

Cubic Mixing Rules

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The accurate description of thermodynamic properties of asymmetric multicomponent fluid systems of industrial interest, over a wide range of conditions, requires the availability of models that are both consistent and mathematically flexible. Specially suited models are those of the equation-of-state (EOS) type, which are built to represent the properties of liquids, vapors, and supercritical fluids. The composition dependence of EOSs is typically pairwise additive, with binary interaction parameters conventionally fit to match experimental information on binary systems. This is the case for the well-known van der Waals quadratic mixing rules (QMRs), which assume multicomponent system describability from binary parameters. In contrast, cubic mixing rules (CMRs) depend on binary and ternary interaction parameters. Thus, CMRs offer the possibility of increasing the model flexibility, i.e., CMRs are ternionwise additive. This means that, through ternary parameters, CMRs make it possible to influence the model behavior for ternary systems while leaving invariant the description of the corresponding binary subsystems. However, the increased flexibility implies the need for experimental information on ternary systems. This is so, unless we have a method to predict values for ternary parameters from values of binary parameters for the ternary subsystems not having ternary experimental information available, when we want to model the behavior of multicomponent fluids. Mathias, Klotz, and Prausnitz (MKP) [*Fluid Phase Equilib.* **1991**, *67*, 31–44] put forward this problem. In this work, we provide a possible solution, i.e., an equation to predict three index ternary parameters from three index binary parameters within the context of CMRs. Our equation matches the Michelsen–Kistenmacher invariance constraint and, in a way, has the pair-based MKP mixing rule in its genesis. The present approach can be extended also to models that are not of the EOS type.

1. Introduction

Models for thermodynamic properties of multicomponent mixtures should be flexible and consistent, i.e., they should be capable of taking advantage to the greatest extent of available experimental data for binary and higher mixtures, while keeping an acceptable qualitative behavior beyond the window of conditions of the experimental data used to tune the model. Flexibility is a mandatory feature for a thermodynamic model for asymmetric systems, such as the high-pressure fluid systems found in technologies that make use of supercritical fluids.

It is generally accepted that a model for multicomponent mixtures should be able to predict the multicomponent behavior only from binary contributions. This is justified on the need for minimizing the experimental effort. Simple equation-of-state (EOS) models for phase equilibria, such as the Soave–Redlich–Kwong (SRK) EOS,¹ used with conventional quadratic mixing rules (QMRs), decouple the problem of representing the fluid properties into two subproblems. On one hand, pure-compound constants such as the critical pressure, the critical temperature, and the acentric factor set the pure-compound behavior. On the other hand, the values for the binary interaction parameters determine the behavior of binary mixtures. Changes in such values do not affect the pure-compound behavior. Thus, the pure-compound vapor pressure curves remain insensitive to the binary interaction parameters. We run out of degrees of freedom when modeling ternary and higher mixtures with QMRs, i.e., the values for the binary interaction parameters coupled to the values for the pure-compound constants completely set the model behavior for ternary and higher mixtures. Models for multicomponent mixtures should match the assumption of

mixture molar volume invariance (MMVI).^{2,3} Such an assumption is the basis for a number of tests² adopted together with other tests in Professor O’Connell’s project “Standardized Validation of Physical Property Models” (SVPPM).⁴ The goal of the SVPPM project is “to develop standardized tests of problems and data that can be utilized to discriminate strengths, weaknesses and inconsistencies of physical properties models used in chemical process design and simulation”.⁴ According to the MMVI constraint, an N -component mixture where a couple of components i and j become “identical” (through a thought experiment), should have its composition-dependent mixture parameter values equal to those of the corresponding $(N - 1)$ -component mixture where the only component corresponding to the i and j components (of the N -component mixture) has a concentration equal to the sum of concentrations of components i and j . When looking for a flexible mixing rule, i.e., for a flexible multicomponent model, Mathias et al.⁵ considered the possibility of using cubic mixing rules (CMRs), but they decided to discard such a choice because of a then regarded as evident need for ternary parameters that would have to be fit from experimental information on ternary systems. Mathias et al.⁵ finally proposed a flexible pair-based (i.e., based on binary parameters) mixing rule for multicomponent systems. If, in the context of CMRs, we found a way of predicting ternary parameters from binary parameters, we would be able to use the CMRs for multicomponent systems, fitting the ternary parameters for all ternary subsystems with experimental information available and predicting such ternary parameters for all ternary subsystems without experimental information available. The purpose of this work is to define one such prediction strategy and to submit it to a number of reliability tests. When fitting ternary parameters in CMRs, we are able, within the universe of the model, to affect the behavior of the ternary

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system while leaving invariant the description of all corresponding binary subsystems and of the pure compounds. This has clear practical consequences. We wrote all the previous statements having in mind molecular models, i.e., excluding group-contribution models. However, what we present in this work would also be applicable, in a way, to group-contribution models.

2. Mixing Rules

2.1. Quadratic Mixing Rules (QMRs). The well-known van der Waals (vdW) quadratic mixing rule (QMR) written for the energy parameter a of a given equation of state (EOS) is the following,

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ji} \quad (1)$$

where

$$a_{ji} = a_{ji}^0 u_{ji} \quad (2)$$

$$u_{ji} = (1 - k_{ji}) \quad (3)$$

$$a_{ij}^0 = (a_i a_j)^{1/2} \quad (4)$$

where N is the number of components, a_i and x_i are, respectively, the (always positive) cohesive energy parameter for component i and the mole fraction in the system for component i , and k_{ji} is the interaction parameter for the (j,i) binary subsystem. Equation 1, written for a binary mixture, gives a quadratic function of the mole fraction x_1 . Since, by construction, such a function satisfies the pure-compound limits, there is only one degree of freedom left, i.e., the vdW rules provide only one interaction parameter k_{ji} per ji binary, i.e., $k_{ij} = k_{ji}$. Also, $k_{ii} = 0$.

2.2. Mathias–Klotz–Prausnitz (MKP) Mixing Rules. Mathias et al.⁵ proposed a mixing rule (MKP mixing rule) that has two degrees of freedom, i.e., a k_{ij} parameter ($k_{ij} = k_{ji}$, $k_{ii} = 0$) and a l_{ij} parameter ($l_{ji} = -l_{ij}$, $l_{ii} = 0$) per binary, both influencing the mixture energy parameter. The pair-based MKP⁵ mixing rule is the following:

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ji}^0 (1 - k_{ji}) + \sum_{i=1}^N x_i \left(\sum_{j=1}^N x_j (a_{ji}^0)^{1/3} (l_{ji})^{1/3} \right)^3 \quad (5)$$

Notice that eq 5 is built as a QMR plus a correction term. When developing eq 5, Mathias et al.⁵ paid attention to the need for flexibility with respect to composition and to the restriction of invariance^{2,3} for the mixture parameters. Several recent works, e.g., refs 6–12, used eq 5 for modeling asymmetric systems. Equation 5 is consistent and flexible. The assumption of “multicomponent system desirability from binary parameters” constrains eq 5, as is the case for vdW quadratic rules, as well as for more sophisticated mixing rules, such as those that combine an EOS with an excess Gibbs energy model¹³ or the theoretically guided mixing rules of ref 14. Mathias et al.⁵ arrived at eq 5 after discarding a three-suffix expression, i.e., a ternionwise additivity form. They did so because of the limitations of two options that they tested for predicting three-index ternary parameters from the corresponding three-index binary parameters.

2.3. Cubic Mixing Rules (CMRs). A mixing rule that is cubic in composition, as the following one, appears to be a more natural extension of the vdW rules than eq 5:

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k a_{ijk} \quad (6)$$

where

$$a_{ijk} = a_{ijk}^0 u_{ijk} \quad (7)$$

$$a_{ijk}^0 = (a_i a_j a_k)^{1/3} \quad (8)$$

$$u_{ijk} = 1 - k_{ijk} \quad (9)$$

For a multicomponent mixture, unary, e.g., u_{333} , binary, e.g., u_{233} , and ternary, e.g., u_{123} , three-indices u_{ijk} parameters appear in eq 6, i.e., eq 6 is ternionwise additive. Notice that positive u_{ijk} variables guarantee positive values for the a mixture parameter.

Equation 6, written for a binary mixture, gives a cubic function of the mole fraction x_1 . In this case, there are two degrees of freedom, i.e., a k_{ijj} parameter and a k_{jij} parameter with $k_{ijj} = k_{jij} = k_{jji}$ and $k_{ijj} = k_{jij} = k_{jji}$. Also $k_{iii} = 0$.

2.4. Relationship between Mathias–Klotz–Prausnitz (MKP) Mixing Rules and CMRs. For a given binary system, it can be shown that it is always possible to find values for parameters k_{ijj} and k_{jij} (eq 6) from known values of parameters k_{ji} and l_{ji} (eq 5) so that eqs 5 and 6 give exactly the same cubic function of x_1 . The relationships, for a system of components 1 and 2, are the following:

$$3a_{112}^0(1 - k_{112}) = a_{12}^0[l_{12} + 2(1 - k_{12})] + a_{11} \quad (10)$$

$$3a_{122}^0(1 - k_{122}) = a_{12}^0[2(1 - k_{12}) - l_{12}] + a_{22} \quad (11)$$

Equations 10 and 11 are linear with respect to all four interaction parameters k_{12} , l_{12} , k_{112} , and k_{122} . Equations 10 and 11 make it possible to find the binary parameters of the cubic mixing rule from known binary parameters of the MKP⁵ mixing rule or vice versa. We obtained eqs 10 and 11 with the aid of the computer algebra software package MAPLE,¹⁵ which is a highly developed symbolic programming language. For correlating binary information, e.g., phase equilibria experimental data, eqs 5 and 6 are indistinguishable. This means that all applications and results, already available in the literature, for binary mixtures modeled with MKP mixing rules (which have been so far only applied to the cohesive parameter) are also results for the CMRs.

The cubic dependence with respect to mole fraction for eqs 5 and 6, implies that the accepted low-density mole fraction dependencies for the virial coefficients are not met. Notice that, when using QMRs in two-parameter EOSs, for both the cohesive energy parameter and the covolume parameter, with a nonzero interaction parameter for the covolume parameter, the accepted form for the composition dependence of the third virial coefficient will already be violated.¹⁶ Besides, Yokozeki¹⁷ has questioned the validity of the generally accepted quadratic dependence on mole fraction for the second virial coefficient.

2.5. Relationship between QMRs and CMRs or MKP Rules. For a binary system, it is always possible to find values for parameters k_{ijj} and k_{jij} so that eq 6 (CMR) becomes identical to eq 1 (QMR). This is because a quadratic function is a particular case of a cubic function. Moreover, it is possible to force the k_{ijj} and the k_{jij} values to be such that the dependence of the mixture energy parameter on composition is linear. Analogous statements are valid for eq 5 when applied to binary systems. Appendix A provides the general expressions that the user must set for u_{ijk} to recover either a quadratic or a linear composition dependence. Notice that we recover the quadratic behavior in eq 5 by setting $l_{ji} = l_{ij} = 0$, which, introduced into eqs 10 and 11, lead to values for parameters k_{112} and k_{122} (as functions of k_{12}) corresponding to quadratic mixing rules for the binary system (1, 2), handled under the cubic mixing rule formalism (eq 6).

2.6. Values of the Three-Index Binary Interaction Parameters k_{ij} and k_{ij} . Appendix B shows that, when using cubic mixing rules, we should not expect to fit experimental information on binary systems using values for the three-index binary interaction parameters within the range to which we are used, from our experience with quadratic mixing rules.

2.7. Ternary Parameters in CMRs. If we wrote eq 6 (CMR) for a ternary system, we would observe the appearance of a ternary k_{ijk} parameter, i.e., a parameter for which all three indices correspond to different compounds. Thus, for a ternary system, eq 6 provides an additional degree of freedom, i.e., the k_{ijk} parameter. The presence of ternary parameters in equations such as eq 6 led Mathias et al.⁵ to conclude that functions of composition such as that of eq 6 were not an acceptable solution to the problem of finding flexible and invariant pair-based mixing rules, because, according to their analysis, such functions would require the availability of experimental information on ternary systems to find values for ternary parameters. This at-first-sight drawback of the presence of ternary parameters would turn into a strength of the model, if we had a method to predict values for ternary parameters in the absence of ternary experimental data. We would use such a prediction method for ternary subsystems with no ternary experimental information available, while, for ternary subsystems with experimental information available, we would optimize the value of k_{ijk} so as to reproduce such experimental data, while leaving invariant the representation by the model of the constituent binary subsystems.

Our problem consists now of finding a consistent expression for the ternary k_{ijk} parameter that relates it to the corresponding binary three-index parameters, which we could use when ternary experimental data are lacking. Finding one such expression that matches the proper limits is the purpose of the present work. To that end, we will later assume that, for a ternary system, each of the three constituent binary subsystems has interaction parameter values so that eqs 5 and 6 are indistinguishable for such a binary subsystem, i.e., we will assume that, for either of the three binary subsystems, the interaction parameters match eqs 10 and 11. In such a case, while the a parameter for the ternary system is completely defined by eq 5, the a parameter for the ternary system remains a function of an unknown ternary k_{ijk} interaction parameter for eq 6. We present in this work a strategy for predicting consistent values for such a k_{ijk} parameter.

3. Partial Parameters

The partial cohesive energy parameter is the derivative $[\partial(na)/\partial n_k]_{T,n_j \neq q}$, where n is the total number of moles, n_k is the number of moles for component k , and T is the temperature. The calculation of partial parameters makes it possible to more thoroughly test whether a proposed composition dependence for a mixture parameter is invariant (see Section 5). Partial parameters are much more sensitive to the interaction parameters than are the parameters of the mixture as a whole. Thus, we best visualize the effect of the interaction parameters in MKP (eq 5), QMRs (eq 1), and CMRs (eq 6), by studying the behavior of the partial parameters rather than the behavior of the parameters of the mixture as a whole. On the other hand, the fugacity coefficient of a component in a mixture, for vdW-like EOSs, depends on partial parameters.¹⁸ We regularly compute the composition of phases at equilibrium through calculations of fugacity coefficients for all the species present in the coexisting phases.¹⁸ The results are typically very sensitive to the values for the interaction parameters. Mathias et al.⁵ tested the invariance of MKP mixing rules through solubility calculations. Although such an approach is valid for testing invariance,

we can alternatively test it by computing mixture and partial parameters, thus avoiding phase equilibria calculations. This is important when developing new models for mixtures, i.e., we have the chance of quickly discarding a model, on the grounds of invariance violations, by just studying the behavior of mixture and partial parameters, before getting into the great effort of generating the codes for phase equilibria calculations. Appendix C presents the expressions for the partial parameters for CMRs, QMRs, and MKP mixing rules.

4. Expression for Estimating Ternary Interaction Parameters from Binary Interaction Parameters

Finding a consistent formula for predicting ternary interaction parameters from binary interaction parameters is not a trivial matter at first sight. Mathias et al.⁵ considered a few options, but they finally discarded them for a number of reasons. More recently, we made another attempt¹⁹ and proposed a preliminary formula that, although more elaborate than the options that Mathias et al.⁵ considered, had to be discarded anyway in this work for the reasons that we later provide.

The alternative formula that we propose in this work arises from combining eqs 6 and 5, in a special way. To produce a more compact final expression, we rewrite eqs 6 and 5, respectively, as follows:

$$A_{\text{cubic}} = \sum_{m=1}^N x_m \left(\sum_{n=1}^N x_n \left(\sum_{p=1}^N x_p A_{m,n,p} \right) \right) \quad (12)$$

$$A_{\text{MKP}} = \left(\sum_{i=1}^N x_i \left(\sum_{j=1}^N x_j Q_{ij} \right) \right) + \left(\sum_{i=1}^N x_i \left(\sum_{s=1}^N x_s M_{s,i}^{(1/3)} \right) \right) \quad (13)$$

where the definitions for variables A_{cubic} , A_{mnp} , A_{MKP} , Q_{ij} , and M_{st} stem easily from comparing eqs 12 and 13 with eqs 6 and 5, respectively. We notice that, for a ternary mixture,

$$Q_{1,1} = a_1 \quad Q_{2,2} = a_2 \quad Q_{3,3} = a_3 \quad (14)$$

$$M_{11} = M_{22} = M_{33} = 0 \quad (15)$$

$$Q_{21} = Q_{12} \quad Q_{31} = Q_{13} \quad Q_{32} = Q_{23} \quad (16)$$

$$M_{21} = -M_{12} \quad M_{31} = -M_{13} \quad M_{32} = -M_{23} \quad (17)$$

$$A_{1,1,1} = a_1 \quad A_{2,2,2} = a_2 \quad A_{3,3,3} = a_3 \quad (18)$$

$$\begin{aligned} A_{1,2,1} &= A_{1,1,2} & A_{1,3,1} &= A_{1,1,3} & A_{2,3,2} &= A_{2,2,3} & A_{1,3,2} &= A_{1,2,3} \\ A_{2,1,1} &= A_{1,1,2} & A_{3,1,1} &= A_{1,1,3} & A_{3,2,2} &= A_{2,2,3} & A_{2,1,3} &= A_{1,2,3} \\ & & & & & & A_{2,3,1} &= A_{1,2,3} \\ A_{2,1,2} &= A_{1,2,2} & A_{3,1,3} &= A_{1,3,3} & A_{3,2,3} &= A_{2,3,3} & A_{3,1,2} &= A_{1,2,3} \\ A_{2,2,1} &= A_{1,2,2} & A_{3,3,1} &= A_{1,3,3} & A_{3,3,2} &= A_{2,3,3} & A_{3,2,1} &= A_{1,2,3} \end{aligned} \quad (19)$$

We look for an expression relating the three-index ternary parameter A_{123} to the three-index binary parameters A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , A_{233} , i.e., we want to find an equation that would make it possible to predict ternary parameters by averaging, somehow, binary parameters. Such an expression should match the following invariance^{2,3} constraints:

$$A_{123} = A_{113} = A_{223} \text{ when components 1 and 2 become "identical"} \quad (20)$$

$$A_{123} = A_{112} = A_{233} \text{ when components 1 and 3 become identical} \quad (21)$$

$$A_{123} = A_{122} = A_{133} \text{ when components 2 and 3 become identical} \quad (22)$$

By expanding eqs 12 and 13 for a binary mixture of components 1 and 2, and considering that $[x_2 = 1 - x_1]$, we obtain two polynomial functions that are cubic with respect to x_1 . By imposing the identity for pairs of polynomial coefficients corresponding to like powers of x_1 , we get the following expressions for Q_{12} and M_{12} in terms of A_{112} and A_{122} :

$$Q_{12} = -\frac{1}{4}a_2 - \frac{1}{4}a_1 + \frac{3}{4}A_{1,1,2} + \frac{3}{4}A_{1,2,2} \quad (23)$$

$$M_{12} = \frac{1}{2}a_2 - \frac{1}{2}a_1 + \frac{3}{2}A_{1,1,2} - \frac{3}{2}A_{1,2,2} \quad (24)$$

Similarly, for the other two binary subsystems of system (1, 2, 3), we write

$$Q_{13} = -\frac{1}{4}a_3 - \frac{1}{4}a_1 + \frac{3}{4}A_{1,1,3} + \frac{3}{4}A_{1,3,3} \quad (25)$$

$$M_{13} = \frac{1}{2}a_3 - \frac{1}{2}a_1 + \frac{3}{2}A_{1,1,3} - \frac{3}{2}A_{1,3,3} \quad (26)$$

$$Q_{23} = -\frac{1}{4}a_2 - \frac{1}{4}a_3 + \frac{3}{4}A_{2,2,3} + \frac{3}{4}A_{2,3,3} \quad (27)$$

$$M_{23} = -\frac{1}{2}a_2 + \frac{1}{2}a_3 + \frac{3}{2}A_{2,2,3} - \frac{3}{2}A_{2,3,3} \quad (28)$$

Notice that the system of eqs 23 and 24 is equivalent to the system of eqs 10 and 11. Again we obtained eqs 23–28 using Maple.¹⁵

By introducing eqs 23–28 into the expression for A_{MKP} of eq 13, we end up setting the variable A_{MKP} in terms of the same variables that, together with variable A_{123} , completely define A_{cubic} of eq 12. Notice that, even in the case where we define the variables Q_{ij} and M_{ij} according to eqs 23–28, the value, at set composition, of A_{MKP} will differ from the value for A_{cubic} for ternary and higher mixtures.

To find an expression for A_{123} , we impose, for an equimolar ternary mixture, the identity between A_{MKP} and A_{cubic} , i.e.,

$$[A_{MKP} = A_{cubic}]_{\text{ternary equimolar mixture}} \quad (29)$$

After introducing eqs 23–28 into eq 13, we solved eq 29 for A_{123} using Maple.¹⁵ The result is eq 30.

$$\begin{aligned} A_{123} = & -\frac{1}{6}a_2 - \frac{1}{6}a_3 - \frac{1}{6}a_1 + \frac{1}{4}A_{1,1,3} + \frac{1}{4}A_{1,3,3} + \\ & \frac{1}{4}A_{2,2,3} + \frac{1}{4}A_{2,3,3} + \frac{1}{4}A_{1,1,2} + \frac{1}{4}A_{1,2,2} + \frac{1}{6}\left(\frac{1}{2}a_3 - \frac{1}{2}a_1 + \right. \\ & \left. \frac{3}{2}A_{1,1,3} - \frac{3}{2}A_{1,3,3}\right)^{(23)}\left(-\frac{1}{2}a_2 + \frac{1}{2}a_3 + \frac{3}{2}A_{2,2,3} - \frac{3}{2}A_{2,3,3}\right)^{(13)} + \\ & \frac{1}{6}\left(\frac{1}{2}a_2 - \frac{1}{2}a_1 + \frac{3}{2}A_{1,1,2} - \frac{3}{2}A_{1,2,2}\right)^{(23)}\left(\frac{1}{2}a_2 - \frac{1}{2}a_3 - \frac{3}{2}A_{2,2,3} + \right. \\ & \left. \frac{3}{2}A_{2,3,3}\right)^{(13)} + \frac{1}{6}\left(\frac{1}{2}a_3 - \frac{1}{2}a_1 + \frac{3}{2}A_{1,1,3} - \frac{3}{2}A_{1,3,3}\right)^{(13)}\left(-\frac{1}{2}a_2 + \right. \\ & \left. \frac{1}{2}a_3 + \frac{3}{2}A_{2,2,3} - \frac{3}{2}A_{2,3,3}\right)^{(23)} + \frac{1}{6}\left(-\frac{1}{2}a_2 + \frac{1}{2}a_1 - \frac{3}{2}A_{1,1,2} + \right. \\ & \left. \frac{3}{2}A_{1,2,2}\right)^{(23)}\left(-\frac{1}{2}a_3 + \frac{1}{2}a_1 - \frac{3}{2}A_{1,1,3} + \frac{3}{2}A_{1,3,3}\right)^{(13)} + \frac{1}{6}\left(-\frac{1}{2}a_2 + \right. \\ & \left. \frac{1}{2}a_1 - \frac{3}{2}A_{1,1,2} + \frac{3}{2}A_{1,2,2}\right)^{(13)}\left(-\frac{1}{2}a_3 + \frac{1}{2}a_1 - \frac{3}{2}A_{1,1,3} + \right. \\ & \left. \frac{3}{2}A_{1,3,3}\right)^{(23)} + \frac{1}{6}\left(\frac{1}{2}a_2 - \frac{1}{2}a_1 + \frac{3}{2}A_{1,1,2} - \frac{3}{2}A_{1,2,2}\right)^{(13)}\left(\frac{1}{2}a_2 - \right. \\ & \left. \frac{1}{2}a_3 - \frac{3}{2}A_{2,2,3} + \frac{3}{2}A_{2,3,3}\right)^{(23)} \quad (30) \end{aligned}$$

Notice that the MKP variables Q_{ij} and M_{st} do not appear in eq 30 because we replaced them by expressions 23–28. We also observe that all three-index variables that appear on the right-

hand side of eq 30 (A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233}) are binary variables.

We find in eq 30 a recipe to predict ternary constants (A_{123}), of cubic mixing rules (eq 6), from binary constants (A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233}) characteristic of the three corresponding binary subsystems. This was the goal of this work.

We can summarize the procedure we used to generate eq 30 as follows. We forced the match between two expressions invariant with respect to composition. Both expressions are equivalent for binary systems. One of them is pair-based (eq 13), while the other one is ternion-based (eq 12). A key step was to rewrite, for the binary subsystems, the pair-based expression in terms of the constants of the ternion-based expression (eqs 23–28). The whole process led to an equation for a three-index ternary variable as a function of three-index binary variables and of pure-compound variables (eq 30).

When setting the “equimolar mixture” constraint in eq 29, we avoid imposing on the model any unsubstantiated hierarchy among the components of the ternary system. Therefore, the equimolar option is the best, in comparison to other options that could be chosen, for the ternary mixture composition, when setting a connection between CMRs and MKP rules.

Equation 30 satisfies constraints 20–22. We illustrate it for the case of constraint 21 in Appendix D. Matching constraints 20–22 is a very stringent test. From looking at eq 30, we notice that A_{123} does not depend exclusively on the binary parameters A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} but also on the pure-compound parameters a_1 , a_2 , and a_3 .

If we use eq 30 for all three-index ternary parameters in eq 6, we obtain an equation that we could classify as a parametrically pair-based equation, since all the three-index interaction parameters entering eq 30 are, in such a case, ultimately binary. However, it seems that it would be improper to classify the combined eqs 6 and 30 as a pairwise additive model. The dependence on just binary parameters is not the only distinguishing feature of a pairwise additive model. The words “pairwise additive” imply a summation of terms, each one consisting of a product of two variables times a binary coefficient. Certainly, such a mathematical structure does not correspond to the combined eqs 6 and 30.

It is interesting to realize that, while Mathias et al.⁵ proposed eq 13 as an alternative solution to the lack of an expression with the properties of eq 30, eq 13 is partially the genesis of eq 30, which, very likely, we would not have been able to propose had eq 13 of Mathias et al.⁵ not been available.

Equation 30 might look complicated at first sight. However, since it gives the variable A_{123} as an explicit function (of pure-compound and binary parameters), A_{123} becomes easy to evaluate. Actually, we can rewrite eq 30 in a slightly more compact way, as we show it in eq D-1 of Appendix D. We generated eq 30 without resorting to distance parameters such as those defined in ref 20 within the context of a pair-based model. The way distance parameters were defined in ref 20 was questioned in the literature.²¹ We can always calculate parameter A_{123} using eq 30, i.e., the function of multiple variables (parameters) that eq 30 sets is always defined in the domain of the real numbers.

For dealing, using eq 6, with multicomponent systems, we would rewrite eq 30 by replacing indices (1, 2, 3) by (i, j, k). We would then use the resulting equation at (i, j, k) values corresponding to all possible combinations, with ($i \neq j, i \neq k, j \neq k$), available to the considered multicomponent system. Among all values of (A_{ijk}) $_{i \neq j, i \neq k, j \neq k}$ thus obtained, we would

keep only those corresponding to subternary systems without experimental information available.

To fix ideas, for a multicomponent system, the computation of interaction parameters for the cubic mixing rules of eq 6 should be done according to the following steps:

(a) Fit the three-index binary parameters k_{ij} and k_{ijk} from experimental information of all binary subsystems, and calculate the binary variables that appear on the right-hand side of eq 30, from the following equation:

$$A_{ijk} = a_{ijk} = a_{ijk}^0 u_{ijk} = (a_i a_j a_k)^{(1/3)} (1 - k_{ijk}) \quad (31)$$

(b) Use, for the ternary subsystems without ternary experimental data available, eq 30 to predict the values for the three-index ternary variables A_{ijk} , and calculate the three-index ternary interaction parameters k_{ijk} from the following equation:

$$k_{ijk} = 1 - \frac{A_{ijk}}{(a_i a_j a_k)^{(1/3)}} \quad (32)$$

(c) Fit the values for the three-index ternary parameters k_{ijk} for ternary systems with known ternary experimental information using such ternary experimental data.

The application of the strategy corresponding to steps (a)–(c) implies taking advantage to the greatest extent possible of available experimental data for binary and ternary systems.

Notice that we have derived eq 30 to satisfy the need for an expression to predict ternary constants while meeting the invariance constraint, i.e., we did not derive eq 30 to force CMRs (eq 6) to produce similar phase equilibrium results to those of the MKP mixing rules (eq 5), at any arbitrary composition condition for ternary and higher mixtures. In spite of this, if the user had strong reasons to believe, for a specific ternary subsystem, in phase equilibrium results obtained using the MKP mixing rules, he/she could disregard eq 30 and fit the ternary parameter of the CMRs so as to match the MKP results, or at least some of the features of the MKP results. In such a case, the MKP results would be used as if they corresponded to experimental data. This choice would make sense only if the binary subsystems were modeled with MKP binary interaction parameters equivalent to the binary three-index parameters of the CMRs (see eqs 10 and 11).

In Appendix E we show, on one hand, that the present approach does not necessarily have to be limited to the case of mixture parameters of EOSs. Otherwise, we can apply it to other composition-dependent properties. On the other hand, we assess in Appendix E the extent to which the use of a ternary parameter improves the description of a ternary real system. The property we consider in Appendix E is the excess molar volume (v^E), which we describe with equations analogous to eqs 12 and 13 but adapted to the case of v^E . For this property, we also derive in Appendix E an equation analogous to eq 30. From comparing experimental data and model calculations, we verify in Appendix E that the model flexibility does increase because of the use of a cubic composition dependence having ternary parameters available for fitting ternary information. To assess the consistency of eq 30, we study in the next section the limits that eq 30 meets and submit eq 30 to a number of tests.

5. Consistency Assessment of Equation 30

5.1. Invariance of Equation 30. Equation 30 satisfies constraints 20–22, i.e., when a couple of components become identical, we get the proper binary value for variable A_{123} (see Appendix D). If all compounds are identical, then we get for

A_{123} a value equal to a_1 ($=a_2 = a_3$), i.e., the proper pure-compound limit.

5.2. Value of k_{123} Parameter at Zero Values for All Three-Index Binary k_{ijk} Parameters. When setting all A_{ijk} variables on the right-hand side of eq 30 as equal to a_{ijk}^0 (eq 8), we always got, for variable A_{123} , a value equal to a_{123}^0 , while performing a test in a numerical way. In other words, a numerical test, where we set arbitrary random values on variables a_1 , a_2 , and a_3 , and also set zero values for all binary three-index k_{ijk} parameters, for all variables on the right-hand side of eq 30 defined according to eq 31, we got, from eqs 30 and 32, a zero value for parameter k_{123} . This is the desired behavior for eq 30. However, we did not find a general demonstration for such behavior. Nevertheless, because of our extensive numerical test, it seems that eq 30 meets, at any condition, the desired limit of a zero k_{123} parameter when we set to zero all three-index binary k_{ijk} parameters.

5.3. Further Testing of Equation 30. We further test eq 30, in several ways, in Appendix F, where we numerically verify that the mixing rules, cubic with respect to mole fraction of eq 6 coupled to eq 30, which predicts ternary three-index parameters from binary three-index parameters, are invariant.^{2,3} The tests in Appendix F are based on computed rather than experimental data. This is appropriate for our goals. The computed data correspond to a ternary system with highly asymmetric binary subsystems. We performed all tests that confirm the invariance of eq 6 coupled to eq 30 under conditions where it is impossible for quadratic mixing rules to describe the chosen binary subsystems and the corresponding ternary system.

6. Remarks and Conclusion

In this work, we propose the use of cubic mixing rules (CMRs, eq 6) for modeling the thermodynamic properties of multicomponent fluid mixtures. CMRs set a dependence on composition that is cubic with respect to the mole fractions of the chemical species present in the mixture, i.e., CMRs are ternionwise additive. The appearance of three-index ternary parameters in CMRs implies the possibility of describing properties that are nonpairwise-additive. This is a clear advantage over models limited by the pairwise-additivity constraint, except when we lack experimental information for one or more ternary subsystems of the multicomponent system that we want to describe. To circumvent this limitation, we derived eq 30, which makes it possible to predict values for three-index ternary parameters of CMRs from the values of the three-index binary parameters that characterize the three binary subsystems corresponding to the ternary parameter to be predicted. We assessed the performance of eq 30 by paying attention to fundamental invariance restrictions that consistent models must meet.^{2,3} We submitted eq 30 to a number of tests in this work that made it possible to verify the invariant character of CMRs coupled to eq 30. The three-index ternary parameters available to CMRs make it possible to influence the model behavior for ternary systems without affecting the model description of the corresponding binary subsystems. We have illustrated this in Appendix E for a real ternary system. Table 1 summarizes our modeling recommendations for multicomponent systems under varying scenarios with regard to availability of experimental information. We developed eq 30 for the cohesive energy parameter of two-parameter *PVT* equations of state, with eq 8 as a combining rule, as our case study. However, the derivations could be easily adapted to the case of combining rules different from that of eq 8, and also to the cases of the mixture covolume

Table 1. Recommendations Involving the Cubic Mixing Rules (CMRs) and the MKP Mixing Rules for Modeling the Behavior of a Multicomponent System under Varying Scenarios^a

no. of ternary subsystems with experimental information available	comment	comment	comment
all	eq 6 (CMR) should be used. All ternary parameters should be fit from experimental information.	eq 30 (A_{123} from binary parameters) could but should not be used.	eq 5 (MKP) could but should not be used because of its lack of ternary parameters.
none	eq 6 (CMR) coupled to eq 30 (A_{123} from binary parameters) could be used. Also eq 5 (MKP) could be used.		
some	eq 6 (CMR) should be used. Ternary parameters should be fit for those ternary subsystems with ternary experimental information available.	eq 30 should be used to predict all ternary parameters corresponding to ternary subsystems lacking experimental ternary information	eq 5 (MKP) could be used but should not be used because of its lack of ternary parameters.

^a Note: The MKP mixing rule and the CMR are indistinguishable for binary systems. They both provide two interaction parameters per binary.

parameter of EOSs and of other parameters of multiparametric EOSs. Moreover, in the future, other researchers could use this work as a starting point in their search for equations alternative to eq 30, for predicting ternary constants from binary constants, while keeping the basic invariance properties of eq 30. Additionally, the strategy we used in this work for dealing with ternionwise additive expressions for mixture parameters can be extended to models for mixture properties such as the excess Gibbs energy, third virial coefficients, excess molar volume (Appendix E), etc., for multicomponent systems. In other words, after focusing on the particular context within which we derived eq 30, we should widen our perspective by considering the implications of the approach here proposed, i.e., rather than a particular model for a given mixture parameter or mixture property, what we have proposed here is a modeling approach, of general applicability, that maximizes the use of available experimental information. Finally, we should mention that the computer algebra software package MAPLE¹⁵ was of great help during the development of this work.

Appendix A: General Expressions for u_{ijk} to Recover Quadratic and/or Linear Composition Dependencies

Quadratic Case. Let us set the following expression for u_{ijk} , which influences eq 7 of the text:

$$u_{ijk} = u_{ijk,Q} = \frac{a_{ij} + a_{ik} + a_{jk}}{3a_{ijk}^0} \quad (\text{A-1})$$

where a_{ij} is defined in eq 2 of the text. After introducing eq A-1 into eq 7 of the text, we get

$$a_{ijk} = \frac{a_{ij} + a_{ik} + a_{jk}}{3} \quad (\text{A-2})$$

Equation A-1 implies that the ternary interactions become decoupled into binary interactions, as eq A-2 shows. Combining eq A-2 with eq 6 of the text and considering the following constraint,

$$\sum_{l=1}^N x_l = 1 \quad (\text{A-3})$$

we obtain

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k \left[\frac{a_{ij} + a_{ik} + a_{jk}}{3} \right] = \sum_{l=1}^N \sum_{m=1}^N x_l x_m a_{lm} \quad (\text{A-4})$$

Thus,

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k a_{ijk}^0 u_{ijk,Q} = \sum_{l=1}^N \sum_{m=1}^N x_l x_m a_{lm} \quad (\text{A-5})$$

where $u_{ijk,Q}$ is defined in eq A-1. In conclusion, if we define u_{ijk} according to eq A-1, we exactly recover a quadratic mixing rule. Let us study the possible cases for u_{ijk} as given by eq A-1, i.e., for $u_{ijk,Q}$. If components i , j and k are identical, then

$$u_{ijk,Q} = u_{iii,Q} = \frac{a_{ii}}{a_{iii}^0} = 1 \quad (\text{when } i, j, \text{ and } k \text{ are "identical"}) \quad (\text{A-6})$$

If components i and j are identical but different from component k , then

$$\begin{aligned} u_{ijk,Q} &= u_{iik,Q} \\ &= \frac{a_{ii} + 2a_{ik}}{3a_{iik}^0} \\ &= u_{jjk,Q} \\ &= \frac{a_{jj} + 2a_{jk}}{3a_{jjk}^0} \quad (\text{if } i \text{ is identical to } j) \end{aligned} \quad (\text{A-7})$$

By renaming index k to j in eq A-7, and from the considerations we made just after we introduced eq 6 of the text, we get

$$u_{iij,Q} = \frac{a_{ii} + 2a_{ij}}{3a_{iij}^0} = u_{iji,Q} = u_{jii,Q} \quad (\text{A-8})$$

By switching indices on eq A-8 and considering that a_{ij} is symmetric, we get

$$u_{jji,Q} = \frac{a_{jj} + 2a_{ij}}{3a_{jji}^0} = u_{ijj,Q} = u_{ijj,Q} \quad (\text{A-9})$$

From eqs 2 and 3 of the text, a_{ij} depends on k_{ij} . Hence, eqs A-8 and A-9 establish how the binary three-index parameters u_{ijj} and u_{jii} must relate to k_{ij} if the cubic mixing rule, eq 6 of the text, has to reproduce exactly a quadratic behavior for the binary subsystem of components i and j .

Combining eqs A-8 and A-9, we obtain

$$3a_{iij}^0 u_{iij,Q} - a_{ii} = 3a_{ijj}^0 u_{ijj,Q} - a_{jj} \quad (\text{A-10})$$

As is also the case for eqs A-8 and A-9, eq A-10 shows that the binary three-index parameters u_{ijj} and u_{jii} are not mutually independent, if the binary subsystem of components i and j has actually a quadratic behavior, which is formally represented as a cubic behavior. To fix ideas, we will write eqs A-8–A-10 for the specific case of $i = 1$ and $j = 2$. From eq A-8,

$$u_{112,Q} = \frac{a_{11} + 2a_{12}}{3a_{112}^0} = \frac{a_1 + 2(a_1a_2)^{1/2}(1 - k_{12})}{3(a_1a_2)^{(1/3)}} = 1 - k_{112,Q} \quad (\text{A-11})$$

Notice that eq A-11 is the same that we get by setting $l_{12} = 0$ in eq 10 of the text. The reason is that the MKP mixing rule (eq 5 of the text) recovers the quadratic rule when we set $l_{ij} = 0$ for every ij pair in the system.

Solving eq A-11 for $k_{112,Q}$, we get,

$$k_{112,Q} = 1 - \frac{(a_1/a_2) + 2(a_1/a_2)^{(1/2)}(1 - k_{12})}{3(a_1/a_2)^{(2/3)}} \\ = 1 - \frac{R_{12} + 2R_{12}^{(1/2)}(1 - k_{12})}{3R_{12}^{(2/3)}} \quad (\text{A-12})$$

By switching indices, we get

$$k_{221,Q} = k_{122,Q} \\ = 1 - \frac{(a_2/a_1) + 2(a_2/a_1)^{(1/2)}(1 - k_{12})}{3(a_2/a_1)^{(2/3)}} \\ = 1 - \frac{R_{12}^{-1} + 2R_{12}^{(-1/2)}(1 - k_{12})}{3R_{12}^{(-2/3)}} \quad (\text{A-13})$$

where

$$R_{12} = a_1/a_2 \quad (\text{A-14})$$

We can draw a number of conclusions from eqs A-12 and A-13. If the ratio R_{12} is 1, and if $k_{12} = 0$, then $k_{112,Q} = 0$ and $k_{122,Q} = 0$. If $k_{12} = 0$ and $R_{12} \neq 1$, then $k_{112,Q} \neq 0$ and $k_{122,Q} \neq 0$. In other words, if a_1 is not equal to a_2 , a zero two-index interaction parameter ($k_{12} = 0$), used for the (1, 2) quadratic binary system, corresponds to nonzero three-index interaction parameters under the formalism of cubic mixing rules, set to exactly reproduce the quadratic rules for the (1, 2) system. If k_{12} and R_{12} do not depend on temperature, then $k_{112,Q}$ and $k_{122,Q}$ are also temperature-independent. In general, a_1 and a_2 depend on temperature in such a way that R_{12} also depends on temperature (e.g., in the SRK EOS¹). In such a case, $k_{112,Q}$ and $k_{122,Q}$ become temperature-dependent both for the case of a temperature-dependent k_{12} and for the case of a temperature-independent k_{12} .

From combining eqs A-12 and A-13, we obtain the relationship that $k_{112,Q}$ and $k_{122,Q}$ must meet, i.e., a constraint involving parameters k_{112} and k_{122} when they give a quadratic rule behavior when using the cubic rule formalism:

$$\frac{3R_{12}^{(2/3)}(1 - k_{112,Q}) - R_{12}}{2R_{12}^{1/2}} = \frac{3R_{12}^{-2/3}(1 - k_{122,Q}) - R_{12}^{-1}}{2R_{12}^{-1/2}} \quad (\text{A-15})$$

Notice that we could have obtained eq A-15 also from eq A-10.

Linear Case. Let us set the following expression for u_{ijk}

$$u_{ijk} = u_{ijk,L} = \frac{a_i + a_j + a_k}{3a_{ijk}^0} \quad (\text{A-16})$$

After introducing eq A-16 into eq 7 of the text, we get

$$a_{ijk} = \frac{a_i + a_j + a_k}{3} \quad (\text{A-17})$$

Equation A-16 implies that the ternary interactions become decoupled into unary contributions, as eq A-17 shows. Combining eq A-17 with eq 6 of the text, we get

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k \left[\frac{a_i + a_j + a_k}{3} \right] = \sum_{l=1}^N x_l a_l \quad (\text{A-18})$$

Thus,

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k a_{ijk,L}^0 u_{ijk,L} = \sum_{l=1}^N x_l a_l \quad (\text{A-19})$$

where $u_{ijk,L}$ is defined by eq A-16. In conclusion, if we define u_{ijk} according to eq A-16, we exactly recover a linear mixing rule. For a binary system, from eq A-16, we have

$$u_{ij,L} = \frac{2a_i + a_j}{3a_{ij}^0} = \frac{2(a_i/a_j) + 1}{3(a_i/a_j)^{(2/3)}} \quad (\text{A-20})$$

$$u_{ij,L} = \frac{a_i + 2a_j}{3a_{ij}^0} = \frac{(a_i/a_j) + 2}{3(a_i/a_j)^{(1/3)}} \quad (\text{A-21})$$

Equations A-20 and A-21 imply that, if we take the linear rule to the cubic formalism, we will in general have nonzero three-index interaction parameters that will be temperature-dependent, for temperature-dependent a_i and a_j . On the other hand, if $a_i = a_j$, then both $k_{ij,L} = 0$ and $k_{ij,L} = 0$.

In this Appendix, we have shown that cubic mixing rules comprise the quadratic and linear mixing rules as particular cases. Moreover, the cubic formalism makes it possible to average the properties of linear, quadratic, and cubic binary subsystems making up a multicomponent system (original quadratic rules can average properties of linear and quadratic binary subsystems).

Important equations in this Appendix are eqs A-12, A-13, A-20, and A-21, which tell us how we must define the three-index interaction parameters for recovering, respectively, a quadratic or a linear behavior for a given binary subsystem.

Appendix B: Values of the Three-Index Binary Interaction Parameters k_{ij} and k_{ij}

Figure B1 shows values for the three-index binary interaction parameters k_{ij} and k_{ij} for cubic mixing rules, which make eq 6 become identical to the quadratic mixing rule (QMR, eq 1) as functions of the interaction parameter k_{ij} for QMRs and of the ratio of pure-compound energy parameters. Consider, for instance, a binary mixture of components A and B such that the ratio a_A/a_B equals 0.001. Suppose that we model such a mixture using quadratic mixing rules with $k_{AB} = 0.4$. Figure B1 tells us that we would obtain exactly the same behavior by modeling the system using cubic mixing rules (eq 6) with $k_{AAB} = -0.298244397$ and $k_{ABB} = -2.459824439$. Notice that these values differ significantly from 0.4. Thus, when using cubic mixing rules, we should not expect to fit experimental information on binary systems using values for the three-index binary interaction parameters within the range to which we are used, from our experience with quadratic mixing rules. Figure B1 also shows that, at $k_{AB} = 0$, the equivalent three-index parameters are, in general, different from zero. It is also clear, from Figure B1, that the interaction parameters for cubic mixing rules (CMRs) equivalent to those for quadratic mixing rules (QMRs) are highly dependent on the ratio of pure-compound parameters.

Appendix C: Expressions of Partial Parameters

C.1. Partial Parameters of CMRs. The expression for the partial parameter $[\partial(na)/\partial n_q]_{T,n_j \neq q}$ ($= \bar{a}_q$) corresponding to the CMRs of eq 6) is the following:

$$\bar{a}_q = -2a + 3 \sum_{l=1}^N \sum_{m=1}^N x_l x_m a_{lmq} \quad (\text{CMR}) \quad (\text{C-1})$$

Notice that the variable a in the first term of the right-hand side of eq C-1 comes from eq 6. From eq C-1, the partial molar parameter \bar{a}_1 when component 1 is infinitely diluted in component 2 (binary mixture) is the following:

$$\bar{a}_1|_{x_1 \rightarrow 0} = \bar{a}_1^\infty = -2a_2 + 3a_{122} = -2a_2 + 3a_{122}^0(1 - k_{122}) \quad (\text{CMR}) \quad (\text{C-2})$$

At the other concentration limit, we have:

$$\bar{a}_2|_{x_2 \rightarrow 0} = \bar{a}_2^\infty = -2a_1 + 3a_{112} = -2a_1 + 3a_{112}^0(1 - k_{112}) \quad (\text{CMR}) \quad (\text{C-3})$$

From eqs C-2 and C-3, we see that, for a binary mixture of components 1 and 2, the infinite dilution partial parameter $[\partial(na)/\partial n_1]_{T, n_2, x_1 \rightarrow 0}$ depends on k_{122} but not on k_{112} , while the partial parameter $[\partial(na)/\partial n_2]_{T, n_1, x_2 \rightarrow 0}$ depends on k_{112} but not on k_{122} . In other words, for a binary system, a given binary parameter controls the mixing rule behavior at one of the infinite dilution limits, independently from the other binary parameter. This is an interesting property of eq 6.

C.2. Partial Parameters of QMRs. The partial molar parameters corresponding to quadratic mixing rules (QMRs, eq 1) have the following expression:

$$\bar{a}_q = -a + 2 \sum_{l=1}^N x_l a_{ql} \quad (\text{QMR}) \quad (\text{C-4})$$

Notice that a in the first term of the right-hand side of eq C-4 comes from eq 1. From eq C-4, for a binary mixture, we write the expressions for the partial parameters at both infinite dilution limits.

$$\bar{a}_1|_{x_1 \rightarrow 0} = \bar{a}_1^\infty = -a_2 + 2a_{12} = -a_2 + 2a_{12}^0(1 - k_{12}) \quad (\text{QMR}) \quad (\text{C-5})$$

$$\bar{a}_2|_{x_2 \rightarrow 0} = \bar{a}_2^\infty = -a_1 + 2a_{21} = -a_1 + 2a_{21}^0(1 - k_{12}) \quad (\text{QMR}) \quad (\text{C-6})$$

From eqs C-5 and C-6, it is clear that both QMR infinite dilution partial molar parameters depend on k_{12} , and thus, we have no independent control on their values.

C.3. Partial Parameters of MKP Mixing Rules. The expression of the partial parameter for component q , corresponding to the MKP mixing rule (eq 5), is the following:

$$\bar{a}_q = - \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ji} + 2 \sum_{l=1}^N x_l a_{ql} + \left\{ -3 \sum_{i=1}^N x_i \left(\sum_{j=1}^N x_j (a_{ji}^0)^{1/3} (l_{ji})^{1/3} \right)^3 + \sum_{i=1}^N 3x_i (a_{qi}^0)^{1/3} (l_{qi})^{1/3} \times \left(\sum_{j=1}^N x_j (a_{ji}^0)^{1/3} (l_{ji})^{1/3} \right)^2 + \left(\sum_{j=1}^N x_j (a_{jq}^0)^{1/3} (l_{jq})^{1/3} \right)^3 \right\} \quad (\text{C-7})$$

Appendix D: Verification of Constraint 21 for Equation 30

Constraint 21 of the text is the following:

$$A_{123} = A_{112} = A_{233} \quad \text{when components 1 and 3 become identical} \quad (21)$$

We can rewrite eq 30 of the text as follows:

$$A_{123} = -(1/6)a_1 - (1/6)a_2 - (1/6)a_3 + (1/4)A_{233} + (1/4)A_{223} + (1/4)A_{122} + (1/4)A_{113} + (1/4)A_{133} + (1/4)A_{112} + (-1/6)U_{13}^{(1/3)}U_{23}^{(2/3)} + (-1/6)U_{23}^{(1/3)}U_{13}^{(2/3)} + (1/6)U_{12}^{(1/3)}U_{13}^{(2/3)} + (1/6)U_{13}^{(1/3)}U_{12}^{(2/3)} + (-1/6)U_{12}^{(1/3)}U_{23}^{(2/3)} + (1/6)U_{23}^{(1/3)}U_{12}^{(2/3)} \quad (\text{D-1})$$

where

$$U_{12} = [(1/2)a_1 - (1/2)a_2 + (3/2)A_{122} - (3/2)A_{112}] \quad (\text{D-2})$$

$$U_{13} = [(1/2)a_1 - (1/2)a_3 + (3/2)A_{133} - (3/2)A_{113}] \quad (\text{D-3})$$

$$U_{23} = [(1/2)a_2 - (1/2)a_3 + (3/2)A_{233} - (3/2)A_{223}] \quad (\text{D-4})$$

Notice that

$$U_{12} = -U_{21} \quad (\text{D-5})$$

$$U_{13} = -U_{31} \quad (\text{D-6})$$

$$U_{23} = -U_{32} \quad (\text{D-7})$$

If components 1 and 3 become identical, then

$$a_3 = a_1 \quad (\text{D-8})$$

$$A_{233} = A_{211} = A_{112} \quad (\text{D-9})$$

$$A_{223} = A_{221} = A_{122} \quad (\text{D-10})$$

$$A_{113} = A_{111} = a_1 \quad (\text{D-11})$$

$$A_{133} = A_{111} = a_1 \quad (\text{D-12})$$

Introducing eqs D-8–D-12 into eqs D-3, D-4, and D-1, we get

$$U_{13} = 0 \quad (\text{D-13})$$

$$U_{23} = U_{21} = -U_{12} \quad (\text{D-14})$$

$$A_{123} = -(1/6)a_1 - (1/6)a_2 - (1/6)a_1 + (1/4)A_{112} + (1/4)A_{122} + (1/4)A_{122} + (1/4)a_1 + (1/4)a_1 + (1/4)A_{112} + 0 + 0 + 0 + 0 + (-1/6)U_{12}^{(1/3)}(-U_{12})^{(2/3)} + (1/6)(-U_{12})^{(1/3)}U_{12}^{(2/3)} \quad (\text{D-15})$$

which gives

$$A_{123} = (1/6)a_1 - (1/6)a_2 + (1/2)a_{112} + (1/2)A_{122} - (1/6)U_{12} + (-1/6)U_{12} \quad (\text{D-16})$$

Introducing the expression D-2 into eq D-16, we obtain

$$A_{123} = A_{112} \quad (\text{D-17})$$

Equation D-17 verifies constraint 21 for eq 30 of the text.

Appendix E: Study of the Excess Molar Volume of the Ternary System Isobutyl Alcohol (1) + Ethanol (2) + 2-Methylpentane (3)—Effect of Ternary Parameters

Muñoz et al.²² measured excess molar volumes at 298.15 K for the system isobutyl alcohol (1) + ethanol (2) + 2-methylpentane (3) and for all three corresponding binary subsystems over the whole composition range. They smoothed their data using an empirical Cibulka–Redlich–Kister equation (eq 3 in ref 22) with 16 fitting parameters. Such a smoothing–interpolating data-treatment equation is useful to generate high-quality pseudo-experimental data.

In this Appendix, we model the excess molar volume (v^E) for this system using eqs 12 and 13 adapted to the case of v^E .

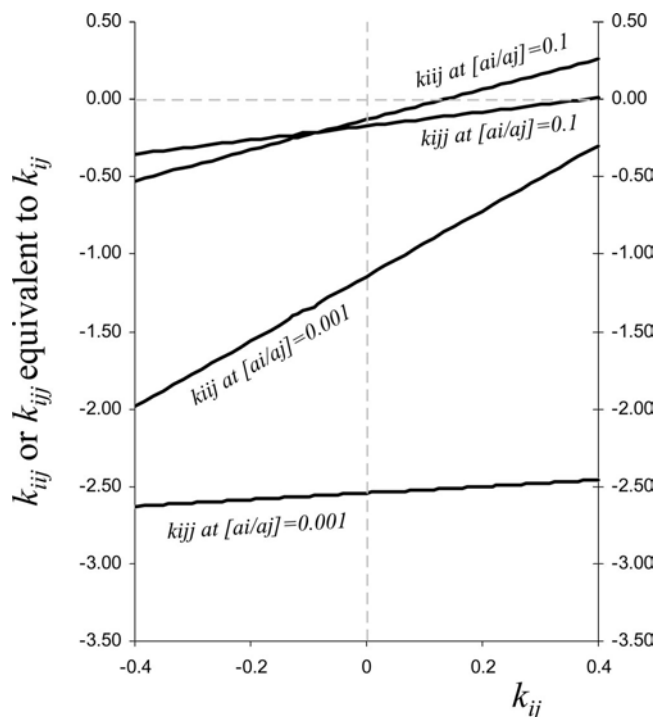


Figure B1. Three-index binary interaction parameters for cubic mixing rules (CMRs, eq 6) making eq 6 become identical to the quadratic mixing rules (QMRs, eq 1), as functions of the interaction parameter k_{ij} for QMRs, for two different values for the ratio of pure-compound energy parameters.

Table E1. Excess Volume Binary Three-Index Parameters^a for the Binary Subsystems of System Isobutyl Alcohol (1) + Ethanol (2) + 2-Methylpentane (3)

isobutyl alcohol (1) + ethanol (2)	isobutyl alcohol (1) + 2-methylpentane (3)	ethanol (2) + 2-methylpentane (3)
$A_{112}^E = 0.03360461971$	$A_{113}^E = -0.2403780601$	$A_{223}^E = 0.3153459826$
$A_{222}^E = 0.07963218110$	$A_{333}^E = 0.4470022964$	$A_{233}^E = 0.5826767275$

^a The units are cm^3/mol for all six parameters.

Our purpose here is to assess the extent to which the use of a ternary parameter improves the description of this ternary real system, i.e., to evaluate the magnitude of the increase in model flexibility associated to the use of a cubic composition dependence.

We adapt eq 12 to the case of v^E as follows:

$$v^E = \sum_{m=1}^N \sum_{n=1}^N \sum_{p=1}^N x_m x_n x_p A_{m,n,p}^E \quad (\text{E-1})$$

where the variables $A_{m,n,p}^E$ are independent from composition and are functions of temperature only, at low pressure (as is the case for the data of ref 22). Equation E-1 is generally applicable to multicomponent systems. We first notice that

$$A_{111}^E = A_{222}^E = A_{333}^E = 0 \quad (\text{E-2})$$

Notice that relationships 19 of the text apply also to variables $A_{m,n,p}^E$ of eq E-1.

We fit the constants of eq E-1 for all three binary subsystems of system isobutyl alcohol (1) + ethanol (2) + 2-methylpentane (3) from the smoothed data of ref 22. By “smoothed data”, we mean pseudo-experimental data generated from eq 3 in ref 22. Table E1 presents the values we obtained for the three-index binary constants of system (1, 2, 3).

At 298.15 K, the systems [isobutyl alcohol (1) + ethanol (2)] and [ethanol (2) + 2-methylpentane (3)] have only positive

excess volumes while the system [isobutyl alcohol (1) + 2-methylpentane (3)] has an excess volume curve that changes sign from positive to negative when going from low to high isobutyl alcohol (1) concentration. This is shown in Figure E1, which presents both the experimental data and a solid line corresponding to eq E-1 used with the values for A_{113}^E and A_{133}^E of Table E1. It would have been impossible to describe the experimental data of Figure E1 by using a multiple summation of degree less than 3 in mole fraction, as would have been the case of a quadratic composition dependence. Thus, for the system here studied, the minimum required complexity level for the composition dependence is the one of eq E-1, among all possible multivariate polynomial functions of composition. The case of Figure E1 illustrates the flexibility associated to the use of a cubic composition dependence.

We adapt eq 13 to the case of the excess molar volume (v^E) as follows:

$$v^E = \sum_{i=1}^N \sum_{j=1}^N x_i x_j Q_{ij}^E + \sum_{i=1}^N x_i \left(\sum_{s=1}^N x_s (M_{s,i}^E)^{1/3} \right)^3 \quad (\text{E-3})$$

$$Q_{11}^E = Q_{22}^E = Q_{33}^E = 0 \quad (\text{E-4})$$

$$M_{11}^E = M_{22}^E = M_{33}^E = 0 \quad (\text{E-5})$$

Notice that relationships 16 and 17 of the text apply also to variables Q_{ij}^E and $M_{s,i}^E$ of eq E-3.

Equation E-3 is a MKP-like expression for the excess molar volume. For binary mixtures, we obtain an absolute equivalence between eqs E-1 and E-3, for system (1, 2), if the parameters relate as follows:

$$Q_{1,2}^E = \left(\frac{3}{4}\right)(A_{112}^E + A_{122}^E) \quad (\text{E-6})$$

$$M_{1,2}^E = \left(\frac{3}{2}\right)(A_{112}^E - A_{122}^E) \quad (\text{E-7})$$

Relationships analogous to eqs E-6 and E-7 are obtained for systems (1, 3) and (2, 3) by renaming indices. Table E2 presents the parameter values that make eqs E-1 and E-3 equivalent for the binary subsystems of the system isobutyl alcohol (1) + ethanol (2) + 2-methylpentane (3).

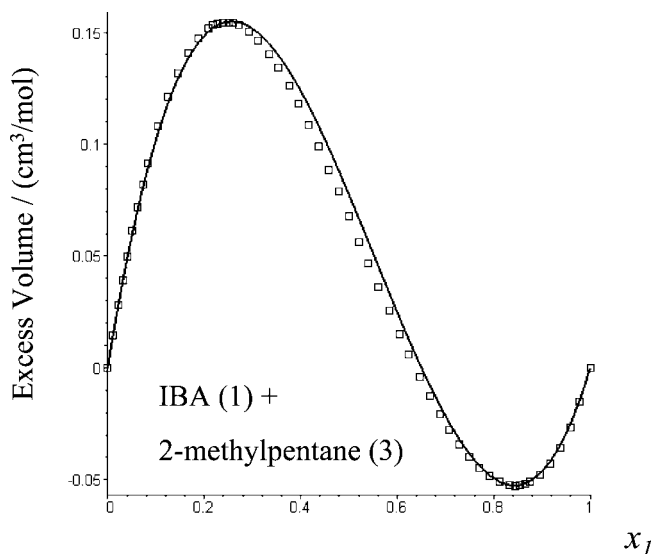


Figure E1. Excess molar volume for the binary system IBA (1) + 2-methylpentane (3) as a function of mole fraction of IBA (1) at 298.15 K. IBA (1) stands for isobutyl alcohol (1). Markers: smoothed experimental data (eq 3 of ref 22). Solid line: eq E-1 at $N = 2$ and parameters A_{113}^E and A_{133}^E from Table E1.

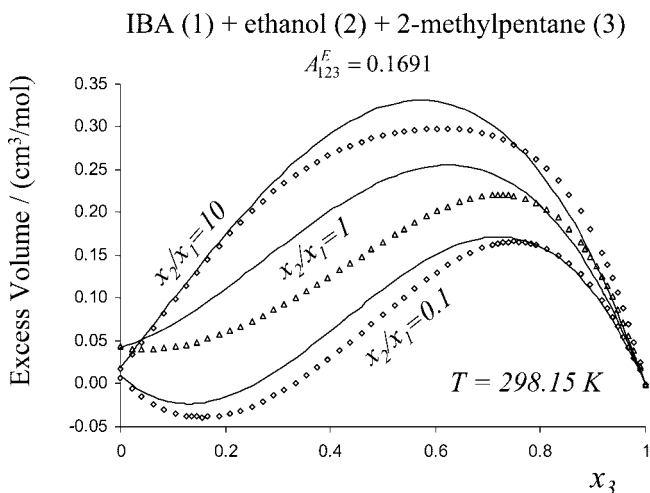


Figure E2. Excess molar volume for the ternary system IBA (1) + ethanol (2) + 2-methylpentane (3) as a function of mole fraction of 2-methylpentane (3) at 298.15 K and at varying ethanol (2)/IBA (1) ratios. IBA (1) stands for isobutyl alcohol (1). Markers: smoothed experimental data (eq 3 of ref 22). Solid lines: eq E-1 with binary three-index parameters from Table E1 and ternary parameter A_{123}^E calculated from eq E-8 ($A_{123}^E = 0.1691 \text{ cm}^3/\text{mol}$).

By following a procedure analogous to that which led us to eq 30 of the text, we find an expression for parameter A_{123}^E . The result is the following:

$$4A_{123}^E = A_{112}^E + A_{122}^E + A_{113}^E + A_{133}^E + A_{223}^E + A_{233}^E + [A_{122}^E - A_{112}^E]^{(1/3)} [A_{133}^E - A_{113}^E]^{(2/3)} + [A_{122}^E - A_{112}^E]^{(2/3)} [A_{133}^E - A_{113}^E]^{(1/3)} + [A_{112}^E - A_{122}^E]^{(2/3)} [A_{233}^E - A_{223}^E]^{(1/3)} + [A_{112}^E - A_{122}^E]^{(1/3)} [A_{233}^E - A_{223}^E]^{(2/3)} + [A_{113}^E - A_{133}^E]^{(2/3)} [A_{223}^E - A_{233}^E]^{(1/3)} + [A_{113}^E - A_{133}^E]^{(1/3)} [A_{223}^E - A_{233}^E]^{(2/3)} \quad (\text{E-8})$$

Equation E-8 makes it possible to predict the ternary parameter A_{123}^E from binary three-index parameters. It comes from imposing the equality between eqs E-1 and E-3 for an equimolar ternary mixture, with binary parameters of eq E-3 given by eqs E-6 and E-7. By introducing the parameters of Table E1 into eq E-8) we obtain $A_{123}^E = 0.1691$. This is a predicted value for parameter A_{123}^E . Figure E2 shows the excess molar volume for the ternary system IBA (1) + ethanol (2) + 2-methylpentane (3) as a function of mole fraction of 2-methylpentane (3) at 298.15 K and at varying ethanol (2)/IBA (1) ratios. IBA (1) stands for isobutyl alcohol (1). The solid lines correspond to eq E-1 with binary three-index parameters from Table E1 and with the ternary parameter A_{123}^E calculated from eq E-8 ($A_{123}^E = 0.1691$). We observe some overprediction of the excess molar volume when the concentrations of components 1 and 2 are similar. We also generated a figure analogous to Figure E2, but for the case of the MKP-like eq E-3 with parameters from Table E2. Such a figure (not shown) was indistinguishable from Figure E2. Thus, in this case, eq E-1 coupled to eq E-8 is indistinguishable from eq E-3. For eq E-3, it is impossible to improve the model performance

Table E2. Excess Volume Parameter Values^a for Equation E-3 Equivalent to Parameters in Table E1

isobutyl alcohol (1) + ethanol (2)	isobutyl alcohol (1) + 2-methylpentane (3)	ethanol (2) + 2-methylpentane (3)
$Q_{1,2}^E = 0.08492760060$	$Q_{1,3}^E = 0.1549681772$	$Q_{2,3}^E = 0.6735170326$
$M_{1,2}^E = -0.06904134204$	$M_{1,3}^E = -1.031070535$	$M_{2,3}^E = -0.4009961173$

^a The units are cm^3/mol for all six parameters.

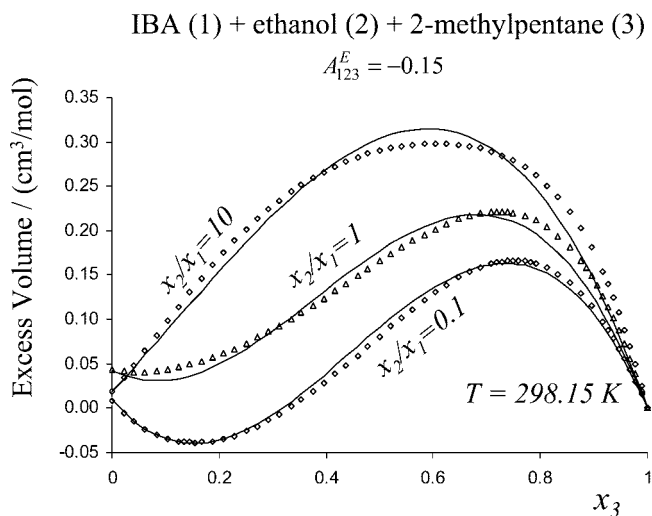


Figure E3. Excess molar volume for the ternary system IBA (1) + ethanol (2) + 2-methylpentane (3) as a function of mole fraction of 2-methylpentane (3) at 298.15 K and at varying ethanol (2)/IBA (1) ratios. IBA (1) stands for isobutyl alcohol (1). Markers: smoothed experimental data (eq 3 of ref 22). Solid lines: eq E-1 with binary three-index parameters from Table E1 and ternary parameter A_{123}^E fit to the ternary experimental data ($A_{123}^E = -0.15 \text{ cm}^3/\text{mol}$).

once the binary parameters have been set at the values of Table E2. In contrast, we can use again eq E-1, but now ignoring eq E-8, i.e., fitting parameter A_{123}^E against the ternary data, having the guarantee that the description of the binary subsystems remains invariant, i.e., remains determined only by the parameter values of Table E1. Figure E3 is analogous to Figure E2 but with the ternary parameter A_{123}^E fit to the ternary experimental data, i.e., set as $A_{123}^E = -0.15$. We observe in Figure E3 a significant improvement in the description of the excess molar volume. In conclusion, it is clear for this case that the model flexibility does increase because of the use of a cubic composition dependence with ternary parameters available for fitting ternary information. This is a confirmation of what we expected from our experience in the manipulation of mathematical expressions, i.e., since the binary subsystems are insensitive to parameter A_{123}^E , the process of freely fitting parameter A_{123}^E , so as to match ternary experimental data, can only lead to an improvement of the model performance.

It is important to stress that, although eq 3 in ref 22 is very accurate for the system isobutyl alcohol (1) + ethanol (2) + 2-methylpentane (3), the information that such an equation contains cannot be extended to multicomponent systems, since it lacks the invariance property. On the other hand, eq E-1 gives an invariant excess molar volume. This is also the case for eq E-3, which lacks parameters that could be fit from ternary information while leaving invariant the description of the corresponding binary subsystems.

Notice that we could define a model for the excess Gibbs energy (g^E) of multicomponent systems analogous to the excess volume model of eq E-1. For a multicomponent system, the parameters of the ternary subsystems could be predicted, when calculating g^E , from an equation analogous to eq E-8, but used for the parameters of the ternion-based g^E model. The availability of a ternary parameter for a g^E model should make

Table F1. Properties of Pure Compounds Considered in Appendix F^a

compound	T_c/K	P_c/Pa	acentric factor	$a/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$ (SRK EOS at 333.13 K)
1	304.21	7 383 000	0.2236	3.425969E+11
2	658.00	1 820 000	0.5764	1.345094E+13
3	900.95	458 309	1.7371	2.202698E+14

^a T_c = critical temperature, and P_c = critical pressure.

possible the description of topologically complex g^E surfaces, as the one shown in Figure 2b of ref 23.

Appendix F: Additional Testing of Equation 30

To further test the performance and properties of eq 30 of the text, we will consider a set of three compounds and the associated binary subsystems and ternary system. An important requirement here, for testing invariance, is that we set values on parameters k_{ij} and k_{ji} for each binary subsystem so that eq 6 does not reduce to eq 1, i.e., values that guarantee that the dependency on mole fraction is not simpler than cubic.

F.1. Pure Components Considered for Testing Equation 30. Table F1 shows the pure-compound properties. We chose the properties so that highly asymmetric binary subsystems would be generated. For this study, we computed, at 333.13 K, the energetic parameters a_1 , a_2 , and a_3 according to the Soave–Redlich–Kwong (SRK) equation of state (EOS).¹

F.2. Interaction Parameters Considered for Testing Equation 30. Table F2 presents the interaction-parameter values for system (1, 2) that we used in this study and the resulting values for the partial parameters at both concentration ends. We considered three cases: quadratic behavior (eq 1) with a zero interaction parameter, quadratic behavior (eq 1) with nonzero interaction parameter, and cubic (eq 6) (or equivalent MKP, eq 5) behavior with nonzero interaction parameters.

Table F2 shows the values for the partial parameters \bar{a}_1 and \bar{a}_2 at both infinite dilution limits, i.e., \bar{a}_1^∞ and \bar{a}_2^∞ , for the three cases that we considered. $(R_{1nz/\varepsilon})_{1,2}$ is the ratio of the infinite dilution partial molar energy parameter for component 1 for QMRs at $k_{12} = 0.23$ over the same property at $k_{12} = 0$ [$(R_{1nz/\varepsilon})_{1,2} = \bar{a}_{1,k_{12}=0.23}^{\text{QMR}}/\bar{a}_{1,k_{12}=0}^{\text{QMR}}$]. $(R_{2nz/\varepsilon})_{1,2}$ gives an analogous result but for component 2 [$(R_{2nz/\varepsilon})_{1,2} = \bar{a}_{2,k_{12}=0.23}^{\text{QMR}}/\bar{a}_{2,k_{12}=0}^{\text{QMR}}$]. Notice that increasing k_{12} from zero to 0.23 implied a simultaneous modification of the values for \bar{a}_1^∞ and \bar{a}_2^∞ , i.e., QMRs do not make it possible to independently control either of the infinite dilution limits. We set the value of $k_{12} = 0.23$ so that a significant departure from the values of \bar{a}_1^∞ and \bar{a}_2^∞ at $k_{12} = 0$ would occur. This is clear from the values of $(R_{1nz/\varepsilon})_{1,2}$ and $(R_{2nz/\varepsilon})_{1,2}$, which Table F2 reports. $(R_{1\text{cubic}/nz})_{1,2}$ is analogous to $(R_{1nz/\varepsilon})_{1,2}$ but compares instead cubic rules to QMRs with nonzero interaction parameter [$(R_{1\text{cubic}/nz})_{1,2} = \bar{a}_{1,\text{sys}12}^{\text{CMR}}/\bar{a}_{1,k_{12}=0.23}^{\text{QMR}}$]. We set the cubic interaction parameters at values such that one of the infinite dilution ends is identical to the corresponding end for QMRs with nonzero interaction parameters [$(R_{1\text{cubic}/nz})_{1,2} = 1.00$], while a significant difference takes place at the other end [$(R_{2\text{cubic}/nz})_{1,2} = \bar{a}_{2,\text{sys}12}^{\text{CMR}}/\bar{a}_{2,k_{12}=0.23}^{\text{QMR}} = 0.77$]. Thus, the values for \bar{a}_1^∞ and \bar{a}_2^∞ of Table F2 for cubic rules (or for equivalent MKP rules), i.e., $\bar{a}_{1,\text{sys}12}^{\text{CMR}}$ and $\bar{a}_{2,\text{sys}12}^{\text{CMR}}$, can never be reproduced by QMRs.

Figure F1 shows both the mixture energy parameter and the partial molar energy parameters as functions of the mole fraction of component 1 for system (1, 2) at 333.13 K, for QMRs with zero (QMRz) and nonzero (QMRnz) interaction parameters and for cubic mixing rules (CMRs). All parameter values are those from Table F1 and Table F2. The differences between the

Table F2. Parameters for the System of Components 1 and 2 at 333.13 K

k_{12}	quadratic (eq 1) mixing rule (QMR) parameters for system (1, 2)				$(R_{1nz/\varepsilon})_{1,2}$	$(R_{2nz/\varepsilon})_{1,2}$
	x_1	x_2	$\bar{a}_1/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$	$\bar{a}_2/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$		
0	0	1	$\bar{a}_{1,\text{sys}12}^{\text{QMR}} = -9.157570\text{E}+12$	$1.345094\text{E}+13$		
0	1	0	$3.425969\text{E}+11$	$\bar{a}_{2,k_{12}=0}^{\text{QMR}} = 3.950770\text{E}+12$		
0.23	0	1	$\bar{a}_{1,k_{12}=0.23}^{\text{QMR}} = -1.014504\text{E}+13$	$1.345094\text{E}+13$	1.11	
0.23	1	0	$3.425969\text{E}+11$	$\bar{a}_{2,k_{12}=0.23}^{\text{QMR}} = 2.963296\text{E}+12$		0.75
k_{12}	cubic (eq 6) mixing rule (CMR) and equivalent MKP (eq 5) mixing rule parameters for system (1, 2)				$(R_{1\text{cubic}/nz})_{1,2}$	$(R_{2\text{cubic}/nz})_{1,2}$
	x_1	x_2	$\bar{a}_1/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$	$\bar{a}_2/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$		
0.309373368	0	1	$\bar{a}_{1,\text{sys}12}^{\text{CMR}} = -1.014504\text{E}+13$	$1.345094\text{E}+13$	1.00	
$k_{112} = 0.1506663546$	1	0	$3.425969\text{E}+11$	$\bar{a}_{2,\text{sys}12}^{\text{CMR}} = 2.281738\text{E}+12$		0.77
$(R_{1nz/\varepsilon})_{1,2} = \frac{\bar{a}_{1,k_{12}=0.23}^{\text{QMR}}}{\bar{a}_{1,k_{12}=0}^{\text{QMR}}}$						
$(R_{2nz/\varepsilon})_{1,2} = \frac{\bar{a}_{2,k_{12}=0.23}^{\text{QMR}}}{\bar{a}_{2,k_{12}=0}^{\text{QMR}}}$						
$(R_{1\text{cubic}/nz})_{1,2} = \frac{\bar{a}_{1,\text{sys}12}^{\text{CMR}}}{\bar{a}_{1,k_{12}=0.23}^{\text{QMR}}}$						
$(R_{2\text{cubic}/nz})_{1,2} = \frac{\bar{a}_{2,\text{sys}12}^{\text{CMR}}}{\bar{a}_{2,k_{12}=0.23}^{\text{QMR}}}$						

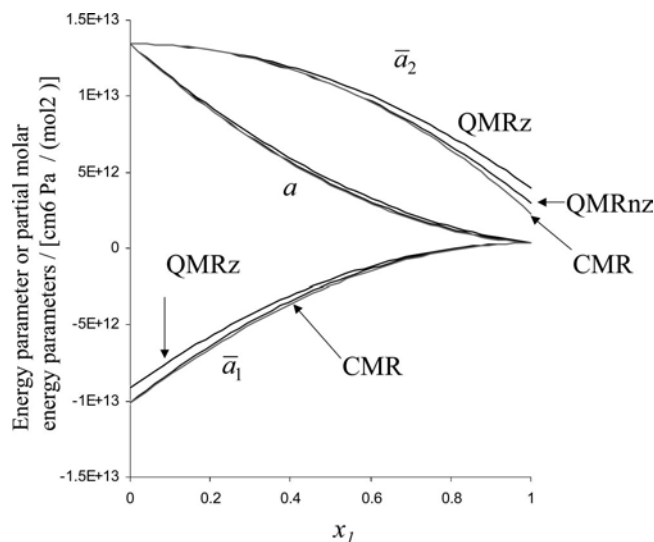


Figure F1. Energy parameter and/or partial molar energy parameters as functions of mole fraction of component 1 for system (1, 2) at 333.13 K. QMRz = quadratic mixing rules (QMRs) with zero interaction parameters. QMRnz = QMRs with a nonzero interaction parameter ($k_{12} = 0.23$). CMR = cubic mixing rules. All parameters are those of Tables F1 and F2.

different mixing rules are not clearly noticeable if we look at the mixture energy parameter (a) curves. The distinction is more clear for the curves corresponding to the partial molar parameters at the infinite dilution ends. For QMRs with a nonzero interaction parameter (QMRnz), parameters \bar{a}_1^∞ and \bar{a}_2^∞ are less than the corresponding values at $k_{12} = 0$. The CMR \bar{a}_2^∞ is less than \bar{a}_2^∞ for QMRs, while, because we imposed it, \bar{a}_1^∞ is the same for CMRs and QMRs with $k_{12} = 0.23$ (QMRnz). Regardless of the k_{12} value used for QMRs, it is impossible for QMRs to simultaneously reproduce the values for \bar{a}_1^∞ and \bar{a}_2^∞ that Figure F1 shows for CMRs. Thus, Figure F1 illustrates the higher flexibility of CMRs with respect to QMRs.

Table F3 is analogous to Table F2 and applies to the system (1, 3). The value 0.28 for k_{13} within QMRs implies a significant departure from the situation where k_{13} is set to zero. We specially notice this when component 3 is infinitely diluted in component 1 [$(R_{3nz/2})_{1,3} = \bar{a}_{3,k_{13}=0.28}^\infty / \bar{a}_{3,k_{13}=0}^\infty = 0.71$]. Also, the parameter values for CMRs imply a significant departure from QMRs with $k_{13} = 0.28$ at one of the infinite dilution limits [$(R_{3cubic/nz})_{1,3} = \bar{a}_{3,sys13}^\infty / \bar{a}_{3,k_{13}=0.28}^\infty = 0.70$] and no departure at all at the opposite end, because we imposed it [$(R_{1cubic/nz})_{1,3} = \bar{a}_{1,sys13}^\infty / \bar{a}_{1,k_{13}=0.28}^\infty = 1$].

Figure F2 is analogous to Figure F1 but for the system (1, 3). This figure corresponds to Table F3. Although Table F3 shows significant differences among QMRs with zero k_{13} , QMRs with nonzero k_{13} , and CMRs, these are hard to see in Figure F2 because of the wide variation ranges for both the mixture energy parameter and the partial molar energy parameters.

Figure F3 shows the energy parameter and the partial molar energy parameters for system (2, 3) at 333.13 K as a function of the mole fraction of component 2. Table F4 gives the interaction parameters for this system. For QMRs, significant differences take place when changing k_{23} from 0 to -0.43 . CMR interaction parameter values are such that \bar{a}_2^∞ is the same as that for QMRs with $k_{23} = -0.43$, while the difference is very important for \bar{a}_3^∞ . Also, in this case, there is no value for k_{23} used for QMRs that is able to reproduce the behavior depicted in Figure F3 for CMRs.

F.3. Tests for Equation 30. The pure-compound and interaction parameter values in Tables F1–F4 make it possible to perform a number of tests on eq 30, as follows.

Table F3. Parameters for the System of Components 1 and 3 at 333.13 K

quadratic (eq 1) mixing rule (QMR) parameters for system (1, 3)						
k_{13}	x_1	x_3	$\bar{a}_1/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$	$\bar{a}_2/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$	$(R_{3nz/2})_{1,3}$	$(R_{3cubic/nz})_{1,3}$
0	0	1	$\bar{a}_{1,k_{13}=0}^{\infty, \text{QMR}} = -2.028958\text{E}+14$	2.202698E+14		
0	1	0	3.425969E+11	$\bar{a}_{3,k_{13}=0}^{\infty, \text{QMR}} = 1.703138\text{E}+13$		
0.28	0	1	$\bar{a}_{1,k_{13}=0.28}^{\infty, \text{QMR}} = -2.077605\text{E}+14$	2.202698E+14	1.02	
0.28	1	0	3.425969E+11	$\bar{a}_{3,k_{13}=0.28}^{\infty, \text{QMR}} = 1.216667\text{E}+13$		0.71
cubic (eq 6) mixing rule (CMR) and equivalent MKP (eq 5) mixing rule parameters for system (1, 3)						
k_{13}	x_1	x_3	$\bar{a}_1/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$	$\bar{a}_2/[(\text{cm}^6 \text{ Pa})/\text{mol}^2]$	$(R_{3cubic/nz})_{1,3}$	$(R_{3cubic/nz})_{1,3}$
0.385042156	0	1	$\bar{a}_{1,sys13}^{\infty, \text{CMR}} = -2.077605\text{E}+14$	2.202698E+14	1.00	
k_{113}	1	0	3.425969E+11	$\bar{a}_{3,sys13}^{\infty, \text{CMR}} = 8.516666\text{E}+12$		0.70
-0.0373223334						

$$(R_{1nz/2})_{1,3} = \frac{\bar{a}_{1,k_{13}=0.28}^{\infty, \text{QMR}}}{\bar{a}_{1,k_{13}=0}^{\infty, \text{QMR}}} = \frac{\bar{a}_{1,sys13}^{\infty, \text{CMR}}}{\bar{a}_{1,k_{13}=0.28}^{\infty, \text{QMR}}}$$

$$(R_{3cubic/nz})_{1,3} = \frac{\bar{a}_{3,sys13}^{\infty, \text{CMR}}}{\bar{a}_{3,k_{13}=0.28}^{\infty, \text{QMR}}}$$

$$(R_{3cubic/nz})_{1,3} = \frac{\bar{a}_{3,sys13}^{\infty, \text{CMR}}}{\bar{a}_{3,k_{13}=0.28}^{\infty, \text{QMR}}}$$

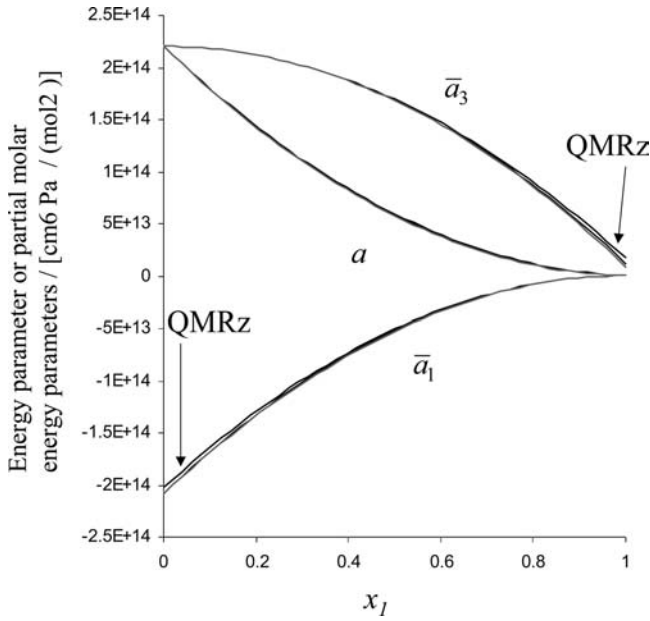


Figure F2. Energy parameter and/or partial molar energy parameters as functions of mole fraction of component 1 for system (1, 3) at 333.13 K. QMRz = quadratic mixing rules (QMRs) with zero interaction parameters. This figure also shows curves for QMRs with a nonzero interaction parameter ($k_{13} = 0.28$) and curves for cubic mixing rules. All parameters are those of Tables F1 and F3.

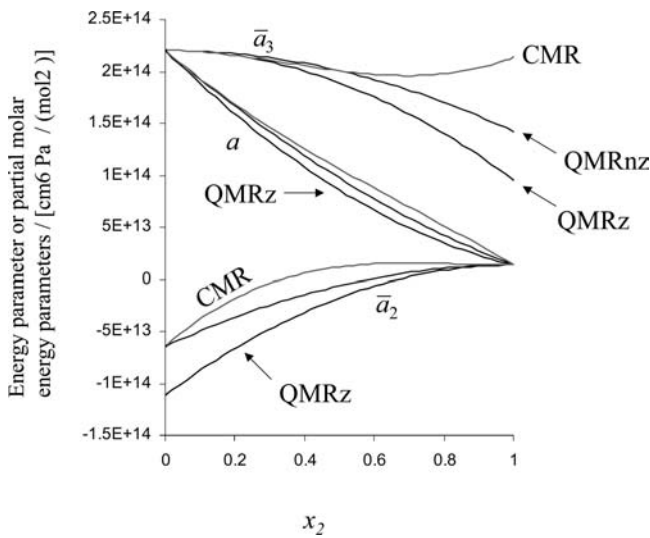


Figure F3. Energy parameter and/or partial molar energy parameters as functions of mole fraction of component 2 for system (2, 3) at 333.13 K. QMRz = quadratic mixing rules (QMRs) with zero interaction parameters. QMRnz = QMRs with a nonzero interaction parameter ($k_{23} = -0.43$). CMR = cubic mixing rules. All parameters are those of Tables F1 and F4.

F.3.1. Quadratic Limit. The relevant interaction parameter values for this test, among all values that Tables F2, F3, and F4 show, are $k_{12} = 0.23$, $k_{13} = 0.28$, and $k_{23} = -0.43$.

MKP rules (eq 5) give the quadratic limit if l_{ij} is set equal to zero in eq 5 for all ij pairs ($M_{st} = 0$ in eq 13). Cubic mixing rules also give the quadratic limit if, as we state in Appendix A, we define a_{ijk} as follows (for all possible (i, j, k) combinations):

$$a_{ijk}^{quad} = \frac{a_{ij} + a_{ik} + a_{jk}}{3} = A_{ijk}^{quad} \quad (A-2a)$$

where a_{ij} corresponds to eq 2. We will verify for the system (1, 2, 3), when considered quadratic, whether, when using eq A-2a

Table F4. Parameters for the System of Components 2 and 3 at 333.13 K

quadratic (eq 1) mixing rule (QMR) parameters for system (2, 3)		cubic (eq 6) mixing rule (CMR) and equivalent MKP (eq 5) mixing rule parameters for system (2, 3)	
k_{23}	x_2	x_3	
0	0	1	$\bar{a}_2^{QMR} = -1.114059E+14$
0	1	0	$\bar{a}_3^{QMR} = 9.541293E+13$
-0.43	0	1	$\bar{a}_2^{QMR} = -6.459448E+13$
-0.43	1	0	$\bar{a}_3^{QMR} = 1.345094E+13$
			$\bar{a}_2^{QMR, k_{23}=-0.43} = 1.422244E+14$
			$\bar{a}_3^{QMR, k_{23}=-0.43} = 1.422244E+14$
			$(R_{2,net})_{2,3} = 0.58$
			$(R_{3,net})_{2,3} = 1.49$
			$(R_{2,net})_{2,3} = 1.00$
			$(R_{3,net})_{2,3} = 1.50$
			$\bar{a}_2^{CMR} = -6.459448E+13$
			$\bar{a}_3^{CMR} = 2.133366E+14$
			$\bar{a}_2^{CMR, k_{23}=-0.43} = 1.345094E+13$
			$\bar{a}_3^{CMR, k_{23}=-0.43} = 1.345094E+13$
			$(R_{2,net})_{2,3} = \frac{\bar{a}_2^{CMR}}{\bar{a}_2^{QMR}} = \frac{\bar{a}_2^{CMR, k_{23}=-0.43}}{\bar{a}_2^{QMR, k_{23}=-0.43}} = -0.43$
			$(R_{3,net})_{2,3} = \frac{\bar{a}_3^{CMR}}{\bar{a}_3^{QMR}} = \frac{\bar{a}_3^{CMR, k_{23}=-0.43}}{\bar{a}_3^{QMR, k_{23}=-0.43}} = -0.43$

Table F5. Verification of the Quadratic Limit for Equation 30^a

from Table F1	from eq 2
$a_{11} = 0.3425969207000000000000 \times 10^{12}$	$a_{12} = 1652946231060.2352737$
$a_{22} = 0.1345093728000000000000 \times 10^{14}$	$a_{13} = 6254631304683.5483505$ (*)
$a_{33} = 0.2202698116000000000000 \times 10^{15}$	$a_{23} = 77837665377366.552505$
from Tables F2, F3, and F4	
$k_{12} = 0.23, k_{13} = 0.28, k_{23} = -0.43$	
from (*) and eq A-2 for the ternary case: $A_{123} = 0.28581747637703445376 \times 10^{14}$ (***)	
note: this result comes from using eq A-2 only once, with indices 1, 2, and 3	
from eqs (*) and eq A-2 for all binary parameters	
$A_{1,1,2} = 0.12161631276068235158 \times 10^{13}$	$A_{1,3,3} = 0.77593024736455698900 \times 10^{14}$
$A_{1,2,2} = 0.55856099140401568491 \times 10^{13}$	$A_{2,2,3} = 0.56375422678244368337 \times 10^{14}$ (**)
$A_{1,1,3} = 0.42839531766890322337 \times 10^{13}$	$A_{2,3,3} = 0.12531504745157770167 \times 10^{15}$
from (*), (**), and eq 30: $A_{123} = 0.28581747637703445377 \times 10^{14}$	
note: this result [which is equal to (***)] comes from using eq A-2 six times, always with two (out of three) indices having equal values.	

^a The interaction parameters are dimensionless. All other variables in this table have units [(cm⁶ Pa)/mol²].

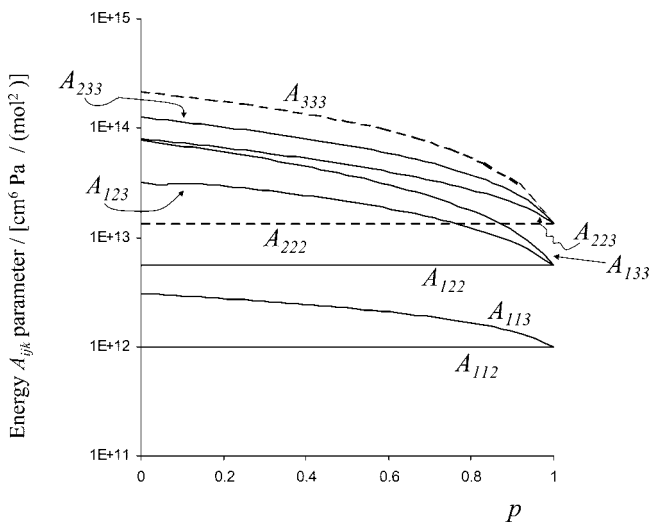


Figure F4. Evolution of the ternary parameter A_{123} (eq 30) as component 3 increases its degree of similarity with respect to component 2 in a linear fashion. This process takes place as p changes from zero to 1. At this limit, component 3 becomes identical to component 2. All parameters are those of Table F6. Binary variables A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} are calculated from eq 31 at $T = 333.13$ K.

for calculating the binary parameters A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} , we get the right value for A_{123} from eq 30. Such a right value is the same as the value that eq A-2 gives when the indices have values 1, 2, and 3. Table F5 shows that indeed eq 30 gives a result equal to that of eq A-2 when applied to the ternary system. Therefore, eq 30 used with eq 6 consistently gives a quadratic behavior for multicomponent mixtures when all binary subsystems behave quadratically. In a previous preliminary work¹⁹ that had the same goals as this work, we proposed a prediction strategy for parameter A_{123} that was more elaborate than the options that Mathias et al.⁵ considered before discarding a mixing rule such as eq 6. However, we discarded in this work our former strategy¹⁹ because it did not give a quadratic behavior for multicomponent mixtures when all binary subsystems behaved quadratically.

F.3.2. Invariance. Now, considering that the ternary system (1, 2, 3) behaves according to the cubic mixing rules of eq 6, let us make component 3 become increasingly similar to component 2, as a parameter p changes from zero to 1, such that, at $p = 0$, the system parameters are those of Table F1 for the pure compounds and those of Tables F2–F4 for the three-index binary parameters k_{ijk} , while, at $p = 1$, component 3 has become identical to component 2. Let us impose a transition, between the two extreme situations, linear with respect to p as

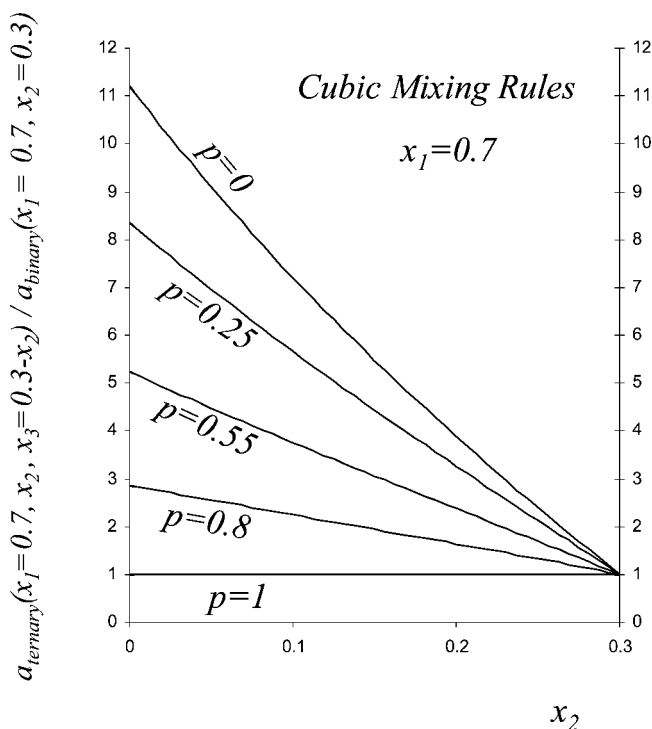


Figure F5. Cubic mixing rules (eq 6): ratio of energy parameter of the ternary system (1, 2, 3) over the energy parameter of the binary system (1, 2) as a function of mole fraction of component 2 in the ternary system. Evolution as component 3 increases its degree of similarity with respect to component 2 in a linear fashion. This process takes place as p changes from zero to unity. At this limit, component 3 becomes “identical” to component 2. All parameters are those of Table F6. Binary variables A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} are calculated from eq 31 at $T = 333.13$ K. Mole fraction for component 1 = $x_1 = 0.7$. a_{123} (= A_{123}) is from eq 30.

Table F6 shows. Notice, from Table F6, that, at $p = 1$, k_{113} becomes equal to k_{112} , k_{133} becomes equal to k_{122} , and, finally, k_{223} and k_{233} become equal to k_{222} , i.e., equal to zero.

F.3.2.1. Invariance of Parameters. Figure F4 shows the evolution of the binary A_{ijk} parameters and of the ternary A_{123} parameter in the range from zero to 1 for parameter p . We generated Figure F4 using the parameters of Table F6 and eq 31 for the binary A_{ijk} parameters and of eq 30 for A_{123} . We observe that, at $p = 1$, A_{233} becomes equal to A_{223} and to A_{222} , i.e., to a_2 ; A_{133} becomes equal to A_{122} ; A_{113} becomes equal to A_{112} ; and the ternary parameter A_{123} becomes equal to A_{122} . This is a verification of the invariance of eq 30, i.e., eq 30 gives the right binary value for the ternary parameter A_{123} when two components become identical. Notice that Figure F4 also shows that the pure-compound parameter A_{333} becomes equal to the

Table F6. Equations for a Linear Transition Where Component 3 Becomes Increasingly Similar to Component 2 as Parameter p Goes from Zero to Unity

$a_1 = 0.3425969207 \times 10^{12} \text{ [(cm}^6 \text{ Pa)/mol}^2]$	(Table F1)
$a_2 = 0.1345093728 \times 10^{14} \text{ [(cm}^6 \text{ Pa)/mol}^2]$	
$a_3 = [(1 - p)0.2202698116 \times 10^{15} + p a_2] \text{ [(cm}^6 \text{ Pa)/mol}^2]$	
$k_{112} = 0.1506635459$	(Table F2)
$k_{122} = -0.4113706603$	
$k_{113} = (1 - p)(-0.3732233339 \times 10^{-1}) + p k_{112}$	(Table F3)
$k_{133} = (1 - p)(-2.040359061) + p k_{122}$	
$k_{223} = (1 - p)(-1.344415570) + p (0.)$	(Table F4)
$k_{233} = (1 - p)(-0.4447156812) + p (0.)$	

pure-component parameter A_{222} at $p = 1$, according to the equation for a_3 as a function of p of Table F6.

F.3.2.2. Invariance of the Coupled Equations 6 and 30.

Figure F4 illustrates a situation of parametric invariance where the system composition does not play a role. On the other hand, Figure F5 shows how eq 30 behaves when coupled to eq 6, i.e., in Figure F5 we observe the performance of the coupled equations in a situation where the (variable) system composition has an influence. In other words, Figure F5 tests the invariance of the cubic mixing rules (eq 6) when combined with eq 30, used for predicting ternary interactions. Figure F5 shows the ratio of the energy parameter calculated as a function of x_2 , at $T = 333.13$ K, for system (1, 2, 3) at $x_1 = 0.7$ (a_{ternary}) over the energy parameter calculated for the binary system (1, 2) at $x_1 = 0.7$ ($x_2 = 0.3$) (a_{binary}). Notice that a_{binary} is a constant in Figure F5. Both energy parameters are calculated using cubic mixing rules (eq 6), with eq 30 used for the calculations for the ternary mixture. The parameters are those of Table F6. We observe that, as component 3 becomes more similar to component 2, i.e., as p goes from zero to 1, the ratio of mixture energy parameters approaches 1, regardless of the relative concentrations of components 2 and 3 in the system. Figure F5 thus reflects the invariance of eq 6 (cubic mixing rules) coupled to eq 30 (recipe for A_{123}). We should observe such invariance also in the behavior of the partial molar parameters.

F.3.2.3. Invariance of Partial Molar Parameters.

Figure F6 shows, for a ternary mixture of components 1, 2, and 3 at set composition, the evolution of the partial molar parameters as component 3 becomes increasingly similar to component 2. For reference, we included the curve for the energy parameter (a) for the mixture. We observe that the partial parameter for component 3 tends to the partial parameter for component 2 as p approaches 1. Thus, Figure F6 also verifies the invariance of the coupled eqs 6 and 30.

Finally, we show in Figure F7 four parametric curves, where the varying parameter is again parameter p for which we again covered the range from zero to 1. A given curve in the figure shows the partial molar parameter of component 3 plotted against the partial molar parameter of component 2. For reference, Figure F7 also shows the identity line where \bar{a}_2 equals \bar{a}_3 . We indicate in Figure F7 the location of the curve end points corresponding to $p = 0$ and to $p = 1$. We observe that, for a given curve, the end point of $p = 1$ is located on the identity line where \bar{a}_2 equals \bar{a}_3 . Consider, for instance, the mixtures with composition $x_1 = 0.1$, $x_2 = 0.3$, and $x_3 = 0.6$ and composition $x_1 = 0.1$, $x_2 = 0.6$, and $x_3 = 0.3$. Both mixtures have the same concentration of component 1. When, at $p = 1$, component 3 becomes identical to component 2, both end points become coincident. This means not only that \bar{a}_2 equals \bar{a}_3 but also that the values of \bar{a}_2 ($=\bar{a}_3$) are the same for both mixtures, i.e., they are independent from the relative concentrations of components 2 and 3. Figure F7 is, therefore, also indicative of the invariance of eq 6 coupled to eq 30. Notice in Figure F7 that the mixtures with compositions $x_1 = 0.7$, $x_2 = 0.2$, and $x_3 = 0.1$ and $x_1 = 0.7$, $x_2 = 0.1$, and $x_3 = 0.2$ also show the

behavior we have just described for the mixtures with $x_1 = 0.1$. The end point at $p = 1$ is different for the pair of curves of $x_1 = 0.7$ with respect to the pair at $x_1 = 0.1$, as expected.

We conclude that the mixing rules that are cubic with respect to mole fraction of eq 6 coupled to eq 30, which predicts ternary three-index parameters from binary three-index parameters, are invariant.^{2,3} Figures F4–F7 are consistent with this conclusion.

F.4. Similarities and Differences between the MKP Mixing Rules and the CMRs When Applied to the System of Components (1, 2, 3).

To fix ideas, we will compare calculation results for the MKP and CMRs when the binary subsystems are equivalent for both mixing rules. For the ternary system of components (1, 2, 3), and using the three-index binary parameters of Tables F2–F4 and the pure-compound parameters of Table F1, we calculate parameters A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} from eq 31, then parameter A_{123} from eq 30, and solve eq 31, for k_{123} . The result is $k_{123} = -2.135341083$. For this value of k_{123} , Figure F8 compares the cubic mixing rules (eq 6) and the MKP (eq 5) mixing rule. Figure F8 corresponds to a ternary mixture of components 1, 2, and 3 at $x_3 = 1/3$ and at varying concentrations for components 1 and 2. A given curve, with the exception of the “Mixt.” curve, corresponds to the ratio of the partial molar-parameter value given by the cubic rules over the value given by the MKP rule, for a given component. The Mixt. curve is analogous to the other curves, but it involves the mixture energy parameter. The left end of Figure F8

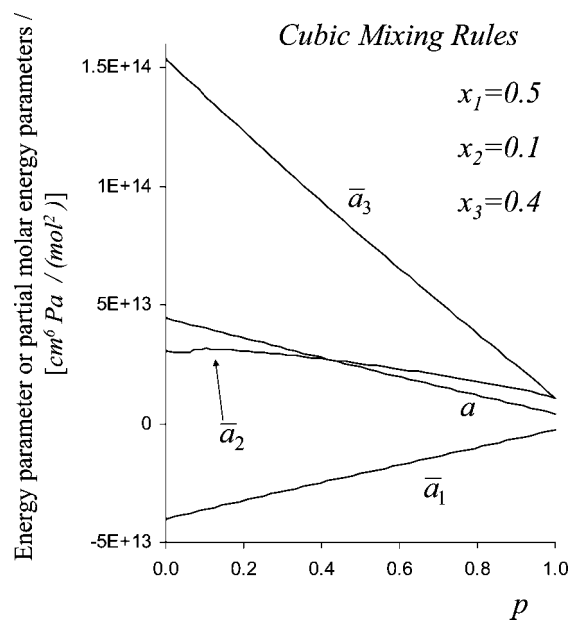


Figure F6. Cubic mixing rules (eq 6): evolution of the partial molar energy parameters, at constant composition, for system (1, 2, 3), as component 3 increases its degree of similarity with respect to component 2 in a linear fashion. This process takes place as p changes from zero to unity. At this limit, component 3 becomes “identical” to component 2. All parameters are those of Table F6. Binary variables A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} are calculated from eq 31 at $T = 333.13$ K. $x_1 = 0.5$, $x_2 = 0.1$, $x_3 = 0.4$; a_{123} ($=A_{123}$) is from eq 30.

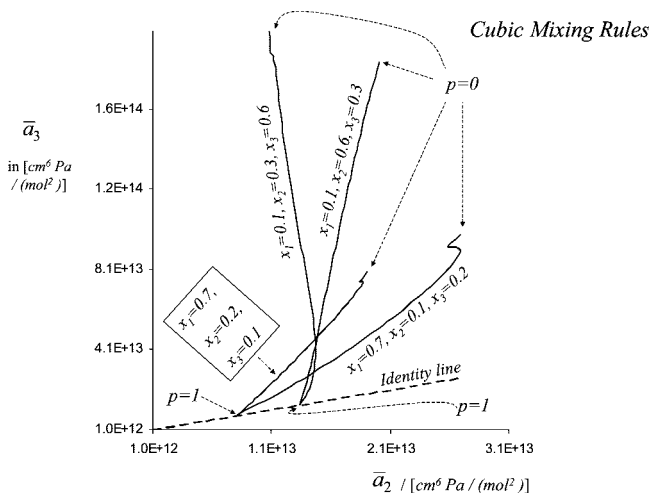


Figure F7. Cubic mixing rules (eq 6), parametric plot: evolution of the partial molar energy parameter for component 3 as a function of the partial molar energy parameter of component 2, for system (1, 2, 3), at four different overall mixture compositions, as component 3 increases its degree of similarity with respect to component 2 in a linear fashion. This process takes place as p changes from zero to 1. At this limit, component 3 becomes identical to component 2. All parameters are those of Table F6. Binary variables A_{112} , A_{122} , A_{113} , A_{133} , A_{223} , and A_{233} are calculated from eq 31 at $T = 333.13$ K. a_{123} ($=A_{123}$) is from eq 30.

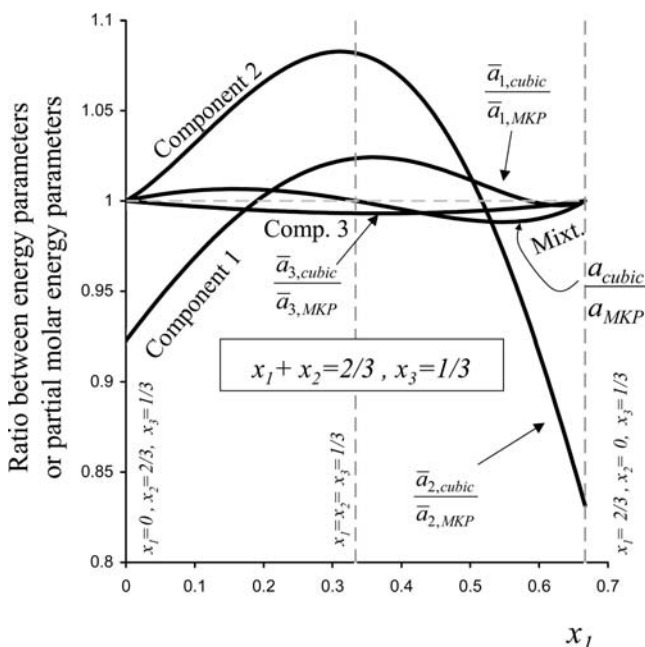


Figure F8. Comparison between the MKP mixing rule (eq 5) and the cubic mixing rules (eq 6) coupled to eq 30 for prediction of ternary parameters: $k_{123} = -2.135341083$; $T = 333.13$ K; system (1, 2, 3); $x_3 = 1/3$. All parameters are those of Tables F1–F4.

corresponds to a mixture where component 1 is infinitely diluted in a binary mixture of components 2 and 3. For these two last components, we observe that the corresponding ratios equal 1 at $x_1 = 0$. This reflects the fact that the values of the interaction parameters of Table F4 for the binary (2, 3) system are equivalent for the MKP and the cubic rule. This is also the reason for the unity value at $x_1 = 0$ for the Mixt. ratio. The right end of Figure F8 corresponds to a binary mixture of components 1 and 3 where component 2 is infinitely diluted. For an equimolar ternary mixture ($x_1 = x_2 = x_3 = 1/3$), we observe that the Mixt. ratio equals 1. We imposed this condition when deriving eq 30, which led to the k_{123} value that we used

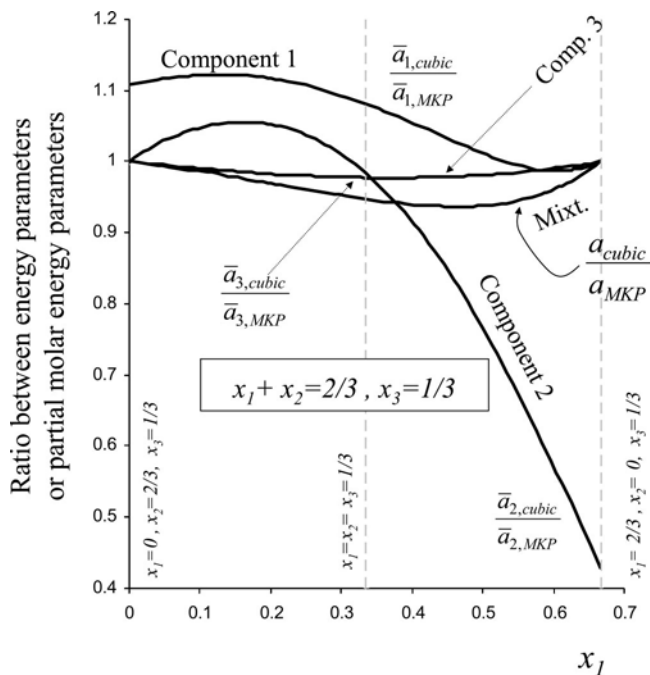


Figure F9. Comparison between the MKP mixing rule (eq 5) and the cubic mixing rules (eq 6): $k_{123} = -1.0$; $T = 333.13$ K; system (1, 2, 3); $x_3 = 1/3$. All parameters are those of Tables F1–F4. Equation 30 was not used to generate this figure.

in Figure F8. This figure illustrates the fact that the MKP rules (eq 5) and the cubic mixing rules (eq 6), coupled to eq 30, are different models that have some common features: they are identical for binary mixtures, and for ternary equimolar mixtures they give the same mixture value for the energy parameter but not for the partial parameters. For the specific case of Figure F8, we observe that the partial molar parameters have values of the same order of magnitude for both models, since all ratios are in the order of 1. An essential difference between the MKP rule and the CMRs is that, while the MKP rule is limited by its pair-based nature, the ternionwise-additive CMRs can be used in a parametrically pair-based mode (eq 6 with eq 30) or with three-index ternary parameters fit from ternary experimental information, i.e., in a ternionwise-additivity mode. We can also use CMRs in a hybrid mode for multicomponent systems, i.e., with ternary parameters fit against experimental information for some of the ternary subsystems, as well as with ternary parameters predicted from eq 30 for the ternary subsystems without experimental information available.

Notice that, in Figure F8, the differences between the MKP rules (eq 5) and the cubic mixing rules (eq 6), coupled to eq 30, correspond to a ternary system that has an exacerbated asymmetry. In contrast, for the real ternary system of Appendix E, we found no differences between a MKP-like model for the excess molar volume and a CMR-like model coupled to an equation analogous to eq 30 for predicting ternary interaction parameters.

Figure F9 is analogous to Figure F8. The difference is that we generated Figure F9 without using eq 30 for predicting k_{123} . The value for k_{123} in Figure F9 is $k_{123} = -1$. The purpose of Figure F9 is to illustrate the case of a system where we do not impose the match of eq 29. Figure F9 shows a result that one would obtain from fitting experimental data available for the ternary system, i.e., Figure F9 corresponds to a situation where we would not need to predict the value for k_{123} using eq 30 or other prediction strategy. We observe, when comparing Figures F8 and F9, that the changes are significant for components 1

and 2, but not for component 3, i.e., for the component that is never at infinite dilution under the constraints of both figures. We also notice in Figure F9 that, for the ternary equimolar mixture, the mixture parameter obtained using the cubic mixing rule does not equal the value for the MKP rules. This is a consequence of not having used eq 30 in the generation of Figure F9.

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