

New Empirical Model for the Excess Gibbs Free Energy: Correlation of Liquid–Liquid Equilibrium for Island-Type Ternary Systems

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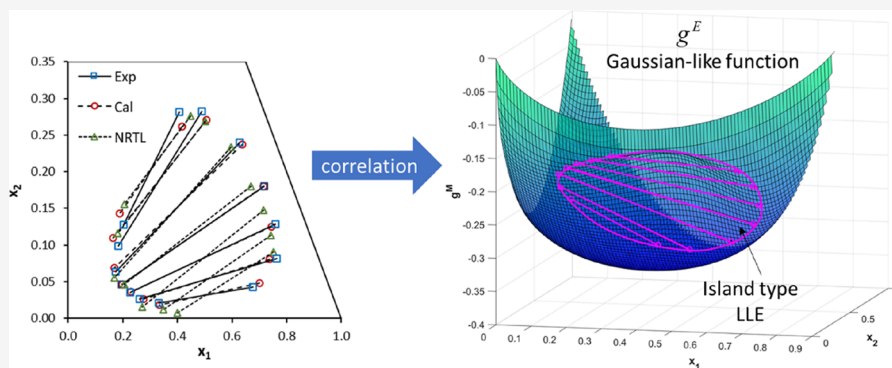
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ABSTRACT: Island-type ternary systems, at constant temperature and pressure, present a closed liquid–liquid miscibility gap in the ternary region while the three binary subsystems are completely miscible. Correlation of this type of phase equilibrium behavior is a challenge. Accordingly, correlation results using classical activity coefficient models (as NRTL or UNIQUAC) are not usually reported in the literature for this type of system. In this paper, the limitations of the NRTL model to correlate LLE data sets for island-type ternary systems are discussed. The lack of flexibility and the uncertainty in the equilibrium solution are the main problems. A new expression for the excess Gibbs free energy is proposed to overcome these limitations with a practical aim. The empirical model proposed has two contributions: a Gaussian-like function and a non-ideal homogeneous term. Both are combined to fulfill the topological requirements of the Gibbs energy of mixing surfaces for island-type ternary systems according to the Gibbs common tangent plane criterion along with the phase stability analysis. The model proposed avoids the uncertainty problems of classical activity models for island-type ternary systems. Additionally, in this model, the relations between the parameter values and the calculated LLE are easily interpreted, which allows generating good initial values and guiding the correlation algorithm when convergence problems occur. Some island-type ternary systems have been selected to illustrate this subject.

1. INTRODUCTION

Liquid–liquid equilibrium (LLE) for island-type or type 0 ternary systems in Treybal classification¹ at constant temperature (T) and pressure (P) presents a ternary heterogeneous region (LL) surrounded by a homogenous one (L), and thus the three binary subsystems involved are completely miscible. The binodal curve defined by this “closed loop” LLE region has two plait points that limit the tie-lines at each end.

Island-type ternary systems are frequently the result of the simultaneous presence of a weak acid and a base that form a soluble salt with a lower miscibility rather than the free base or the free acid. Becker and Richter² determined the binodal curves for island-type ternary systems formed by carboxylic acid (1) + tertiary amine (2) + hydrocarbon (3), like the dichloroacetic acid (1) + 1-methyl-2-pyrrolidinone (2) + 1-hexene (3) mixture at 293.15, 303.15, and 313.15 K. “Closed loop” miscibility gaps can also occur in systems containing two polymers and a low-molecular-weight solvent.³

The correlation of island-type LLE data is a challenge due to the topological requirements of the Gibbs energy of mixing (g^M) surface. In this regard, the g^M curves for the three binary subsystems included in the ternary system must be homogeneous (L), and therefore convex, over the entire composition range. However, at the same time, the g^M surface must present a ternary heterogeneous region (LLE), where common tangent planes must exist connecting the two conjugated equilibrium compositions. Moreover, these tangent planes must not intersect the g^M surface at any other composition in order to guarantee the minimum energy for

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the system and thus the stability of the solution. It is evident that these are very demanding requirements for the g^M function.

In this regard, it is relevant that equilibrium databases such as DECHEMA Chemistry Data Series⁴ do not present NRTL⁵ nor UNIQUAQ⁶ binary interaction parameters for island-type ternary systems while they provide regression results for all type 1 and 2 ternary systems (Treybal classification¹). Moreover, most papers dealing with island-type ternary systems only provide experimental LLE data, but they do not usually report results of data fitting obtained with any suitable model.^{2,3}

Moreover, as far as we know, the regression tools included in commercial software packages for chemical process design as CHEMCAD⁷ or Aspen Plus⁸ are not specifically prepared to correlate LLE data sets of these systems. In other words, they do not include the possibility of imposing total miscibility for the three binary subsystems while the LLE ternary region is fitted, as required in island-type ternary systems to avoid inconsistent correlation results.⁹ Only very few papers have been found that provide correlation results for island-type ternary systems. For example, Novák et al.¹⁰ employed the regular-solution model with temperature-dependent parameters to describe critical curves of LLE in ternary systems where the appearance of a closed loop LLE region was discussed. Řehák et al.¹¹ used the NRTL⁵ and Wilson¹² models, both modified with a ternary correction, for the regression of the phenol (1) + tetrahydrofuran (2) + water (3) system at 423.15 K. Olaya et al.¹³ and Carbonell-Hermida et al.⁹ applied the NRTL model⁵ for the LLE correlation of some island-type ternary systems: water (1) + dimethyl sulfoxide (2) + tetrahydrofuran (3) at 293.15 K⁴ and trichloroacetic acid (1) + antipyrine (2) + water (3) at 303.15 K.⁴ Zuber et al.¹⁴ studied the application of a stochastic algorithm to fit the experimental LLE data of the first of these two systems using the NRTL and UNIQUAC models.

In principle, classical activity coefficient models such as NRTL⁵ are capable of generating g^M surfaces with the basic requirements of island-type ternary systems. Nevertheless, the lack of flexibility of these models for this specific application can only produce rough correlation results in most cases and many uncertainty problems. These difficulties are added to those of a non-linear optimization problem, where some local solutions, with similar estimation of composition, can be found.^{15–17} Figure 1 shows different possibilities for binary g^M curves. Figure 1a presents a homogeneous (convex in the complete composition range) g^M curve. Figure 1b shows a g^M curve with a good definition of the LLE points (common tangent line) that correspond with phases I and II. Figure 1c shows a poor definition of the common tangent line (LLE). Finally, in Figure 1d, a g^M curve with two metastable LLE solutions has been represented. In type 1 or 2 ternary systems, only when the differences in compositions between the two conjugated equilibrium points are small, the g^M curve becomes very linear between the common tangent points (tie-line ends), producing uncertainty in the LLE solution (as in Figure 1c). However, for island-type ternary systems, this problem is almost always present, regardless of the proximity of the end of the tie-lines. The reason seems to be that for classical activity coefficient models, it is difficult to provide a g^M function (surface for ternary systems) with a compatible topology with sectional cuts as the one represented in Figure 1b (good definition of the common tangent points) when the g^M curves

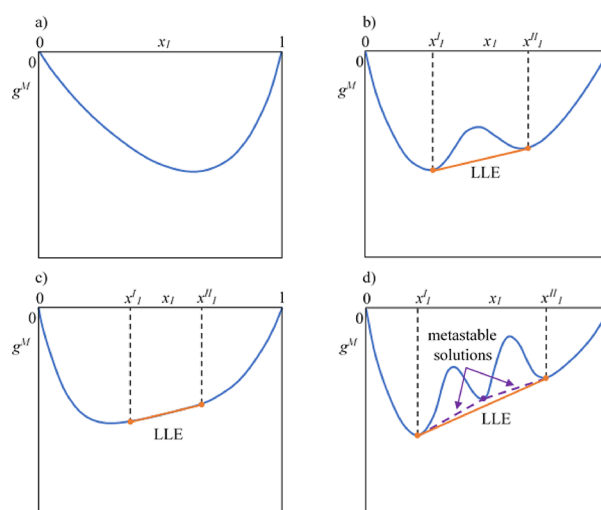


Figure 1. Different possibilities for g^M curves in binary mixtures: (a) homogeneous, (b) heterogeneous (good definition of the LLE), (c) heterogeneous (poor definition of the LLE), and (d) some metastable LLE solutions.

for the three binary subsystems must be necessarily convex in all the composition interval, as the one represented in Figure 1a. It has been checked that classical activity coefficient equations, as NRTL, tend to provide g^M cuts in the ternary region as the one represented in Figure 1c. In these cases, the convex/concave transitions required by the Gibbs common tangent plane equilibrium condition are almost inappreciable, with the aforementioned uncertainty problems.

This paper aims to advance the search for a possible solution to this problem. For this, experimental data for some island-type ternary systems, with different shapes for the heterogeneous region, have been selected in order to analyze the problems that arise during the fitting process and look for some practical solutions. First, the NRTL model⁵ was used to correlate the island-type ternary systems selected, and after analyzing the limitations found, an alternative empirical activity coefficient model was proposed and applied.

2. LIMITATIONS OF THE NRTL MODEL IN LLE DATA CORRELATION FOR ISLAND-TYPE TERNARY SYSTEMS

In some previous papers, some limitations of the NRTL equation (representative of classical activity coefficient models) in the correlation of LLE data for island-type ternary systems were discussed.^{9,13} The most evident limitation is its lack of flexibility to reproduce with the required precision the experimental LLE behavior of different island-type ternary systems.

LLE data correlation for this type of system presents a particular difficulty due to the topological requirements of the g^M surface: in the ternary region, a heterogeneous zone must exist where common tangent planes define the conjugated liquid compositions (LLE), while the three binary subsystems must be totally miscible.

It has been previously discussed¹³ that these restrictive conditions, which are required for the g^M function (surface) to describe island-type ternary systems, are only accomplished when the g^M curve for one of the three binary subsystems is much more negative (dissimilar binary system) than the other two g^M binary curves. This is the only way to provide the

required convex/concave transitions in the g^M surface to reproduce the “closed loop” LLE region, while convex g^M curves for the three binary subsystems must be guaranteed. However, it has also been checked that the g^M surface generated in these conditions by classical models as NRTL is extremely flat. Figure 2 shows the g^M surface of the water (1) +

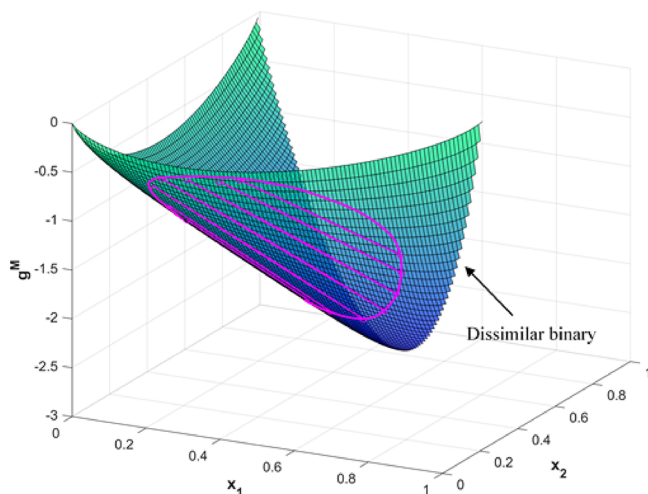


Figure 2. Gibbs energy of mixing g^M surface and tie-lines (NRTL model (ref 9)) for the island-type water (1) + dimethyl sulfoxide (2) + tetrahydrofuran (3) ternary system at 293.15 K. Compositions in mole fractions.

dimethyl sulfoxide (2) + tetrahydrofuran (3) ternary system at 293.15 K⁴ generated with the NRTL model (parameters in ref 9). It can be observed that the g^M surface is almost plane between the equilibrium points and the smooth convex/concave transitions required to reproduce the LLE region (common tangent equilibrium criterion) are barely noticeable. This fact is even more evident by inspection of sectional cuts of the g^M surface in the direction of some calculated tie-lines (Figure 3). This figure shows that the g^M curves are

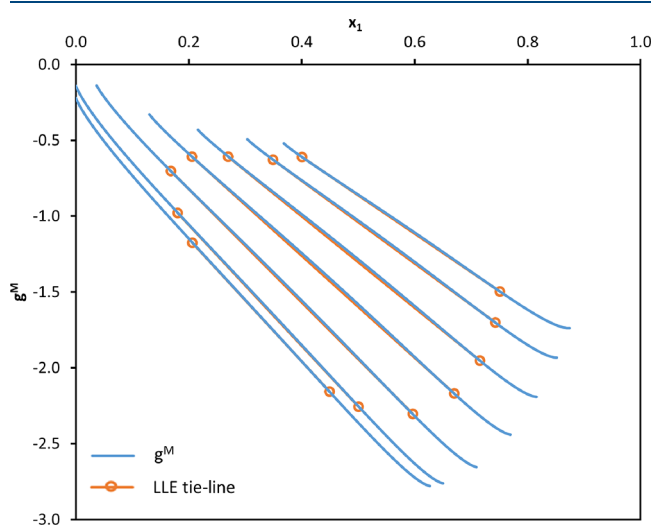


Figure 3. Gibbs minor common tangent criterion for the island-type water (1) + dimethyl sulfoxide (2) + tetrahydrofuran (3) ternary system at 293.15 K. Sectional cuts of the g^M surface (NRTL model (ref 9)) in the direction of calculated tie-lines. Compositions in mole fractions.

considerably linear between the equilibrium points leading to uncertainty in the LLE calculations due to the poor definition of the common tangent points to the g^M function. This uncertainty, shown from the common tangent equilibrium criterion, is also affecting other alternative phase equilibrium conditions such as the isoactivity, frequently used for LLE data correlations.

Attending the several limitations of the NRTL model, and by extension of other classical activity coefficient models, to correlate LLE data for island-type ternary systems, a new set of empirical equations has been proposed. The topological requirements for the Gibbs energy of mixing function to overcome the existing limitations have been considered in the formulation of these equations. The proposed equations can be considered a practical alternative to the classical activity coefficient models for LLE data correlation of island-type ternary systems.

3. PROPOSED CORRELATION PROCEDURE

3.1. Selected Systems. In this paper, experimental data for four island-type ternary systems (one of them at different temperatures) were selected.^{2,4} Table 1 shows these systems

Table 1. Selected Island-Type Ternary Systems at Atmospheric Pressure

system	ternary system	T (K)	ref.
S1	water (1) + dimethyl sulfoxide (2) + tetrahydrofuran (3)	293.15	4
S2	acetic acid (1) + dimethyl formamide (2) + cyclohexene (3)	291.15	2
S3	dichloroacetic acid (1) + 1-methyl-2-pyrrolidinone (2) + 1-hexene (3)	293.15	2
S4	dichloroacetic acid (1) + N-formylpiperidine (2) + cyclohexane (3)	298.15	2

and the temperature conditions. LLE tie-lines have been published for system S1,⁴ whereas for systems S2 to S4, only points on the binodal curve, but no tie-lines, have been experimentally measured,² as far as we know. Thus, the correlation results obtained in the present paper for these last systems can only be used to reproduce such binodal curves but not to calculate LLE tie-lines. Because experimental LLE data for island-type ternary systems are very scarce and also due to the shape and position of the miscibility gaps in systems S2 to S4, the consideration of such systems is of interest in the present work, in spite of not having for them LLE tie-lines. Moreover, only the system S1 had been previously fitted (using the NRTL model) with not very satisfactory results.^{9,13}

3.2. Empirical Model Proposed. With the aim of finding a possible solution to the correlation problem of LLE data for island-type ternary systems, the topological requirements of the g^M were considered. Thus, the proposed equation for the excess Gibbs free energy (g^E) must not introduce discontinuities and, added to the ideal contribution, it must provide a g^M surface compatible with the LLE behavior for island-type ternary systems, satisfying the Gibbs common tangent equilibrium criterion as well as the phase stability test. Several mathematical functions were investigated but, among all of them, only a Gaussian-like function (g^E_C) (eq 1) satisfied all the requirements. This equation is an extension, for ternary systems, of the one proposed in a previous work for the simultaneous VLE data correlation of a binary system with an

ionic liquid.¹⁸ The use of a Gaussian-like function for the excess Gibbs energy allows us to introduce the required convex/concave transition in the Gibbs energy of mixing when added to a homogeneous (ideal or non-ideal) contribution. Moreover, the simple relation existing between the parameters of a Gaussian-like function and the topology of the function itself is a great advantage to control the characteristics of the LLE region, as explained later in this paper.

It should be noted that the g_C^E contribution only affects the ternary region since it vanishes for the binary subsystems as it follows from eq 1. Consequently, a second contribution in the excess Gibbs free energy was needed to modify the g^M function of the three binary subsystems that must be homogeneous, but not necessarily ideal. This contribution (g_H^E) (eq 2) provides a convex function when A , B , and C parameters are positive. This function, added to the ideal Gibbs energy of mixing, generates homogeneous (convex) liquid behavior for the liquid mixtures that can become highly non-ideal depending on the parameter values. It allows the change of orientation of the LLE area providing more flexibility to the model.

$$g_C^E = a \cdot \exp \left[- \frac{b_1(x_1 - c_1)^2 + b_2(x_2 - c_2)^2 + b_3(x_3 - c_3)^2}{x_1^d x_2^e x_3^f} \right] \quad (1)$$

$$g_H^E = (A - 1)x_1 \ln x_1 + (B - 1)x_2 \ln x_2 + (C - 1)x_3 \ln x_3 \quad (2)$$

where x_1 , x_2 , and x_3 are the mole fractions of the components ($x_3 = 1 - x_1 - x_2$), a , b_1 , b_2 , b_3 , c_1 , c_2 , c_3 , d , e , and f are the parameters of the g_C^E contribution, and A , B , and C are the parameters of the g_H^E contribution.

Thus, the proposed model for the excess Gibbs free energy (g^E) (eq 3) and also for the activity coefficient (eq 4) is the result of two contributions: a Gaussian-like function (g_C^E) (eq 1), which modifies the g^M surface by better defining the convex/concave LLE transitions, and the homogeneous Gibbs free energy (g_H^E) (eq 2), which confers flexibility to the model with regard to the homogeneous but non-ideal liquid mixtures.

$$g^E = g_H^E + g_C^E \quad (3)$$

$$\ln \gamma_i = \ln \gamma_{i,H} + \ln \gamma_{i,C} \quad (4)$$

The activity coefficient model given by eq 4 can be deduced by applying eq 5 along with eqs 1–3.

$$\ln \gamma_i = g^E + \left(\frac{\partial g^E}{\partial x_i} \right)_{T,P} - \sum_{j=1}^c x_j \left(\frac{\partial g^E}{\partial x_j} \right)_{T,P} \quad (5)$$

The proposed equations for g^E allow the existence of common tangent planes to the g^M surface at each pair of conjugated equilibrium compositions (tie-lines), which must not intersect the g^M surface at other points. Also, each tangent plane must only contain one LLE equilibrium data (tie-line).

The equations proposed do not consider any classical contribution to the excess Gibbs energy as those given by NRTL or UNIQUAC. However, it should be noticed that the use of the Gaussian-like function given by eq 1 as a contribution to be added to the NRTL equation, with the aim of extending its application to island-type LLE, was also considered in this study. However, this possibility was later

discarded because multiple, and so metastable, LLE solutions arose in many cases (Figure 1d), causing additional problems to find the stable LLE solution. This situation occurs by combination of two concave regions in the g^E function, the one that comes from NRTL (for certain combination of parameters) and the one that comes from the Gaussian-like function, which is always present. To avoid this problem of multiple solutions, the NRTL parameters could be restricted to those values that guarantee homogeneous liquid behavior, and so the LLE splitting would be provided exclusively by the Gaussian-like function. However, a more convenient alternative to the NRTL model has been used in the present work for the homogeneous non-ideal g^E contribution (g_H^E), eq 2, with only three parameters instead the six parameters required by NRTL for ternary systems. These have been the main reasons for the selection of the two contributions to formulate the excess Gibbs energy used in the present work.

3.3. Interpretation of the Model Parameters. One of the advantages of the proposed model is that the relation between the parameter values and the characteristics of the calculated LLE can be quite easily interpreted. This feature allows the generation of good initial guesses and also guides and improves the correlation results when necessary, e.g., when the optimization algorithm does not converge to the global minimum. The interpretation of the fitting parameters in eq 1 regarding their influence on the LLE behavior is presented below and it has been schematically represented in Figure 4. In

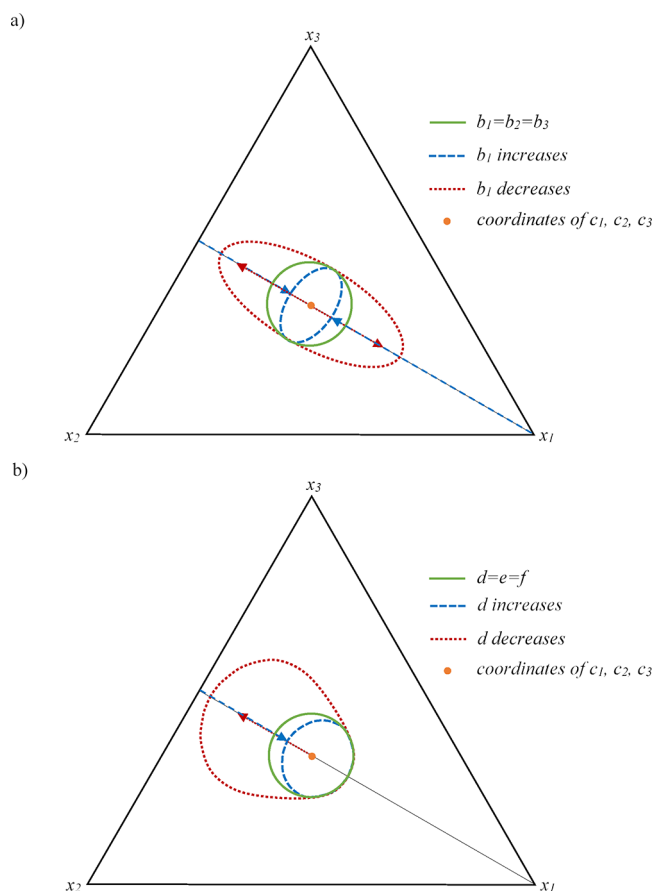


Figure 4. Schematic representation of the effect on the LLE region of the parameter values modification (g_C^E function): (a) change in the parameter b_1 and (b) change in the parameter d .

Table 2. Correlation Results^{a,b} for Island Type Ternary Systems: Model Parameters for g_C^E and g_H^E , Objective Function (O.F.), and Mean Deviations (%)

system	T (K)	g_C^E parameters									
		a	b_1	b_2	b_3	c_1	c_2	c_3	d	e	f
S1	293.15	0.099389	0.52779	3.1690	0.23049	0.45425	0.11078	0.43497	9.9950×10^{-5}	0.93210	0.74818
S2	291.15	2.1085	8.2965×10^{-3}	0.024257	1.1667×10^{-7}	0.20697	0.19303	0.60000	2.2869	2.9492	2.7567
	293.15	2.0471	0.56398	1.2639	1.0000×10^{-6}	0.18346	0.21504	0.60150	2.1302	1.5873	0.80343
S4	298.15	1.4548	9.6174×10^{-3}	0.010836	1.0000×10^{-4}	0.09397	0.05436	0.85167	3.3480	1.6976	2.0642

system	T (K)	g_H^E parameters			σ (%)	O.F.
		A	B	C		
S1	293.15	0.21102	0.68366	0.12009	1.23	0.00641
S2	291.15	6.7849	0.17906	6.5263	1.95	0.0274
	293.15	10.553	1.0079×10^{-6}	9.2776	2.60	0.0484
S4	298.15	6.8010	0.54941	4.6584	1.39	0.0150

^aResults for S2–S4 are exclusively for the miscibility gap but not for LLE (tie-line) calculations. ^bNo acceptable correlation results for S3 at 293.15 K.

Figure 4a,b, the orange point represents the location of the maximum of g_C^E and the green circle represents the position of the Gaussian function with constant parameters ($b_1 = b_2 = b_3$ and $d = e = f$), which is related to the position of the LLE region.

The parameter a (“height”) is the maximum value of g_C^E and so when its value increases or decreases, the maximum of the function (“the peak of the bell of the Gaussian-like function”) reaches higher or lower values, respectively. The parameters b_1 , b_2 , and b_3 are related to the “width” of this same function. Each of these parameters is associated with the composition of one component: b_1 with x_1 , b_2 with x_2 , and b_3 with x_3 . The increase or decrease in their values will narrow or widen, respectively, the bell of the g_C^E function in the direction defined by the bisector that starts from each vertex of the equilibrium diagram ($x_i = 1$): b_1 in the direction of the bisector that starts from $x_1 = 1$, b_2 in the direction of the bisector that starts from $x_2 = 1$, and b_3 in the direction of the bisector that starts from $x_3 = 1$. In Figure 4a, the effect of increasing (blue discontinuous line) or decreasing (red discontinuous line) the parameter b_1 on the shape of the LLE region is schematically represented, which can be extrapolated to the parameters b_2 and b_3 . The parameters d , e , and f are related to the “propagation” of the bell of the g_C^E Gaussian-like function changing its extension. Each of these parameters is also associated with the composition of one component: d with x_1 , e with x_2 , and f with x_3 . An increase or decrease in their values will retract or propagate, respectively, the function in the direction defined by the bisector that starts from each vertex of the equilibrium diagram ($x_i = 1$): d in the direction of the bisector that starts from $x_1 = 1$, e in the direction of the bisector that starts from $x_2 = 1$, and f in the direction of the bisector that starts from $x_3 = 1$. Figure 4b presents the effect of changing the parameter d and the consequences can be extrapolated to the parameters e and f . The parameters c_1 , c_2 , and c_3 represent the “location” (composition in mole fractions) of the maximum of g_C^E , so they must accomplish the mass balance. Equation 1 allows us “to control” the position and shape of the LLE region in a certain way as well as the slope of the tie-lines in a relatively easy and intuitive way, which could solve frequent convergence problems and improve the LLE correlation results. The particular characteristics of eq 1 have allowed us to find these relations between the fitting parameter values, which must always be positive, with the position and shape of the LLE region.

Moreover, A , B , and C are the parameters of g_H^E that modify the non-ideal behavior of the binary subsystems. These three parameters must be positive in order to guarantee total miscibility of the three binary mixtures, as is required in island-type ternary systems.

3.4. Optimization Algorithm. The equilibrium condition used in the correlation algorithm is based on the isoactivity criterion, so the calculated compositions must satisfy the equilibrium function (E.F.) given by eq 6:

$$\text{E. F.} = \sum_{n=1}^{\text{nd}} \sum_{i=1}^3 (a_{i,n}^I - a_{i,n}^{II})^2 < \varepsilon \quad (6)$$

where $a_{i,n}$ is the activity of component i in tie-line n , I and II represent the two phases in equilibrium, nd is the total number of equilibrium data, and ε is a low tolerance value ($\varepsilon < 10^{-9}$) guaranteeing the fulfillment of the isoactivity equilibrium condition.

The fitting parameters were optimized using the Solver optimization tool in Excel worksheet with the GRG (Generalized Reduced Gradient) Nonlinear Method^{19,20} to minimize the composition objective function O.F. defined in eq 7:

$$\text{O. F.} = \min \sum_{n=1}^{\text{nd}} \sum_{i=1}^3 [(x_{i,n}^{I,\text{exp}} - x_{i,n}^{I,\text{cal}})^2 + (x_{i,n}^{II,\text{exp}} - x_{i,n}^{II,\text{cal}})^2] \quad (7)$$

subject to E. F. < ε

where $x_{i,n}$ is the mole fraction of component i in tie-line n and exp and cal represent the experimental (or supposed) and calculated equilibrium data, respectively. Modeling binodal curves (miscibility gaps) involves implicitly establishing the equilibrium condition among two points (liquid mixtures) on them. In other words, any calculated binodal curve (by an activity coefficient model) will always reproduce conjugated liquid phases in equilibrium. Each point on the miscibility curve must have a tangent plane to the calculated Gibbs energy of mixing (g^M) surface which, at the same time, will also be necessarily tangent to other different points on that binodal curve (conjugated liquid mixture), because otherwise, the starting point would be a homogeneous mixture consequently out of the miscibility curve. Thus, the correlation of the binodal curves for systems S2 to S4, as that of any system, requires in some way tie-line data. Because for these systems, as to our knowledge, no tie-line data is available, we had to

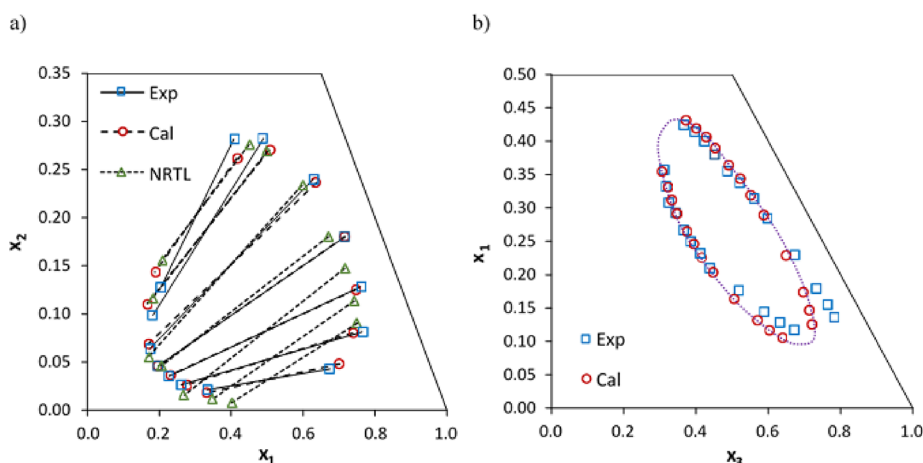


Figure 5. Experimental and calculated data with the proposed empirical model for island-type ternary systems: (a) system S1 at 293.15 K (tie-lines) and (b) system S2 at 291.15 K (binodal curve). Parameters in Table 2. System S1 also includes calculated data with the NRTL model (parameters in ref 9). Compositions in mole fractions.

assume some hypothetical (supposed) tie-lines (their ends lying on the binodal curve) to obtain a set of parameters that can only be used to correlate the miscibility gap. Thus, the set of parameters obtained for these systems is one possible, but not unique, solution for the miscibility gap description, since no real tie-line data have been used in the correlation. Despite the inconvenience of not having tie-line data, we still find considering these S2–S4 systems to illustrate some aspects of the model presented very interesting.

Mass balance must be accomplished in each phase. Flash calculations in global mixtures located at the middle point of the experimental tie-lines were performed to establish a correspondence between experimental and calculated LLE data. In order to characterize the quality of the fittings, the mean deviation (%) between experimental or supposed (*exp*) and calculated (*cal*) LLE data has been obtained using eq 8

$$\sigma(\%) = 100 \sqrt{\frac{\sum_{n=1}^{\text{nd}} \sum_{i=1}^3 [(x_{i,n}^{I,\text{exp}} - x_{i,n}^{I,\text{cal}})^2 + (x_{i,n}^{II,\text{exp}} - x_{i,n}^{II,\text{cal}})^2]}{6\text{nd}}} \quad (8)$$

where all variables have been previously defined.

4. RESULTS

Table 2 shows the parameters of the proposed model, O.F. values (eq 7), and mean deviations (eq 8) obtained in the correlation of the island-type data sets presented in Table 1.

The results presented in Table 2 show that, with the proposed equations for the excess Gibbs free energy (eqs 1 and 2) along with the correlation procedure used, these data sets are satisfactorily fitted, with the exception of system S3 at 293.15 K that will be discussed later. Figure 5 shows a comparison between experimental and calculated data for systems S1 at 293.15 K (tie-lines) and S2 at 291.15 K (binodal curve). For system S1, the correlation results obtained with the NRTL model⁹ have been included for comparison. For systems S2 to S4, it was not possible to find an acceptable correlation result of the binodal curves using the NRTL model. Similar representations for systems S2 at 293.15 K and S4 at 298.15 K are presented in Figures S1 and S2 in the Supporting Information. From these results, it follows that the proposed model has been able to reproduce consistently the miscibility behavior of these island-type ternary systems. NRTL binary

interaction parameters⁵ for system S1 had been previously published,^{9,13} but the mean deviations obtained (5.83% in ref 13 and 3.92% in ref 9) were higher than the one obtained in the present paper (1.23%).

The Gibbs minor common tangent criterion has been used to discard any possible metastable solution and to guarantee the consistency of the fitting parameters in all the composition range. For that aim, 3D figures and sectional cuts were made to analyze the topology of the g^M surface versus composition (in mole fractions) and to check the existence of common tangent planes at each pair of calculated equilibrium mixtures, which must not intersect the g^M function at any other composition. As an example, Figure 6 shows the calculated g^M surfaces and the tie-lines and binodal curve obtained in the correlation of systems S1 at 293.15 K and S2 at 291.15 K using the proposed model. Also, for system S1, sectional cuts were obtained for a better visualization of the common tangent equilibrium criterion. Figure 7 presents sectional cuts in the directions defined by some calculated tie-lines for system S1 at 293.15 K. The curves obtained in these sectional cuts of the g^M surface show a good definition of the common tangent line. This means that the equilibrium compositions can be calculated without the frequent uncertainty problems found when using classical activity coefficient models, as previously discussed.^{9,13,21} When the NRTL model was used in the correlation of the system S1 at 293.15 K, the g^M surface was extremely flat (Figure 2) and the sectional cuts in the direction of calculated tie-lines were practically linear in the heterogeneous ternary region (Figure 3). Using the proposed model, these problems are not present as shown in Figure 6a and Figure 7.

We have also checked that, with the proposed model, the existence of a “dissimilar” binary g^M curve to generate the convex/concave transitions (LLE) in the ternary g^M surface is not a requirement as it happens when the NRTL model is used.¹³ Figure 8 shows the three binary g^M curves for the systems S1 at 293.15 K and S2 at 291.15 K calculated with eqs 1 and 2 (correlation parameters in Table 2). As expected in island-type ternary systems, the three binary g^M curves are totally miscible for both S1 and S2 systems. It can be concluded that the existence of a dissimilar binary g^M curve does not seem to be a requirement for the empirical equations proposed in this paper to model LLE island-type ternary

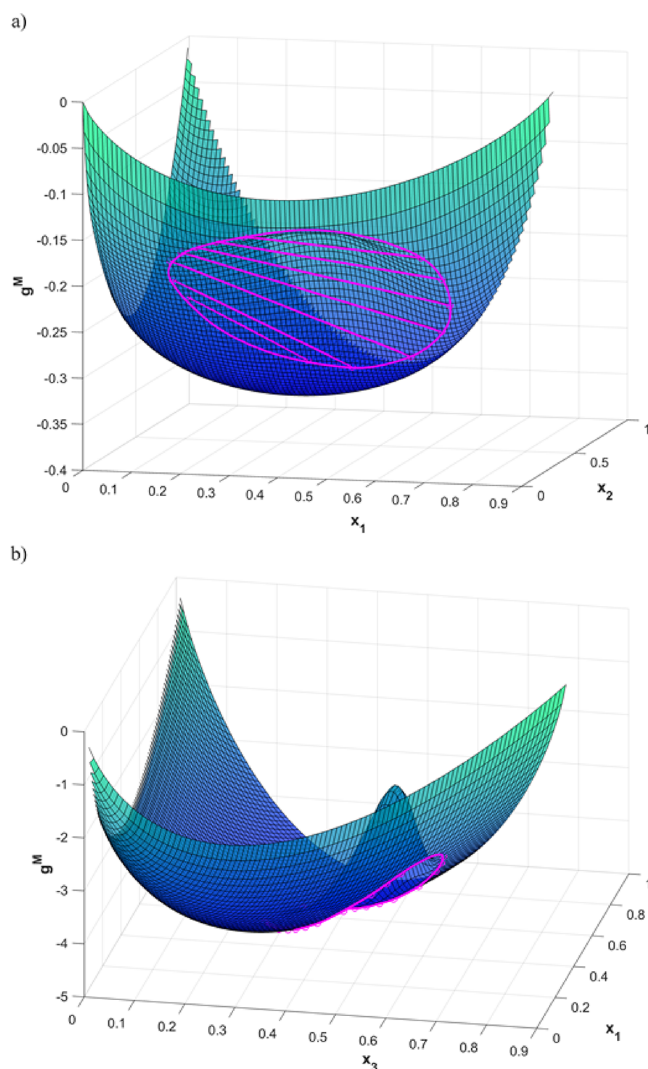


Figure 6. Calculated g^M surface and for island-type ternary systems: (a) system S1 at 293.15 K (tie-lines) and (b) system S2 at 291.15 K (binodal curve). Parameters in Table 2. Compositions in mole fractions.

systems because the convex/concave transitions required can be easily reproduced by the Gaussian-like function (g^E_C) (eq 1).

4.1. Artificial Composition Variables. Despite the advantages of the proposed set of equations (eqs 1 and 2) to correlate island-type ternary systems, it is possible to find specific systems that present special difficulties for their fitting. This is the case of system S3 at 293.15 K for which it has not been possible to obtain an acceptable regression result probably due to the difficulty of reproducing the large heterogeneous region of this system. To solve this limitation, different alternatives have been evaluated, being the introduction of a change of variable in the composition for the g^E_C contribution, the one that has provided better correlation results among all of them. This calculation strategy consists of defining three new artificial composition variables (z_1 , z_2 , and z_3) as a function of mole fractions (x_1 , x_2 , and x_3) and two new optimization parameters (cv_1 and cv_2) according to eqs 9–11:

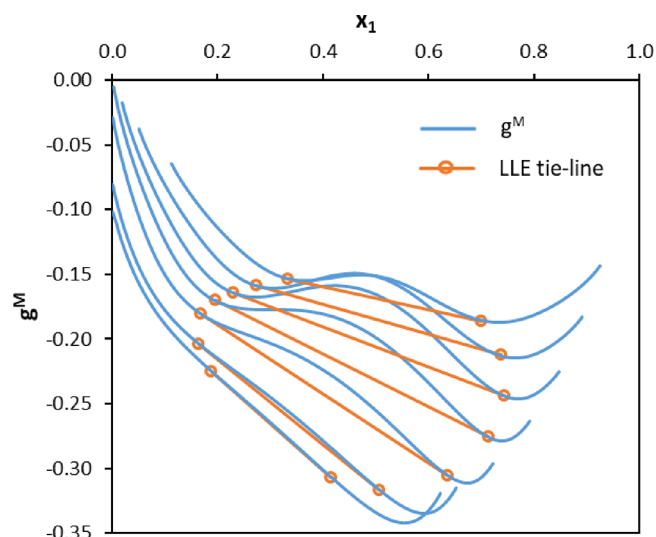


Figure 7. Sectional cuts of the g^M surface in the direction of calculated tie-lines and Gibbs common tangent criterion for island-type ternary system S1 at 293.15 K. Parameters in Table 2. Compositions in mole fractions.

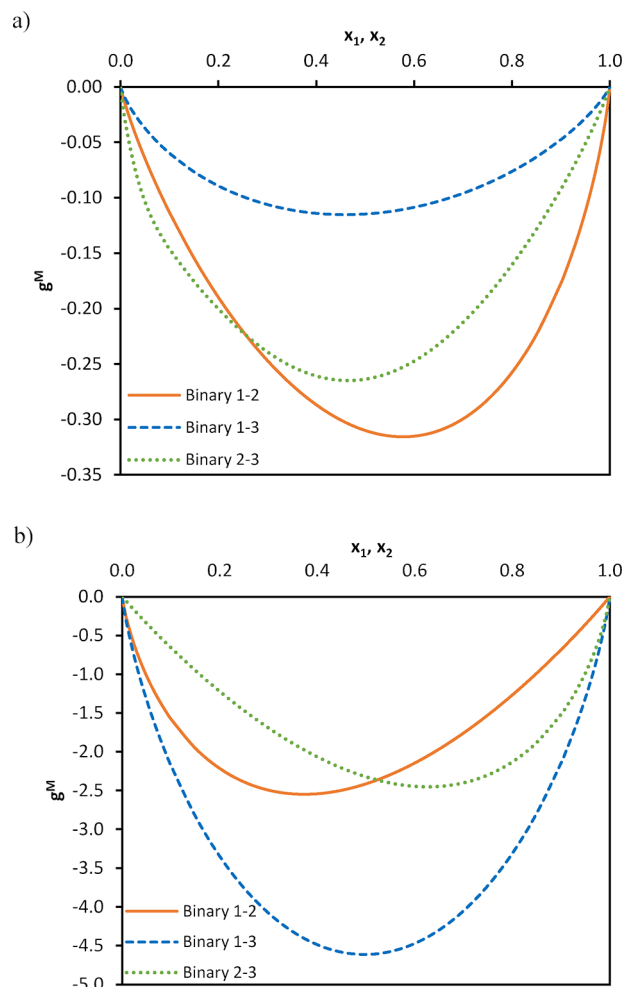


Figure 8. Representation of the g^M curves for the three binary subsystems of island-type ternary systems: (a) S1 at 293.15 K and (b) S2 at 291.15 K. Parameters in Table 2. Compositions in mole fractions.

Table 3. Correlation Results^a for Island-Type Ternary Systems: Model Parameters for g_C^E (with Artificial Composition Variables) and g_H^E , Objective Function (O.F.), and Mean Deviations (%)

system	T (K)	g_C^E parameters									
		a	b_1	b_2	b_3	c_1	c_2	c_3	d	e	f
S1	293.15	0.085623	1.0214	3.6037	1.0000×10^{-4}	0.52597	0.13456	0.33947	1.0000×10^{-6}	0.84195	0.99264
S2	291.15	0.40112	0.010947	0.014581	1.0000×10^{-4}	0.27619	0.27786	0.44595	2.7835	3.5561	1.8070
	293.15	0.40040	0.011193	0.015625	1.0000×10^{-4}	0.28216	0.26986	0.44798	3.0512	3.4207	1.8805
S3	293.15	0.10071	4.0293×10^{-3}	0.21113	0.17306	0.41087	0.42039	0.16874	1.9249	1.5154	0.21350
S4	298.15	1.4120	8.8389×10^{-3}	0.011793	1.0000×10^{-4}	0.09422	0.06084	0.84494	3.4614	1.6093	2.1253

system	T (K)	g_H^E parameters			artificial composition parameters			O.F.
		A	B	C	cv_1	cv_2	σ (%)	
S1	293.15	0.18906	0.51234	0.045049	1.1342	0.81522	0.935	0.00367
S2	291.15	0.71628	0.25474	0.20810	1.1843	0.39915	0.710	0.00424
	293.15	0.79906	0.41378	0.19205	1.1093	0.41839	0.841	0.00551
S3	293.15	1.2582	0.099856	0.49365	0.76014	0.034439	1.48	0.0330
S4	298.15	6.8126	0.51365	4.3973	0.90708	0.85779	0.799	0.00498

^aResults for S2–S4 are exclusively for the miscibility gap but not for LLE (tie-line) calculations.

$$z_1 = \frac{x_1}{x_1 + cv_1x_2 + cv_2x_3} \quad (9)$$

$$z_2 = \frac{cv_1x_2}{x_1 + cv_1x_2 + cv_2x_3} \quad (10)$$

$$z_3 = \frac{cv_2x_3}{x_1 + cv_1x_2 + cv_2x_3} \quad (11)$$

and use them in the g_C^E contribution (eq 1) replacing mole fractions (x_i). The artificial composition variables fulfill the mass balance $z_1 + z_2 + z_3 = 1$ for any values of cv_1 and cv_2 .

This approach implies two additional optimization parameters in the model, which might be necessary to model certain particularly complex island-type ternary systems. The change in the composition variables combined with the proposed empirical model (eqs 1 and 2)) has provided the required flexibility to the equations to allow a quite satisfactory correlation result for system S3 that presents particular fitting problems. Although this calculation strategy that uses a higher number of parameters is not strictly necessary for all other systems, since the results obtained for them were acceptable, it has been applied to all of them in order to quantify the reduction in deviations achieved.

Table 3 presents the correlation results for all island-type ternary systems listed in Table 1 with the proposed model (eqs 1 and 2)) including the use of artificial composition variables (eqs 9–11) in the g_C^E (eq 1) contribution: fitting parameters, O.F. values (eq 7), and mean deviations (eq 8). Mean deviations go from 0.710% for system S2 at 291.15 K to 1.48% for system S3 at 293.15 K. The introduction of the artificial variables in the g_C^E contribution has made it possible to obtain lower mean deviation values for all the correlations. Figure 9 shows a comparison between experimental and calculated binodal curves for system S3 at 293.15 K, obtained using the procedure presented. Similar representations for the other systems listed in Table 1 are presented in Figures S3–S6 in the Supporting Information. From these representations, it follows that the modified g_C^E has been able to reproduce the miscibility gap of these systems quite well, considering the particular complexity of this type of correlations. For example, the miscibility gap for system S3 could not be correlated using the NRTL model, not even approximately.

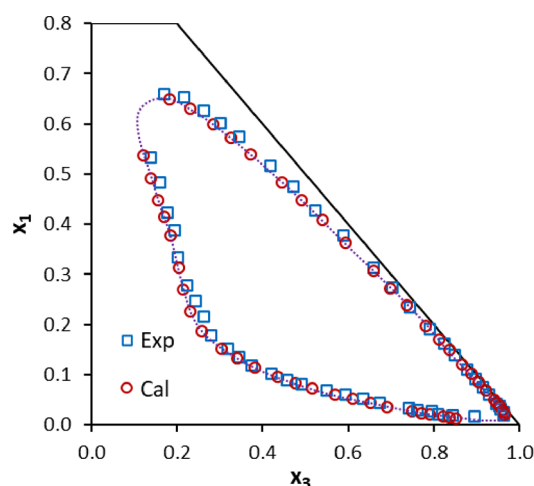


Figure 9. Experimental and calculated binodal curve for the island-type ternary system S3 at 293.15 K. Parameters in Table 3. Compositions in mole fractions.

The Gibbs minor common tangent criterion has been used to verify the stability of the regression results by inspection of the g^M 3D representation. As an example, Figure 10 shows the g^M surface for system S3 at 293.15 K. In this figure, it can be observed that the common tangent planes to each point on the g^M surface describing the binodal curve are well defined, avoiding the frequent problems of uncertainty in equilibrium calculations when using the NRTL model for island-type ternary systems. These checks were made for all systems in Table 1 to ensure that, for each tie-line or point on the binodal curve, a common tangent plane to the g^M surface versus compositions (mole fractions) exists, which does not intersect the g^M surface at any other point, guaranteeing the minimum energy and so the stable solution. It has been shown that the validation of the correlation solutions by means of the inspection of the Gibbs energy of mixing function along with the minor common tangent equilibrium criterion is a very valuable tool to avoid inconsistent correlation solutions that too frequently are found in the literature.^{21,22} In Figure 11, all the correlation results obtained for the same island-type ternary system (S1) have been represented along with the experimental LLE data. The calculated data include the results

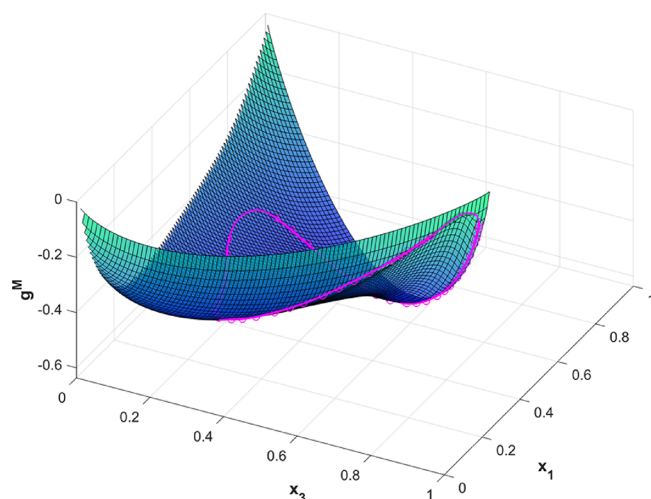


Figure 10. Calculated g^M surface and binodal curve for the island-type ternary system S3 at 293.15 K. Parameters in Table 3. Compositions in mole fractions.

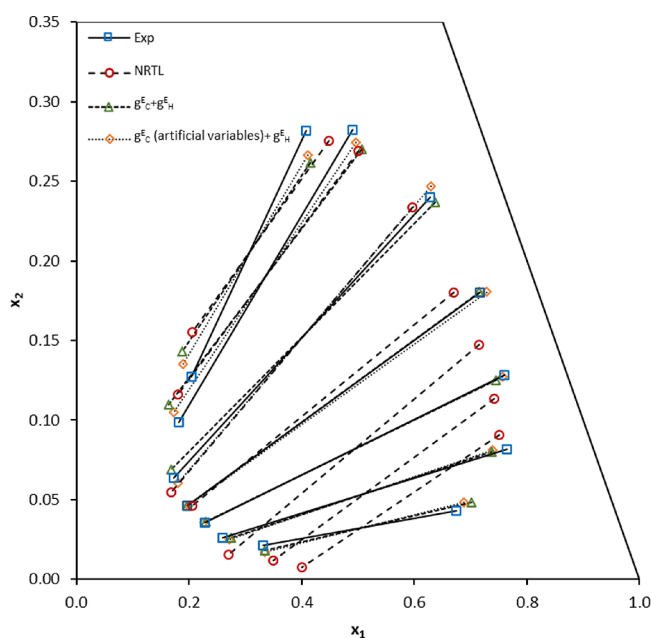


Figure 11. Experimental and calculated data for island-type ternary system S1 at 293.15 K. Calculated data include: the NRTL model (parameters in ref 9), the originally proposed model (parameters in Table 2), and the one using artificial composition variables (parameters in Table 3). Compositions in mole fractions.

obtained using the NRTL model, the proposed model (eqs 1–3) and artificial composition variables (eqs 9–11) in the proposed model. The figure shows a significant improvement of the correlation results using the proposed empirical equation compared with the NRTL model. Moreover, the use of artificial composition variables does not significantly improve the results for this system. The empirical equations and calculation strategies proposed in the present paper can be considered as one possible practical solution to the island-type LLE correlation problem, although other possible alternatives could be found for that purpose.

5. CONCLUSIONS

Some important limitations of classical activity coefficient models like NRTL for the correlation of island-type LLE data have been confirmed. The lack of flexibility and the extremely flat g^M surfaces generated, which cause uncertainty in equilibrium calculations, are the main problems of the application of these models to island-type ternary systems. To overcome these problems with a practical aim, an alternative empirical activity coefficient model has been proposed. The proposed model has allowed a good definition of the convex/concave transitions in the g^M surface, which avoids uncertainty problems, while the total miscibility of the three binary subsystems included in the ternary system is preserved as it is required for island-type ternary systems.

The proposed model for the excess Gibbs free energy is the result of two contributions: a Gaussian-like function (g^E_C) and a non-ideal homogeneous Gibbs free energy (g^E_H), which are able to fulfill the requirements of the g^M for island-type LLE, according to the Gibbs minor common tangent equilibrium criterion. These equations have allowed the correlation of island-type data for different ternary systems that could not be fitted with classical activity coefficient models like NRTL. The deviations obtained have been acceptable, especially when considering the difficulty of this type of correlations. Also, a good definition of the common tangent planes to the g^M surfaces has been obtained in all cases, preventing the uncertainty problems of the classical activity coefficient models, when they are used for island-type systems. Another advantage of the proposed model is that the relations between the values of the parameters and the calculated LLE can be easily established. This allows the generation of good initial guesses for the parameters and guides the correlation algorithm when convergence problems occur. Artificial composition variables have been used in the g^E_C contribution, providing the model a greater flexibility that may be necessary for the correlation of systems with particularly complex behavior. The number of parameters in the equations proposed is somewhat high, but it has not been possible in this study to obtain acceptable correlation results with a lower number of parameters. The solution presented is not unique, but it could be considered as a practical alternative to the classical activity coefficient models, like NRTL or UNIQUAC, to overcome some limitations and obtain better results for LLE data correlation of island-type ternary systems.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c04384>.

Representations of the experimental and calculated data using the proposed model (PDF)

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<https://pubs.acs.org/10.1021/acs.iecr.2c04384>

Notes

The authors declare no competing financial interest.

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NOMENCLATURE

A, B, C	parameters of the homogeneous contribution to the excess Gibbs free energy (g^E_H)
$a, b_1, b_2, b_3, c_1, c_2, c_3, d, e, f$	parameters of the Gaussian-like contribution to the excess Gibbs free energy (g^E_C)
$a_{i,n}$	activity of component i in tie-line n
cv_1, cv_2	parameters of the artificial composition variables
E.F.	equilibrium function
g^E	excess Gibbs free energy (dimensionless)
g^M	Gibbs free energy of mixing (dimensionless)
LLE	liquid–liquid equilibrium
nd	number of LLE data
O.F.	objective function
P	pressure (Pa)
T	temperature (K)
VLLE	vapor–liquid–liquid equilibrium
x_i	mole fraction of component i in liquid phase
z_i	artificial mole fraction of component i

Greek symbols

γ_i activity coefficient of component i
 σ mean deviation (%)

Superscripts

I, II liquid phases in equilibrium
 cal calculated
 exp experimental or supposed

Subscripts

C Gaussian-like contribution of the proposed model for the excess Gibbs free energy
 H homogeneous contribution of the proposed model for the excess Gibbs free energy
 i, j components
 n LLE data

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