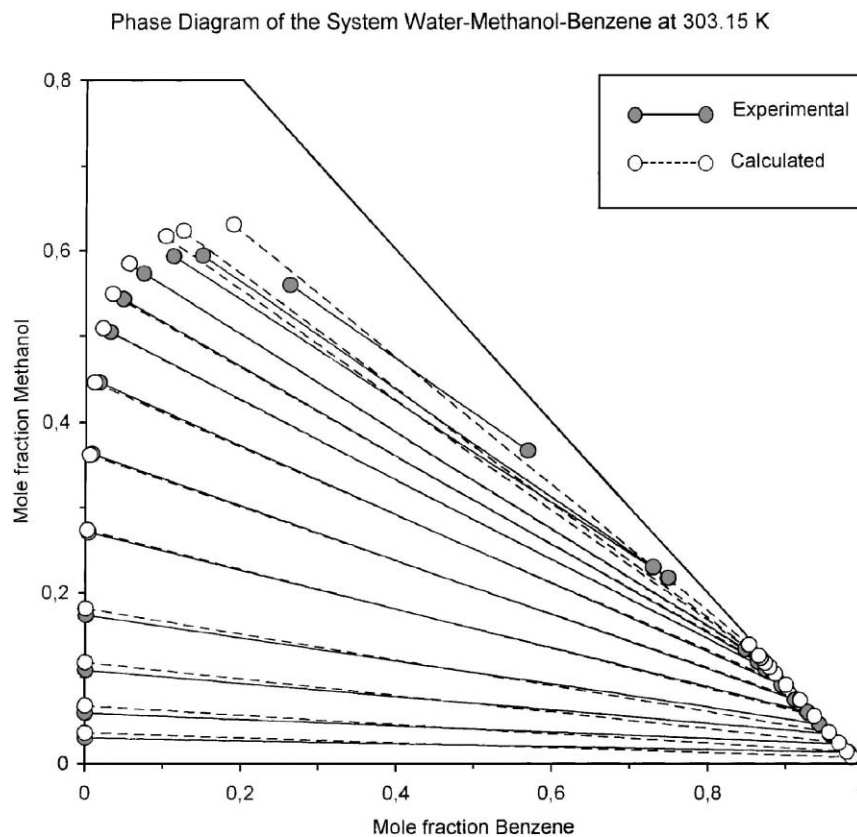


Fig. 1. Liquid–liquid equilibria for the water–methanol–benzene system at 303.15 K. Experimental data taken from [19]. Calculated values obtained using the PRCRP equation of state and the limit form of the G3PCD excess function model.

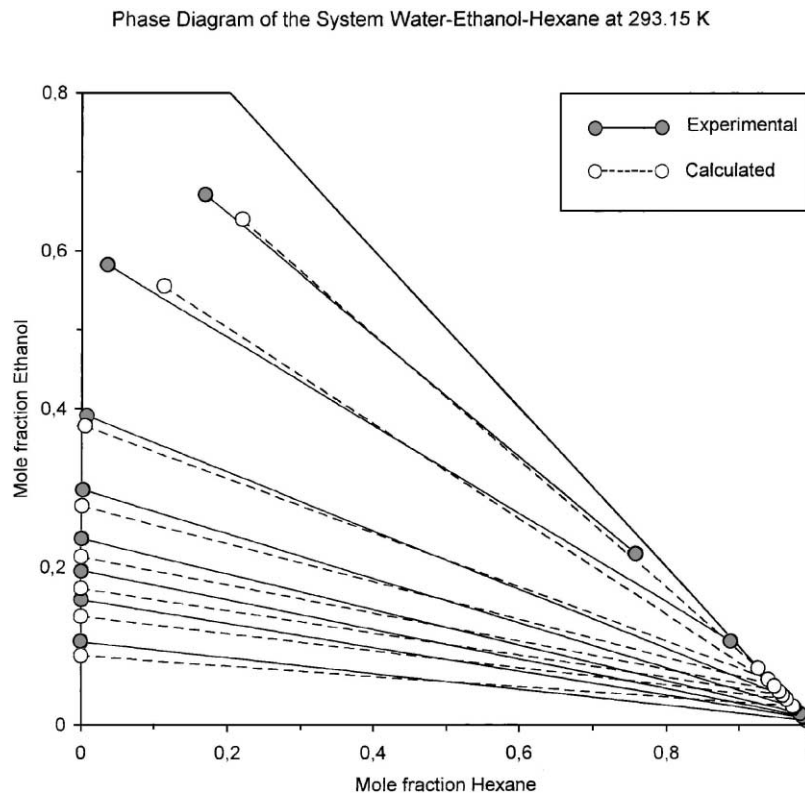


Fig. 2. Liquid-liquid equilibria for the water-ethanol-hexane system at 293.15 K. Experimental data taken from [19]. Calculated values obtained using the PRCRP equation of state and the limit form of the G3PCD excess function model.

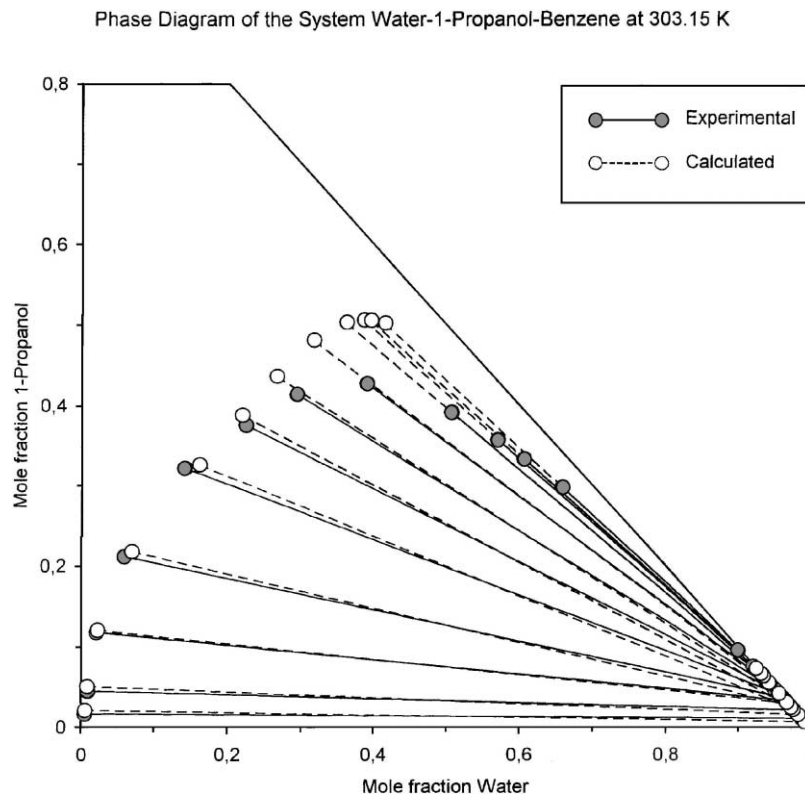


Fig. 3. Liquid-liquid equilibria for the water-1-propanol-benzene system at 303.15 K. Experimental data taken from [19]. Calculated values obtained using the PRCRP equation of state and the limit form of the G3PCD excess function model.

water–methanol and water–benzene using both the 2PCD and 3PCD excess function models. Thus, as shown in Table 3, we can see that there is not a sensible improvement on the representation of the vapor–liquid equilibria for the system water–methanol using the 3PCD excess function model with respect to those obtained with the 2PCD one. Similarly, we have not found differences in using either the 2PCD or 3PCD model when they are applied on the representation of the liquid–liquid equilibrium data for the system water–benzene.

Therefore, we cannot expect any improvement on the prediction of the liquid–liquid equilibria for the system water–methanol–benzene in spite of using more parameters. Nevertheless, it should be mentioned that the representation of the vapor–liquid equilibria for the system methanol–benzene is greatly improved when the 3PCD excess function model is considered.

Fig. 2 shows the predictions of the liquid–liquid equilibria for the system water–ethanol–hexane at 293.15 K using the limit form of the G3PCD excess function model with $e_{ij}^{(2)} = 0.5$ and the interaction parameters of the 2PCD excess function model. This figure shows that for this system, with exception of the two last tie lines, this model is able to predict correctly the experimental behavior.

Fig. 3 presents the predicted liquid–liquid equilibria for the system water–1-propanol–benzene at 303.15 K using the limit form of the G3PCD excess function model with $e_{ij}^{(2)} = 0.5$ and the 2PCD excess function model parameters $E_{ij}^{(0)}$ and $E_{ij}^{(1)}$ given in Table 1.

Similar results were obtained when the G3PCD excess function model is applied to the prediction of the above systems using the three estimated parameters $E_{ij}^{(0)}$, $E_{ij}^{(1)}$, and $e_{ij}^{(2)}$, also given in Table 1. Prediction of the liquid–liquid equilibria for these systems using the G2PCD excess function model was also carried out. The obtained results were, as expected, less satisfactory than those obtained with the G3PCD model.

5. Conclusions

A simple but consistent generalization of the 2PCD, Eq. (8), and 3PCD, Eq. (10), mixing rules have been presented. These mixing rules in conjunction with excess function models and associated to equations of state can be applied to multicomponent systems. It is shown that these generalized expressions do not present the shortcomings related to the invariance problem and that of dilution effect existing in the Schwartzentruber–Renon type mixing rules when these are applied to multicomponent mixtures. The performance of the suggested mixing rules was demonstrated on the prediction of ternary vapor–liquid and liquid–liquid equilibria using estimated interaction parameters obtained from binary phase equilibrium data. In addition, it is shown that a more satisfactory prediction of

the ternary vapor–liquid and liquid–liquid equilibria can be obtained by using the limit form of the G3PCD excess function model. Therefore, it seems that to obtain a better prediction of the thermodynamic properties of multicomponent systems it is more convenient to get a less accurate representation of all the singularities for the binary systems.

Besides, it is important to point out that the PRSV [12] and the PRCRP [13] equations of state give similar results when both equations are applied with the same excess function on the representation of binary vapor–liquid and liquid–liquid equilibrium data. Similar conclusions are derived when these equations are applied to the prediction of ternary vapor–liquid and liquid–liquid equilibria. This is due mainly to that both equations of state give an excellent correlation of the pure-component vapor pressures.

Appendix A. The PRSV equation of state

The PRSV equation of state [12] was established through Eqs. (1) and (4) in conjunction with constants $c_1 = 1 - \sqrt{2}$ and $c_2 = 1 + \sqrt{2}$. For pure components, parameters a and b are estimated as,

$$a = \left(0.457235 \frac{R^2 T_c^2}{P_c} \right) \alpha(T) \quad (\text{A.1})$$

and

$$b = 0.077796 \frac{RT_c}{P_c} \quad (\text{A.2})$$

where the temperature function $\alpha(T)$ was defined by Stryjek and Vera [12] as,

$$\alpha(T) = \left\{ 1 + \left[\kappa_0 + \kappa_1 \left(1 + \left(\frac{T}{T_c} \right)^{0.5} \right) \left(0.7 - \frac{T}{T_c} \right) \right] \times \left(1 - \left(\frac{T}{T_c} \right)^{0.5} \right) \right\}^2 \quad (\text{A.3})$$

with

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (\text{A.4})$$

where ω is the acentric factor, T_c and P_c are the critical temperature and pressure, and κ_1 is a constant specific for each fluid.

Appendix B. The PRCRP equation of state

The PRCRP equation of state [13] was established through Eqs. (1) and (4) in conjunction with constants $c_1 = 0$ and $c_2 = 2 + \sqrt{2}$. For pure components, parameters a and b are estimated as,

$$a = \begin{cases} a_m & \text{if } T \leq T_b \\ a_s & \text{if } T \geq 1.25T_b \\ Xa_s + (1 - X)a_m & \text{if } T_b \leq T \leq 1.25T_b \end{cases} \quad (\text{B.1})$$

Table 6
Pure-component properties and parameters m_0 , m_1 and m_2 used in the PRCRP equation of state

Component	T_c (K)	P_c (bar)	T_b (K)	m_0	m_1	m_2	$T_{\min} - T_{\max}$ (K)	dP/P (%)	N_p	Reference
Pentane	469.65	33.680	309.21	0.74428	1.92415	0.42290	207.97–297.98	0.19	13	[21]
							286.43–309.97	0.03	9	[22]
Hexane	507.43	30.124	341.89	0.81114	2.29511	0.55634	300.26–321.26	0.06	8	[23]
							286.18–342.69	0.01	16	[22]
Benzene	562.15	48.970	353.24	0.68993	2.25148	0.62126	287.70–354.07	0.04	19	[22]
							294.16–378.15	0.05	19	[24]
Heptane	540.26	27.348	371.57	0.87860	2.54606	0.63021	299.08–372.43	0.04	20	[22]
Octane	568.82	24.855	398.81	0.94488	2.82804	0.72155	326.08–399.72	0.02	19	[22]
Acetone	508.15	47.015	329.20	0.81844	1.68549	0.27537	310.83–329.17	0.02	8	[25]
Methanol	512.65	80.959	337.70	1.15812	1.15727	−0.13199	273.05–328.43	0.05	13	[26]
							288.05–356.83	0.05	20	[27]
Ethanol	513.92	61.370	351.44	1.27246	1.63796	−0.05154	274.87–336.53	0.15	15	[28]
							288.15–337.65	0.07	18	[29]
1-Propanol	536.78	51.676	370.30	1.24520	3.34835	0.73782	262.59–356.03	0.04	25	[30]
							273.15–351.70	0.14	8	[31]
Water	647.37	221.200	373.15	0.85710	1.35795	0.16530	293.15–323.15	0.06	6	[32]
							292.77–366.63	0.04	25	[27]
							276.50–370.50	0.15	27	[30]
							321.29–370.25	0.15	15	[33]
							333.32–377.73	0.05	19	[27]
							293.19–389.48	0.05	27	[30]
							287.45–389.45	0.16	27	[30]
							273.15–373.15	0.01	52	[34]

where

$$a_m = a_0 \left\{ 1 + m_1 \left[1 - \left(\frac{T}{T_b} \right)^{0.5} \right] - m_2 \left(1 - \frac{T}{T_b} \right) \right\} \quad (\text{B.2})$$

$$a_s = a_c \left\{ 1 + m_0 \left[1 - \left(\frac{T}{T_c} \right)^{0.5} \right] \right\}^2 \quad (\text{B.3})$$

and

$$X = \frac{(T - T_b)^2}{(T - T_b)^2 + (1.25T_b - T)^2} \quad (\text{B.4})$$

where a_0 is the value of $a(T)$ estimated at the normal boiling temperature T_b , while parameters a_c , b , and m_0 are, in turn, obtained from the critical properties and the normal boiling temperature of pure components, i.e.,

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (\text{B.5})$$

$$m_0 = \frac{(a_0/a_c)^{0.5} - 1}{1 - (T_b/T_c)^{0.5}} \quad (\text{B.6})$$

$$b = 0.045572 \frac{RT_c}{P_c} \quad (\text{B.7})$$

Relevant pure-component properties are given in Table 6.

References

- [1] A.Z. Panagiotopoulos, R.C. Reid, *Am. Chem. Soc.* 300 (1986) 571.
- [2] Y. Adachi, A. Sugie, *Fluid Phase Equil.* 28 (1986) 103.
- [3] R. Stryjek, J.H. Vera, *Fluid Phase Equil.* 25 (1986) 279.
- [4] J. Schwartztruber, H. Renon, *Ind. Eng. Chem. Res.* 28 (1989) 1049.
- [5] M.L. Michelsen, H. Kistenmacher, *Fluid Phase Equil.* 58 (1990) 229.
- [6] P.M. Mathias, H.C. Klotz, J.M. Prausnitz, *Fluid Phase Equil.* 67 (1991) 31.
- [7] J. Schwartztruber, H. Renon, *Fluid Phase Equil.* 67 (1991) 99.
- [8] D.Y. Peng, D.B. Robinson, *Ind. Eng. Chem. Fund.* 15 (1976) 59.
- [9] A. Pénéoux, W. Abdoul, E. Rauzy, *Fluid Phase Equil.* 47 (1989) 115.
- [10] O. Redlich, J.N.S. Kwong, *Chem. Rev.* 44 (1949) 233.
- [11] E. Rauzy, *Doctoral Dissertation*, Université d'Aix-Marseille II, Marseille, 1982.
- [12] R. Stryjek, J.H. Vera, *Can. J. Chem. Eng.* 64 (1986) 323.
- [13] B. Carrier, M. Rogalski, A. Pénéoux, *Ind. Eng. Chem. Res.* 27 (1988) 1714.
- [14] R. Sandoval, G. Wilczek-Vera, J.H. Vera, *Fluid Phase Equil.* 52 (1989) 119.
- [15] M.S. Zabaloy, J.H. Vera, *Fluid Phase Equil.* 119 (1996) 27.
- [16] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York, 1987.
- [17] J. Gmehling, U. Onken, *Vapor-liquid Equilibrium Data Collection: Binary Systems*, Chemistry Data Series, Vol. I, Dechema Publishers, Frankfurt, Germany, 1977.
- [18] A. Maczynski, A. Bilinski, P. Oracz, T. Treszczanowicz, *Verified Vapor-Liquid Equilibrium Data: Binary Systems of C₄₊ Hydrocarbons and Alcohols*, Thermodynamic Data for Technology Series A, Vol. 6, PWN-Polish Scientific Publishers, Warsaw, 1982.
- [19] J.M. Sørensen, W. Artl, *Liquid-Liquid Equilibrium Data Collection: Ternary Systems*, Chemistry Data Series, Vol. V, Part 2, Dechema Publishers, Frankfurt, Germany, 1979.
- [20] J. Griswold, S.Y. Wong, *Chem. Eng. Symp. Ser.* 48 (1952) 18.
- [21] G.H. Messerly, R.H. Kennedy, *J. Am. Chem. Soc.* 62 (1940) 2988.

- [22] C.J. Willingham, W.J. Taylor, J.M. Pignocco, F.D. Rossini, *J. Res. Natl. Bur. Stand.* 35 (1945) 219.
- [23] T.M. Letcher, F.J. Marsicano, *J. Chem. Thermodyn.* 6 (1974) 509.
- [24] D. Ambrose, *J. Chem. Thermodyn.* 13 (1981) 1161.
- [25] I. Brown, F. Smith, *Aust. J. Chem.* 10 (1957) 423.
- [26] T. Boublik, K. Aim, V. Fried, E. Hala, *The Vapor Pressures of Pure Substances*, Elsevier, Amsterdam, 1975.
- [27] D. Ambrose, C.H.S. Sprake, *J. Chem. Thermodyn.* 2 (1970) 631.
- [28] T. Boublik, K. Aim, *Coll. Czech. Chem. Commun.* 37 (1972) 3513.
- [29] H.F. Gibbard, J.L. Creek, *J. Chem. Eng. Data* 19 (1974) 308.
- [30] Thermodynamic Research Center, *Thermodynamic Tables. Vapor Pressure*, The Texas A&M University System, College Station, TX, 1988.
- [31] C.B. Kretschmer, R.J. Wiebe, *J. Am. Chem. Soc.* 71 (1949) 1793.
- [32] J. Singh, G.C. Benson, *Can. J. Chem.* 46 (1968) 1249.
- [33] I. Brown, F. Smith, *Aust. J. Chem.* 12 (1959) 407.
- [34] N.B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd Edition, Wiley, New York, 1975.