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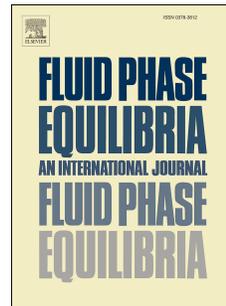
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**The unavoidable necessity of considering temperature dependence of the liquid
Gibbs energy of mixing for certain VLE data correlations**

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Abstract

Running vapor-liquid equilibrium (VLE) data correlation with interaction parameters independent of temperature is a common practice that may lead to incongruous situations, which may remain unnoticed. A non-negligible number of VLE data sets for binary systems appear very poorly correlated in literature by using any of the existing models with constant parameters and without any apparent explanation. This paper illustrates the unavoidable necessity of considering the temperature dependence for the parameters of the models used to formulate the activity coefficients of the liquid mixtures (such as NRTL, UNIQUAC, Wilson, among others) in order to adequately represent certain experimental data. For these systems, such an approach is mandatory and not a choice. Moreover, there are certain cases where even considering such temperature dependence of the parameters of the liquid phase is not enough and other alternatives must be used in order to enable a coherent correlation of the VLE data.

In addition, a strategy has been suggested that allows knowing in advance when the parameters should be considered temperature dependent. The attractive feature of this proposal is that the answer to the question of whether a T-dependence is necessary is obtained just from the experimental VLE data, without using any particular model for the Gibbs energy of mixing for the liquid phase. New results of VLE data correlation showing markedly improved fittings are presented for some of the systems poorly correlated in literature, showing the potential of the procedure.

Keywords: vapor-liquid equilibrium, VLE correlation, NRTL, activity coefficient model, Gibbs energy of mixing.

1. Introduction

Local composition models such as NRTL or UNIQUAC are frequently used to represent the non-ideality of the liquid phases in the correlation of phase equilibrium data where liquid phases are present. This is the case of liquid-liquid equilibrium (LLE) and vapor-liquid equilibrium (VLE). Commercial design programs such as Aspen Plus [1] or CHEMCAD [2] use them to run phase equilibrium calculations, though they may dramatically fail in representing certain systems. We have been working lately in analyzing the capabilities and limitations of these activity coefficient models. As a result of this work, we have identified some severe limitations of such models to represent VLE (or VLLE) in ternary azeotropic systems [3], as well as certain binary VLE and ternary LLE behaviors [4][5]. With the aim of improving previous poor correlation results that are published in literature, we have proposed some modifications of these equations that provide substantially improved results [6]. Nevertheless, we have found certain systems, such as that shown in Fig. 1(a) [7], where we have failed, and the correlation of such data has been not possible even using very flexible models.

Data in Fig. 1(a) show a very poor correlation with the NRTL model (similar results are obtained with other classical models [7]), though the experimental VLE data appear very smooth and quite symmetric with respect to the line $y=1-x$. Some VLE data sets showing more scatter or more non-symmetric behavior are better correlated. We found at that moment no reason to explain such behavior and neither is any reason provided in literature. To correlate these systems at constant pressure (P) we, as the authors in the literature cited, have used parameters independent of temperature. In LLE or VLE data correlation at constant temperature (T), it is obviously not necessary to use any dependence with temperature in the model. However, in VLE or VLLE correlation data at constant P, the temperature is different for each equilibrium composition. The temperature dependence in local composition models is extremely weak (as is the case of the NRTL model) unless this dependence is included in the parameters. Despite this, it is common practice to use constant parameters with temperature in these models. The isobaric VLE data of quite a few systems have could be correlated with sufficient accuracy in this way, explaining their widespread use. Although considering the variation of the binary interaction parameters of the models with temperature is not new and it is included in some process simulation packages such as Aspen Plus [1] or CHEMCAD [2], they are frequently considered as constant. For instance, the VLE Data

Collection by DECHEMA [8] includes the correlation with different models (Margules, Wilson, NRTL and UNIQUAC) of the experimental equilibrium data sets collected, but no variation of the parameters with temperature is considered. Similarly, many of the published papers (even recently) that include the correlation of experimental VLE data do not consider it. Only for some isobaric VLE data sets with a wide range of temperatures that can include partial liquid miscibility (VLLE) is this option sometimes taken into account [9]. For the other VLE data sets, the addition of such dependence seems to be considered only as a way of increasing *slightly* the flexibility of the model equation. Probably because it is at the expense of using many more parameters, this possibility is rarely used.

It is common practice to start the isobaric VLE correlation process using the most elementary version of the models, i.e. equations in their original forms and constant parameters with temperature. When the results obtained are poor, running the correlations in this way, some authors try to improve them. In some cases, the correlation results can be improved simply running the fitting again with some minor modifications, as for example starting from different initial values for the unknowns, improving the convergence of the equilibrium calculation algorithm or using a different objective function. If all these strategies do not solve the problem, then the use of a greater number of parameters in the model is sometimes considered, for example using T-dependent parameters. If even so, the correlation results were poor, very few researchers would consider the use of some modifications of the classical models, such as the addition of some term including ternary parameters among others. Regrettably, all these possibilities do not guarantee the solution to the VLE correlation data in all the cases either, and there are still many data sets that cannot be adequately correlated, at least for the moment. All these aspects are usually known by the researchers in the field. However, the remarkable aspect is that when this sequence is followed, because the researcher does not stop in the first step, it is frequently performed as a “trial and error process” without analysing the real reasons for the existing limitations in each case. In our opinion, this analysis could increase the possibilities of making significant progress in this field.

When attempting to understand the difficulties arising in the correlation of certain VLE data sets, and only after we analyzed the topology of the Gibbs energy of mixing

functions for the liquid ($g^{M,L}$) and vapor ($g^{M,V}$) phases was when we realized the true nature of one of the existing problems, i.e.: for some specific systems (not necessarily with a wide range of temperature nor LL splitting) the use of T-dependence in the parameters is *mandatory* and not a choice. In other words, for these systems, the widespread practice of not including the dependence of the model parameters with temperature in VLE data correlation (always referred to constant P) is itself *inconsistent*.

In these cases, this practice should be avoided in order not to continue with possible misinterpretations. It is very important to emphasize that *this is not a trivial question arising out of the necessity for some systems of higher flexibility in the model that can be provided by the higher number of parameters fitted when they are dependent on temperature*. Differently, this is a new insight about the inconsistency of assuming that the parameters are constants with temperature in isobaric VLE data correlation of some systems. Such inconsistency could and should be identified previously to avoid such useless effort. For these systems, no model (neither actual nor hypothetical) could represent the VLE experimental data, unless a strong dependence with temperature was considered.

In other words, the very weak influence of temperature in the existing activity coefficient models and the common practice of using constant interaction parameters with temperature lead in many cases to demand something that is simply *impossible* and that, as will be shown in the next section, could be known in advance. Regrettably, the variation of the parameters with temperature does not solve all the problems related to VLE data correlations and in such cases, other solutions must be derived and applied. Thus, the objective of this paper is to explain in detail and illustrate with examples all these assertions, which could have important consequences on the VLE data correlation. Besides, a graphical procedure is proposed to identify those VLE data sets that unavoidably require T-dependence in the parameters of the model, which could and should be used previously in the correlation process.

2. Discussion

In this discussion, we consider binary systems to facilitate the visualization of the graphical representations, but the conclusions could be extended to ternary or multicomponent systems.

2.1 Most of the information for VLE regressions is in the vapor phase

The Gibbs stability criterion establishes that in order to have VLE, a common tangent line must exist between the Gibbs energy of mixing functions for the vapor and the liquid phases, $g^{M,V}$ and $g^{M,L}$ curves respectively in Fig. 2, providing the global minimum of the Gibbs energy. In this Figure, z_1 is the mole fraction of the lightest component in the binary global mixture (M) of components 1 and 2; x_1^L and y_1^V are used for the molar fractions (component 1) in the liquid and vapor phases at equilibrium, L and V respectively.

If we consider ideal behavior of the vapor phase (a common practice in literature for moderate pressures), the dimensionless $g^{M,V}$ curve for a binary system (if the pure liquid at T and P of the mixture is considered as the reference state) is given by:

$$g^{M,V} = \frac{G^{M,V}}{RT} = y_1 \ln\left(\frac{P \cdot y_1}{p_1^0}\right) + y_2 \ln\left(\frac{P \cdot y_2}{p_2^0}\right) \quad \forall y_1, y_2 \in [0,1] \quad (1)$$

where p_i^0 is the vapor pressure for the pure component i and P is the total pressure. The deduction of this equation is in Appendix A.

Eq. (1) sets the $g^{M,V}$ curve at each temperature. Besides, the two experimental equilibrium compositions x_1^L and y_1^V in Fig. 2 are known for each VLE datum. If we combine all this information along with the Gibbs common tangent line equilibrium condition, the $g^{M,L}$ value and its derivative at each T for the liquid phase (L) in equilibrium are univocally defined, as shown next. The derivative to the $g^{M,V}$ curve of the vapor phase at the mole fraction of the vapor (y_1^V) is the following:

$$\left(\frac{dg^{M,V}}{dy_1}\right)_{T,P}^V = \left[\ln\left(\frac{y_1^V \cdot p_2^0}{y_2^V \cdot p_1^0}\right) \right] \quad (2)$$

The value of the Gibbs energy of mixing of the liquid phase is given by:

$$(g^{M,L})^L = \left(\frac{G^{M,L}}{RT} \right)^L = (x_1^L - y_1^V) \left(\frac{dg^{M,V}}{dy_1} \right)^V + (g^{M,V})^V \quad (3)$$

that can be rewritten using Eqs. (1) and (2) as

$$(g^{M,L})^L = (x_1^L - y_1^V) \left[\ln \left(\frac{y_1^V \cdot p_2^0}{y_2^V \cdot p_1^0} \right) \right] + \left[y_1^V \ln \left(\frac{P \cdot y_1^V}{p_1^0} \right) + y_2^V \ln \left(\frac{P \cdot y_2^V}{p_2^0} \right) \right] \quad (4)$$

The derivative to the $g^{M,L}$ curve of the liquid phase at the mole fraction of the liquid (x_1^L) must be equal to the one for the vapor phase at y_1^V :

$$\left(\frac{dg^{M,L}}{dx_1} \right)^L = \left(\frac{dg^{M,V}}{dy_1} \right)^V = \left[\ln \left(\frac{y_1^V \cdot p_2^0}{y_2^V \cdot p_1^0} \right) \right] \quad (5)$$

Consequently, the value of $g^{M,L}$ at the liquid equilibrium composition (x_1^L) and the slope of the tangent line to this function at this same point, are both fixed at each temperature T and the pressure P (Eqs. (4) and (5) respectively) by: the vapor pressures of the pure components at T and the experimental compositions for both V and L phases at equilibrium (y_1^V and x_1^L , respectively).

This means that because we are not using any model to represent the non-ideality of the vapor phase, relevant information about the liquid phase (fixed T and P), that is the $g^{M,L}$ value and its derivative at x_1^L , is determined by the vapor composition y_1^V . The vapor composition, in turn, determines the $g^{M,V}$ function and its derivative at y_1^V (ideal gas model). This insight give us a different way to provide the correlations of VLE data sets: a hypothetically “perfect” correlation of VLE data sets will be obtained when a set of parameters of the model used for the non-ideality of the liquid phase is found ($g^{M,L}$ cal) that satisfactorily reproduces the $g^{M,L}$ values and its derivatives obtained from the vapor phase, at all the experimental liquid compositions ($g^{M,L}$ exp). This is the reason why we say that the vapor phase provides the most relevant information about the behavior that must be required of the model used for correlating the liquid phase. In other words, the vapor phase determines exactly the value and the slope of the $g^{M,L}$ curve at each one of the liquid equilibrium compositions. Usually, this treatment of the problem is not considered because other different objective functions are used for VLE data correlation. The normal practice is to use the following objective function:

$$\text{O.F}(\gamma) = \min \sum_{j=k}^n \sum_{i=1}^2 \left(\frac{\gamma_{i,k}^{\text{exp}} - \gamma_{i,k}^{\text{cal}}}{\gamma_{i,k}^{\text{exp}}} \right)^2 \quad (6)$$

where i and k are used for the components and VLE data, respectively, n denotes the total number of VLE data, the activity coefficient named as *cal* is the one obtained using the NRTL equation (S5 in Appendix A), and the activity coefficient *exp* is obtained from the experimental data using this equation (considering ideal vapor phase)

$$\gamma_i^{\text{exp}} = \left(\frac{P y_i}{p_i^o X_i} \right) \quad (7)$$

In addition, the usual condition for bubble temperature calculations given by Eq. (8) must be used:

$$\text{F.O} = \sum_{k=1}^n \left(\sum_{i=1}^2 \frac{p_{i,k}^o \gamma_{i,k} X_{i,k}}{P} - 1 \right)^2 = 0 \quad (8)$$

This procedure, although correct, does not by itself help to know the true nature of the existing limitations in those cases for which the results for VLE data correlations are poor. Rarely are the $g^{\text{M,L}}$ and the $g^{\text{M,V}}$ curves discussed nor is a phase stability analysis run, which may lead to misinterpretations. Bollas and col. [9] emphasize the importance of including the phase stability check in the estimation of the parameters and propose a bilevel optimization method for this purpose. In the present paper, we would like to emphasize the crucial role that the topology of the Gibbs energy of mixing functions, $g^{\text{M,L}}$ and the $g^{\text{M,V}}$, has to understand the reasons for many poor VLE data correlation results.

2.2. Study cases

Let us consider the following examples:

- *Example 1:* 3-methylphenol (1) + alpha ethylnaphtalene (2) at 760 mmHg
- *Example 2:* methyl tert butyl ether (1) + tert-butanol (2) at 760 mmHg

The experimental VLE data for these two examples have been extracted from Dechema Chemistry Data Series [7], as well as the NRTL parameters obtained in the fitting of the data. The election of these specific systems is not especially relevant and has been done

exclusively because they allow the aspects discussed in this paper to be illustrated, but other systems could have been selected for this purpose.

2.2.1. Example 1

The results published for the VLE data correlation of this example using any of the existing activity coefficient models are very poor. For example, the published results using the NRTL model have been graphically represented in Figs. 1(a)-(d), where T vs. the x,y and y vs. x diagrams, and also the calculated $g^{M,L}$ points and the slopes of the tangent lines to $g^{M,L}$ have been represented, respectively, together with the experimental values for comparison. Binary interaction parameters for this correlation [7] are shown in Table 1(a), along with the objective function calculated with Eq. (6) and deviations in temperature and compositions (mean and maximum). It is evident from this Table and Figs. 1(a) and (b) that this system has not been satisfactorily fitted with the NRTL model, but neither is a better result achieved with any other model such as UNIQUAC, Wilson, etc., all of them providing similar deviations [7]. The objective function and deviation values are extremely high using any of the existing models.

From the point of view presented here, the optimal correlation for the VLE experimental data would require a satisfactory description of the $g^{M,L}$ function and its derivatives calculated from the vapor phase, to satisfy the Gibbs minor common tangent equilibrium condition, regardless of the objective function used (e.g. the activity coefficient function given by Eq. (6)). In other words, if a “perfect” fitting were to be achieved, the model (with the parameters obtained) would satisfy the existence of a common tangent line among the vapor and the liquid g^M curves (as shown in Fig. 2). Therefore, to analyze any kind of difficulties in the correlation of some specific systems, such as the one presented in example 1, we consider it very valuable to use this not frequently used perspective. We have plotted the $g^{M,L}$ values and the slopes of their tangents for example 1, both calculated from the experimental vapor phase data (i.e.: according to Eqs. (4) and (5) and the corresponding ones calculated with the NRTL model. A good correlation would result in good agreement between both series of data, but Figs. 1(c) and (d) show that this is not the case of this example. We have checked that for some VLE data sets, such as those corresponding with example 1, it is *impossible* to simultaneously achieve both correlations, the required $g^{M,L}$ and the slope values of their tangent lines, due to the *incompatibility* between both fittings. In other

words, a unique and smooth curve able to adequately fit the required $g^{M,L}$ points would never have the required derivatives (slopes) to have a common tangent line with the $g^{M,V}$ curve (for the vapor phase) in order to fulfill the VLE equilibrium condition. This is evident from Fig. 3(a) where all the pairs of conjugated V and L phases in equilibrium at each T appear connected with a straight line that is clearly secant (no tangent) to one smooth curve passing through all the $g^{M,L}$ points. The $g^{M,V}$ curves (gas ideal) at each one of these experimental temperatures have been represented for all the composition range in Fig. 3(b). It must be taken into account that the NRTL equation, and other local compositions models, has a very slight and barely perceptible variation with T when the binary interaction parameters are constant. It is shown in Fig. 1(c), where the $g^{M,L}$ curves have been represented for the two extreme experimental temperatures and almost the same curve is obtained. Consequently, it is possible to realize that the problem in these cases is that we are trying to fit the experimental VLE data with an almost unique and constant curve for all the different $g^{M,L}$ points at different temperatures. But nevertheless for the vapor phase different $g^{M,V}$ curves exist at each T (given by Eq. (1) and represented in Fig. 3(b). This is not a problem of the model itself, for example of its lack of flexibility. Any model with such a weak T-dependence would present exactly the same limitation, however flexible it was, because a very high T dependence is indispensable in these cases. In other words, as long as the tie-lines connecting the two conjugated VLE phases are clearly secant (far from being tangent) to the smooth $g^{M,L}$ curve connecting all the $g^{M,L}$ points, it would not be possible to carry out an acceptable correlation of the experimental VLE data without a high T dependence in the model. The reason is that one unique curve passing through the $g^{M,L}$ values required by the experimental VLE data has values for the slopes of the tangents to the $g^{M,L}$ function (at each experimental point) that are very far from those required to satisfy the necessary and sufficient minor common tangent equilibrium criterion with the vapor phase. If T-dependent parameters were used in the $g^{M,L}$ model, each one of the $g^{M,L}$ points (at each experimental T) would belong to a different $g^{M,L}$ curve. In this way, it could be possible to simultaneously satisfy both the $g^{M,L}$ values and the slopes of its tangents required by the equilibrium condition, as shown later in this paper. The restriction of not consider the variation (or just a weak variation) with T in the $g^{M,L}$ non-ideal liquid phase (common practice) is not only very demanding to perform VLE data correlation, but also leads to *dead-end situations* for some systems such as the one in example 1.

Despite not being relevant to this discussion, we would like to point out that the value for $g^{M,V}$ in Fig. 3 is not zero for 2-component (pure) due to the deviation between the Antoine parameters provided by [7] and the boiling temperature included in the VLE data set for this 2-component.

Next, we show another example of this type of inconsistency that is present in many sets of VLE data for systems with one homogeneous azeotrope of minimum-boiling temperature.

2.2.2. Example 2

The experimental VLE data for the system used in example 2 reveal the existence of a *homogeneous* azeotrope. However, when we represent the $g^{M,L}$ function obtained from the vapor phase to satisfy the common tangent equilibrium condition (Fig. 4), we realize that the consideration of the model parameters as constant (a single curve containing all the $g^{M,L}$ points at different T), would unavoidably lead to a *heterogeneous* (instead of homogeneous) azeotropic point. This Figure shows a common tangent line to the $g^{M,L}$ curve at two different liquid compositions (LLE) for all global mixtures from $x_1=0.5$ to 0.9 (molar fractions) approximately. Consequently, the phase stability analysis would predict the existence of LLE and thus of one heterogeneous azeotropic point (VLLE). This LLE solution would be the stable solution, being the VLE in that region of compositions the metastable solutions. Besides, we can observe that in this case neither could the required slopes of the tangents to the $g^{M,L}$ curve be satisfied by any model without T dependence, as shown in Fig. 4 where some of these conjugated VLE lines are secant (no tangent) to the smooth $g^{M,L}$ curve passing through all the experimental points. At this point, we could ask ourselves how this type of system is correlated in literature, where this analysis is not frequently carried out and where T-dependence is not considered. From the previous discussion, it follows that the unavoidable result for the correlation of this type of system must be very far from the experimental VLE data and, consequently, no acceptable fitting could be achieved in these cases, and this is exactly what is found in literature. For example, the correlation result reported in the Dechema Data Collection [7] (for instance using the NRTL model) for this system, corresponds with parameters and deviations shown in Table 2(a). Fig. 5 shows the representation of the calculated and experimental values for comparison. The correlation with NRTL is clearly poor. The result obtained corresponds with calculated

$g^{M,L}$ curves that do not present LL splitting (see Fig. 5(c)) and thus reproduces a homogeneous azeotrope as required, but neither the values of $g^{M,L}$ nor its derivatives can be reasonably fitted (Figs. 5(c)-(d)), and consequently neither the activity coefficients nor the equilibrium compositions.

We are familiar with this type of poor correlation results for systems exhibiting high non-ideality. Nevertheless, the point exposed in the present paper is that it is an *incoherence* to attempt the correlation of this type of systems without taking into account the needed variation of the $g^{M,L}$ function with temperature, for the previously discussed reasons. In the next section, we will show that the only way of obtaining a consistent variation of $g^{M,L}$, which reproduces the required values for $g^{M,L}$ and its derivatives (common tangent line with the vapor phase), but at the same time does not exhibit LLE (i.e.: a heterogeneous azeotropic point), is to admit that the $g^{M,L}$ function strongly depends on temperature. This alternative is frequently obviated when extremely poor correlation results are presented in literature for this type of system.

2.3. Improving previous correlation results

Some systems are satisfactorily correlated using constant values for the NRTL (or any other classical model) parameters with T. However, other systems would *necessarily* require the inclusion of a high T-dependence in the model to achieve consistent and good (near to the experimental data) fitting results. Obviously, there may also be systems that cannot be correlated even with this latter treatment. Additional modifications to the classical models will be necessary in these cases. The necessity (or not) of considering T-dependence in the model parameters can be detected prior to the correlation process itself by means of the construction and inspection of a diagram equivalent to the ones represented in Fig. 3(a) and Fig. 4, for examples 1 and 2, respectively. For systems that can be correctly fitted using classical models with T-independent parameters, this type of representation shows an aspect such as the one in Fig. 6 that corresponds to the methanol (1) + water (2) binary system at 760 mmHg [10]. In this Figure, the tie-lines connecting the conjugated V and L phases in equilibrium are close to being tangent to one single and smooth $g^{M,L}$ curve connecting all L phases at different temperatures. So, the common tangent line condition can be satisfied without T-dependence in the model, unlike what happens in Fig. 3(a) and Fig.

4, where the conjugated VLE lines are secant. To do these graphical representations only the experimental data are necessary and, consequently, they could be inspected previously in the correlation process to decide whether to include or not dependence with T in the parameters.

To consider T dependence in the binary interaction parameters of the model we have used the one included in ASPEN PLUS Chemical Process Optimization Software [1]:

$$\tau_{ij} = a + \frac{b}{T} + c \cdot \ln T + d \cdot T \quad (9)$$

When the NRTL model is used for the correlation, the dependence with T may also be used in the non-randomness parameter:

$$\alpha_{ij} = e + f \cdot (T - 273.15K) \quad (10)$$

where a, b, c, d, e and f are the parameters of the model, which can be obtained by correlation of the experimental VLE data and T is temperature (K). These equations combined with the activity coefficient model can provide a high T dependence in the $g^{M,L}$ function, being able to reproduce very different curves at each one of the temperatures of the VLE data set, if the data require it. For a practical purpose, we have not restricted α_{ij} in Eq. (10) during the correlation process to attain the better approximation to the experimental VLE data, regardless of its supposed physical meaning.

We have carried out the correlation of the VLE data sets for examples 1 and 2 using Eqs. (6)-(8) along with Eqs. (9) and (10) and the NRTL model. We name these correlations as NRTL f(T) to distinguish them from those carried out using constant parameters with T in the NRTL model. Next, the results obtained are presented and discussed.

2.3.1. Example 1: NRTL f(T)

The parameters obtained in the VLE data correlation for example 1 using the NRTL f(T) model are presented in Table 1(b). The value achieved for the objective function (Eq. (6)) and for the deviations in temperature (ΔT) and vapor component mole

fractions (Δy_i) are much lower than those previously published for NRTL with constant parameters. Fig.7 shows the very good agreement achieved between the calculated and experimental VLE data from different points of view: the typical T vs. x,y and y vs. x diagrams (Fig. 7(a-b)), but also the required and calculated $g^{M,L}$ and slope values at each point (Fig. 7(c-d)). These two last representations correspond with the interpretation of the VLE by means of the Gibbs common tangent equilibrium condition. We can see that now, unlike the results presented in Fig. 1, it has been possible to simultaneously satisfy the $g^{M,L}$ and slope values required at each equilibrium point. For that, the model has needed a very high T-dependence, as is evident in Fig. 8, where the calculated $g^{M,L}$ curves (at each calculated T) have been represented using the parameters in Table 1(b). Without such dependence with T, it would not have been possible to achieve the satisfactory fitting of this experimental VLE data set. The curves also show metastable LLE solutions that correspond with common tangent lines between two liquid phases at the same temperature. However, the phase stability test shows that VLE is the stable solution for all the composition range, which validates this correlation result. For example, in Fig. 9 we present the graphical representation of the phase stability check for one VLE point (at $T_{cal}=225.6^\circ\text{C}$) to illustrate this aspect.

2.3.2. Example 2: NRTL $f(T)$

Table 2(b) presents the results we obtained in the correlation with NRTL $f(T)$ of the VLE data set for example 2. These results have been represented in Fig. 10, following the same structure as Fig. 7 for example 1. Also for this example, it is observed that the addition of a high T-dependence in the NRTL parameters seems to be absolutely necessary to simultaneously fit the required $g^{M,L}$ values and their slopes as a function of x_1 , as is evident from Fig. 11 where the whole $g^{M,L}$ curves for each temperature calculated have been represented. However, although this correlation result seems to be capable of fitting the experimental data satisfying the common tangent equilibrium condition for the required VLE, the solution is misleading. The reason is that one no desirable LLE region inevitably appears when increasing the temperature and, unlike example 1, in this case, the predicted LLE solution is not a metastable solution. Fig. 12 shows this situation for two specific temperatures (61.16°C and 53.81°C), where $g^{M,V}$ curves have been also represented along with $g^{M,L}$ curves for checking the stability of the solutions. The first one of these temperatures is between the boiling temperatures of

both components of the system, one VLE region and one non-desirable but stable LLE region appears. The second one is between the boiling temperature of the light component and the azeotrope (minimum-boiling point) and, consequently, two VLE regions exist in addition to the non-required LLE. Consequently, we can assert that the parameters presented in Table 2(b) are inconsistent for the VLE data correlation of this example 2. At this point, we could ask ourselves the reason why LLE splitting is metastable in example 1 and stable in example 2. If we consider that when decreasing the temperature the $g^{M,V}$ curve moves upwards (Fig. 3(b)) “uncovering” the $g^{M,L}$ curve for the heaviest component region it is evident that, when the LLE splitting is close to the lighter component (as in example 1) and it also vanishes with decreasing temperature, there will be a high probability of metastable LLE (Fig. 9 shows this situation at one specific T). On the contrary, when the LLE splitting is close to the heaviest component (as in example 2) and it is accentuated with decreasing temperature, the LLE solution will be stable, invalidating the VLE correlation result for those systems presenting homogeneous liquid phase.

At this point, the question is: Would it be possible to find a consistent solution to the correlation of example 2 using NRTL or any other classical model? From this analysis, we can conclude the particular topology that these experimental VLE data for example 2 require of the $g^{M,L}$ function to satisfy the Gibbs minor common tangent equilibrium criterion. As we have discussed previously in this paper, if ideal vapor phase is considered, the equilibrium in the liquid phase at each temperature is defined by a single point ($g^{M,L}$) and a single derivative ($dg^{M,L}/dx_1$). For the rest of the $g^{M,L}$ curve at each T, we have no information and, as a consequence, many curves could satisfy the equilibrium conditions, although not necessarily the phase stability criterion. In Fig. 13(a) we have drawn at each temperature: the liquid equilibrium composition (blue point) and the slope of the tangent line at this point given by the line path marked by the common tangent line with the ideal vapor (dashed line). The model should satisfy these requirements without providing any stable LLE. In Fig. 13(a) we have also drawn one among the infinitely possible sets of $g^{M,L}$ curves that would satisfactorily reproduce the VLE data for system 2 at all the experimental temperatures. In Fig. 13(b) only one VLE datum has been selected and five different $g^{M,L}$ curves that satisfy the equilibrium requirements with the vapor phase, at the experimental T, have been drawn as an example. The extremely high flexibility required for the model to represent these VLE

data is evident from these Figures. If we consider that $g^{M,L}$ curves start from zero at the ends and should not have any common tangent close to the pure 2-component (left side in Fig. 13) to avoid stable LLE solutions, it is evident that some VLE data (as the one represented in Fig. 13(b)) require certain part of the $g^{M,L}$ curve close to a straight line while others are sharply curved. In other words, because some tie-lines connecting the conjugated V and L phases in equilibrium cross the ordinate-axis very close to zero ($(g^{M,L})_{x_1=0}$ very small in absolute value and negative) it is very difficult for the model to consistently represent the VLE behavior of the system without leading to non-existing LLE solutions.

This example illustrates the reason why NRTL or any other classical model, even considering the influence of temperature, may fail to fit some VLE data sets with a consistent solution regarding phase stability. These models do not possess the extremely high flexibility that is sometimes required by the equilibrium data. To satisfactorily correlate the VLE data for this type of system a new model for the non-ideality of the liquid phase, capable of reproducing curves as the ones shown in Fig. 13, should be proposed. If this function does not exist because the requirements are too demanding, the only way of fitting these types of VLE data would be to consider the non-ideality of the vapor phase. In such a case, the $g^{M,V}$ curves could change providing new values for $g^{M,L}$ and for the required slopes at each temperature, increasing the possibilities of finding a satisfactory solution to the correlation.

However, another important aspect should also be considered: those cases in which common tangent lines connecting conjugated V (ideal) and L phases in equilibrium cross the ordinate-axis at $g^{M,L} \geq 0$. If experimental VLE data that can be considered as correctly measured provide any of both situations at one or more temperatures, the non-ideality of the vapor phase must necessarily be taken into account in the correlation process. In the first case, when $(g^{M,L})_{x_1=0} = 0$, because the model could never reproduce a straight line as part of the $g^{M,L}$ curve. In the second one, with $(g^{M,L})_{x_1=0} > 0$, because it would involve a positive value for the chemical potential of the 2-component in the mixture, being $\mu_2^{\text{solution}} > \mu_2^{\text{pure}}$ since $\mu_2^{\text{pure}} = 0$ (standard state), which is inconsistent with the formation of the liquid solution. This situation could reveal some inconsistency in the experimental VLE data, but if these data are considered correct, the only solution to their fitting is to assume non-ideality of the vapor phase, to the point of obtaining $\mu_i^{\text{solution}} < \mu_i^{\text{pure}}$ for all the temperatures. In this sense, we have checked that the weak

change that traditional equations of state (EOS) provide at moderate pressure for non-ideal $g^{M,V}$ functions (comparing with ideal $g^{M,V}$) could not be enough to satisfactorily correlate the VLE data for these type of systems. In these cases, other alternative models should be inspected to provide a solution to the correlation problem of these systems, but this matter will be considered in a future work.

3. Conclusions

The present paper shows the reason why many VLE data sets could not be adequately fitted using any model with temperature independent parameters. It is concluded that it is *compulsory*, for many systems, to consider the variation of $g^{M,L}$ with temperature in the correlations of VLE experimental data. In these cases, it is not a matter of increasing the flexibility of the model due to the higher number of parameters used, but it is required by the VLE data set itself. In these cases, no model, no matter how capable it is, would be able to fit the data without such T dependence. Because the classical models for the activity coefficients are almost constant with temperature, the T-dependence is included in the binary interaction parameters. The Gibbs minor common tangent criterion has been the tool to identify the true nature of the problem that these systems present, and to achieve a solution. The analysis carried out shows that many of the correlation results reported in literature as poorly correlated could be significantly improved taking into account a high T-dependence in the model parameters to satisfy the equilibrium condition required. In some cases, the presence of metastable solutions (e.g LLE) is unavoidably required to achieve a satisfactory VLE correlation result and thus invalidating them. For this reason, the validation of the parameters obtained by means of checking phase stability is always necessary. In others, the presence of some stable LLE regions will invalidate the solution found. To overcome this last situation we could act in two steps: 1) find a new and extremely flexible non-classical model for the non-ideality of the liquid phase and, when it fails, 2) consider the non-ideality of the vapor phase (probably with some non-classical EOS). Some strategies have been suggested to know, prior to the correlation process, whether it will be or not be necessary to include T-dependence in the binary interaction parameters of classical activity coefficient models and whether even considering this T-dependence, the correlation will fail using classical models for both the liquid and vapor non-idealities. The topology of the g^M function (for both vapor and liquid phases) is the essential tool

in this approach to the VLE correlation problem because it contains all the information that must be satisfied by the correlation models.

Nomenclature

a, b, c, d, e, f	parameters
G^M, g^M	Gibbs energy of mixing ($J \cdot mol^{-1}$ and dimensionless, respectively)
n	number of VLE data
O.F	objective function
P	pressure (Pa)
p^o	vapor pressure (Pa)
R	gas constant ($J \cdot K^{-1} mol^{-1}$)
T	temperature (K)
VLE	vapor-liquid equilibrium
VLLE	vapor-liquid-liquid equilibrium
x_i	molar fraction of component i in liquid phase
y_i	molar fraction of component i in vapor phase

Greek symbols

α_{ij}	non-randomness NRTL factor
γ_i	activity coefficient for component i
τ_{ij}	NRTL binary interaction parameter

Superscripts

exp	experimental
calc	calculated
L	liquid phase
V	vapor phase

Subscripts

i, j	components
k	VLE data

Appendix A. Supplementary information

Supplementary information associated with this article can be found in the online version.

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Table 1

Correlation results of the experimental VLE data for example 1 using the NRTL model:

a) with constant parameters (NRTL) [7], and b) with parameters dependent on temperature (NRTL f(T)). The objective function calculated by Eq. (6) and the mean and maximum deviations in T and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	2801.03	-1243.30	0.2876			
	O.F(γ)	mean ΔT	max ΔT	mean Δy_1	max Δy_1	
	2.917	11.14	21.07	0.0915	0.3343	
(b) NRTL f(T)						
ij	a_{ij}	b_{ij} (K)	c_{ij}	d_{ij} (K ⁻¹)	e_{ij}	f_{ij} (K ⁻¹)
12	14.7344	-8552.80	-3.49106	0.140469	0.124098	-0.000585
21	357.016	-219396	54.3861	-1.16978	-0.090166	-0.000149
	O.F(γ)	mean ΔT	max ΔT	mean Δy_1	max Δy_1	
	0.0316	1.145	3.997	0.0056	0.0095	

Table 2

Correlation results of the experimental VLE data for example 2 using the NRTL model: a) with constant parameters (NRTL) [7], and b) with parameters dependent on temperature (NRTL f(T)) that represent a *misleading* solution. The objective function calculated by Eq. (6) and the mean and maximum deviations in T and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	2183.52	-480.874	0.2857			
	O.F(γ)	mean ΔT	max ΔT	mean Δy_1	max Δy_1	
	1.673	0.771	2.79	0.0605	0.171	
(b) NRTL f(T)						
ij	a_{ij}	b_{ij} (K)	c_{ij}	d_{ij} (K ⁻¹)	e_{ij}	f_{ij} (K ⁻¹)
12	0	389.813	0	0	1.0324	0
21	239.404	7.59394	0.000998	0.068932	0	0.000425
	O.F(γ)	mean ΔT	max ΔT	mean Δy_1	max Δy_1	
	0.2506	0.292	0.838	0.0124	0.0423	

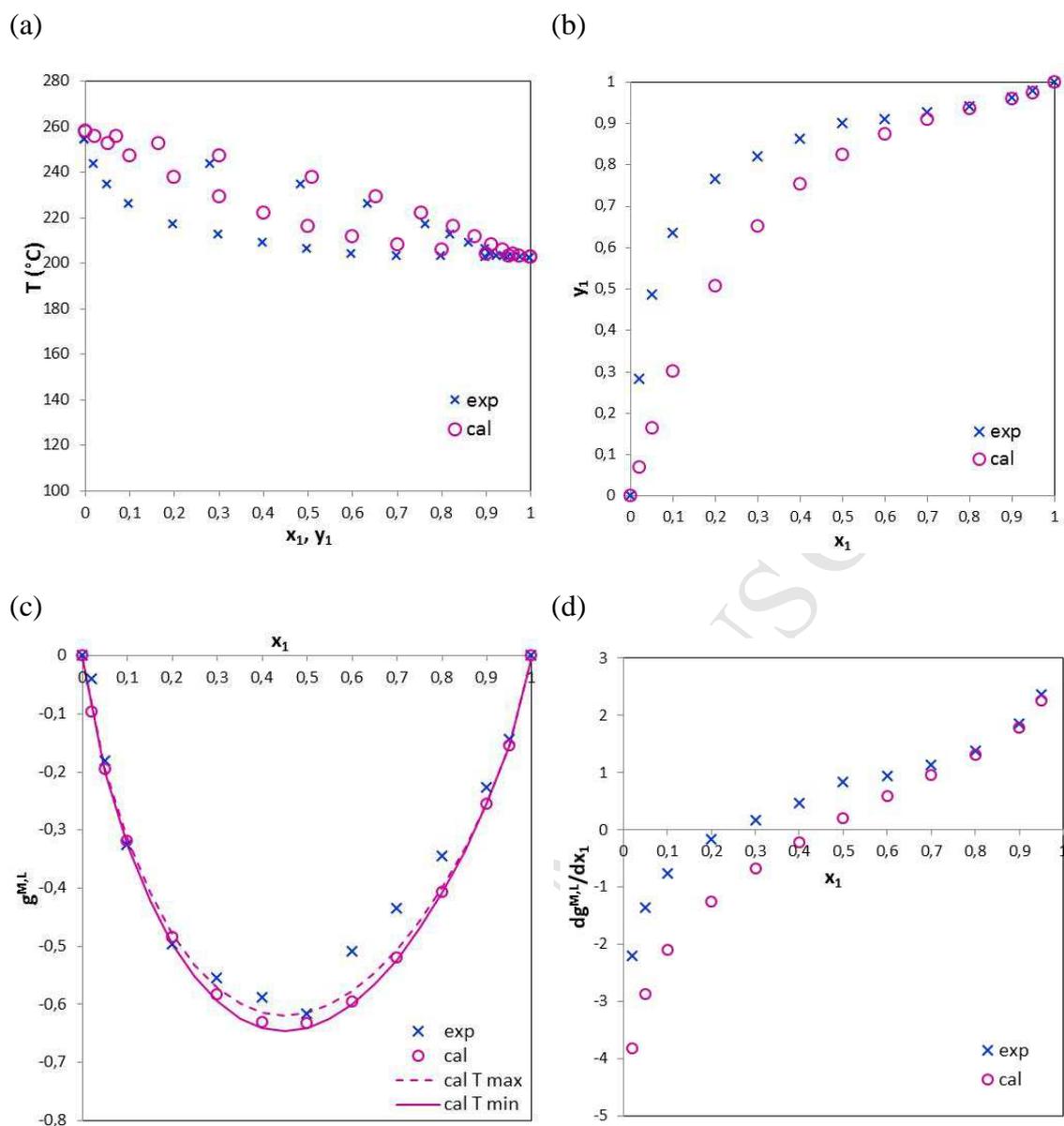


Fig. 1. Experimental data and correlation results using the NRTL model [7] for example 1: a) T vs. x, y , b) y vs. x , c) $g^{M,L}$ vs. x_1 and d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1 . Parameters are given in Table 1(a).

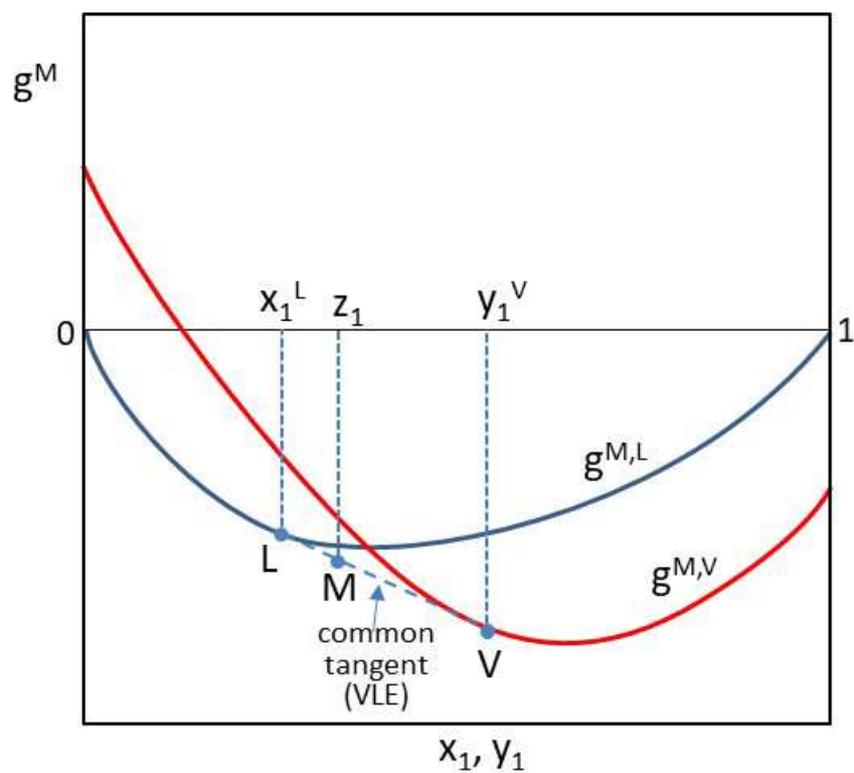
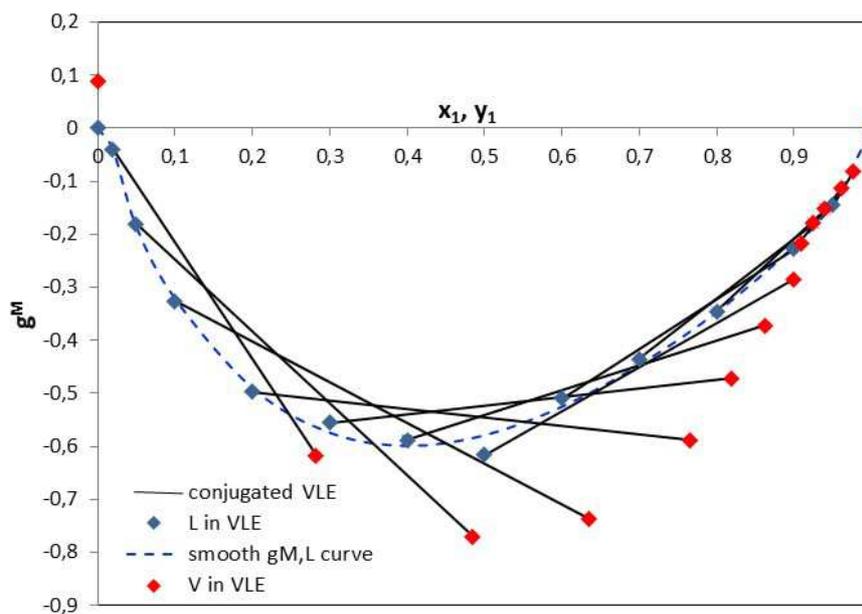


Fig. 2. Qualitative representation of the Gibbs minor common tangent equilibrium criterion applied to VLE of a binary system at some specific T and P.

(a)



(b)

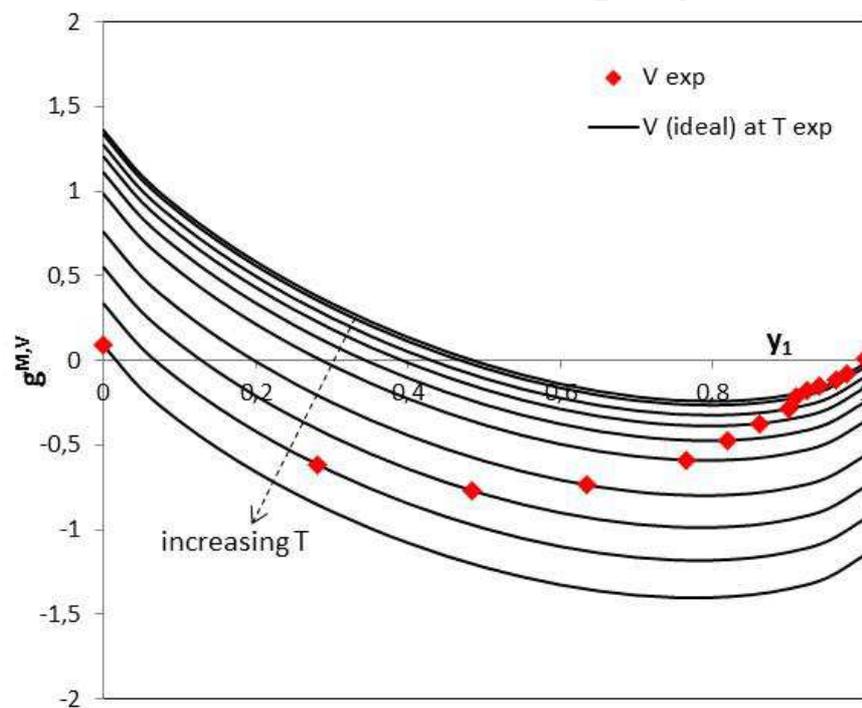


Fig. 3. For example 1 have been represented: (a) the straight lines connecting the conjugated VLE phases that are tangent to the $g^{M,V}$ curves represented in (b) and a smooth $g^{M,L}$ curve passing through all the L phases, and (b) $g^{M,V}$ curves (ideal gas) including the points for the experimental vapor phases (V).

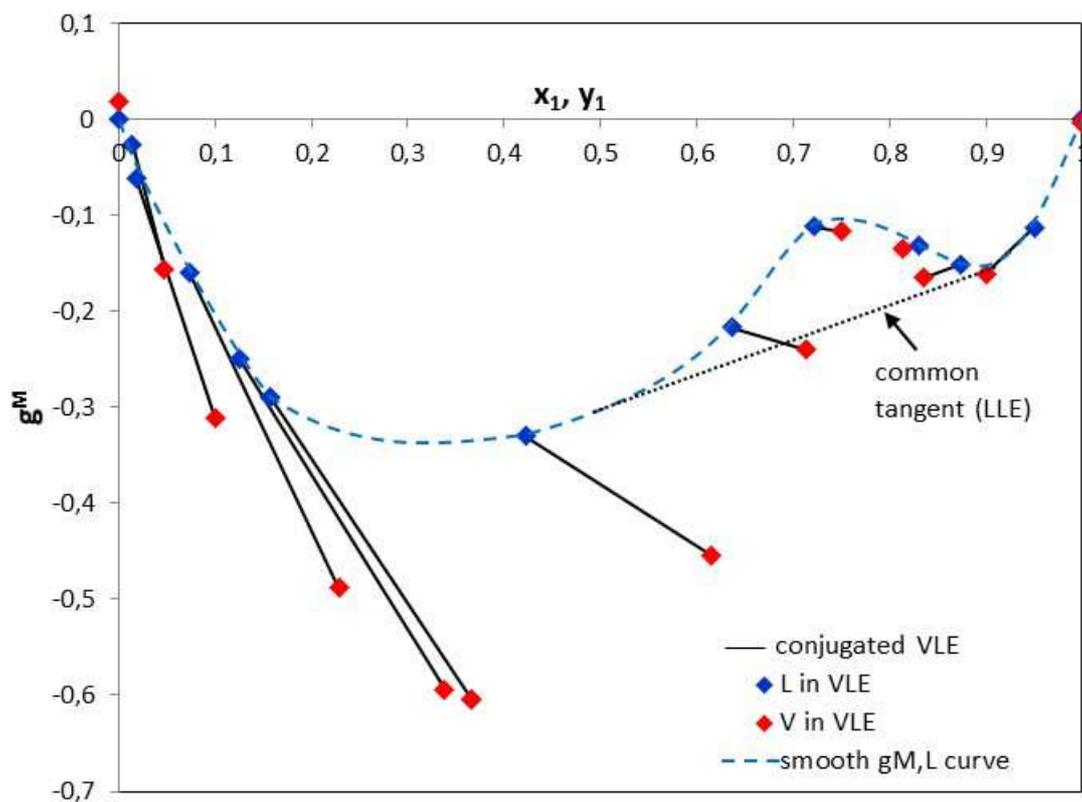


Fig. 4. Representation of the straight lines connecting the conjugated VLE phases that are tangent to the $g^{M,V}$ curves (ideal gas) for example 2. A smooth $g^{M,L}$ curve for $g^{M,L}$ passing through all L phases has been included showing LLE splitting.

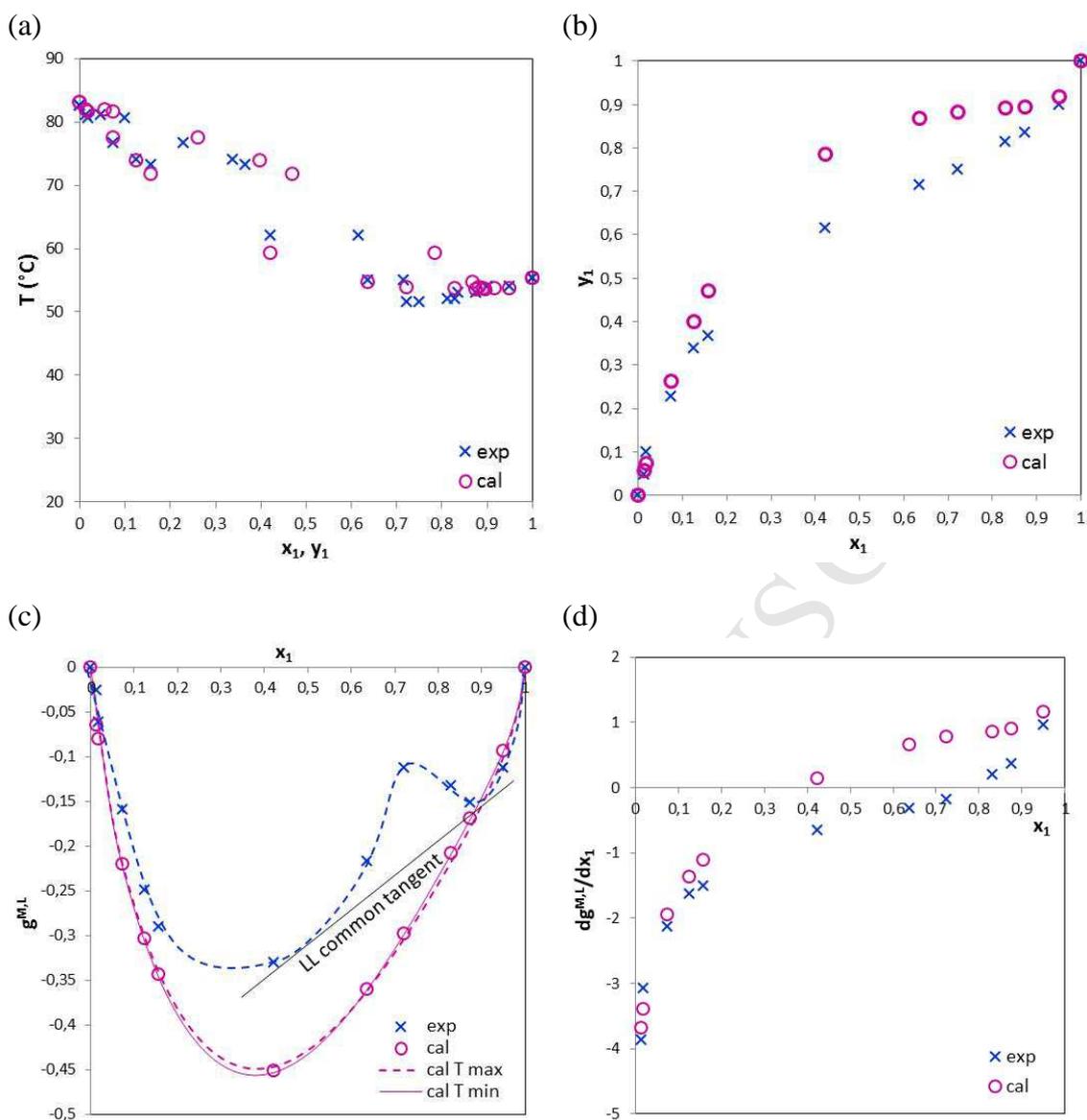


Fig. 5. Experimental data and correlation results using the NRTL model for example 2: (a) T vs. x, y , (b) x vs. y , (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1 . Parameters are given in Table 2(a) [7].

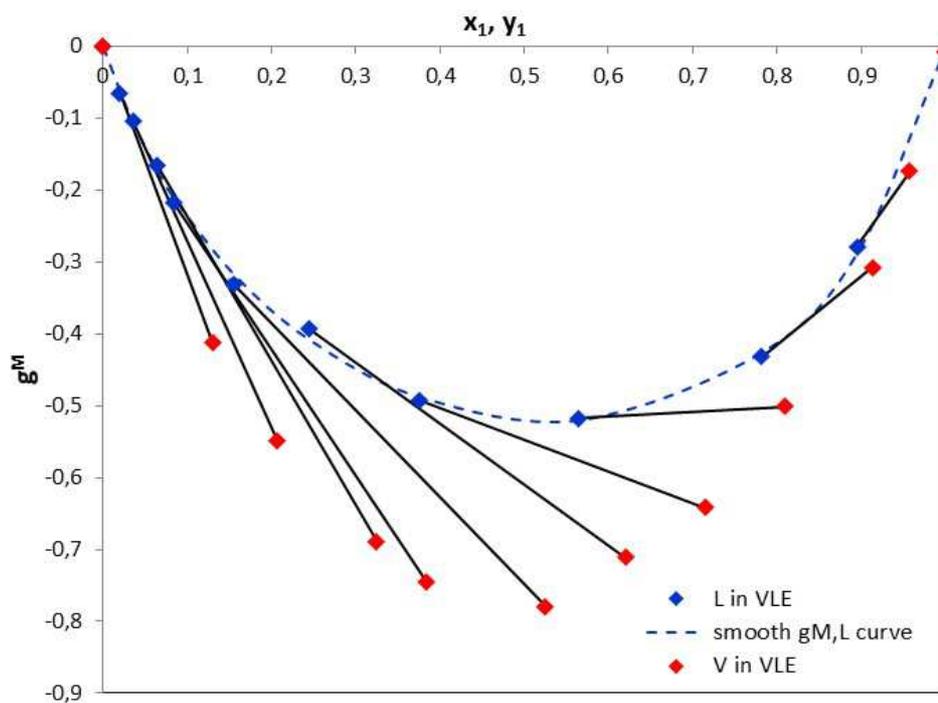


Fig. 6. Representation of the straight lines that connect the conjugated VLE phases for the methanol (1) + water (2) binary system at 760 mmHg and are tangent to the $g^{M,V}$ curves (ideal gas) [10]. A smooth curve for $g^{M,L}$ passing through all the L phases has been included.

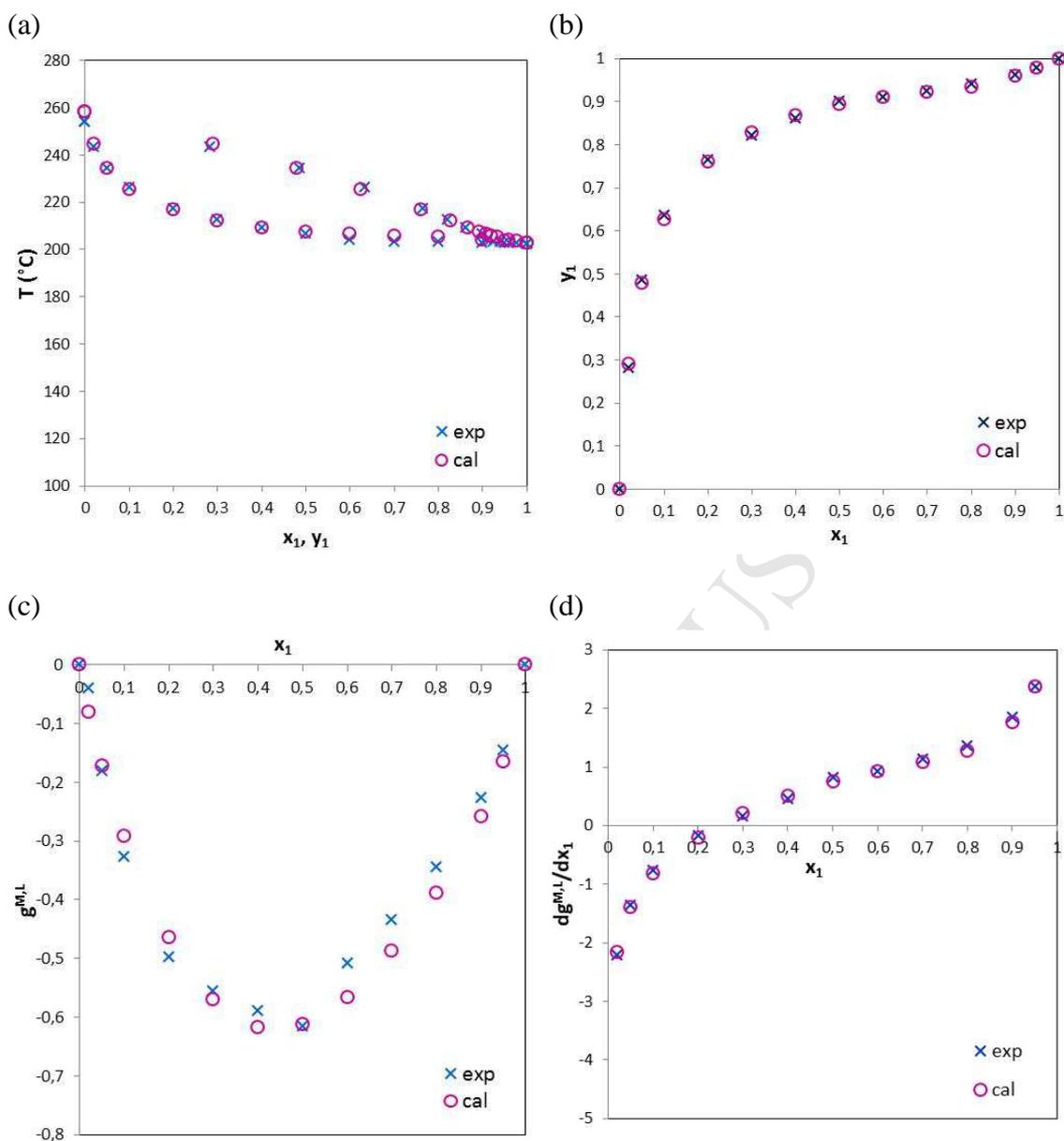


Fig. 7. Experimental data and correlation results using the NRTL $f(T)$ model for example 1: (a) T vs. x, y , (b) x vs. y , (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1 . Parameters are given in Table 1(b).

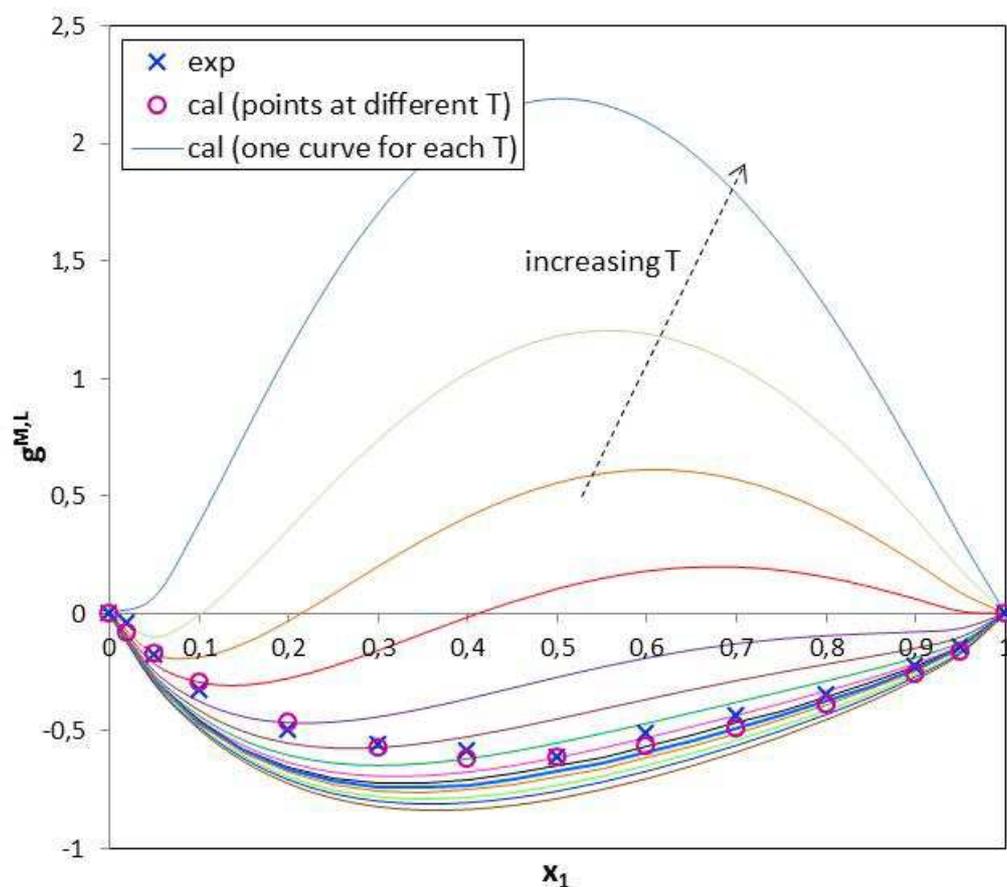


Fig. 8. Experimental (exp) and calculated (cal) Gibbs energy of mixing points for the liquid phases ($g^{M,L}$) using the NRTL $f(T)$ model for example 1 (each point is at a different T). The complete $g^{M,L}$ curves obtained as result of the correlation at each T have been included. Parameters are given in Table 1(b).

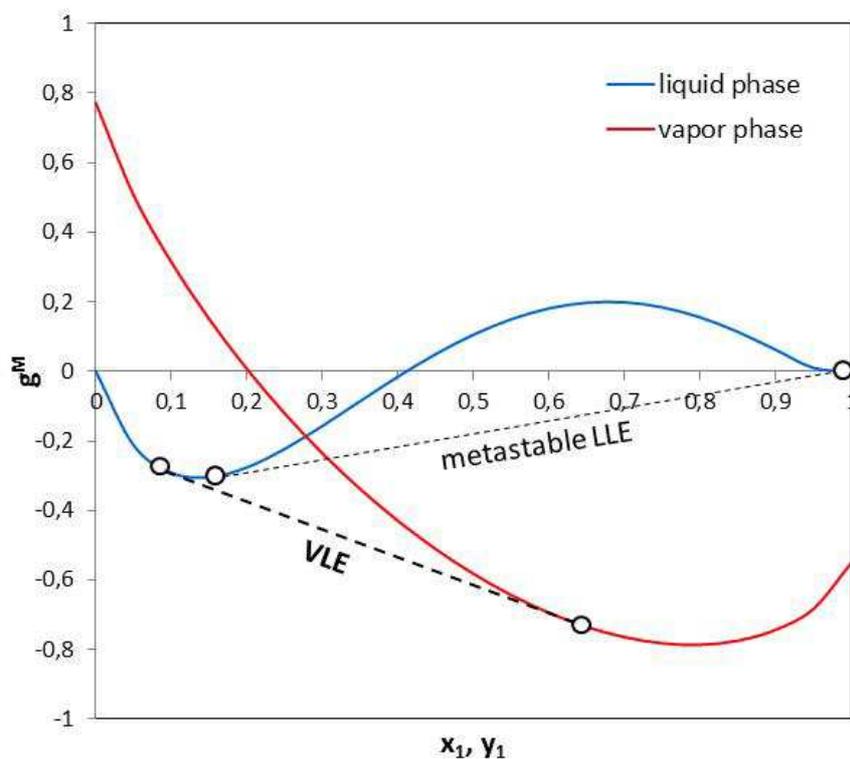


Fig. 9. Stability checking of the correlation results obtained for example 1 using the NRTL $f(T)$ model (parameters in Table 1(b)). This example is for one VLE datum at $T(\text{cal})=225.6^\circ\text{C}$, showing the metastable LLE and the required and stable VLE solution.

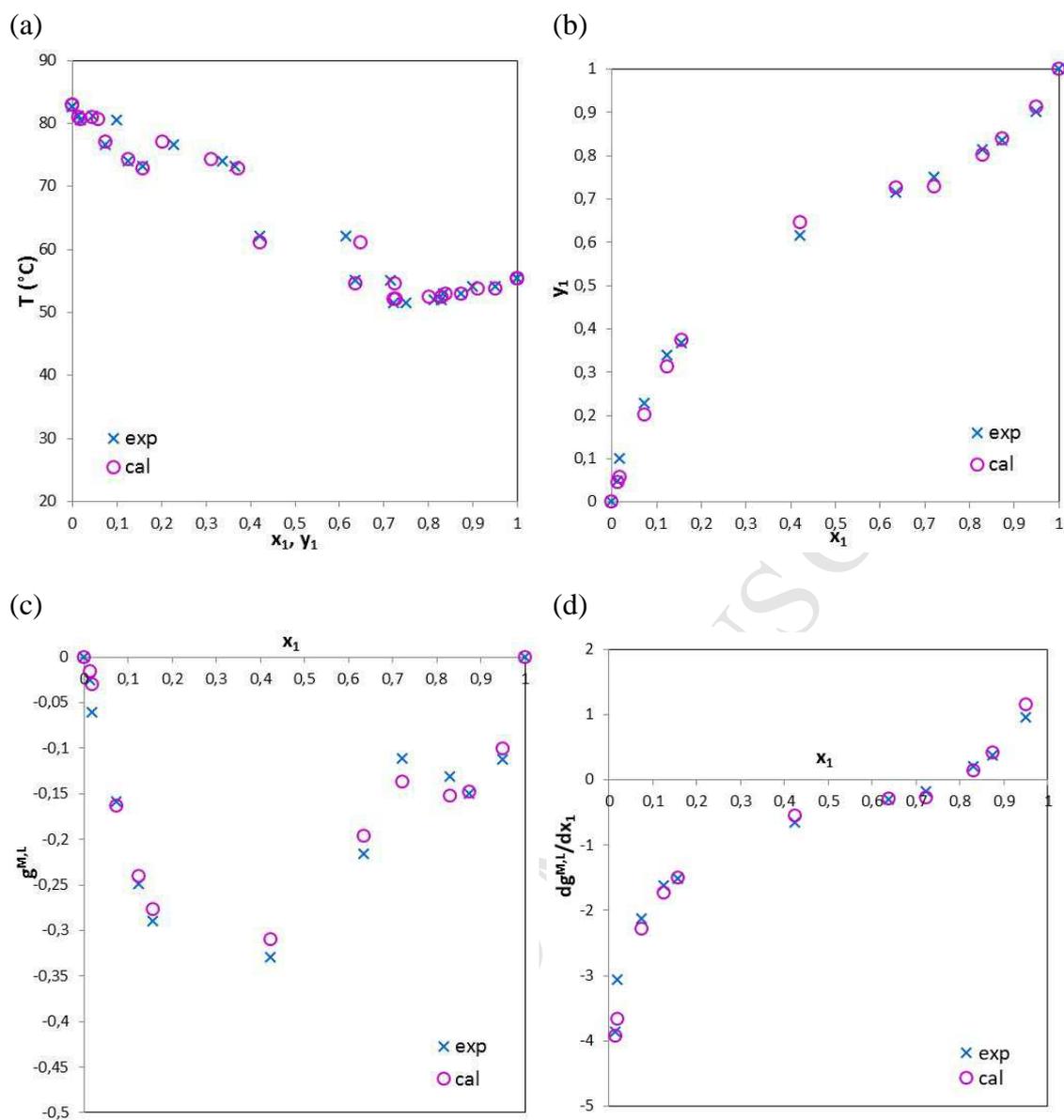


Fig. 10. Experimental data and *misleading* correlation results using the NRTL $f(T)$ model for example 2: (a) T vs. x, y , (b) x vs. y , (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1 . Parameters are given in Table 2(b).

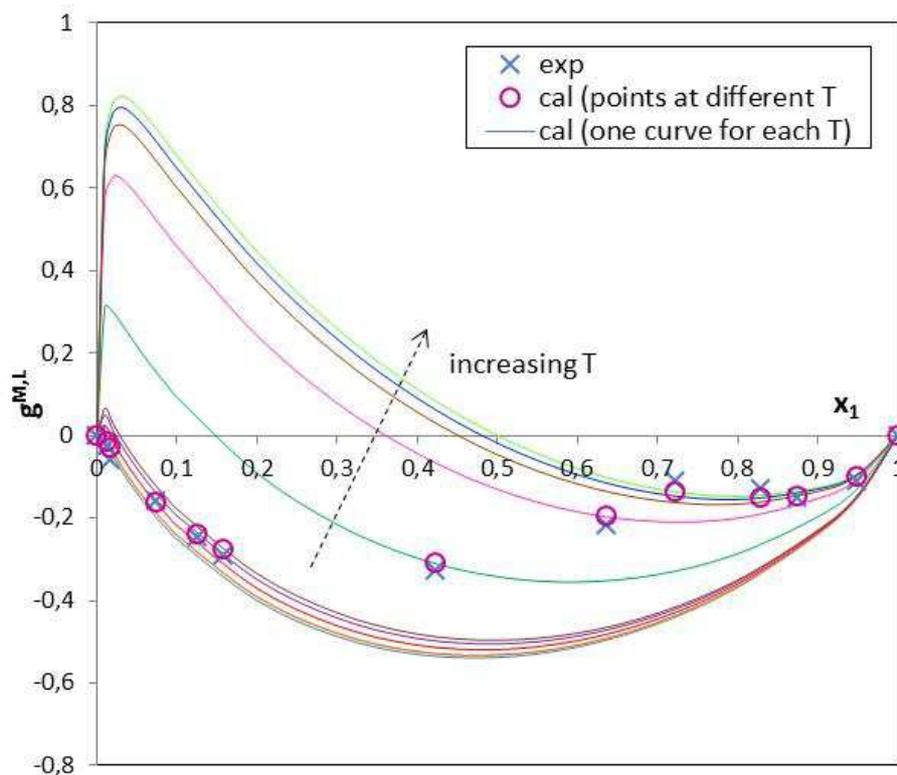
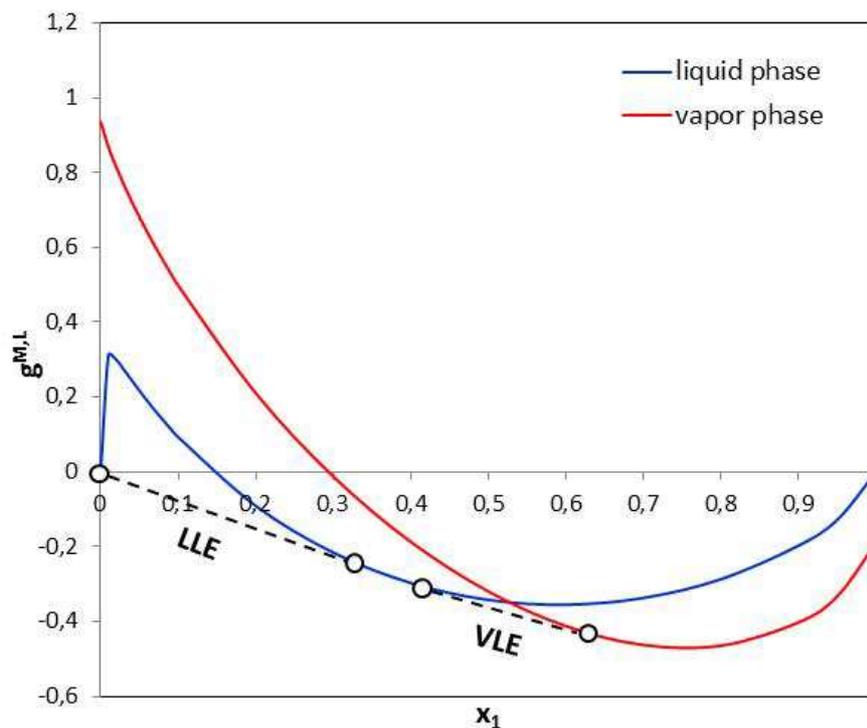


Fig. 11. Experimental (exp) and calculated (cal) Gibbs energy of mixing points for the liquid phases ($g^{M,L}$) using the NRTL $f(T)$ model for example 2 (each point is at a different T). The complete $g^{M,L}$ curves obtained as result of the correlation at each T have been included, presenting a region of LLE splitting. Parameters are given in Table 2(b).

(a)



(b)

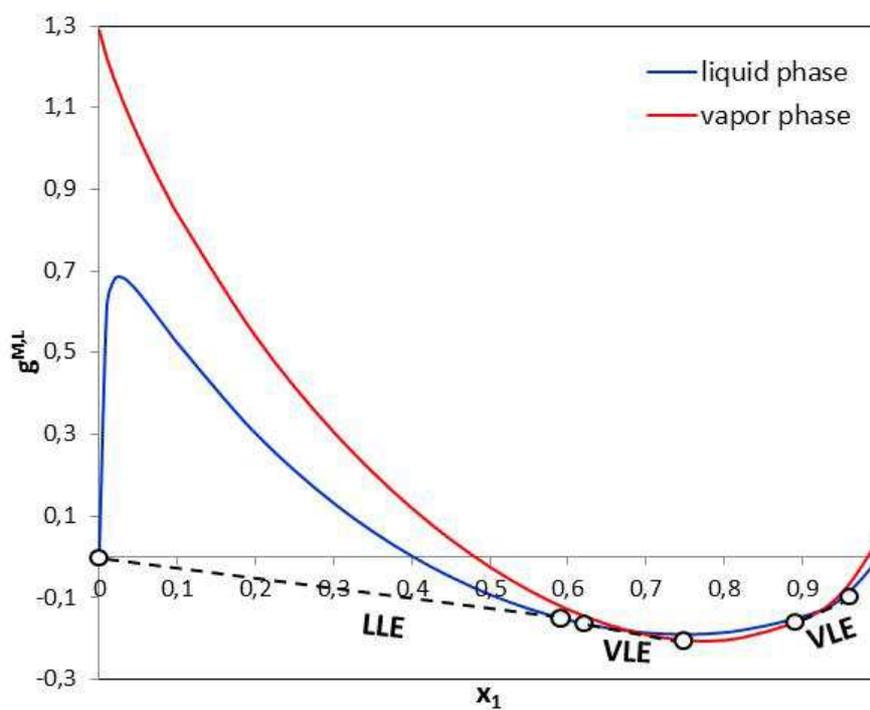
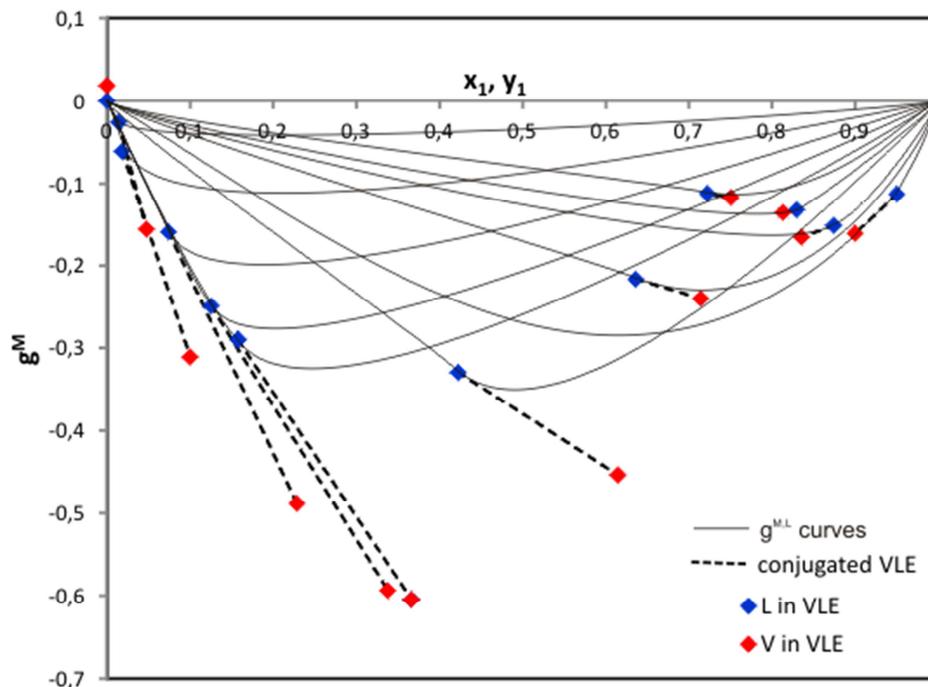


Fig. 12. Phase stability checking of the correlation results obtained for example 2 using the NRTL $f(T)$ model (parameters in Table 2(b)). This example is for two specific temperatures: (a) $T(\text{cal})=61.16^\circ\text{C}$ and (b) $T(\text{cal})=53.81^\circ\text{C}$, showing one undesirable LLE region in addition to the required VLE, invalidating these correlation results.

(a)



(b)

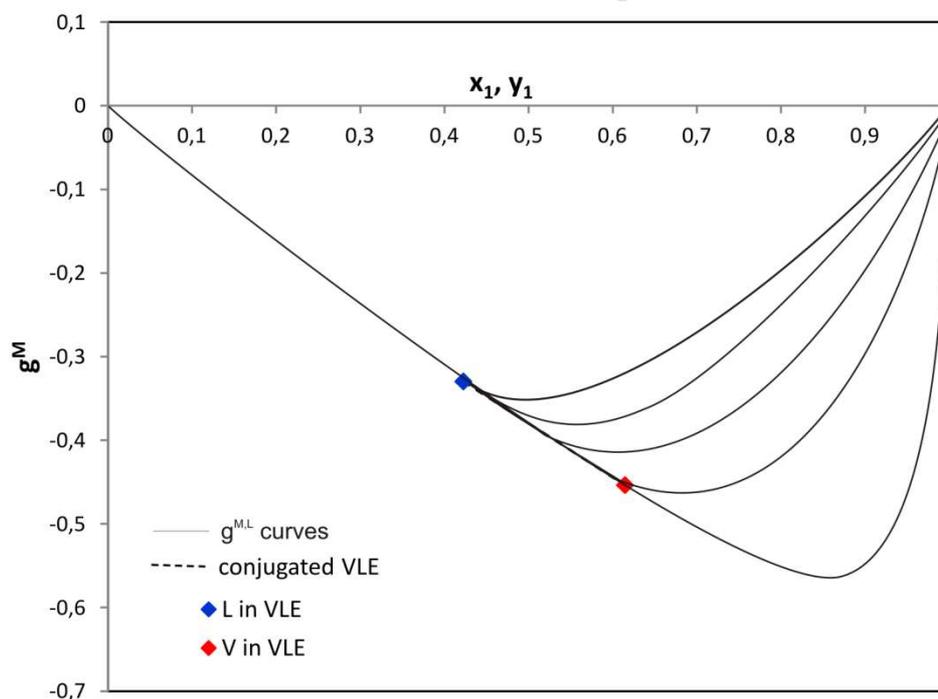


Fig. 13. Approximation to the required $g^{M,L}$ curves at constant T to satisfactorily correlate the VLE data for example 2: (a) one possible curve for each one of the VLE data, and (b) different possibilities for just one VLE datum.