Comparative study of mixing rules for cubic equations of state in the prediction of multicomponent vapor–liquid equilibria

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Abstract

Some common volume-independent mixing rules and the problems associated with them are reviewed. Reported experimental data of a highly non-ideal quaternary mixture and all its constituent binaries and ternaries are used for adjusting binary interaction parameters and comparing the performance of each mixing rule in predicting vapor–liquid equilibria (VLE). The parameters in each mixing rule were obtained fitting experimental binary data only. The ternary and quaternary VLE calculations were then used to test the capability of the mixing rules to predict multicomponent VLE. It is shown that the VLE of those systems can be adequately reproduced with a cubic equation of state using Wong and Sandler's mixing rule with Wilson's excess Gibbs energy function thanks to its simultaneous correction of several inconveniences. It is also shown that mixing rules should be tested with multicomponent mixtures.

Keywords: Theory; Equation of state; Cubic; Mixing rules; Vapor–liquid equilibria; Mixtures; Polar

1. Introduction

Cubic equations of state are a convenient form of calculating vapor-liquid equilibria, VLE, and may be used for pure substances and mixtures. With a small number of parameters they may be used to obtain information that depends on the state of a fluid in a wide variety of circumstances.

This representation, though, is not perfect, since it shows differences with respect to experimental information. That is why efforts have been made to improve the equations, trying to obtain the least possible error.

For pure substances, a powerful one is the Peng–Robinson–Stryjek–Vera equation, or PRSV (Stryjek and Vera, 1986a). In this work we studied this equation as representative of cubic equations

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of state. In particular, we are interested in testing how well it predicts vapor-liquid equilibria (VLE). For pure substances, it gives acceptable results for practical purposes, and for mixtures the results are strongly dependent on the mixing rule that is adopted. Different expressions for the mixing rules have been proposed, and binary parameters have been added. Each of these mixing rules has its virtues and its defects. The main purpose of this work is to compare the performance of some of the mixing rules that have been proposed in the last few years.

Much of the work that has been previously done in this direction was limited to binary mixtures, but quite often accurate results for multicomponent mixtures are needed. It is desirable to be able to predict the behavior of these mixtures with pure component parameters and, at most, binary parameters. The idea is to be reasonably confident of obtaining acceptable results for mixtures with any number of components using information derived exclusively from pure substance and binary mixture experiments.

Another desirable characteristic in an equation of state is generality, i.e., that it can be applied in as many cases as possible. It has been observed that the largest errors in non-electrolyte systems usually occur in mixtures that have polar compounds, compounds that form hydrogen bonds, or substances with very different physical or chemical properties. In consequence, a mixing rule will be better if it enables the equation of state to predict well VLE in such a mixture.

It is difficult to evaluate precisely and systematically the relative merits of different mixing rules from existing papers, since there is no widely used basis of comparison. Another aim of this work is to present many of the most simple and popular mixing rules on a common denominator for making as fair an evaluation as possible. For achieving this, we used the same compounds and pure compound parameters for all mixing rules; binary parameters were calculated with the same experimental data, optimization algorithm, and objective function; the same algorithm is employed for VLE calculations; and the results are compared using the same multicomponent experiments. The parameters in each mixing rule were obtained fitting experimental binary data only. The ternary and quaternary VLE calculations were then used to test the capability of the mixing rules to predict multicomponent VLE.

2. Mixing rules

The PRSV equation of state is given by:

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2}$$

where P is the system's pressure, R the gas constant, T the temperature, v the molar volume, and a and b the characteristic parameters of the equation of state. Parameters a and b are calculated for pure substances as shown by the following equations:

$$a = 0.45723553 \frac{R^2 Tc^2}{Pc} \alpha$$

$$b = 0.077796074 \frac{RTc}{Pc}$$

$$\sqrt{\alpha} = 1 + \left[\kappa_0 + \kappa_1 \left(1 + \sqrt{\frac{T}{Tc}} \right) \left(0.7 - \frac{T}{Tc} \right) \right] \left(1 - \sqrt{\frac{T}{Tc}} \right)$$

$$\kappa_0 = 0.378893 + 1.4897153\,\omega - 0.17131848\,\omega^2 + 0.0196554\,\omega^3$$

where Tc is the critical temperature, Pc is the critical pressure, ω is Pitzer's acentric factor, and κ is an adjustable parameter characteristic of each pure component.

The mixing rules proposed for the first cubic equation of state, Van der Waals's equation, are

$$b = \sum_i x_i b_i \tag{1}$$

and

$$a = \left(\sum_i x_i \sqrt{a_i} \right)^2 \tag{2}$$

These equations may be used for systems of similar hydrocarbons, but for others the errors are too large. New parameters must be added that are not dependent on pure compounds alone, but on pairs of compounds, so that interactions between different substances in the mixture may be considered. The parameters are empirical, and are obtained by regression from experimental VLE data of each pair of components that constitute the system. The introduction of binary parameters in the mixing rule for a gives

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left(1 - k_{ij} \right) \tag{3}$$

where k_{ij} is the binary parameter of the components i and j that satisfies these relations:

$$k_{ij} = k_{ji}$$

and

$$k_{ii} = k_{jj} = 0$$

If all the binary parameters are set to zero, we return to Eq. (2). Eq. (3) is sometimes known as the classical mixing rule. For a mixture with n components, $n(n-1)/2$ binary parameters are needed. As a rule, good results are obtained in systems with non-polar compounds. Some commercial process simulators use Eqs. (1) and (3) for cubic equations of state. It seems that the energy parameter (i.e., a) is the more important in obtaining good agreement with VLE experimental data, so more effort has been made to propose a better mixing rule for a than for b.

It is desirable to extend the applicability of cubic equations of state to any type of mixture by varying the way a is computed and introducing different binary interaction parameters. Once these parameters are obtained, no additional information will be necessary for calculating equilibria in complex mixtures.

2.1. Problems associated with mixing rules

Mixing rules attempt to extend the predictive power of equations of state to the most diverse group of mixtures. A valid way of comparing the relative merits of different rules is to see how well each attacks highly non-ideal mixtures, as those formed by compounds with great differences in properties

(like boiling point, size, polarity, hydrogen bonds formation, etc.). Not one has been found yet that satisfactorily solves all the problems posed by these "difficult" mixtures. Many have been proposed, but most of them have more or less serious problems or limitations.

There is a number of mixing rules that involve not only the mentioned elements (composition, binary parameters, and pure compound parameters), but also volume. This has the inconvenience of destroying the cubic nature of the equation of state without introducing significant improvements that justify the change. For this reason they are not included in this study.

A common shortcoming is the "Michelsen–Kistenmacher syndrome" (Michelsen and Kistenmacher, 1990). If an equimolar mixture of A and B is formed, with the pure component parameters and the corresponding binary parameters we can calculate a. The same mixture can be formed in the following way: 50% of A, 25% of B and 25% of B. We have divided component B in two equal parts, which is to say that we have not done anything to the original mixture, so its properties should be the same. If the mixing rule is not invariant to this division (i.e., the rule has the above mentioned syndrome) for the second case we obtain a different a. This may be a serious problem. For example, it has been noted that wrong results may be obtained in the solubility of water in benzene–cyclohexane mixtures as a consequence of this lack of invariance (Mathias et al., 1991).

A simple way of finding out if a mixing rule is invariant consists in algebraically expanding the summation that calculates a for a binary mixture of A and B. Then repeat the procedure for a ternary mixture of A, B, and C. For this last expression, change all Cs for Bs and simplify, eliminating interaction parameters of B with B. If it is not possible to arrive at an expression identical to that of the binary mixture, the mixing rule has the Michelsen–Kistenmacher syndrome.

In the virial equation of state, the second virial coefficient of a gaseous mixture is computed according to

$$B = \sum_i \sum_j x_i x_j B_{ij} \tag{4}$$

where B is the second virial coefficient. We can see that it depends quadratically on composition. If we arrange a cubic equation of state and expand it into a power series in density, we can arrive to an expression that is approximately equivalent to the second virial coefficient:

$$B = b - \frac{a}{RT}$$

Because Eq. (4) is a result of statistical mechanics, some authors consider it desirable that the equivalent of the second virial coefficient in an equation of state be also quadratic in composition, which means that

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \tag{5}$$

Having a quadratic second virial coefficient (QSVC) would make the equation of state theoretically correct in this respect. The legitimacy of imposing such a restriction is arguable. The equations we are discussing apply for both the liquid and vapor phases, while the virial equation can only be used for the gaseous state. Besides, it is not clear how this matter affects results.

To know if a mixing rule produces a QSVC take the expression for b and subtract from it the expression of a divided by RT. If it is not possible to arrive at Eq. (5) this way, the mixing rule does not produce a QSVC.

One aspect about binary interaction parameters that is often mentioned is their dependency on temperature. It has been noted that adjusting them at different temperatures for the same binary produces different values. For some mixtures this variation is small; for others it is somewhat greater and approximately linear (Chang et al., 1983). Polynomials have been proposed to model this variation, but their use is not generalized, since it implies an increased number of parameters. In this work, the temperature dependence of the parameters in the mixing rules, is not studied.

A convenient mixing rule may be characterized by
- being simple,
- having few parameters,
- being invariant to the division of a component into identical subcomponents (not having the Michelsen-Kistenmacher syndrome),
- predicting equally well VLE of binary and multicomponent mixtures,
- predicting equally well VLE of non-polar mixtures and highly non-ideal mixtures,
- predicting well other properties, such as entropy, enthalpy, etc,
- predicting well liquid–liquid and liquid–liquid–vapor equilibria, and
- being able to use the values of the parameters previously determined with a "gamma–phi" model.

It may not be possible to achieve all these requisites, but having these ideas in mind has helped to dramatically expand the applicability of cubic equations of state. In this work we study mixing rules considering their performance in predicting VLE, an area of great interest.

2.2. Some important mixing rules

We will mention some important mixing rules without being exhaustive. For making their study easier, we can classify them into several groups, depending on the characteristic we are most interested in. One classification divides them according to the number of binary parameters they possess; another one, according to their being or not invariant. They may also be divided in rules that produce a QSVC and rules that do not. Finally, they may be divided depending on the characteristic of explicitly involving or not an energy function model (Gibbs or Helmholtz; this point will be explained later on). We will call those rules that do not use such a model "simple".

Unless otherwise stated, the mixing rule for b given by Eq. (1) will be used. It must also be noted that although the letter k is used to refer to binary interaction parameters in general, it stands for a different parameter and may have a completely different value in each mixing rule.

The binary parameters have two subindices. Mixing rules in which $k_{ij} = k_{ji}$ are described as having symmetric binary parameters. If $k_{ij} \neq k_{ji}$, the mixing rule is described as not having symmetric parameters.

The mixing rules included in this work are the following.

2.3. Van der Waals or classical

This rule is probably the most widely used, despite being generally limited to non-polar and slightly polar mixtures. It is simple, invariant, produces a QSVC, and its parameter is symmetric.

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left(1 - k_{ij}\right)$$

2.4. Two parameter classical

A binary parameter for b is added to the classical rule (Shibata and Sandler, 1989). This rule is also simple, invariant, produces a QSVC, and both of its parameters are symmetric.

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left(1 - k_{ij}\right)$$

$$b = \sum_i \sum_j x_i x_j \frac{1}{2} \left(b_i + b_j\right) \left(1 - d_{ij}\right)$$

2.5. Panagiotopoulos–Reid

This rule (Panagiotopoulos and Reid, 1986) is simple, not invariant, does not produce a QSVC, and has two parameters, since k is not symmetric. It is entirely equivalent to those by Adachi and Sugie (1986), Melhem et al. (1989), and Schwartzentruber and Renon (1991), and to the GMR2 (Sandoval et al., 1989).

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left[1 - k_{ij} + x_i \left(k_{ij} - k_{ji}\right)\right]$$

2.6. Margules type Stryjek–Vera

This rule is simple, not invariant, does not produce a QSVC, and its parameter is not symmetric (Stryjek and Vera, 1986b).

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left(1 - x_i k_{ij} - x_j k_{ji}\right)$$

2.7. Van Laar type Stryjek–Vera

This rule is simple, not invariant, does not produce a QSVC, and its parameter is not symmetric (Stryjek and Vera, 1986b).

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left(1 - \frac{k_{ij} k_{ji}}{x_i k_{ij} + x_j k_{ji}}\right)$$

2.8. Sandoval–Wilczek–Vera–Vera (GMR3)

This rule (Sandoval et al., 1989) is simple, not invariant, does not produce a QSVC, its parameter k is not symmetric, and its parameter l is symmetric (it needs three constants per binary).

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left[1 - \overline{k_{ij}} - x_i \Delta k_{ij} - x_j \Delta k_{ji} - l_{ij} \left(x_i - x_i^2 + x_j - x_j^2\right)\right]$$

$$\overline{k_{ij}} = \frac{k_{ij} + k_{ji}}{2}$$

$$\Delta k_{ij} = k_{ij} - \overline{k_{ij}}$$

$$\Delta k_{ji} = k_{ji} - \overline{k_{ij}}$$

2.9. Mathias–Klotz–Prausnitz

This rule is simple, invariant, does not produce a QSVC and its parameter is not symmetric (Mathias et al., 1991)

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \left(1 - k_{ij}\right) + \sum_i x_i \left[\sum_j x_j \left(a_i a_j\right)^{\frac{1}{6}} \left(k_{ij} - k_{ji}\right)^{\frac{1}{3}} \right]^3$$

2.10. Huron–Vidal

In this rule (Huron and Vidal, 1979), the authors consider that the true parameters of the cubic equation of state are a/b (energy) and b (covolume), instead of a and b. They show that there is a relationship between the infinite pressure limit of the excess Gibbs energy and the mixing rules, and derive an expression for the mixing rule for a/b from this relationship. The parameter b is calculated as in Eq. (1), and the energy parameter is calculated as follows:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g_\infty^E}{L}$$

Any excess Gibbs energy model may be used in place of g_∞^E. The constant L depends on the equation of state used. For the PRSV equation of state its value is given by

$$L = \frac{1}{2\sqrt{2}} \ln\left(\frac{2 + \sqrt{2}}{2 - \sqrt{2}} \right)$$

The rule does not produce a QSVC. The excess Gibbs energy model used will determine the number of parameters and if the equation is invariant or not.

2.11. Kurihara–Tochigi–Kojima

This rule (Kurihara et al., 1987) uses an excess Gibbs energy model, which will determine the number of parameters and if it is invariant or not. It does not produce a QSVC.

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} - \frac{b}{L} g_\infty^E$$

2.12. Wong–Sandler

This rule (Wong and Sandler, 1992) was derived considering the excess Helmholtz energy at infinite pressure, but equations used for the excess Gibbs energy at low pressure may be used in place

Table 1
Mixing rules tested

No.	Mixing rule	g^E model	parameters	QSVC	Invariant
1	classical	no	1	yes	yes
2	two parameter classical	no	2	yes	yes
3	Panagiotopoulos–Reid	no	2	no	no
4	Stryjek–Vera (Margules)	no	2	no	no
5	Stryjek–Vera (Van Laar)	no	2	no	no
6	Sandoval–Wilczek–Vera–Vera	no	3	no	no
7	Mathias–Klotz–Prausnitz	no	2	no	yes
8	Huron–Vidal	Redlich–Kister	2	no	no
9	Huron–Vidal	Redlich–Kister	3	no	no
10	Huron–Vidal	Van Laar	2	no	yes
11	Huron–Vidal	Wilson	2	no	yes
12	Huron–Vidal	NRTL	3	no	yes
13	Kurihara–Tochigi–Kojima	Redlich–Kister	2	no	no
14	Kurihara–Tochigi–Kojima	Redlich–Kister	3	no	no
15	Kurihara–Tochigi–Kojima	Van Laar	2	no	yes
16	Kurihara–Tochigi–Kojima	Wilson	2	no	yes
17	Kurihara–Tochigi–Kojima	NRTL	3	no	yes
18	Wong–Sandler	Redlich–Kister	3	yes	no
19	Wong–Sandler	Redlich–Kister	4	yes	no
20	Wong–Sandler	Van Laar	3	yes	yes
21	Wong–Sandler	Wilson	3	yes	yes
22	Wong–Sandler	NRTL	4	yes	yes

of A_∞^E, since A^E is both, almost independent of pressure and almost equal to G^E at low pressure. One important advantage of this mixing rule is that the parameters determined with a "gamma–phi" model can be used, for example, the one reported in Gmehling and Onken (1977). The excess energy model will determine if the rule is invariant or not, and the number of parameters will be that of the chosen model plus one. The rule does produce a QSVC.

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{A_\infty^E}{L}$$

$$b = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \frac{1}{RT}\sum_i x_i \frac{a_i}{b_j} + \frac{A_\infty^E}{LRT}}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij})$$

Table 1 summarizes the classification. Five different models for the excess Gibbs energy were chosen.

2.13. Redlich–Kister expansion

$$g^E = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots \right]$$

where A, B, C, etc., are the temperature-dependent binary parameters (Smith and Van Ness, 1987). One may use as many as needed. We test this model with two and three parameters.

2.14. Van Laar's model

$$g^E = \frac{ABx_1 x_2}{Ax_1 + Bx_2}$$

where A and B are the temperature-dependent binary parameters (Smith and Van Ness, 1987). Both models were originally proposed for binary mixtures. A simple way of extending them to multicomponent systems that does not involve extra parameters (Reid et al., 1987) is used here

$$g^E = \sum_{all\,pairs} g_{ij}^E$$

2.15. Wilson's model

$$\frac{g^E}{RT} = -\sum_i x_i \ln\left(\sum_j x_j \Lambda_{ij} \right)$$

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\frac{-a_{ij}}{RT} \quad for\ i \neq j$$

$$\Lambda_{ij} = 1 \quad for\ i = j$$

where a_{ij} is the binary parameter, and is not symmetric (Smith and Van Ness, 1987). The molar volumes may be substituted for the corresponding b parameter of the components (Bazúa, 1978).

2.16. Non random two liquids (NRTL) model

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j x_j \frac{\Delta g_{ji}}{RT} \exp\frac{-\alpha_{ij}\Delta g_{ji}}{RT}}{\sum_k x_k \exp\frac{-\alpha_{ki}\Delta g_{ki}}{RT}}$$

Table 2
Activity coefficients at infinite dilution (Gmehling and Onken, 1977)

Binary mixture (1-2):	γ_1^∞:	γ_2^∞:
ethanol-chloroform	4.37	1.75
ethanol-hexane	81.28	9.52
ethanol-acetone	1.79	2.01
chloroform-hexane	1.34	2.34
chloroform-acetone	0.42	0.29
hexane-acetone	5.20	4.24

where Δg_{ij} is a non-symmetric binary parameter and α_{ij} is a symmetric binary parameter (Smith and Van Ness, 1987).

3. Criteria for comparing the mixing rules

For practical purposes, the fundamental comparison criterion is that the predictions of the equation of state resemble as closely as possible experimental results. Since we look for generality too, we tested the different mixing rules with a highly non-ideal mixture. We selected the system ethanol–chloroform–hexane–acetone and all its subsets of binary and ternary systems.

The selection of the system was based on the heterogeneity of its components. Each one may be considered as representative of a family of chemical compounds, and their interactions are considered among the most difficult that do not produce splitting in the liquid phase. Ethanol is representative of substances that form hydrogen bonds and is also a polar compound (1.7 Debyes). Chloroform is a moderately polar compound (1.1 Debyes); hexane represents non-polar compounds, and acetone

Table 3
Temperature, number of experimental points, part, and pages in volume I of the Vapor–Liquid Equilibrium Data Collection, (Gmehling and Onken, 1977), for all the systems studied in this work

System	Temperature (K)	No. of points	Part	Pages
ethanol–chloroform	328.15	23	2a	292
ethanol–acetone	321.15	14	2a	325
ethanol–hexane	308.15	9	2a	450
chloroform–acetone	323.15	31	3 + 4	104–105
chloroform–hexane	317.15	9	6a	424
acetone–hexane	328.15	9	3 + 4	224
ethanol–chloroform–acetone	328.15	36	2c	626–627
ethanol–chloroform–hexane	328.15	36	2a	651–652
ethanol–acetone–hexane	328.15	21	2a	663
chloroform–acetone–hexane	328.15	37	3 + 4	376–377
ethanol–chloroform–acetone–hexane	328.15	84	2a	700–701

Table 4
Critical temperature, critical pressure, acentric factor and the adjustable parameter of the PRSV equation of state (Stryjek and Vera, 1986a; Proust and Vera, 1989)

Substance	Tc (K)	Pc (MPa)	ω	$\kappa 1$
ethanol	513.92	6.148	0.64439	− 0.03374
chloroform	536.55	5.472	0.21754	+ 0.02899
hexane	507.3	3.01236	0.30075	+ 0.05104
acetone	508.1	4.696	0.30667	− 0.00888

highly polar compounds (2.9 Debyes) (Reid et al., 1987). Besides, there is the interaction of acetone, a Lewis base, with the acidic proton of the chloroform.

A measure of the non-ideality of the binary system is the activity coefficient at infinite dilution. The farther away from unity, the more non-ideal the system is. The activity coefficients at infinite dilution for all pairs are given in Table 2.

The VLE experimental data were taken from the first volume of the Vapor–Liquid Equilibrium Data Collection, (Gmehling and Onken, 1977). For the same system there are usually several sets of data reported by different authors, or by the same ones but at different pressures or temperatures. In order to select a set of data for fitting the binary parameters, we chose the ones that had the following characteristics (in order of importance):

• isothermal data positive consistency tests made by the compilers on binary systems
• temperature as close as possible to 328.15 K
• the largest number of experimental data.

All the selected systems were isothermal, and all the binaries had a positive consistency test. Information about the last two criteria and the exact location of the data used (pages in volume one of Gmehling and Onken, 1977) are summarized in Table 3.

The pure component parameters used in the PRSV equation of state are summarized in Table 4 (Stryjek and Vera, 1986a; Proust and Vera, 1989).

All the binary interaction parameters were calculated using the chosen binary experimental data sets with a non-linear least squares optimization algorithm. The objective function involved the error in bubble pressure for every point, since the bubble pressure is very sensitive to variations of the binary parameters and its measurement is usually more precise and exact than that of vapor composition.

Table 5 contains the adjusted binary interaction parameters for all the binary systems studied in this work. For the mixing rules 12 and 22 (Huron–Vidal and Wong–Sandler with NRTL model), two sets of parameters are presented. The first set, referred as 12a and 22a, corresponds to the selection of α_{12} parameter equal to 0.3, for all binary systems, and the corresponding optimization of the rest of the parameters. In the second set, referred as 12b and 22b, the α_{12} was chosen to improve the representation of the binary data. For the mixing rule 17 (Kurihara–Tochigi–Kojima with NRTL model), α_{12} was preset to 0.3 for all binary systems.

It has been mentioned that an advantage of using explicit excess energy function models is that the parameters previously obtained for these models may be used in the context of the equation of state. This is true for the Wong-Sandler mixing rule tested in this work. Nevertheless, to make a fair

Table 5
Adjusted binary interaction parameters for all the binary systems studied in this work

Binary rule	C-E:	A-E:	H-E:	A-C:	C-H:	A-H:
1: $k_{12} =$	0.055948	0.022162	0.046736	−0.059312	0.001263	0.101823
2: $k_{12} =$	0.436739	0.080193	0.449970	0.115763	−0.193156	−0.020266
$d_{12} =$	0.442700	0.066080	0.444841	0.197188	−0.224350	−0.151848
3: $k_{12} =$	0.023284	0.017088	−0.000533	−0.064625	−0.001298	0.125298
$k_{21} =$	0.096713	0.030027	0.131068	−0.053857	0.003305	0.081934
4: $k_{12} =$	0.096713	0.030027	0.131068	−0.053857	0.003305	0.081934
$k_{21} =$	0.023284	0.017088	−0.000533	−0.064625	−0.001298	0.125298
5: $k_{12} =$	0.038087	0.018116	0.029885	−0.064795	0.000580	0.129525
$k_{21} =$	0.126223	0.032908	1.558887	−0.054459	1946.092	0.085747
6: $k_{12} =$	0.097796	0.031086	0.168299	−0.049537	0.011433	0.082368
$k_{21} =$	0.023959	0.017611	0.018412	−0.060875	0.009747	0.125714
$l_{12} =$	−0.001857	−0.001702	−0.057780	−0.009449	−0.021694	−0.000944
7: $k_{12} =$	0.096713	0.030027	0.131068	−0.053857	0.003305	0.081934
$k_{21} =$	0.023284	0.017088	−0.000533	−0.064625	−0.001298	0.125298
8: $A =$	1.186041	0.799618	2.856351	−0.907957	0.694837	1.916849
$B =$	0.534765	0.008833	0.247259	0.131652	0.215245	0.092481
9: $A =$	1.201954	0.793417	2.686829	−0.958722	0.458100	1.914228
$B =$	0.538260	0.008093	0.218140	0.129552	0.148562	0.091846
$C =$	−0.041375	0.015017	0.483482	0.083004	0.448660	0.006239
10: $A =$	0.827495	0.790766	2.605483	−1.049608	0.514831	1.827449
$B =$	1.9967182	0.808685	3.159043	−0.796135	1.020841	2.014510
11: $\Lambda_{12} =$	1.033226	0.660495	0.0	1.151766	1.217027	0.298073
$\Lambda_{21} =$	0.101125	0.615915	0.0	1.920717	0.281936	0.196674
12a: $\Delta g_{12} =$	6.442710	1.253589	6.515528	−2.331118	3.941753	3.688518
$\Delta g_{21} =$	−0.999822	1.028282	4.103136	0.202086	−1.180357	2.644668
$\alpha_{12} =$	0.3	0.3	0.3	0.3	0.3	0.3
12b: $\Delta g_{12} =$	7.980523	1.261908	7.350555	−3.429350	3.610141	4.152376
$\Delta g_{21} =$	−2.31263	1.077558	4.816512	1.416934	−0.895928	1.428069
$\alpha_{12} =$	0.2	0.4	0.35	0.165	0.35	0.1
13: $A =$	1.011725	0.402061	1.128815	−0.945525	0.017590	1.543686
$B =$	0.548859	0.061722	0.877308	0.133504	0.032688	0.012499
14: $A =$	1.028152	0.399040	1.050139	−0.996219	−0.169727	1.549920
$B =$	0.552468	0.061362	0.863908	0.131407	−0.020585	0.014015
$C =$	−0.042706	0.007312	0.220360	0.082888	0.355690	−0.014833
15: $A =$	0.672392	0.346032	0.610399	−1.089020	0.009987	1.531253
$B =$	1.898155	0.477095	3.998565	−0.831592	3579.337	1.556303
16: $\Lambda_{12} =$	1.231206	1.093996	1.335926	1.179570	2.009365	0.379291
$\Lambda_{21} =$	0.094888	0.563242	0.0	1.937814	0.321510	0.347554
17: $\Delta g_{12} =$	6.735455	1.982798	9.595510	−2.34208	2.998466	2.521985
$\Delta g_{21} =$	−1.507470	−0.666182	−1.765344	0.114938	−2.182317	2.325827
$\alpha_{12} =$	0.3	0.3	0.3	0.3	0.3	0.3
18: $A =$	1.030609	0.939914	3.014254	−1.160707	0.486393	2.109329
$B =$	0.640934	0.027304	0.419111	0.152722	0.169369	0.066285
$k_{12} =$	0.119353	−0.025536	0.045727	0.029870	0.107619	0.071504
19: $A =$	1.916663	1.896595	2.854765	−1.276314	0.301704	2.214972
$B =$	0.657014	−0.004101	0.383225	0.151580	0.114093	0.089372

Table 5 (continued)

Binary rule	C-E:	A-E:	H-E:	A-C:	C-H:	A-H:
$C =$	−0.026132	0.118593	0.530709	0.092671	0.507101	−0.032080
$k_{12} =$	−0.206890	−0.433751	0.035787	0.051196	0.078731	0.040211
20: $A =$	2.400685	0.906035	0.539089	−1.386848	0.575933	2.029737
$B =$	3.815334	0.961765	7.546194	−1.088621	1.144636	2.154514
$k_{12} =$	−0.662625	−0.022986	0.640863	0.052177	0.004295	0.077869
21: $\Lambda_{12} =$	1.140652	0.657211	0.354426	1.157768	0.530047	0.346755
$\Lambda_{21} =$	0.062076	0.553251	0.0	1.988746	0.069343	0.540408
$k_{12} =$	0.072933	−0.004420	0.313571	−0.044079	−0.407625	0.323170
22a $\Delta g_{12} =$	7.649960	1.909516	8.747919	6.641377	4.329942	2.415394
$\Delta g_{21} =$	1.561030	1.444729	5.184522	−4.214071	−0.854111	2.828915
$\alpha_{12} =$	0.3	0.3	0.3	0.3	0.3	0.3
$k_{12} =$	−0.342874	−0.1004	−0.049578	−0.295106	−0.045985	0.221868
22b $\Delta g_{12} =$	9.773597	1.909516	11.687510	−4.885692	8.008030	3.628222
$\Delta g_{21} =$	3.530380	1.444729	10.744970	2.182953	3.310367	2.246872
$\alpha_{12} =$	0.2	0.3	0.2	0.1	0.4	0.1
$k_{12} =$	−0.931873	−0.1004	−0.9137922	0.046271	−0.660050	0.097518

The letters refer to the binary mixtures with C = chloroform, E = ethanol, A = acetone, H = hexane. NRTL parameters are in kJ mol^{-1}. Mixing rule numbers refer to Table 1.

comparison, the parameters for this mixing rule were obtained following the procedure described above.

4. Results and conclusions

One way to discriminate the mixing rules is to examine their worst performance. The rules whose largest errors are consistently lower than those of other mixing rules will be preferred, since their predictions will be more reliable in a wider variety of systems. In this work we use mainly this criterion for selecting the best mixing rules. Table 6 contains the greatest errors in binary systems (it includes the errors in the hexane–ethanol mixture, the most difficult one) and Table 7 contains the largest errors in the quaternary system and the worst predictions in the ternary systems. Since the objective function involved the bubble pressure, our evaluation relies heavily on these results, but without completely neglecting the errors in composition.

A look at the results reveals a fact not sufficiently stressed: mixing rules that make good predictions of VLE in a binary system may give unacceptable results for multicomponent mixtures. From this it is clear that an evaluation must consider the ability to correctly predict the VLE of a mixture of at least three components.

Looking at Tables 6 and 7, we conclude that mixing rules 3, 6, and 7 (refer to Table 1 for the rules' names) are clearly the best simple mixing rules. Their predictions for the quaternary system are better than for the worst ternary. Rules 3 and 7 are equivalent for binary systems, but mixing rule number 7 is invariant. Although, this fact does not seem to have a significant impact on the results. A closer look at the complete results reveals that mixing rule number 6 (Sandoval–Wilczek–Vera–Vera) is the best simple rule.

Table 6

Standard and greatest errors for the ethanol-hexane system, and maximum standard and greatest errors for all other binary systems [a]

No.	Hexane-ethanol				Rest of binary systems			
---	Greatest error		Standard error		Greatest error		Standard error	
	$P\%$	y	$P\%$	y	$P\%$	y	$P\%$	y
1	20.44	0.1210	13.86	0.0862	9.17ce	0.0543ce	5.70ce	0.0379ce
2	12.83	0.0890	6.93	0.0532	4.09ah	0.0369ah	2.66ah	0.0242ah
3	6.10	0.0531	3.22	0.0291	1.09ch	0.0220ac	0.54ch	0.0137ac
4	6.10	0.0531	3.22	0.0291	1.09ch	0.0220ac	0.54ch	0.0137ac
5	8.68	0.1191	3.97	0.0559	3.45ce	0.0223ac	1.77ce	0.0139ac
6	1.35	0.0365	0.86	0.0179	0.99ce	0.0205ac	0.48ce	0.0124ac
7	6.10	0.0531	3.22	0.0291	1.09ch	0.0220ac	0.54ch	0.0137ac
8	4.90	0.0474	2.77	0.0261	1.28ch	0.0218ac	0.70ch	0.0135ac
9	3.35	0.0237	1.53	0.0173	1.02ce	0.0383ch	0.47ce	0.0210ch
10	4.37	0.0446	2.64	0.0249	2.61ce	0.0224ac	1.34ce	0.0140ac
11	6.88	0.0620	4.12	0.0368	3.17ce	0.0229ac	1.70ce	0.0143ac
12a	1.76	0.0315	1.17	0.0166	2.16ce	0.0224ac	1.16ce	0.0140ac
12b	0.58	0.0196	0.30	0.0126	1.98ce	0.0223ac	1.07ce	0.0139ac
13	3.08	0.0409	1.56	0.0207	1.11ce	0.0218ac	0.57ch	0.0135ac
14	2.38	0.0296	1.16	0.0168	1.02ce	0.0331ch	0.47ce	0.0181ch
15	4.97	0.0329	2.29	0.0189	3.08ce	0.0224ac	1.56ce	0.0140ac
16	9.01	0.0385	3.79	0.0276	3.46ce	0.0230ac	1.81ce	0.0144ac
17	2.86	0.0259	1.39	0.0142	2.38ce	0.0224ac	1.27ce	0.0140ac
18	4.68	0.0457	2.63	0.0252	1.23ch	0.0216ac	0.67ch	0.0134ac
19	3.22	0.0231	1.48	0.0170	1.02ce	0.0371ch	0.45ce	0.0203ch
20	2.79	0.0449	1.43	0.0234	1.12ch	0.0221ac	0.50ch	0.0138ac
21	3.32	0.0281	2.11	0.0193	3.56ce	0.0229ac	1.89ce	0.0143ac
22a	0.51	0.0180	0.27	0.0124	2.16ce	0.0218ac	1.18ce	0.0136ac
22b	0.39	0.0176	0.21	0.0140	1.22ce	0.0220ac	0.31ce	0.0137ac

[a] Mixing rule numbers refer to Table 1. The letters after the numbers refer to the binary mixtures with c = chloroform, e = ethanol, a = acetone, h = hexane. The errors are: error $= (\Delta P / P)\%$, error $= \Delta y$, standard error $= \sqrt{(\Sigma \text{error}^2/\text{NP})}$. NP = number of points.

It is evident that the multicomponent version we adopted for the Van Laar and Redlich–Kister models did not work in the Huron–Vidal, Kurihara–Tochigi–Kojima, and Wong–Sandler rules (numbers 8, 9, 10, 13, 14, 15, 18, 19, and 20). In some cases, these mixing rules did very well for binary systems, but their performance for the multicomponent systems gave very high errors that are not acceptable. Therefore, these mixing rules are discarded for future work.

For the mixing rules 12 and 22 (Huron–Vidal and Wong–Sandler with NRTL model), two sets of parameters were used, as referred above. The results for the binary systems show a good improvement when α_{12} was optimized (rules 12b and 22b). This improvement is not sustained in the multicomponent systems, and better results were obtained when α_{12} was set to a unique value for all binaries. Therefore, we recommend to use the NRTL model with a constant value for α_{12} when the model is to be applied to multicomponent mixtures. In the following discussion we adopt only the results for rules 12a and 22a when referring to NRTL model.

Table 7
Maximum standard and greatest errors for the quaternary and the ternary systems [a]

No.	Quaternary system				Ternary systems			
	Greatest error		Standard error		Greatest error		Standard error	
	$P\%$	y	$P\%$	y	$P\%$	y	$P\%$	y
1	71.18	0.3864	17.90	.1571	17.25ech	0.1173ech	10.78ech	0.0637ech
2	13.17	0.0678	6.34	0.0332	12.06ech	0.0708ace	5.81ach	0.0388ech
3	4.13	0.0768	1.88	0.0258	9.86ech	0.061ace	6.56ech	0.0270ech
4	14.32	0.0916	8.57	0.0307	16.05aeh	0.0918ech	10.82aeh	0.0420aeh
5	29.90	0.1227	20.40	0.0587	21.19aeh	0.1372ech	14.34aeh	0.067aeh
6	3.65	0.0739	1.77	0.0253	8.73ech	0.0633ech	6.01ech	0.0265ech
7	5.00	0.0655	2.39	0.0214	8.45ech	0.0611ace	4.67aeh	0.0272aeh
8	18.96	0.0693	13.06	0.0312	19.24aeh	0.0663aeh	12.61aeh	0.0391aeh
9	18.26	0.0689	12.08	0.0319	19.34aeh	0.0636aeh	12.69aeh	0.0385aeh
10	80.76	0.1920	47.30	0.0820	56.36aeh	0.1592aeh	34.50aeh	0.0956aeh
11	7.72	0.0534	3.29	0.0132	5.78ech	0.0646ace	2.24ace	0.0210ech
12a	4.04	0.0362	1.92	0.0121	4.75ace	0.0384ach	2.50ace	0.0179ach
12b	5.70	0.0475	2.97	0.0128	5.42ace	0.0411ach	3.11ace	0.0191ach
13	7.63	0.0723	4.85	0.0228	7.65aeh	0.0569ace	4.46aeh	0.0265aeh
14	7.46	0.0716	4.19	0.0232	7.87aeh	0.579ace	4.51aeh	0.0264aeh
15	24.48	0.1060	17.63	0.0447	16.48aeh	0.0966aeh	12.96aeh	0.0556aeh
16	4.26	0.0686	2.10	0.0149	7.26aeh	0.0619ace	5.12aeh	0.0243ech
17	3.83	0.0351	1.86	0.0153	7.28aeh	0.0450aeh	5.10aeh	0.0214aeh
18	14.97	0.0725	10.11	0.0294	16.51aeh	0.0655aeh	10.69aeh	0.0373aeh
19	20.29	0.0733	14.07	0.0279	20.87aeh	0.0634aeh	14.26aeh	0.0311aeh
20	46.15	0.1392	32.39	0.0564	25.99aeh	0.0986aeh	17.38aeh	0.0588aeh
21	3.69	0.0530	1.18	0.0119	4.89ace	0.0640ace	2.33ace	0.0210ech
22a	4.67	0.0373	2.20	0.0119	5.94ach	0.0775ach	3.49ach	0.0165ach
22b	8.06	0.0459	3.29	0.0208	12.96ech	0.0490aeh	7.26ech	0.0240aeh

[a] Mixing rule numbers refer to Table 1. The letters after the numbers refer to the ternary mixtures with c = chloroform, e = ethanol, a = acetone, h = hexane. The errors are: error = $(\Delta P / P)\%$, error = Δy, standard error = $\sqrt{(\Sigma \text{error}^2 / NP)}$. NP = number of points.

Of all the Huron–Vidal versions, mixing rule number 12 seems to be preferable for multicomponent mixtures. From mixing rules 13 through 17, mixing rule 17 (Kurihara–Tochigi–Kojima with NRTL model) appears to be the most reliable one, and from mixing rules 18 through 22, mixing rule 21 (Wong–Sandler with Wilson's model) is the best.

In the comparison of the three mixing rules based on excess energy models, the following conclusions can be drawn. When the NRTL model is used (rules 12, 17, and 22), the Wong–Sandler rule is much better than the other two for binary systems, but for multicomponent systems, the Huron–Vidal rule is slightly better. When the Wilson's model is used (rules 11, 16, and 21), the Wong–Sandler rule is better in almost all cases. From the results of this study, it seems that the Wong–Sandler mixing rule has an advantage over the Huron–Vidal rule for almost all binary systems, and in some cases, the improvement is quite significant. This advantage is greatly reduced when both rules are applied to multicomponent systems.

The three best simple mixing rules (numbers 3, 6, and 7) are, in general terms, inferior to mixing rule 12, with the noteworthy exception of the quaternary system, where their bubble pressure

predictions are clearly better. Mixing rule 12 calculates better vapor compositions than mixing rule 6 (the best simple one), but its bubble pressure predictions are not always better.

Wilson's model seems to be particularly well suited to work with the different mixing rules, even better than the NRTL model, which is the one that is usually tested. Van Laar's model was altogether unsuccessful, probably due to the extension to multicomponent mixtures. Redlich–Kister's expansions did not work well (except in the Kurihara–Tochigi–Kojima mixing rule, but here they were also superseded by Wilson's model), and from the results, it does not seem that adding more parameters will help. It is clear that mixing rule 21 (Wong–Sandler) is the best one in most cases. In fact, this is the only rule that never gave an error in bubble point pressure greater than 5% for all the 309 experimental points. The results obtained with it for the quaternary system support the opinion that binary interaction parameters are enough for multicomponent VLE calculations, so that ternary or higher order parameters are not necessary. We recommend it as the best mixing rule. If a two parameter mixing rule is needed, probably mixing rule 12 (Huron–Vidal with NRTL model) is the best choice.

Although many sources of difficulties are present in the selected system (multicomponent VLE, hydrogen bonds, polar-nonpolar interactions, etc.), the effect of the invariance of the mixing rules was not clear, and a general conclusion cannot be drawn, because of the nature of the system studied. On the other hand, this work allows us to make a more general conclusion on the overall performance of mixing rules that can be helpful when choosing a particular equation. Many characteristics of a good mixing rule are seen in mixing rule 21 (Wong–Sandler), the best one: it is invariant, it explicitly involves an excess energy function, it uses Wilson's model, and it produces a QSVC. By itself, none of these characteristics ensures the general success of a mixing rule, but a proper combination of properties significantly improves the power of the equation of state.

It must be mentioned that the results obtained in this work, though illustrative, should be regarded with care, since they should be confirmed with tests in a wider variety of conditions and with many more systems.

5. List of symbols

A,B,C constants in the Redlich–Kister expansion
A,B constants in Van Laar's model
a_{ij} binary parameter in Wilson's model
A_∞^E molar excess Helmholtz energy at infinite pressure
a parameter in PRSV equation of state
B second virial coefficient
b parameter in PRSV equation of state
d binary interaction parameter
g^E molar excess Gibbs energy
g_∞^E molar excess Gibbs energy at infinite pressure
k binary interaction parameter
L constant of a cubic equation of state
l binary interaction parameter
P pressure

R	gas constant
T	Temperature
v	molar volume
x	mole fraction

Greek letters

α	function of temperature in the PRSV equation of state
α_{ij}	binary parameter in the NRTL model
γ_i^{∞}	activity coefficient at infinite dilution
Δg_{ij}	binary parameter in the NRTL model
κ_0	function of the acentric factor
κ_1	polar parameter
Λ_{ij}	function in Wilson's model
ω	acentric factor

Subscripts

c	critical property
ij	component index

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