G^E Models and Algorithms for Condensed Phase Equilibrium Data Regression in Ternary Systems: Limitations and Proposals

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Abstract: Phase equilibrium data regression is an unavoidable task necessary to obtain the appropriate values for any model to be used in separation equipment design for chemical process simulation and optimization. The accuracy of this process depends on different factors such as the experimental data quality, the selected model and the calculation algorithm. The present paper summarizes the results and conclusions achieved in our research on the capabilities and limitations of the existing G^E models and about strategies that can be included in the correlation algorithms to improve the convergence and avoid inconsistencies. The NRTL model has been selected as a representative local composition model. New capabilities of this model, but also several relevant limitations, have been identified and some examples of the application of a modified NRTL equation have been discussed. Furthermore, a regression algorithm has been developed that allows for the advisable simultaneous regression of all the condensed phase equilibrium regions that are present in ternary systems at constant T and P. It includes specific strategies designed to avoid some of the pitfalls frequently found in commercial regression tools for phase equilibrium calculations. Most of the proposed strategies are based on the geometrical interpretation of the lowest common tangent plane equilibrium criterion, which allows an unambiguous comprehension of the behavior of the mixtures. The paper aims to show all the work as a whole in order to reveal the necessary efforts that must be devoted to overcome the difficulties that still exist in the phase equilibrium data regression problem.

Keywords: Correlation algorithm, LLLE, LLSE, local composition models, NRTL, phase equilibria, simultaneous correlation.

1. INTRODUCTION

Modelling of phase equilibria is essential for simulation and optimization of separation processes in the chemical industry. The accuracy of the phase equilibrium data regressions depends on different factors: the experimental data quality, the selected model to describe the excess Gibbs energy (G^E) and the correlation algorithm.

The most frequently used methods to solve the equilibrium calculation problem are: the K-value method and the Gibbs energy minimization [1,2]. The K-value method is very common and usually applied to many equilibrium calculation algorithms, most of all for VLE [3-5], and also for LLE [6,7]. Generally, successive substitution methods or Newton or quasi-Newton methods, which strongly depend on starting values, are used to apply this criterion [2]. However, the K-value method imposes a necessary but not sufficient phase equilibrium condition and can give multiple solutions corresponding to local minima. On the contrary, only one single solution minimizes the Gibbs energy of mixing (g^M in eq. 1) and, therefore, satisfies the second law of thermodynamics:

$$g^M = G^M /RT = G^I/RT + G^E/RT \qquad (1)$$

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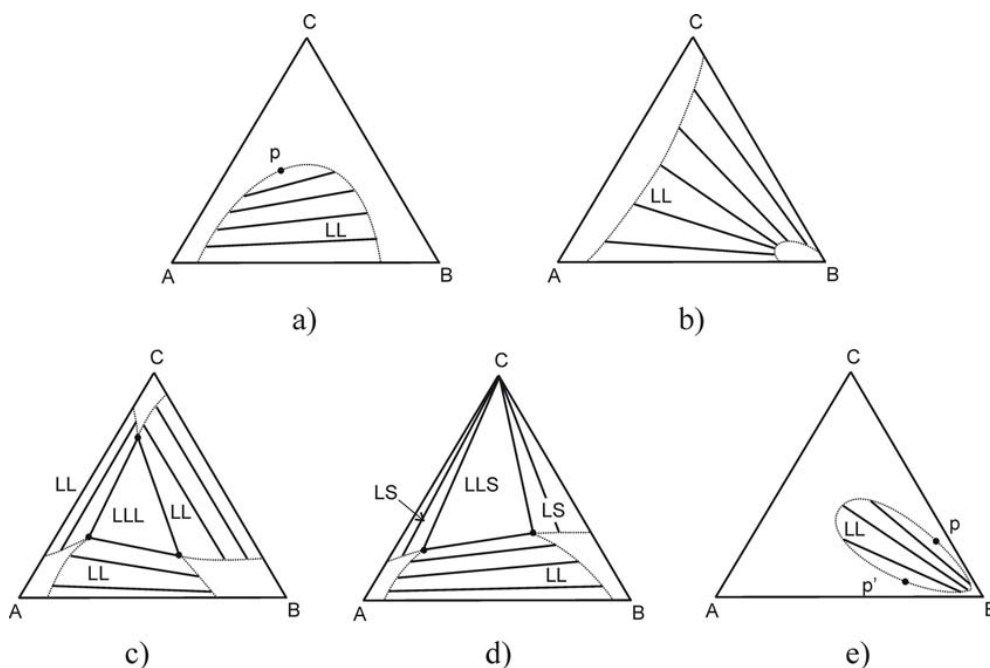
where g^M is the dimensionless Gibbs energy of mixing, G^I and G^E are the ideal and excess Gibbs energy of mixing ($J \cdot mol^{-1}$), respectively, T is the temperature (K) and R is the gas constant ($J \cdot K^{-1} \, mol^{-1}$).

Thus, methods for Gibbs energy minimization are preferred versus K-value methods, since they unambiguously define the phase equilibrium state of a system. These methods have been applied through different techniques, which are mainly classified in three groups: tangent plane criterion [8,9], maximum area [10], and equal area [11]. The common tangent plane condition, which has been the base for the present work, allows a geometrical interpretation of the equilibrium that provides a clear understanding of the phase behavior for mixtures and a better definition of the capabilities and limitations of the models and the regression strategies used.

1.1. Condensed Phase Equilibrium Regression Background

Fig. (**1**) shows an example for each type of ternary system according to the Treybal classification [12]. Most of the ternary systems, with condensed phase equilibria, that are measured and correlated in the literature, are type 1 and 2 [12]. Less effort has been dedicated to singular type 0 (island) or complex type 3 or 4 systems. An illustrative example is that in the DECHEMA *Chemistry Data Series Collection* [13] the type 1 or 2 LLE data for ternary systems represent around 95% of the data included.

Fig. (1). Treybal classification for ternary systems [12]: **a)** type 1; **b)** type 2; **c)** type 3; **d)** type 4 and **e)** type 0 (island).

The existing models for the excess Gibbs energy (G^E) are not always capable of managing with sufficient accuracy the equilibrium data regression of these frequent type 1 and 2 systems, with only one or two equilibrium regions. Many examples can be easily located in the literature, e.g. in the *Chemistry Data Series Collection* the following systems are correlated with NRTL [14] and UNIQUAC [15] models, but neither of them provides an accurate fitting: a) the type 1 system Methanol (1) + Diphenylamine (2) + Cyclohexane (3) at 298ºK ([13], Vol. V-2, p. 129) and b) type 2 system Isopropylbenzene (1) + 2-Methylpropanoic acid (2) + Water (3), 288ºK ([16], Vol. V-4, Sup 1. p. 245).

Regarding systems with salts (type 4), only solubility data for aqueous and non-aqueous binary systems with electrolytes are collected in DECHEMA *Chemistry Data Series Collection* [17], NIST Standard Reference Database [18] and DETHERM database [19] which compiles data from different sources such as DECHEMA e.V, *Dortmund Data Bank* (DDB) [20], *Electrolyte Data Collection* (ELDAR) [21] and *Thermophysical database* (INFOTHERM) [22]. Generally these databases do not include LLE or SLE data in the entire composition space of ternary systems with salts (type 4) or they allow finding SLLE but do not provide results for the simultaneous correlation of all the existing equilibrium regions. As far as we know, type 0 and 3 systems are very scarce and never correlated. However, equilibrium data for all these types 0, 3 and 4 ternary systems are of interest in very important industrial applications:

- Type 0 (island) systems present a ternary LLE region, where the three binary subsystems are completely miscible. These systems can appear from the simultaneous presence of a hydrocarbon and a weak acid

and base, forming a soluble but less miscible salt [23]. They also appear for ternary systems with two polymers and a low molecular weight solvent [24]. No correlations of type 0 systems and no reference about the capacity of models to reproduce the phase equilibrium behavior of these systems have been found.

- Type 3 systems appear in mixtures of water, oil and non-ionic surfactants forming microemulsions with a LLLE region (tie-triangle) in a certain range of temperatures. Those systems are of interest for industrial cosmetic production, herbicides, paints, lubricants, etc. [25], and are especially important for the petroleum industry where they are used to recover residual oils [26-28]. These systems are not usually correlated ([13] Vol. 2, p. 69) or, sometimes, partial regressions are found: for example, in some papers the LLLE tie-triangle is correlated and the three partially miscible binaries are predicted with the previously optimized parameters [29], which often lead to serious deviations in the LLE data for the binary subsystems.

- Type 4 systems, including inorganic salts, are frequently used for favouring the unequal distribution of the solute between the two liquid phases in equilibrium [30-34]. The most common effect is the solute enrichment of the organic phase ("*salting-out*") to improve the extraction efficiency. This type of systems present different equilibrium regions (LLE, LSE and LLSE), but the simultaneous regression of all these equilibrium regions is scarcely tackled and the results obtained are not accurate. Sometimes only LLE data are determined and correlated or, when the complete diagram is experimentally obtained, only the LLE data are regressed (e.g. only the LLE region of system Water + Aconitic

Acid + 1-Pentanol at 303.15K is correlated with UNIQUAC, although the complete diagram is determined [32]).

The capacity of a model to simultaneously represent all the equilibrium regions of a system at constant T and P, using a unique set of parameters, should be considered as a necessary requirement, since all the equilibrium regions are closely linked. However, regressions for only one of the regions of a complex system (e.g. type 3 or 4) are frequently found in the literature [29, 32]. Consequently, the obtained parameters, which do not describe all the equilibrium regions existing in the system, can lead to serious problems when they are used in chemical process simulation packages. Advantages of global versus local correlations for separation equipment design calculations are evident, since parameters are valid for all the composition space. A model that provides an accurate description of the thermodynamic properties of a system, in the entire diagram, facilitates the plant design improvement strategies, the solution of problems and the process control [35].

1.2. Limitations of Models and Commercial Regression Tools

The modern chemical industry is in continuous growth and the money and time invested in the determination of experimental data is high, thus the existence of equations that allowed the accurate prediction of the thermodynamic properties of the different systems would be very interesting [36]. The use of binary parameters, exclusively obtained from binary equilibrium data would considerable decrease the necessary experimental work. However, many authors distrust the physical meaning of the parameters and their predictive capability [37,38].

Despite the significant contribution of NRTL and UNIQUAC to phase equilibrium data modelling in the past four decades, the results obtained show that the predictive capability, originally attributed to their binary parameters, cannot be generalized. These models do not generally yield reliable results when extrapolated from binary systems to ternary or multicomponent systems. On the other hand, binary parameters for a certain binary subsystem are different when the third component changes in the correlation of different ternary systems [38]. Another proof of the lack of predictive sense is that a set of experimental ternary equilibrium data can be correlated by very different parameter sets. Consequently, binary parameters obtained by direct correlation of a set of ternary experimental data, cannot be used to describe the phase equilibrium of any other multicomponent mixture that includes any of the binary subsystems correlated.

According to published papers referred to in the previous section, the difficulty of excess Gibbs energy models such as NRTL for the simultaneous correlation of all the different equilibrium regions in type 3 or 4 systems is evident. Many topological conditions must be fulfilled by the g^M surface, as is required by the tangent plane criterion, in order to

simultaneously reproduce LLE and LLLE in type 3 systems and LLE, LSE together with LLSE (ShLE, ShLLE, ShSLE for hydrated phases) in the case of type 4 systems. These difficulties frequently lead to poor results when all the equilibrium regions are simultaneously regressed or partial fittings are carried out for those complex systems. Besides, for singular systems, such as island type ternary systems no correlation was found in literature, which suggested that, perhaps, G^E models were not able to simultaneously reproduce systems with a ternary splitting region (LLE), where the g^M surface must permit the existence of conjugated points with a common tangent plane, where the three binary subsystems are completely miscible.

In some recent works, models have been modified by adding new parameters to increase their flexibility. Simple thermodynamic models are preferred for industrial applications versus more sophisticated models with a high number of parameters, unless a clear advantage is evident [35]. For example, Chen and col. [39] correlated the LLE data of some quaternary systems using ternary and quaternary interaction parameters in an extension of the UNIQUAC model, which was not able to reproduce the quaternary systems only with binary data.

On the other hand, commercial equilibrium data regression tools do not allow for the simultaneous regression of different equilibrium regions in type 3 or 4 ternary systems, neither data regression of island type systems. For example, ChemCAD [40] specifies that only deals with the regression of type 1 and 2 systems. Fig. (**2**) shows the correlation results of a type 3 system using the DECHEMA Data Preparation Package (DPP) [41]. Binodal curves starting from each binary subsystem are obtained, and a series of false crossed tie-lines corresponding to metastable solutions are found, where the LLLE tie-triangle, shaded in Fig. (**2**), should be located. However, the program is not able to calculate it.

In addition, convergence failures of commercial regression tools are very frequent. The user usually has to continue testing from another starting point with a trial and error procedure because no details about the error source and what to do next are provided. More robust programs should be developed or improved, in order to guarantee that the best solution that the model can provide, to minimize the composition deviations, is always obtained.

Considering those deficiencies still present in the commercial programs, many authors keep on working in the design of robust algorithms to reject false and metastable solutions and facilitate the convergence. For example, McDonald and Floudas (1995) [42] work on global optimization strategies with Mixed Integer Non linear Programming methods (MINLP), Dominguez and col. (2002) [43] develop Interval Arithmetic methods and Nagatani and col. (2008) [44] work in Stochastic methods. These are only some examples that evidence the necessity of dedicating more effort in the development of robust algorithms that allow avoiding the typical problems that still arise.
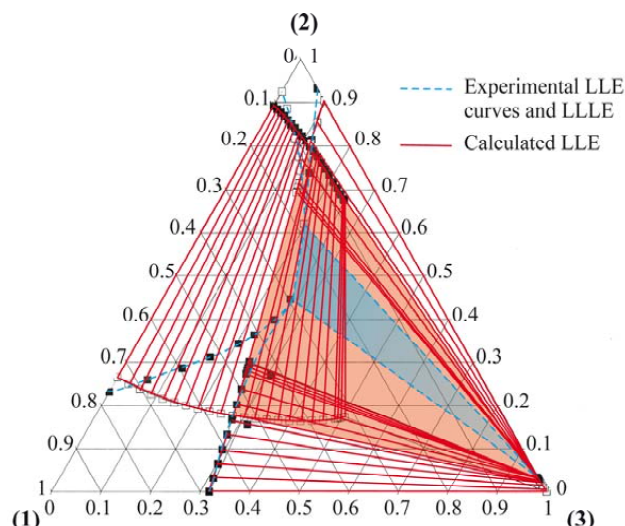
Fig. (2). Equilibrium data regression results obtained with DECHEMA Data Preparation Package [41] for the system Hexanol (1) + Nitromethane (2) + Water (3) at 294°K ([13], Vol. V-2, pp. 77) using the NRTL model (α_{ij}=0.2): A_{12}(K)=160.25; A_{21}=755.94; A_{13}=-118.51; A_{31}=2080.4; A_{23}=447.51; A_{32}=744.12.

2. OBJECTIVES

According to the background exposed in sections 1.1 and 1.2, the following objectives were proposed:

- Analysis of objective functions to formulate the phase equilibrium condition and assessment of the fulfilment of this condition in the results published in the literature and provided by the regression tools.

- Topological study of the characteristics that the g^M surface must present in order to reproduce all the equilibrium regions present in ternary systems types 0, 1, 2, 3 and 4.

- Proposal of a robust algorithm for the simultaneous correlation of the equilibrium regions of ternary systems types 0, 1, 2, 3 and 4 that overcomes the limitations found in the most common commercial regression tools, and that leads to consistent results in all the composition space.

- Application of the algorithm for the correlation of ternary systems types 0, 1, 2 and 3 (including LLLE tie-triangles) to systems that were not previously correlated, or for which the provided parameters were inconsistent; and also to water + organic solvent + inorganic salt (type 4) ternary systems, where the salt appears with anhydrous and hydrated forms, complicating substantially the equilibrium diagram.

- Examination of the capabilities and limitations of NRTL for the correlation of the different types of ternary systems. Proposal of new ideas to obtain more flexible models and their application for equilibrium data regression of different systems.

3. METHODOLOGY PROPOSED

Regarding the existing limitations in commercial regression tools, our research group has developed a robust methodology implemented in a computer program for the condensed phase equilibrium data correlation of ternary systems. This methodology has been based on the study of the g^M function topology, to simultaneously reproduce all the equilibrium regions present in type 0, 1, 2, 3 and 4 systems at constant T and P. In the present section, the general aspects of this algorithm and the novel strategies proposed are stated as follows:

- Selection of the excess Gibbs energy model.

- Calculation of the Gibbs energy for the solid phases (type 4 systems).

- Equilibrium criterion selection and fulfilment.

- Limiting composition region for the LLE calculation.

- Plait point location.

- Geometrical procedure for the approximate calculation of the LLLE in type 3 ternary systems.

- Application of the extended "vector method" when special LLE convergence problems arise.

- Estimation of the model parameters:

  o Definition of a robust comparison criterion between calculated and experimental compositions.

  o Application of NRTL binary parameter restrictions:

    ▪ NRTL binary parameter value restrictions to reproduce total or partial miscibility condition.

    ▪ NRTL binary parameter value restrictions to reproduce island type ternary systems.

- Validation of the results according to the "lowest common tangent plane" stability criterion.

3.1. Selection of the Excess Gibbs Energy Model

NRTL and UNIQUAC are the models that provide better results in the binary and ternary LLE data regressions [13]. Supposedly, the structural parameters of UNIQUAC, taking into consideration shape and size of molecules, provide it with a better capacity for representing liquid mixtures. However, this model does not always give better results than NRTL.

With an illustrative aim, part 2 of volume V of DECHEMA *Liquid-liquid Equilibrium Data Collection* [13], where NRTL and UNIQUAC specific parameters are presented for 78% of the compiled systems, was analysed. From the deviations obtained, it can be concluded that the capacity of regression for both models is similar. Fig. (**3**) shows how the percentage of systems with lower deviation is slightly higher for NRTL than for UNIQUAC (40% vs. 36%) obtaining, for the rest of the systems, the same standard deviation with both equations.
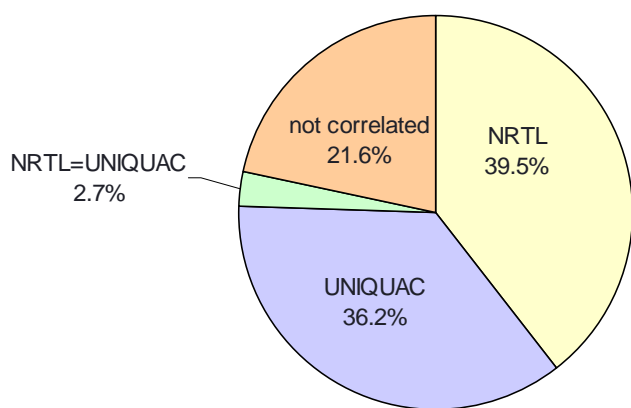
Fig. (3). Percentage of ternary systems (types 1 and 2) compiled in DECHEMA [13] that are better correlated with each model (NRTL and UNIQUAC).

In our work, NRTL has been selected as a representative local composition model. The binary parameters for this model have been obtained by the simultaneous correlation of equilibrium data in all the regions that each ternary system correlated presents at constant T and P.

3.2. Calculation of the Gibbs Energy for the Solid Phases (Type 4 Systems)

Since for type 4 ternary systems, the presence of solid phases must be considered, the Gibbs energy value for the solid (g^S) has been calculated as the chemical potential change from the pure liquid (reference state) to the pure solid salt at the T and P conditions, using a thermodynamic cycle [45]. In case of hydrated salts being present, the Gibbs energy (g^{Sh}) was calculated as the hydrating energy change that occurs when the hydrated salt is formed from the reference state: the sub-cooled molten salt and the liquid water [46].

3.3. Equilibrium Criterion Selection and Fulfilment

Generally, papers dealing with phase equilibrium data regressions only show the optimized parameter set and the mean deviation. As a consequence, it is not possible to check the equilibrium criterion fulfilment of the solution. We selected some papers (from the *Journal of Chemical & Engineering Data* and *Fluid Phase Equilibria,* since 1977) where, contrarily, the set of calculated tie-lines, as a result of the regression process, were presented. The analysis of these papers showed that the phase equilibrium condition was not correctly fulfilled in many cases [47]:

- In only 2 of 7 papers were all the calculated tie-lines correct.

- Among papers showing errors, four of them had more than 35% incorrect tie-lines and in one paper all the calculated tie-lines presented were wrong.

To evaluate the magnitude of these deviations for all the incorrect tie-lines, the stable splitting was calculated for the

middle point of each "false" tie-line. Deviations of more than 28% in the mole fraction were obtained.

On the other hand, it was observed that even with commercial BIP regression tools (ChemCAD [40]) false equilibrium solutions could be obtained [47].

For every set of parameters involved in the regression procedure, the equilibrium compositions must be calculated to compare them with the experimental ones. These calculated compositions must be *real equilibrium compositions* and must therefore satisfy the equilibrium criterion, for example formulated as the isoactivity condition for LLE:

$$OF(a) = \sum_{t=1}^{n} \sum_{i=1}^{c} (a_{i,t}^{I} - a_{i,t}^{II})^2 \qquad (2)$$

where $a_{i,t}^{P}$ is the activity of component i in liquid phase P(I and II) for tie-line number t, n is the number of tie lines and c is the number of components.

Despite the correct fulfilment of eq. (2), calculated compositions may be very different from the experimental data. The composition objective function (eq. (3)) would only decrease as far as the model is capable of reproducing the experimental phase equilibrium data:

$$O.F(x) = \sum_{t=1}^{n} \sum_{p=1}^{np} \sum_{i=1}^{c} \left[\left(x_{i,t}^{p} \right)_{exp} - \left(x_{i,t}^{p} \right)_{cal} \right]^2 \qquad (3)$$

where $x_{i,t}^{P}$ is the molar fraction of component i in liquid phase p for tie-line number t and np is the number of phases.

Despite the fact that these ideas are widely known, the acceptance of simplifications during data regression is surprisingly common. The wrong results found in literature reveal that a decrease in the composition deviations could have been promoted by "relaxing" the isoactivity requirement for the calculated tie-lines. This is obviously an unacceptable practice since the accuracy of the regression is distorted; the parameter values obtained as correlation results are not valid and neither standard deviation nor any other data fit indicator obtained is valuable.

In a previous paper [48], problems were illustrated for a type 1 ternary system when the isoactivity criterion is used as the equilibrium condition in liquid phase splitting calculations. For a certain global mixture, a set of different "tie-lines", all of them with O.F.(a) $<10^{-12}$, have been obtained. Evidently, only one single tie-line can be correct, and the rest are false solutions. Therefore, it can be concluded that O.F.(a) values lower than 10^{-12}, which could be apparently sufficient, do not guarantee the isoactivity condition. This example shows that the isoactivity criterion is sometimes not sensitive enough to calculate LLE data and, as a consequence, problems in finding the true solution can arise depending on the method or algorithm used for the optimization. From this work it was confirmed that if the equilibrium condition is relaxed to improve the numerical method convergence, especially when the isoactivity criterion is used, false solutions could be wrongly accepted.

The isoactivity criterion and the common tangent plane equilibrium condition were compared in the surroundings of the solution, and it was concluded that the latter provides a better definition of the stable splitting, since it is more sensitive to deviations.

In our proposed methodology, the common tangent plane equilibrium conditions, as proposed by Iglesias-Silva and col. [49], have been used to define the equilibrium between liquid phases. Moreover, we have applied these equations to describe all kinds of equilibrium regions (LS, LLS, LLL,...) present in type 0, 1, 2, 3 and 4 ternary systems. Additionally, the equilibrium equations of the common tangent plane have been formulated with the "*Complex Step Derivative Approximation Technique*" [50] that avoids the typical error of using numerical finite differences and the use of extensive analytical expressions that change every time the g^M model is modified. The application of this tangent plane criterion reduces to the simultaneous solution of the system of $(c-1)\cdot np$ non-linear equations. The Newton-Raphson method is the numerical method used to solve these systems of equations.
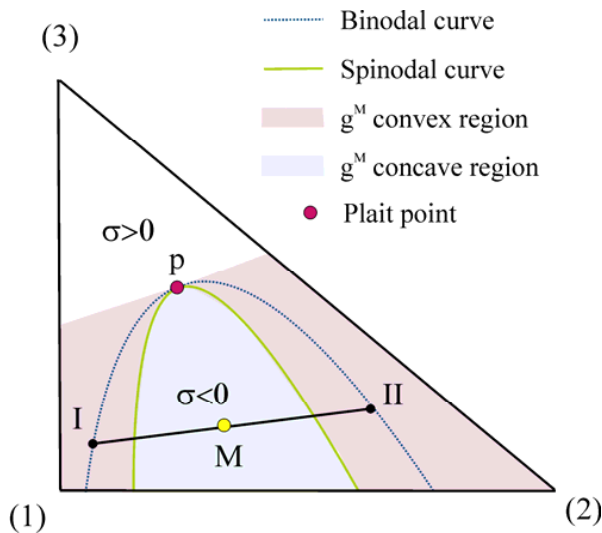
3.4. Limiting Composition Region for the LLE Calculation

The stability criterion for a homogeneous phase in a c-component system is that the matrix of the derivatives:

$$\frac{\partial^2 g^M}{\partial x_i \cdot \partial x_j} > 0 \quad i, j = 1,2,....c\text{-}1 \tag{4}$$

should be positive definite [51].

In the correlation program developed [52], the calculation of the solutions for the determinant of the Hessian matrix (σ) provides the spinodal curve that allows the separation between the convex region ($\sigma > 0$), where the liquid equilibrium compositions (I and II) must be searched, from the concave region ($\sigma < 0$) where all unstable mixtures (M) must be located (Fig. **4**).

Fig. (4). Limited composition region for the liquid-liquid equilibrium search.

This procedure excludes trivial solutions, improves the convergence since it avoids most of the problems arising from multiple solution roots and the need for smart composition initial guesses, and is less time consuming because it avoids searching for equilibrium splitting in the composition range with no g^M curvature changes.

3.5. Plait Point Location

For each iteration of the model parameters through the optimization procedure, the LLE calculation requires the uniform distribution of the unstable global mixture points (M). The previous location of the plait point in a ternary system, before the binodal curve or LLE calculations, helps with that mixture points distribution. In the plait point, it must be simultaneously accomplished [53, 54]:

$$\sigma = \begin{vmatrix} \dfrac{\partial^2 g^M}{\partial^2 x_1} & \dfrac{\partial^2 g^M}{\partial x_1 \partial x_3} \\[2ex] \dfrac{\partial^2 g^M}{\partial x_3 \partial x_1} & \dfrac{\partial^2 g^M}{\partial^2 x_3} \end{vmatrix} = 0 \qquad \delta = \begin{vmatrix} \dfrac{\partial \sigma}{\partial x_1} & \dfrac{\partial \sigma}{\partial x_3} \\[2ex] \dfrac{\partial^2 g^M}{\partial x_3 \partial x_1} & \dfrac{\partial^2 g^M}{\partial^2 x_3} \end{vmatrix} = 0$$

$$\omega = \begin{vmatrix} \dfrac{\partial \delta}{\partial x_1} & \dfrac{\partial \delta}{\partial x_3} \\[2ex] \dfrac{\partial^2 g^M}{\partial x_3 \partial x_1} & \dfrac{\partial^2 g^M}{\partial^2 x_3} \end{vmatrix} \geq 0 \tag{5}$$

These conditions unequivocally define the plait points (p in Fig. (**4**) and Fig. (**1**)) of the splitting equilibrium region of the system.

3.6. Geometrical Procedure for the Approximate Calculation of the LLLE in Type 3 Ternary Systems

In the case of type 3 ternary systems that include a tie-triangle (LLLE), the number of heterogeneous regions increases. Therefore, the confinement to limited composition regions for the LLE calculations using the previous procedure (section 3.4) is more complex. An alternative method has been developed to calculate the LLL tie-triangle first, which is very valuable for the subsequent confinement of the composition regions for the LL tie-line calculations. The presence of three-liquid equilibrium phases (LLLE tie-triangle) implies the existence of three points on the g^M surface with a lower common tangent plane (Fig. **5**). A procedure has been proposed to separate the regions where every one of the three liquid equilibrium points must be confined [55]. The use of these LLLE restricted composition regions during the calculation or correlation of type 3 ternary systems, improves the convergence of the numerical methods that are typically very sensitive to the initial-guess values used. Alternatively, if the algorithm [55] evolved providing planes that progressively defined smaller regions, the LLLE solution (Fig. **5b**) would be found geometrically.
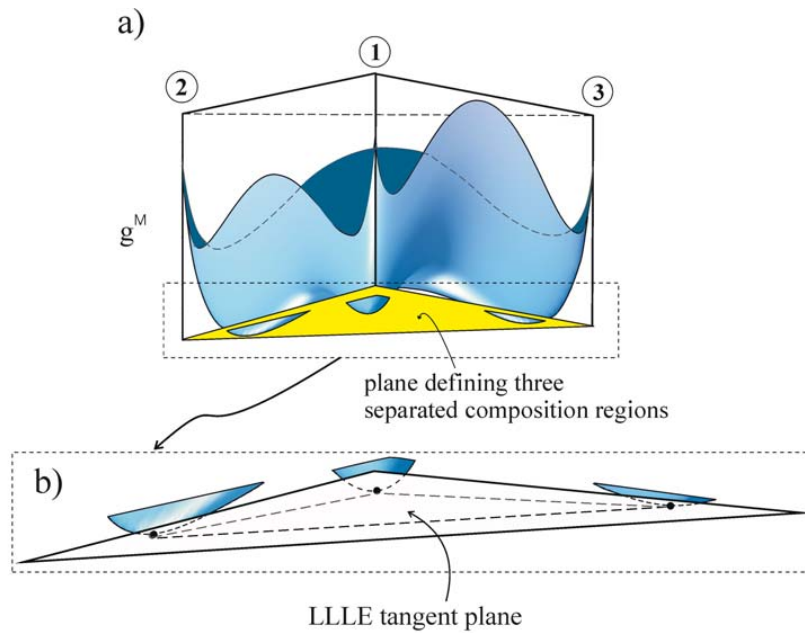
Fig. (5). Gibbs Energy surface (g^M) for a type 3 ternary system to illustrate the proposed method: **a)** a plane is formed to intersect the g^M surface giving three separate composition regions and **b)** the LLLE calculation is performed with liquid compositions limited to these regions.

3.7. Application of the Extended "Vector Method" when Special LLE Convergence Problems Arise

A procedure based on the vector method (originally proposed by Eubank, 1992 [10]) has been devised [48] and is used in the correlation program only when convergence problems appear in the tie-line calculation, due to flat g^M surfaces or near the plait point zone:

- First, an α-angle range for the ternary global mixture M (Fig. **6**) is defined. For a sheaf of straight lines passing through the composition of the mixture M, the two common tangent points (I, II) to the g^M function in the sectional plane corresponding to each direction defined by the α-angle (i.e. close to the plait point) are obtained (necessary condition for LLE).

- Among all pairs of calculated compositions, the "true" tie-line corresponds to the minimum value for the Gibbs energy of mixing (g^{tl}) (sufficient condition).

This method is really useful for cases with convergence problems or with special uncertainty (e.g. close to the plait point). We have checked that for all these problematic situations, the guided calculations carried out by this modified vector method guarantee that the LLE solution is obtained.

3.8. Estimation of the Model Parameters

The model parameter optimization is carried out by minimizing the OF defined by eq. (6) using the Flexible Simplex Method [56]. This OF can generally be applied for all type of ternary systems (types 0, 1, 2, 3 and 4). The OF considers two contributions: one corresponding to the LLE regions (OF_{LL}), and the other one corresponding to the SLE regions (O.F$_{SL}$).
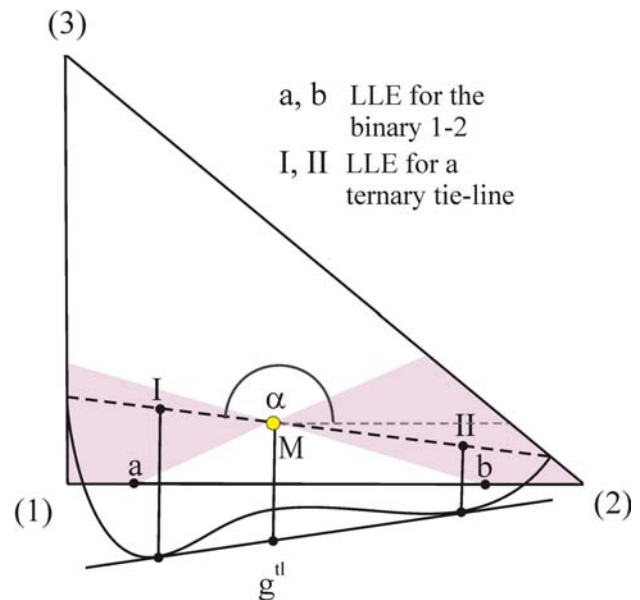
Fig. (6). Graphical representation of the modified vector method.

$$OF = OF_{LL} + OF_{SL} =$$

$$\sum_{t=1}^{n_{LL}} \sum_{P=1}^{np_{LL}} \sum_{i=1}^{c} \left[\left(x_{i,t}^P\right)_{\exp} - \left(x_{i,t}^P\right)_{cal} \right]^2 + \sum_{t=1}^{n_{SL}} \sum_{i=1}^{c} \left[\left(x_{i,t}^L\right)_{\exp} - \left(x_{i,t}^L\right)_{cal} \right]^2 \quad (6)$$

where $x_{i,t}^P$ is the molar fraction of component i in liquid phase p for tie-line LL number t and $x_{i,t}^L$ is the molar fraction of component i in the liquid phase L for tie-line SL number t; n_{LL} and n_{SL} refer to the number of tie-lines in LLE and SLE regions, respectively; n_{pLL} is the number of liquid phases in each LL tie-line (n_{pLL}=2); exp and cal refer to experimental and calculated data, respectively.

For ternary systems types 0, 1, 2 and 3, the OF_{SL} contribution vanishes. In type 3 systems, for the evaluation of the LLLE in eq. (6), the tie-triangle is considered to be divided into three LL tie-lines (each one with $n_{pLL}=2$).

For the equilibrium data correlation in type 4 ternary systems including inorganic salt forming hydrates, the ShLLE and ShSLE tie-triangles are also considered to be divided into tie-lines: the ShLLE region is considered to be divided into one LLE pair and two ShLE pairs, and the ShSLE tie-triangle is formed by the SLE and ShLE pairs. LLE and SLE (ShLE) tie-lines are included, respectively, in the OF_{LL} and OF_{SL} contributions of eq. (6).

3.8.1. Definition of a Robust Comparison Criterion between the Experimental and Calculated Equilibrium Data

In order to evaluate the accuracy of an experimental data fitting, for each parameter iteration, calculated compositions should be compared with the experimental data during the optimization procedure. The usual criteria to obtain the calculated LL data point to be compared with each experimental tie-line are:

- To calculate the tie-line by fixing the composition of one component i in a phase p equal to the experimental value

$$\left(x_i^p\right)_{cal} = \left(x_i^p\right)_{exp} \tag{7}$$

- To calculate the tie-line that passes through the unstable global mixture point obtained as the middle point of the experimental tie-line

$$\left(z_i\right)_{cal} = \left(z_i\right)_{exp} \tag{8}$$

- To select, among all the t calculated tie-lines, the nearest (minimum distance d) to the experimental tie-line:

$$\left(x_{i,t}^p\right)_{cal} = \min d = \min\left[\sum_{i=1}^{c}\left[\left(x_{i,t}^p\right)_{exp} - \left(x_{i,t}^p\right)_{cal}\right]^2\right]^{0.5} \tag{9}$$

However, all these comparison criteria can generate calculation problems. For example, Fig. (**7a**) qualitatively shows how a set of parameters, during the optimization process, can give a binodal curve smaller than the experimental one. The use of one of the two criteria (eq. (7) and (8)) can lead to LLE splitting calculations in the homogeneous phase region, with the consequent convergence problems.

Additionally, a more complex situation can occur when the set of parameters being evaluated can reproduce an additional splitting region (i.e. LLE) that does not exist in the experimental system (Fig. **7b**). A quantitative example of this situation was discussed in detail in [52]. With any of the conventional comparison criteria (eqs. (7) to (9)), the real quality of the guessed parameter set would not be evaluated because non-desirable equilibrium regions generated by the parameters would not be taken into account.

For these reasons, we propose a comparison criterion that always evaluates, at each iteration loop, all the equilibrium regions described by the tested parameters in the entire composition diagram. The calculated equilibrium data are obtained for a set of unstable global mixtures uniformly distributed in the heterogeneous regions predicted. Comparable experimental data are uniformly interpolated using the same criteria. In this way, a real measurement of the accuracy of the fitting is obtained.

3.8.2. Application of NRTL Binary Parameter Restrictions

During the optimization procedure, the model parameter values should be restricted to obtain consistent results with the phase equilibrium behavior of the system. In this way, apart from the recommended NRTL parameter range found in the literature [57,58], a novel condition is deduced to guarantee a consistent total or partial miscibility behavior between the experimental and calculated system, at least for the binary subsystems.
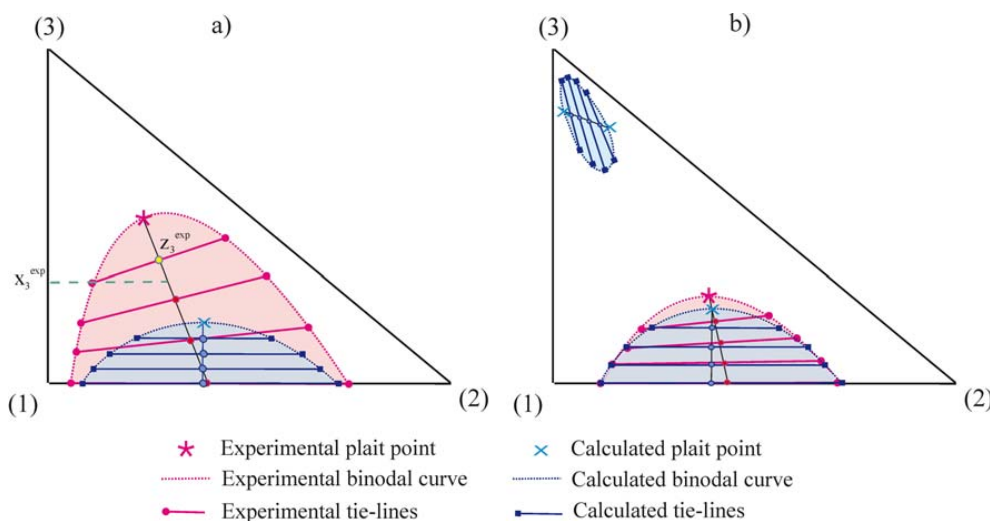
Fig. (7). Representation of the comparison criterion between experimental and calculated LLE data for two situations where the number of experimental and calculated LLE regions: a) is the same; b) is different.

a. NRTL Binary Parameter Value Restrictions to Reproduce Total or Partial Miscibility Condition

A relationship between the NRTL model parameters, that allows imposing the requirement of the expected total or partial miscibility behavior for each one of the binary subsystems taking part of the multicomponent system, is desirable in order to avoid convergence problems. This restriction would allow consistent equilibrium behavior for each tested set of parameters during the optimization algorithm. Therefore, inconsistent situations would be avoided, such as those presented in DECHEMA *Chemistry Data Series Collection*: (a) Heptane (1) + Toluene (2) + Dimethyl sulphate (3) at 17ºC, where a type 1 system has been correlated with NRTL parameters reproducing two partially miscible binary subsystems (type 2 system), and (b) Hexane (1) + Methyl-ester cis-9-octadecenoic acid (2) + Acetonitrile (3) at 25ºC, where a type 2 system has been correlated with NRTL parameters that correspond with a type 1 system ([13], Vol. 2, p. 436 and 190, respectively). More examples of these inconsistent situations are given by Reyes-Labarta and col. [59].

In a previous work [60], we showed the representation of the conjugated A_{ij} parameters (NRTL) for miscible and partially miscible pairs, which were clearly divided into two regions. In Fig. (**8**) the equivalent graph is presented for the NRTL dimensionless parameters (τ_{ij} and τ_{ji}) and α_{ij}=0.2. The boundary definition $\tau_{ji} = f(\tau_{ij})$ is given by the following equations:

$\tau_{ij}<-3$ $\qquad$ $\tau_{ji}= -1.833\cdot\tau_{ij}+ 1.423$ $\qquad$ (10a)

$-3<\tau_{ij}<7$ $\qquad$ $\tau_{ji} = -4.191\cdot10^{-3}\cdot\tau_{ij}^{3} + 9.089\cdot10^{-2}\cdot\tau_{ij}^{2}$

$\qquad\qquad\qquad - 1.206\cdot\tau_{ij}+ 2.481$ $\qquad$ (10b)

$\tau_{ij}>7$ $\qquad$ $\tau_{ji} = -0.545\cdot\tau_{ij} + 0.7758$ $\qquad$ (10c)

The above restrictions depend on the non-randomness parameter (α_{ij}). The representation of τ_{ji} versus τ_{ij} for different values of α_{ij} shows that the variation of the frontier is not very significant, although for high values of α_{ij} ($\alpha_{ij} > 0.43$) the behavior starts to differ from the general trend [61].

b. NRTL Binary Parameter Value Restrictions to Reproduce Island Type Ternary Systems

In LLE island type ternary systems at constant temperature and pressure, a binodal curve lies around a heterogeneous two liquid region (LL) that is entirely surrounded by a homogeneous one liquid region (L). Therefore, there is complete miscibility in each one of the three binary subsystems involved (defined by convex g^{M} binary curves), which simultaneously coexist with a LL ternary region (concave g^{M} surface region).

We have found conditions for the NRTL binary parameters that allow the formation of island type ternary systems [62]. From a systematic study, it was concluded that the main requirement for the ternary LLE island region was the existence of a binary subsystem with a very low g^{M}_{min} value (dissimilar) compared to the other two binary
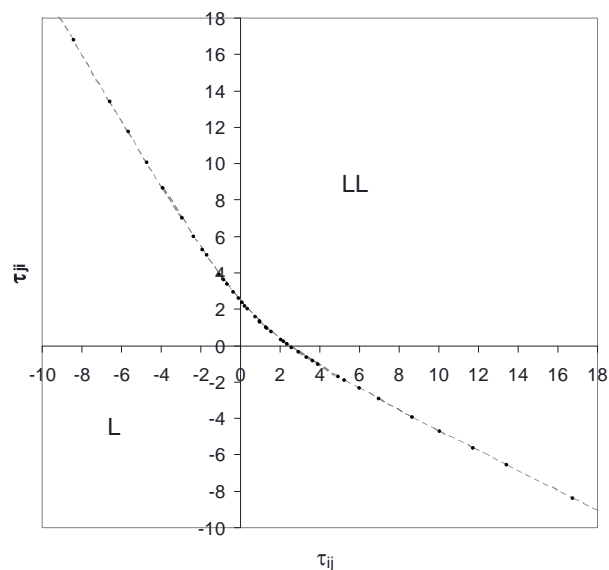
Fig. (8). Miscible (L) and partially miscible (LL) regions and boundary using the NRTL model, as a function of the dimensionless conjugated binary parameters τ_{ij} and τ_{ji}, with α_{ij}=0.2.

subsystems. In addition, it was observed that the island type binodal curve is preferably located in the opposite side of the "dissimilar binary" (Fig. **9**).

The representation of the sum of the conjugated binary interaction parameters ($A_{ij} + A_{ji}$) versus the g^{M}_{min} value [62] showed that the negative values of such sum corresponded to the dissimilar binary and the positive sum corresponded to the other two binary subsystems. These conclusions led to the following restrictions for the dimensionless parameters, which are used in the equilibrium data regression of this type of system:
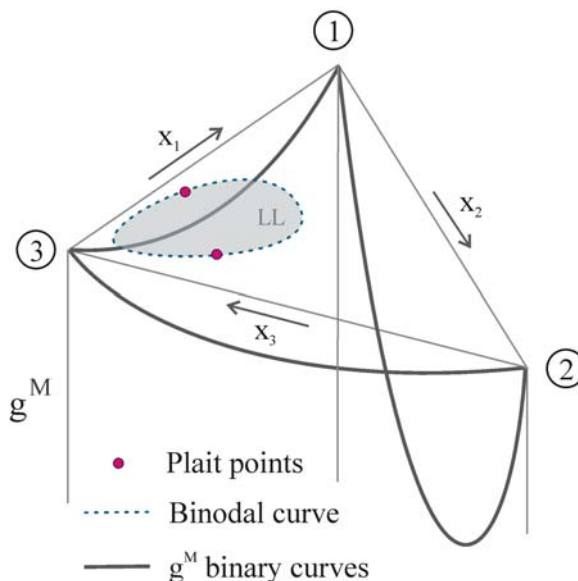
Fig. (9). Section of a triangular prism where the three g^{M} binary subsystem curves and the ternary binodal curve are represented for an island type ternary system.

$$\tau_{12} + \tau_{21} < 0 \text{ "dissimilar binary subsystem"} \qquad (11)$$

$$\tau_{13} + \tau_{31} > 0 \qquad (12)$$

$$\tau_{23} + \tau_{32} > 0 \qquad (13)$$

These conditions must be combined with the fulfilment of $\tau_{ji} < f(\tau_{ij})$ ($f(\tau_{ij})$ defined in eq. (10)) to guarantee the total miscibility of the three binary subsystems, giving the following conditions for the NRTL parameters that allow island type ternary systems to be generated:

$$-\tau_{12} > \tau_{21} \text{ "dissimilar binary subsystem"} \qquad (14)$$

$$-\tau_{13} < \tau_{31} < f(\tau_{13}) \qquad (15)$$

$$-\tau_{23} < \tau_{32} < f(\tau_{23}) \qquad (16)$$

3.9. Validation of the Results According to the "Lowest Common Tangent Plane" Stability Criterion

According to the methodology proposed in section 3.4, all the equilibrium compositions calculated are restricted to convex regions of g^M. Thus, false equilibrium solutions corresponding to Gibbs global maxima, that are also solutions of the common tangent plane criterion, are avoided. However, since local minima can also be found, it is necessary to check that the obtained solutions correspond to the global minima for the Gibbs energy.

For each equilibrium solution, the tangent plane π passing through the conjugated equilibrium phases is calculated in order to confirm that it does not intersect the g^M surface at any other point. The sign of the difference between the calculated tangent plane (π) and the g^M surface must be negative or zero in the complete composition space, which guarantees that the lowest tangent common plane has been located:

$$\pi - g^M(x_1^p, x_2^p) = \frac{\partial g^M}{\partial x_1}(x_1 - x_1^p) + \frac{\partial g^M}{\partial x_2}(x_2 - x_2^p) \leq 0 \qquad (17)$$

3.10. Application of the Proposed Strategies in the Regression Algorithm

The algorithm including all the strategies summarized in this section, for the simultaneous correlation of all the existing equilibrium regions in types 0 (island), 1, 2, 3 and 4 ternary systems, has been implemented in Visual Basic 2005® [63].

For types 0, 1 and 2 systems, compositions for LLE calculations are restricted to limited regions according to the method described in section 3.4. The only difference between these systems lies in the location of the unstable global mixture points (M) that are distributed between the plait points (type 0), previously calculated according to section 3.5, the partially miscible binaries (type 2), or between the partially miscible binary and the plait point (type 1 and type 2 with two LLE regions), depending on the type of system. The equilibrium conditions are solved together with the restrictions for the composition confinement (section 3.4) to calculate the LLE data. The modification of the vector method (section 3.7) is used only when problems of convergence arise, especially near the plait point.

In the case of a type 3 system, the geometrical method described in section 3.6 allows the confinement of three separate composition regions where every one of the three liquid phases in the LLLE tie-triangle are located. The solution of the LLLE equations restricted to that condition provides the LLL tie-triangle, which is very valuable for the subsequent confinement of the composition regions for the LL tie-line calculations. The mixture points (M) for these LLE regions are distributed among each side of the LLLE tie-triangle and the corresponding partially miscible binary.

For type 4 systems, calculation starts with the SLLE tie-triangle determination. Since the solid Gibbs energy is fixed (g^S), only liquid phases of this triangle should be confined to the convex regions according to the method described in Fig. (**4**) for type 1 systems. Once the SLLE is calculated, LLE and SLE regions are determined. SLE calculation is simple since the solid phase compositions and their Gibbs energy values are (g^S or g^{Sh}) are fixed. In these regions, unstable global mixture points (M) are distributed using the SLE binary solubility and the rest of previously determined regions (LLE, SLLE,...) as references.

Conditions for the NRTL binary parameters values described in section 3.8.2 that guarantee the total or partial miscibility for each one of the binary subsystems included in the ternary system have proved to be very efficient during the optimization procedures. Moreover, the application of the proposed robust composition comparison criterion (section 3.8.1) guarantees the consistency of the solution in all the composition space.

4. RESULTS AND DISCUSSION

4.1. Correlation Results

Table **1** collects all the ternary systems correlated in the present research, together with the reference to the paper where the regression has been presented and discussed.

Results obtained show that the NRTL model, despite evident limitations, has more capabilities than expected. Some Types 1 and 2 systems, which had not been regressed before or, if they were, inconsistent results had been obtained, have been consistently correlated using the robust proposed methodology.

For type 3 systems, the NRTL model has been able to simultaneously generate all the equilibrium regions present (LLE and LLLE), though deviations between experimental and calculated equilibrium data are too high for some of them. The scarce compatibility between the calculated binary subsystems and the calculated LLL tie-triangle demonstrates the lack of capability of the NRTL equation to simultaneously model all the equilibrium regions present in this type of systems.

Table 1. Compilation of the Systems Correlated with the NRTL Model, using the Proposed Algorithm

System	Components	Type	Equilibrium Regions	Reference Paper
1	Water + Dimethyl sulfoxide + Tetrahydrofurane, 20 ℃	0	LL	[62]
2	Trichloroacetic acid + Antipyrine + Water, 30 ℃	0	LL	[62]
3	Furfural + Formic acid + Water, 35 ℃	1	LL	[59]
4	Water + Acetic acid + Dichloromethane, 19 ℃	1	LL	[59]
5	Toluene + Acetaldehyde + Water, 17 ℃	1	LL	[59]
6	Propyl acetate + Formic acid + Water, 35 ℃	1	LL	[59]
7	1-Butanol + Methanol + Water, 60 ℃	1	LL	[59]
8	4-Methyl-2-pentanone + Acetonitrile + Water, 30 ℃	1	LL	[59]
9	Acetonitrile + 1-Propanol + Hexane, 25 ℃	1	LL	[59]
10	Propenoic acid + Propanoic acid + Water, 70 ℃	2	LL	[59]
11	Hexane + 2,5-Dimethyl-THF + 1,2-Ethanodiol, 120 ℃	2	LL	[59]
12	Trichloroethene + Furfural + Water, 20 ℃	2	LL	[59]
13	1-Hexanol+ Nitromethane + Water, 40 ℃	2	LL	[59]
14	Hexane + 9-Octadecenoic acid (cis), Methyl ester + Acetic acid, nitrile, 25 ℃	2	LL	[52]
15	Propanoic acid, Nitrile + Heptane + Octane, 1,8-oxy, perfluoro, 25 ℃	2	LL	[52]
16	Isopropilbencene + 2-Methyl-propanoico acid + Water, 15℃	2	LL	[64]
17	1-Nonanol + Nitromethane + Water, 23 ℃	3	LLL, LL	[55]
18	1-Hexanol + Nitromethane + Water, 21 ℃	3	LLL, LL	[55]
19	Lauryl alcohol + Nitromethane + Glycol, 22 ℃	3	LLL, LL	[55]
20	Water + 1-Butanol + NaCl, 25 ℃	4	LL, LLS, LS	[60]
21	Water + 3-Pentanol + NaCl, 25 ℃	4	LL, LLS, LS	[60]
22	Water + Acetone + NaCl, 25 ℃	4	LL, LLS, LS	[60]
23	Water + Ethanol + NaCl, 25 ℃	4	LS	[60]
24	Water + 1-Butanol + LiCl, 25 ℃	4	LL, LLS, LS, LSh, LSSh	[65]
25	Water + 1-Pentanol + LiCl, 25℃	4	LL, LLS, LS, LSh, LSSh	[64]

Type 4 systems with solid phases have also been correlated, even with the presence of hydrated solids. For the latter, the most important difficulty was the simultaneous fitting of both the LLE and ShLLE regions. Many topological conditions must be fulfilled by the Gibbs energy surface, as is required by the tangent plane criterion, in order to simultaneously reproduce so many different hetero-geneous regions and different aggregation state phases.

The results obtained in the correlation of type 0 (island ternary systems) using the NRTL equation have demonstrated that this model is able to generate a LLE ternary region where all three binary subsystems are completely miscible. However, deviations obtained for all the systems correlated have been considerably high.

4.2. Analysis of NRTL Limitations. Methods for Improving Models for Phase Equilibria Composition Calculations

Many geometrical conditions must be accomplished by the g^M surface defined by the model, in order to fulfil the common tangent plane equilibrium conditions necessary to reproduce, with accuracy, the existing equilibrium regions of ternary systems in the complete composition space. Difficulties arise especially for types 3 or 4 systems regression since they have so many different equilibrium regions to be simultaneously correlated, and for type 0 systems that require a singular change of curvature among the ternary space and the binary subsystems. As we commented on before, even for some type 1 and 2 systems

the NRTL model shows limitations to reproduce the equilibrium with precision.

In order to establish the lack of flexibility of NRTL to correlate the condensed phase equilibrium data for many ternary systems, a systematic study was carried out [66]. It was concluded that there are "gaps" where it is not possible to find parameters to reproduce homogeneous g^M curves with, for instance, different minimum values (g^M_{min}) located at a given x_i composition (Fig. **10a**). This, together with the fact that each partially miscible binary subsystem can only be appropriately reproduced by a unique pair of binary parameters, may provide a considerable limitation for the flexibility of the model to reproduce distinct phase equilibrium behaviors. Fig. (**10a**) shows an example of the systematic study for $x_{2min} = 0.35$, where a "gap" appears since parameters found for the corresponding g^M_{min} values in

that range lead to LL phase splitting. For a type 1 ternary system with the 1-3 pair partially miscible, the existence of such "gaps" is not desirable for any of the homogeneous binary subsystems (e.g. 1-2 and 2-3 binary in Fig. **10b**). The combination of the parameter values found for the homogeneous binary subsystems 1-2 and 2-3, with the partially miscible binary pair 1-3, are responsible for the size of the binodal curve and the slopes of the calculated tie-lines. The existence of "gaps" imposes serious limitations in the LL equilibrium regions that the model can define, what has been schematically represented in Fig. (**10b**).

A more flexible model should be capable of reproducing g^M binary curves that are compatible with the same LL splitting and it must avoid the existence of "gaps". As an example, a modification of NRTL was proposed including a new parameter per component (F_i):
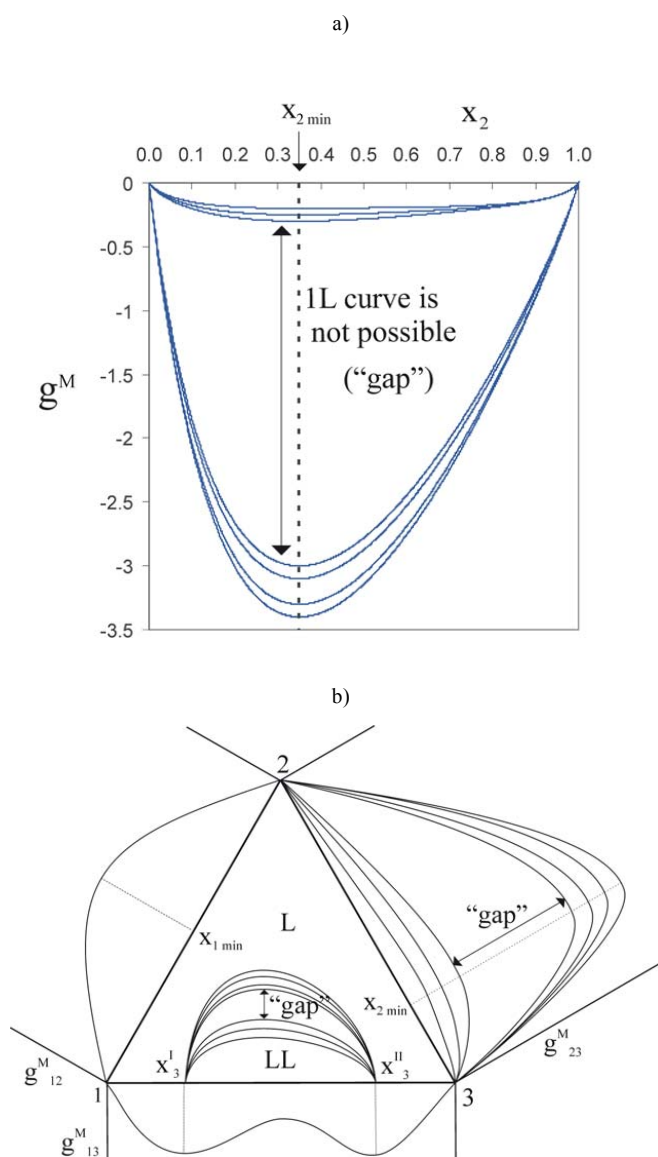
Fig. (10). Schematic representation of the limitations of the NRTL model for a type 1 system: **a**) systematic study of the homogeneous g^M binary curves for $x_{2min}=0.35$; **b**) g^M binary curves for a type 1 ternary system where the existence of "gaps" constraints the LL region calculated by the model.

Table 2.   Compilation of Systems Correlated by using the Modified NRTL Model

System	Components	Type	Equilibrium Regions	Reference Paper
26	1-Hexanol + Nitromethane + Water, 21ºC	3	LLL, LL	[66]
27	Methanol + Diphenilamine + Ciclohexane, 25ºC	1	LL	[66]
28	1-Nonanol + Nitromethane + Water, 23ºC	3	LLL, LL	[64]
29	Isopropylbenzene + 2-Methyl-propanoic, acid + Water, 15ºC	2	LL	[64]

$$\frac{G^E}{RT} = \sum_i F_i \cdot x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} \tag{18}$$

where F_i are the *new parameters* proposed for the modified model. The rest of parameters are defined as in the original model [14].

Regressions of some systems have been improved by using the modified model (Table **2**). Results obtained with both models have been compared in previous works [64,66].

The capability of the existing G^E models so far is not sufficient to correlate the phase equilibrium data of many systems. The insistence of using theoretical based models and exclusively with a few binary parameters, are desirable characteristics but perhaps too strict to respond to the complex behavior of the molecular interactions in the liquid mixtures. Until a theoretical and more flexible model is developed, a practical treatment based on the topology analysis of the g^M function, according to the common tangent plane criterion, and without the traditional limitations has shown to be an effective way to obtain better results.

CONCLUSIONS

The present paper summaries previous works that have been focused on the study of the deficiencies found in algorithms and G^E models for the regression of condensed phase equilibrium data in ternary systems and the proposal of alternatives to avoid them.

A robust algorithm has been developed not only to correlate equilibrium data for type 1 and 2 ternary systems, but also for the correlation of type 3, type 0 (island), and type 4 ternary systems, which are not usually included in the capabilities of many of the existing commercial tools for data reduction. It includes novel strategies intended to avoid the well-known convergence faults and also to guarantee the consistency of the parameters obtained. In the referred papers, the importance of the g^M topology for analysing the characteristics that the g^M function must accomplish, in order to reproduce all the existing equilibrium regions in the different type of ternary systems (type 0, 1, 2, 3 and 4), has been demonstrated. This analysis is very useful to validate the results obtained, and to evaluate the capabilities of the G^E models.

From the results obtained it can be concluded that the new g^M function needs to be more flexible than the local composition models (NRTL and UNIQUAC) in order to represent the phase equilibria of singular and complex systems. A simple modification of NRTL has been tested only as an example to show how slight modifications can considerably improve results.

To increase the G^E function flexibility should be a major objective in phase equilibria calculations, but a change of mind will be necessary to dismiss the limitations, desirable but too severe, traditionally imposed to the models.

CONFLICT OF INTEREST

None declared.

ABBREVIATIONS

a	=	Activity
A_{ij}	=	Binary interaction parameters (K) for components i and j
c	=	Number of components
G^E	=	Excess Gibbs energy (J·mol⁻¹)
G^I	=	Ideal Gibbs energy of mixing (J·mol⁻¹)
G^M, g^M	=	Gibbs energy of mixing (J·mol⁻¹ and dimensionless, respectively)
LLE	=	Liquid-liquid equilibrium (tie-line)
LLLE	=	Liquid-liquid-liquid equilibrium (tie-triangle)
n	=	Number of tie-lines
np	=	Number of phases
nLL	=	Number of liquid-liquid tie-lines
nSL	=	Number of liquid-solid tie-lines
O.F	=	Objective function
p	=	Plait point
P	=	Pressure (Pa)

R	=	Gas constant $(J \cdot K^{-1} \, mol^{-1})$
SLE	=	Solid-liquid equilibrium
SLLE	=	Solid-liquid-liquid equilibrium
ShLE	=	Hydrated solid-liquid equilibrium
ShLLE	=	Hydrated solid-liquid-liquid equilibrium
ShSLE	=	Hydrated solid-solid-liquid equilibrium
T	=	Temperature (K)
VLE	=	Vapour-liquid equilibrium

Greek symbols

α_{ij}	=	Non-randomness NRTL factor
π	=	Tangent plane
τ_{ij}	=	Binary interaction parameters (K) for components i and j

Subscripts

exp	=	Experimental
calc	=	Calculated
i	=	Component number
LL	=	Liquid-liquid equilibrium
min	=	Minimum
SL	=	Liquid-solid equilibrium
t	=	Tie-line number

Superscripts

L	=	Liquid phase
M	=	Unstable global mixture
p	=	Phase p

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