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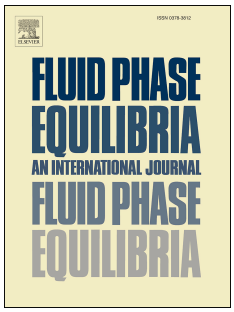

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Procedure for the correlation of normal appearance VLE data, where the classical models dramatically fail with no apparent reason

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Abstract

The necessity of using a pressure (P) or temperature (T) dependence in the Gibbs energy of mixing of the liquid phase ($g^{M,L}$) for some isothermal (or isobaric) VLE data sets, respectively, is discussed in this paper. A graphical representation, directly obtained from the experimental data, is proposed as a method to clearly classify the behaviour of the systems and select the adequate model (i.e. including when appropriate the T or P dependence) to correlate them. The result is that many of the poorly fitted systems in the literature could be precisely modelled using the correct procedure with adequate functions of P or T. Some suitable examples are used to illustrate the validity of these ideas, providing satisfactory correlation results for those systems in the literature. The ideas presented in this paper reveal important aspects related to the inappropriate application of some thermodynamic consistency (TC) tests to evaluate the quality of VLE data sets.

Keywords: activity coefficient model, NRTL, VLE, phase equilibrium, data correlation.

1. Introduction

A revision of the published vapor-liquid equilibrium (VLE) data for binary systems, and their correlation results, shows that quite a high number of these sets presents a very poor fitting with insufficient justification. In other words, some VLE behaviours apparently close to ideality cannot be modelled using any of the activity coefficient equations, when other comparable data showing similar trends can be satisfactorily correlated. For these poorly correlated systems, the parameters obtained are published

along with very high values of deviations between experimental and calculated properties, without any explanation for the true reasons behind such results.

Experimental VLE data at low and moderate pressures are frequently fitted using an activity coefficient model such as NRTL [1] or UNIQUAC [2]. These local composition models to formulate the dimensionless Gibbs energy of excess ($g^E = G^E/RT$) of non-ideal solutions, or alternatively the activity coefficient of each component, do not include dependence with total pressure (P) and the dependence with temperature (T) when included is very weak. To overcome this limitation, in the case of the correlation of isobaric VLE data, the binary interaction parameters are occasionally formulated with a certain mathematical function of T. For example, the chemical process simulation package Aspen Plus [3] includes the following expression:

$$\tau_{ij} = a + \frac{b}{T} + c \cdot \ln T + d \cdot T \qquad (1)$$

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

$$\alpha_{ij} = e + f \cdot (T - 273.15K) \qquad (2)$$

where a, b, c, d, e and f are the parameters of the model, which can be obtained by correlation of experimental VLE data, and T is temperature (K). This is an accepted empirical procedure to provide a stronger T-dependence in the model.

However, the case of pressure is different. It is widely accepted that at low and moderate pressures, the influence of P on the Gibbs energy of mixing (g^M) for the liquid phases, calculated as the sum of the ideal (g^{id}) and excess (g^E) contributions, is negligible. We have only found one paper [4] in which the effect of pressure is considered in the g^M function for the liquid phase, within a multi-parametric empirical equation used as part of the checking of thermodynamic consistency of VLE data sets. The widespread assumption that activity coefficients are virtually independent of pressure leads to the common practice of fitting isothermal VLE data sets with no dependence of P in the liquid mixtures. For example, this is the procedure used in the VLE Data Collection by DECHEMA [5] that includes the correlation with different models (Margules, Wilson, NRTL and UNIQUAC) of experimental VLE data sets. In this data base no variation of the parameters with pressure (isothermal data) or with T

(isobaric data) is considered. This is a common occurrence in the published papers on this topic. The effect of P is only considered for isothermal VLE data at high pressures, but in these cases, state equations (EOS) instead of activity coefficient models are frequently used.

This approximation is related to the incompressibility of the liquid phases at low pressures, for which it is well accepted. As consequence, when an acceptable correlation of the experimental isothermal VLE data set at low P is not possible, it is believed that the lack of capability (flexibility) of the activity coefficient model is responsible. Even though this fact could be correct in some cases, in the present paper we show that for others, the variation with P in the $g^{M,L}$ function is *compulsory*, because otherwise an inconsistent situation is obtained.

In a previous paper [6], we achieved similar conclusions for temperature, demonstrating that for some isobaric VLE data sets, the use of additional T-dependence, like the one represented in Eqs. (1) and (2), is not a question of increasing the flexibility of the model because of the higher number of parameters used, but is demanded by the VLE data set itself. The key point is that in these cases, no model, no matter how capable it is, would be able to fit the data without such T dependence. In other words, in these cases the notion of fitting VLE data without T dependence in the interaction parameters is meaningless. In the paper, we started with the vapor phase (ideal gas) and used the Gibbs minor common tangent equilibrium condition to obtain the dimensionless $g^{M,L}$ ($G^{M,L}/RT$) values and the slopes ($dg^{M,L}/dx_1$) at each experimental liquid composition (molar fraction). With this information we identified those cases where a unique $g^{M,L}$ curve was not able to simultaneously satisfy all these $g^{M,L}$ values and its derivatives ($dg^{M,L}/dx_1$), requiring a high T-dependence, like the one in Eq. (1), to overcome the weak (or non-existent) influence of temperature in the activity coefficient models used.

Parallel reasoning to that of temperature has been carried out in the present paper for pressure, for those VLE data sets obtained under isothermal conditions. Nevertheless, in this case the conclusions are even more significant because, unlike temperature, the variation with pressure is not usual, neither in the parameters nor directly in the activity coefficient models for liquid mixtures. Moreover, we show that it is possible to know, just by checking the experimental VLE data set without using any model and before proceeding with the correlation data, if a P-dependence will be required. This reduces the frequent trial-and-error approaches that are common in equilibrium data fitting.

The ideas presented lead to a classification of the VLE data sets that allows the application of the most adequate correlation procedure in each case. We present some examples to illustrate all these ideas. New correlation results are presented in the present paper that accurately describe the experimental VLE data for systems that had been poorly correlated in literature. Moreover, the findings of this paper have direct consequences for the application of some tests frequently used to evaluate the thermodynamic consistency of the VLE data sets, which are included in the last part of the paper.

2. Theoretical Development

In order to have vapor-liquid equilibrium, 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, providing the global minimum of the Gibbs energy (Gibbs stability criterion), as shown qualitatively in Fig. 1 [6]. 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.

At moderate pressures, ideal behavior of the vapor phase is frequently considered. In these cases, 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 Eq. (3):

$$g^{M,V} = \frac{G^{M,V}}{RT} = y_1 \ln\left(\frac{P\cdot y_1}{p_1^o}\right) + y_2 \ln\left(\frac{P\cdot y_2}{p_2^o}\right) \qquad \forall\ y_1, y_2 \in [0,1] \qquad (3)$$

where p_i^o is the vapor pressure for the pure component i and P is the total pressure.

Eq. (3) sets the $g^{M,V}$ curve at each pressure for isothermal VLE data sets. The two experimental equilibrium compositions x_1^L and y_1^V in Fig. 1 are known for each VLE datum. The combination of this information along with the necessary and sufficient Gibbs common tangent equilibrium condition univocally set the $g^{M,L}$ value and its derivative at each P for the liquid phase (L) in equilibrium with each vapor phase (V), providing the following equations:

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

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

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

From this point of view, a hypothetically "perfect" correlation of VLE data sets will be obtained when a set of parameters of the model used for the activity coefficient of the liquid phase is found that satisfactorily reproduces the $g^{M,L}$ values and its derivatives obtained from the vapor phase $g^{M,V}$. 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 (L).

Many of the isobaric or isothermal VLE data sets correlated in literature satisfy these conditions using $g^{M,L}$ functions that are almost constant with temperature or constant with pressure, respectively. This is the case of all the systems that have been satisfactorily fitted.

In paper [6], we focused on isobaric conditions and showed that for some specific VLE data sets it is not possible to satisfy simultaneously both, the value and the slope of the $g^{M,L}$ curve, at each one of the liquid compositions. This treatment of the problem, which is not frequently considered, has demonstrated its relevant role in the understanding of the true nature of the limitations regarding correlation of isobaric VLE data. In the present paper, these arguments are extended and applied to isothermal conditions.

3. Study cases

We have selected the following VLE data sets from the DECHEMA Chemistry Data Series to illustrate our ideas:

Example 1: toluene (1) + 1-pentanol at 30ºC [7]

Example 2: water (1) + acetic acid (2) at 30ºC [8]

Example 3: hexane (1) + ethanol (2) at 30ºC [9]

Example 4: acetonitrile (1) + water (2) at 20ºC [8]

Example 5: diisopropyl ether (1) + ethylbenzene at 50ºC [10]

Example 6: hexane (1) + 2-nitropropane (2) at 25ºC [11]

In Fig 2, the $g^{M,V}$ and the required $g^{M,L}$ values have been represented for the first three systems (examples 1-3) at the experimental molar fractions for all the VLE data, showing the tie-lines that connect the conjugated V and L phases in equilibrium. These tie-lines indicate the slopes of the common tangents that must exist between the L and V phases in equilibrium for ideal vapor behaviour. In these three cases it is possible to draw one hypothetical smooth curve passing through all the liquid points that satisfy the required slopes at each point. This means that it *could* be possible to find a good correlation of the experimental VLE data using a model for $g^{M,L}$ with no dependence on pressure (just one curve for all the equilibrium points at different pressures). In fact, all these three systems have been adequately fitted in literature using the NRTL model without using P-dependence in the $g^{M,L}$ function [7,8,9]. We have selected these systems to show, in addition, different possibilities of appearance in the g^{M} vs x,y representation of the VLE tie-lines for systems that do not require dependence on pressure. In example 1, the vapor phases are out of the trajectory of the $g^{M,L}$ points (Fig. 2(a)), while they are located very close to that trajectory in system 2 (Fig. 2(b)). Finally, system 3 is representative of cases with an azeotrope point (Fig. 2(c)).

Now we consider the experimental VLE data for the acetonitrile (1) + water (2) at 20ºC (example 4). The results published for the VLE data correlations for this example using any of the existing activity coefficient models are very poor [8]. For example, the results published using the NRTL model have been represented in Figs. 3(a)-(d), where P versus the molar fractions x and y, the equilibrium curve y versus x, 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. Table 1(a) shows the binary interaction parameters along with the objective function calculated with Eq. (6) and deviations in pressure and vapor molar fractions (mean and maximum).

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

In Eq. (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 denoted *cal* is the one obtained using the model, and *exp* is obtained from the experimental data using the following equation (considering ideal vapor phase)

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

The comparison between activity coefficients in Eq (6) has been used as objective function because this is the most widely used procedure, e.g. DECHEMA Chemistry Data Series [5][7-11].

It is noticeable from Table 1(a) and Figs. 3(a) and (b), that this system could not be satisfactorily fitted with the NRTL model. Neither have other equations such as UNIQUAC, Wilson, etc., provided better results [8].

From the approach presented in the present paper, the satisfactory correlation of the experimental VLE data would require a precise description of the $g^{M,L}$ function and its derivatives calculated from the vapor phase, to satisfy the Gibbs minor common tangent equilibrium condition. This condition must be satisfied regardless of the objective function used (e.g. the activity coefficient function given by Eq. (6)).

Therefore, to analyse the difficulties in the correlation of some specific systems, it is very useful to plot the $g^{M,L}$ values and the slopes of their tangents lines, both calculated from the experimental vapor phase data (i.e.: according to Eqs. (4) and (5)) and compare them with the ones calculated with the NRTL model. Figs. 3(c) and (d) show that there is a lack of good agreement between both series of data. When this information is represented showing all the conjugated V and L phases in equilibrium (at each P) connected with a straight line (Fig. 4), it is observed that these tie-lines are clearly secant (not tangential) to any smooth curve passing through all the L points. This smooth curve would represent any hypothetical model for the activity coefficient with no variation with P. This fact reveals that for some isothermal VLE data sets, like the one in this example, the fitting of the equilibrium data with any hypothetical model (as capable as we can imagine), without taking into account the variation of the $g^{M,L}$ curve with pressure, is simply *impossible*. Attempting this task is hopeless and, what is more, it would be possible to identify in advance, which are these special cases of isothermal VLE, by means of a representation as the one in Fig 4. In this type of figure, the incompatibility among the required $g^{M,L}$ values and slopes for the L phases obtained from the vapor (ideal) phases can be easily observed. As long as the tie-lines connecting the two conjugated VLE phases are clearly secant (far from being tangential) to any smooth $g^{M,L}$ curve connecting all the L points, it will not be possible to carry out an

acceptable correlation of the experimental VLE data without an adequate P dependence in the model. This situation (example 4) is the opposite to those represented in Fig. 2 (examples 1, 2 and 3), in which the VL tie-lines are tangent to a smooth $g^{M,L}$ curve that connects all the liquid phases, making it possible to find a model like NRTL without P-dependence that adequately reproduces this curve.

For systems such as the one discussed (example 4), if the behaviour of the vapor phase is adequately represented by the ideal model (accepted at low or moderate pressures), the only possibility of overcoming the reached *dead-end situation,* and consequently of making compatible the isothermal VLE data, is to assume the effect of pressure in the liquid phases. If P-dependent parameters are used in the activity coefficient model, each one of the $g^{M,L}$ points (at each experimental P) would belong to a different $g^{M,L}$ curve and so it *could* be possible to satisfy simultaneously both the $g^{M,L}$ values and the slopes of its tangents required by the VLE condition, as will be shown next. If even then the results obtained are not acceptable, the only option is to consider non-ideal vapour behaviour.

P-dependence in the NRTL parameters

To consider P dependence in the binary interaction parameters of the model we have used a formulation similar to the one included in the Aspen Plus Chemical Process Optimization Software [3] for temperature (Eq. (1)):

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{P} + c_{ij} \cdot \ln P + d_{ij} \cdot P \qquad (8)$$

If necessary, when the NRTL model is used for the correlation, the dependence with P can also be used in the non-randomness parameter:

$$\alpha_{ij} = e_{ij} + f_{ij} \cdot P \qquad (9)$$

where a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij} and f_{ij} are the parameters of the model, which can be obtained by correlation of the experimental isothermal VLE data, i and j are the components of the system.

It is important to point out that the NRTL parameters published using the "conventional" procedure, for example the DECHEMA Chemistry Data Series [5], could be used as starting point of the correlation in which the influence of pressure is

considered. To do that, the previously published NRTL parameters for VLE data correlations (e.g. in cal/mol) should be transformed into dimensionless values (dividing by RT) to obtain the "a_{ij}" parameter in Eq. (8). Using this procedure, we make sure that the conventional solution (known in many cases) is present in the optimization from the beginning and any other solution of the fitting process will be always better than that, for those cases where P-dependence is necessary.

We carried out the correlation of the VLE data for the binary system acetonitrile (1) + water (2) at 20ºC (example 4) using this procedure, combining the Eqs. (8) and (9) with the activity coefficient model (NRTL) and the objective function in Eq. (6). The correlation results obtained, labelled as NRTL f(P), are shown in Table 1(b) and Fig. 5. For practical purposes, we did not restrict α_{ij} during the correlation process to attain a better approximation to the experimental VLE data, regardless of its supposed physical meaning, but the use of P-dependence in α_{ij} was not necessary since f=0 in Eq. (9).

These results reveal that allowing a P dependence in the $g^{M,L}$ function leads to very satisfactory correlation results. The calculated pressures and vapor molar fractions reproduce the experimental values very well. This is because using the proposed procedure it was possible to satisfy simultaneously the required $g^{M,L}$ and $dg^{M,L}/dx_1$ (named in some parts of this paper as slopes) values, as shown in Fig. 6. In this figure, it is also possible to observe the evolution of the $g^{M,L}$ curves with pressure which was necessary to satisfy the VLE requirements, in the interval of pressures of this data set. In Fig. 6(b) both $g^{M,L}$ and $g^{M,V}$ curves are simultaneously represented for P=62.8 mmHg, as an example to show the fulfilment of the Gibbs common tangent equilibrium condition., The required common tangents between the liquid and vapor phases are also satisfied for all other pressures in this VLE data set. We would like to remark that to achieve this correlation result, unstable LLE splitting is provided by the model at some pressures. However, the stable solution in all these cases correspond with vapor and liquid phases in equilibrium, as it is shown in Fig. 6(b) for one specific pressure. For this reason, stability must be checked in all the phase equilibria calculations.

It is important to remark that only the L and V points (corresponding with the VLE tie-lines) and those to the left of L and to the right of V have real existence. Compositions between L and V equilibrium points are not stable and so, points on the curve in this interval are fictitious. Therefore, the calculated $g^{M,L}$ curves in Fig. 6 allow satisfying the

equilibrium conditions reproducing faithfully the experimental VLE data and, at the same time, the influence of pressure *at the existing liquid mixtures* remains weak.

The same correlation procedure has been applied to other VLE data sets very poorly fitted in literature with any model, as the examples 5 and 6. Also in these cases, the addition of pressure in the model is required to make the vapor and liquid behaviour compatible with the experimental equilibrium data measured. In Tables 2 and 3 and Figs. 7 and 8, we present the correlation results for these two systems. These results show the necessity of considering P-dependence in the $g^{M,L}$ function (labelled as NRTL f(P)) to achieve an acceptable fitting of the experimental data.

3. Procedure for the correlation of VLE data

There are a considerable number of VLE data sets, both isobaric and isothermal, with a very standard appearance that inexplicably cannot be satisfactorily correlated with any of the existing models to formulate the non-idealities of the liquid mixtures. From the point of view presented in this paper for isothermal conditions, and in a previous paper [6] for isobaric conditions, we have demonstrated that for these systems no model, as highly flexible as can be imagined, can fit the data if P or T dependence, respectively, are not included in the parameters of the model.

Analysing the g^{M} curves for many VLE data sets at constant T or P, both for azeotropic and non-azeotropic systems, we have identified the following types of behaviours:

i. Group 1: formed by the majority of systems. These are systems that exhibit a smooth experimental $g^{M,L}$ curve that can adequately accommodate the common tangents to the vapor and liquid phases in equilibrium (Fig. 2)
ii. Group 2: formed by a non-negligible number of VLE data sets, both isothermal and isobaric, that exhibiting a smooth experimental $g^{M,L}$ curve cannot accommodate the common tangents to the vapor and liquid phases in equilibrium.
    - Group 2A. Includes those systems that can be perfectly correlated by considering an adequate variation of the $g^{M,L}$ with T or P (Figs. 6 and 7). Usually, this approach will provide a satisfactory correlation of all variables, including the activity coefficients, $g^{M,L}$, vapor molar fractions y_i and T or P.
    - Group 2B. Requires in addition a strong non-ideality of the vapor phase to enable the coupling of the vapor and liquid phases common tangents to the

g^M functions. At low and moderate pressures, conventional equations of state (EOS) do not provide, in most cases, a remarkable modification of the ideal vapor behaviour. As an alternative for these cases, a Wilson type equation could be adequate to formulate the fugacity coefficient (φ_i).

Most of the systems fitted satisfactorily in literature belong to group 1. Related to group 2, in the present paper we have presented some examples of isothermal VLE data sets of group 2A and those for isobaric conditions are in [6]. Next we discuss one example that belongs to group 2B: water (1) + n,n-dimethylacetamide (2) a P=200 mmHg [12]. For this system, the correlation results obtained using NRTL, or any other classical model, describe the experimental equilibrium data poorly. Moreover, the addition of a very flexible T-dependence in the binary interaction parameters, such as that given in Eq. (1), does not solve the problem. In this and other similar cases, the only possibility to make the experimental VLE data compatible with the equilibrium condition (formulated by the common tangent line) is, in addition, the substantial modification of the ideal $g^{M,V}$ function. In many cases, it cannot be achieved using typical EOS. We have used a Wilson type equation for non-ideal $g^{M,V}$ behaviour with good results (taking into account that this equation does not allow phase splitting which the vapour phase requires). Table 4 shows the correlation results obtained for this system using the different procedures discussed. In Fig. 9 comparison of experimental and calculated results obtained with parameters presented in Table 4(b) have been represented showing a satisfactory fitting of the data. In all cases like this one that belongs to group 2B, a very high number of parameters is necessary to achieve an acceptable fitting of the experimental VLE data. However, the important aspects of this matter are as follows: i) the necessity of this high number of parameters is totally justified, and ii) these parameters have been selected based on a process where the requirements of the experimental behaviour have been considered. In some cases, fitting parameters are added without any criterion, in an attempt to achieve better correlation results. This practice is not recommended at all. For example, consider the case discussed in this paper where the $g^{M,L}$ function requires P (or T) dependence and, as a consequence, as much as we increase the number of parameters in the $g^{M,L}$ model, the fitting is simply impossible without such consideration. There is a famous aphorism in physics: ‘‘Give me four parameters and I can fit an elephant. Give me five and I can wag its tail’’. This humorous comment could lead to thinking, erroneously, that increasing the number of

fitting parameters will allow the easy reproduction of any phase equilibrium behaviour. Regrettably, this is not true because the correct functionality also has to be also present in the equations and, on many occasions, this is very difficult to achieve. The combination of adequate functions containing the required number of parameters along with the checking of Gibbs stability criterion is the key to reaching a satisfactory correlation result. Nowadays, with the great computing capacity of computers, nobody need use a poor fitting solution to avoid handling multiple parameters in the equations.

4. Implications on thermodynamic consistency tests

The ideas discussed in the present paper have some implications on the veracity of the results obtained when applying some typical thermodynamic consistency (TC) tests for the evaluation of the experimental VLE data. Wisniak et al. [13] present an excellent summary of the state of the art in TC tests application. The fulfilment of the Gibbs-Duhem (GD) equation is the criterion most widely used for consistency of the VLE data:

$$\int_{T(x_1=0)}^{T(x_1=1)} \frac{h^E}{RT^2} dT - \int_{P(x_1=0)}^{P(x_1=1)} \frac{v^E}{RT} dP + \int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \qquad (10)$$

where h^E and v^E are, respectively, the excess enthalpy and volume in the mixing process.

Because this equation can be handled in different ways, a variety of TC tests can be found in the literature that are frequently combined to produce a unique quality factor for the VLE data set. For example, the NIST Thermodata Engine (TDE) software package [14] includes the algorithm proposed by Kang et al. [15] to assess the quality of experimental VLE data. This algorithm consists of a combination of five tests: Herington Test (Area Test) [16], Van Ness Test [17], Point Test [18], Infinite Dilution Test [19] and Pure Component Consistency Test [15]. The result of this algorithm is the so-called global quality factor (Q_{VLE}) for the VLE data set. Some of these tests have been seriously questioned in literature [13,20,21,22] . However, its use is still widespread, to the point that it is a requirement in many journals and data banks, for the acceptance of experimental VLE data sets.

The results presented in the present paper provide additional reasons to question the way in which some of these tests are applied. For example, the Van Ness Test is regarded as a modelling capability test in which the NRTL equation is frequently used [15], but using constant binary parameters with pressure and with a very weak variation with temperature. For example, the Thermodata Engine TDE uses a version of NRTL with five parameters for binary mixtures: $A_{12}^{A}, A_{21}^{A}, A_{12}^{B}\ A_{21}^{B}, \alpha_{12}$ [23]. For isobaric data sets, temperature dependence of the parameters is represented as follows:

$$A_{ji} = A_{ji}^{A} + \frac{A_{ji}^{B}}{T} \tag{11}$$

For isothermal data sets, binary interaction parameters are considered to be composition-dependent

$$A_{ji} = A_{ji}^{A} + A_{ji}^{B}\left(x_i - x_j\right) \tag{12}$$

Therefore, the temperature dependence considered in the model to test the quality of the data is very weak and the pressure dependence does not exist. Because it has been demonstrated that some isobaric and isothermal VLE data sets require that the Gibbs energy of mixing function *necessarily* includes a marked dependence with T or P, respectively, and trying the fitting otherwise would be incongruous, it is clear that the penalization of these experimental VLE data for it would neither be correct nor justified. In other words, the same invalidated VLE data set could pass the TC test with a high quality factor Q^{VLE}, if an adequate form of the model considering conveniently T or P, was used.

Considering that some TC tests are based on the capacity of modelling of the experimental VLE data, but in their application not all the available tools to achieve an adequate fitting are frequently used, the result is that on many occasions the experimental VLE data sets are wrongly penalized as not thermodynamically consistent. In these cases, the problem is in the application of the TC tests and not in the data itself.

Recently, Fernández et al. [24] have proposed a more rigorous method to evaluate the consistency of experimental data in VLE and VLLE that avoid the necessity of using several tests simultaneously. The application of this method requires using a mathematical model for the Gibbs energy of mixing that adequately represents the

experimental behaviour of the system. The authors propose one that is a function of P, T and molar fractions in accordance with the ideas established in the present paper.

We now focus on the Area Test in the version by Herington for isobaric VLE data. This test proposes an approximation to evaluate the excess enthalpy term in the Gibbs-Duhem equation (Eq. (13)):

$$\int_{T(x_1=0)}^{T(x_1=1)} \frac{h^E}{RT^2} dT + \int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \qquad (13)$$

This excess enthalpy term could be considered as a correction of the fulfilment of the Area (or equal-area) test by Redlich-Kister (restricted to constant T and P) for isobaric VLE data in which T is variable. This term requires data that are difficult to measure but that are not negligible, especially for mixing processes accompanied by strong thermal effects. Otherwise, only when both T and P are constant is possible to assure that the activity coefficients for components 1 and 2 (for a binary mixture) cross each other, allowing both required positive and negative areas in the Redlich-Kister test to be evaluated. This is shown in Fig. 10(a) where a qualitative $g^{M,L}$ surface is represented as a function of $\psi = \psi_o$ (T for isobaric or P for isothermal data) and molar fraction x. In this case, the projection of all the $g^{M,L}$ curves at constant ψ that correspond with the experimental VLE data is a unique curve which necessarily provides the crossing in the $\ln\gamma_i$ curves for i=1 and 2 (Fig. 11(a)). Otherwise, every point representative of each VLE datum is located in a different $g^{M,L}$ curve (Fig. 10(b)) and in this case the $\ln\gamma_i$ curves could not cross each other, as shown in Fig. 11(b). An example of system showing this type of behaviour is water (1) + n,n-dimethylacetamide at P=200 mmHg [12]. The question that arises is how this could affect the application of the Herington test. Without going into details about the equations proposed by Herington, because they have been extensively described in literature [13,16], the method is based on the information of a very scarce number of systems. Its application to those systems with strong thermal effects, like those under discussion, could produce false results. The magnitude required in the excess enthalpy term for those systems with non-crossing $\ln\gamma_i$ curves, and consequently without changes in the sign of the area in the Redlich-Kister plot [25], is much higher than the values provided by the Herington method. As result, the test could declare some data sets as inconsistent when in practice they are not. This is an additional critique to the Herington method, whose lack of rigor has already been

discussed in several papers [13,20,21,22], but is still used in some very popular algorithms for TC evaluation of VLE data sets.

5. Conclusions

Many of the experimental VLE data sets that appear poorly correlated in the literature using activity coefficient models such as NRTL or UNIQUAC require a strong dependence on temperature (constant P) or any on pressure (constant T) in the Gibbs energy of excess function, which are not frequently considered. For this type of systems, the use of such functions is not an option but a necessity and no hypothetical model, as flexible as we can imagine, could fit the data unless this dependence is considered. A type of graphical representation, based on the analysis of the g^M function for the vapor and liquid phases, is suggested to show when P (or T) dependence in the model is required. The advantage of this method is that it can be carried out before the correlation procedure using exclusively experimental VLE data. This is very useful in order to avoid frequent trial-and-error procedures finishing on many occasions with non-satisfactory fitting results for systems that could be well fitted. It is also important to identify those systems where the vapor phase cannot be considered as ideal and the $g^{M,V}$ function must be strongly modified to obtain a good correlation of the experimental VLE. A classification of the systems has been presented based on their characteristics for an optimal model correlation in the context of VLE data. Moreover, the aspects discussed in this paper revel the inadequate application of the thermodynamic consistency tests that is made in many cases and whose result could be the wrong quality penalization of experimental VLE data sets. Finally, we suggest that authors should assure not only the quality of the data but also the correlation results they obtain, and journals should share this responsibility, establishing the required measurements.

Nomenclature

a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}, f_{ij}	parameters
A_{ij}	binary interaction parameters (cal mol^{-1})
g^{id}	ideal Gibbs energy (dimensionless)
g^E	excess Gibbs energy (dimensionless)

G^M, g^M	Gibbs energy of mixing ($J \cdot mol^{-1}$ and dimensionless, respectively)
h^E	excess enthalpy ($J\ mol^{-1}$)
n	number of VLE data
O.F	objective function
P	pressure (Pa)
p^o	vapor pressure (Pa)
Q^{VLE}	global quality factor for the VLE data set
R	gas constant ($J \cdot K^{-1}\ mol^{-1}$)
v^E	excess volume ($m^3\ mol^{-1}$)
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
z_i	molar fraction of component i in the binary global mixture

Greek symbols

α_{ij}	non-randomness NRTL factor
γ_i	activity coefficient for component i
φ_i	fugacity coefficient
τ_{ij}	NRTL binary interaction parameter
Ψ	T for isobaric or P for isothermal data

Superscripts

cal	calculated
exp	experimental
L	liquid phase
V	vapor phase

Subscripts

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i, j	components
k	VLE data

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Table 1

Correlation results of the experimental VLE data for example 4 using the NRTL model: a) with constant parameters (NRTL) [8], and b) with parameters dependent on pressure (NRTL f(P)). The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	1133.67	890.574	0.5296			
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.893	5.68	16.48	0.0511	0.1485	
(b) NRTL f(P)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	44.4118	0.873161	-6.87589	-0.158597	0.147648	0
21	-452.753	-2.59140	77.1902	-0.566901	-0.039320	0
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.0145	0.972	1.735	0.0044	0.0086	

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Table 2

Correlation results of the experimental VLE data for example 5 using the NRTL model: a) with constant parameters (NRTL) [10], and b) with parameters dependent on pressure (NRTL f(P)). The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	835.626	-461.593	0.2749			
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.649	6.65	14.7	0.0293	0.0620	
(b) NRTL f(P)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	41.6503	65.5484	-13.1781	-0.039177	-0.171954	0
21	1.21027	-31.3570	0.699303	-0.011635	0.681666	0
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.0638	4.22	18.8	0.0061	0.019	

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Table 3

Correlation results of the experimental VLE data for example 6 using the NRTL model: a) with constant parameters (NRTL) [11], and b) with parameters dependent on pressure (NRTL f(P)). The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	847.988	780.622	0.6421			
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.396	8.52	20.5	0.0112	0.0318	
(b) NRTL f(P)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	46.9449	243.191	-3.38461	0.046585	0.199393	0
21	-7.85728	52.2899	2.52101	-0.027135	-0.577396	0
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.102	1.10	3.18	0.0053	0.0186	

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Table 4

Correlation results of the experimental VLE data for water (1) + n,n-dimethylacetamide (2) at 200 mmHg using the NRTL model: a) with constant parameters (NRTL) [12], and b) with parameters dependent on temperature (NRTL f(T)) and non-ideal vapor phase. The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	3.0940	-53.8757	0.3024			
	O.F(γ)	mean ΔT (ºC)	max ΔT (ºC)	mean Δy_1	max Δy_1	
	0.898	0.770	1.986	0.0374	0.0941	
(b) NRTL f(T) and non-ideal vapor phase (Wilson)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	-0.001587	697.900	-0.804139	0.008289	0.2	0
21	-0.080572	153.715	0.018984	-0.002705	0.2	0
	A_{ij} (Wilson)					
12	0.794					
21	1.779					
	O.F(γ)	mean ΔT (ºC)	max ΔT (ºC)	mean Δy_1	max Δy_1	
	0.020	0.317	1.202	0.0047	0.0299	

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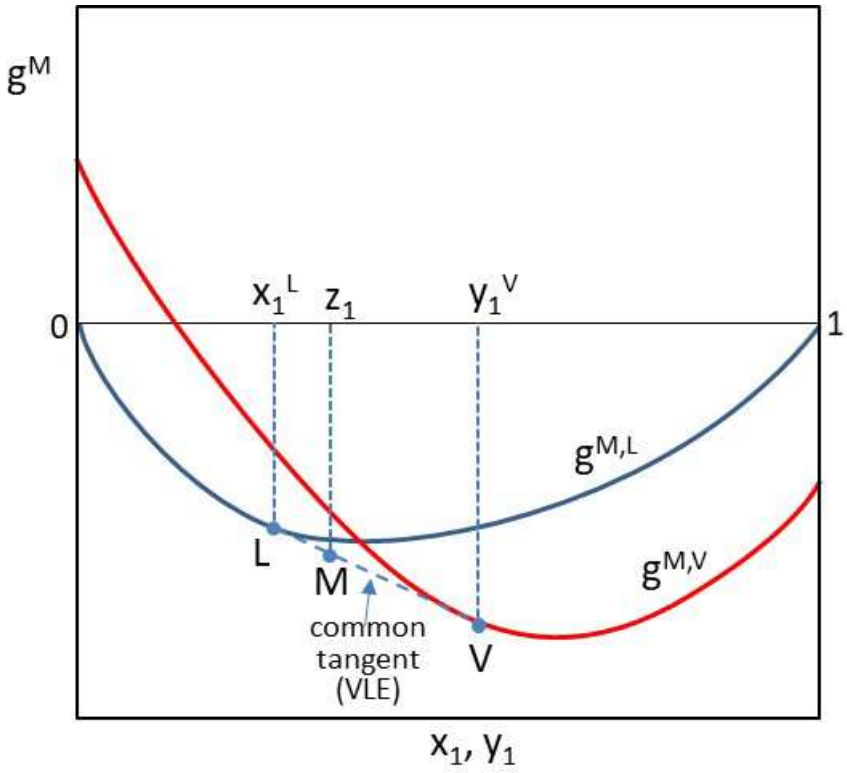

Fig. 1. Qualitative representation of the Gibbs minor common tangent equilibrium criterion applied to VLE of a binary system at some specific T and P.

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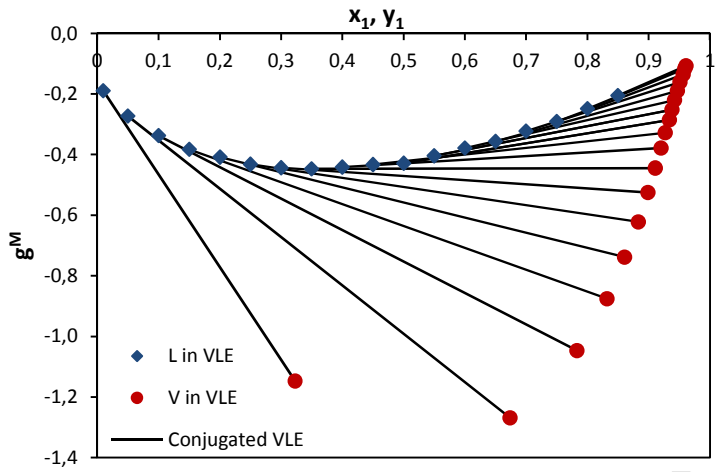

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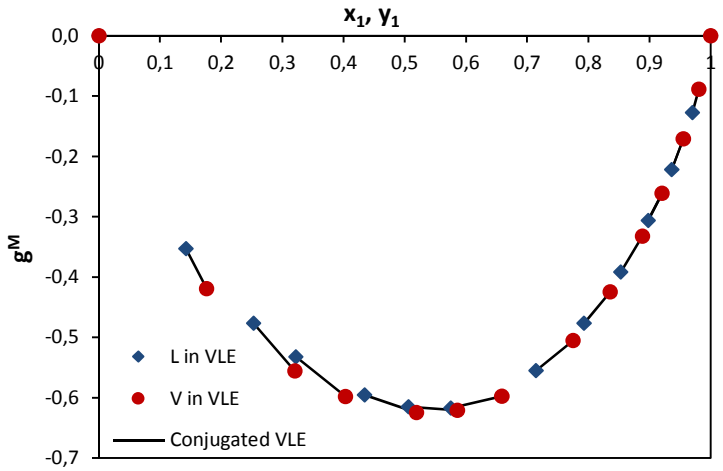

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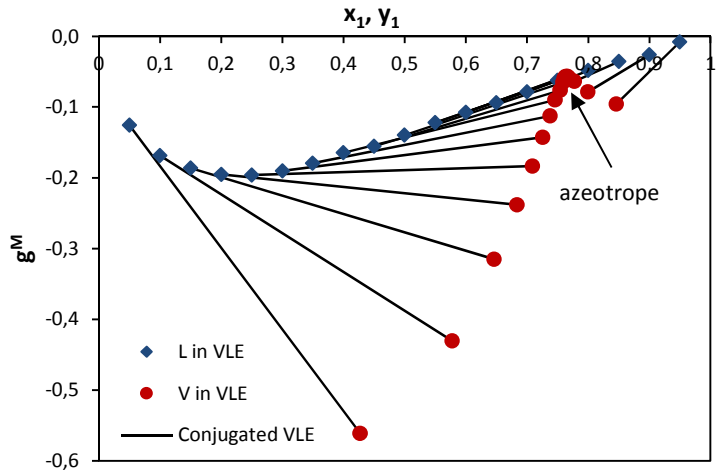

Fig. 2. Representation of the straight lines that connect the conjugated VLE phases and are tangent to the $g^{M,V}$ curves (ideal gas) for systems that do not require P-dependence in the $g^{M,L}$ function: a) example 1, b) example 2, and c) example 3.

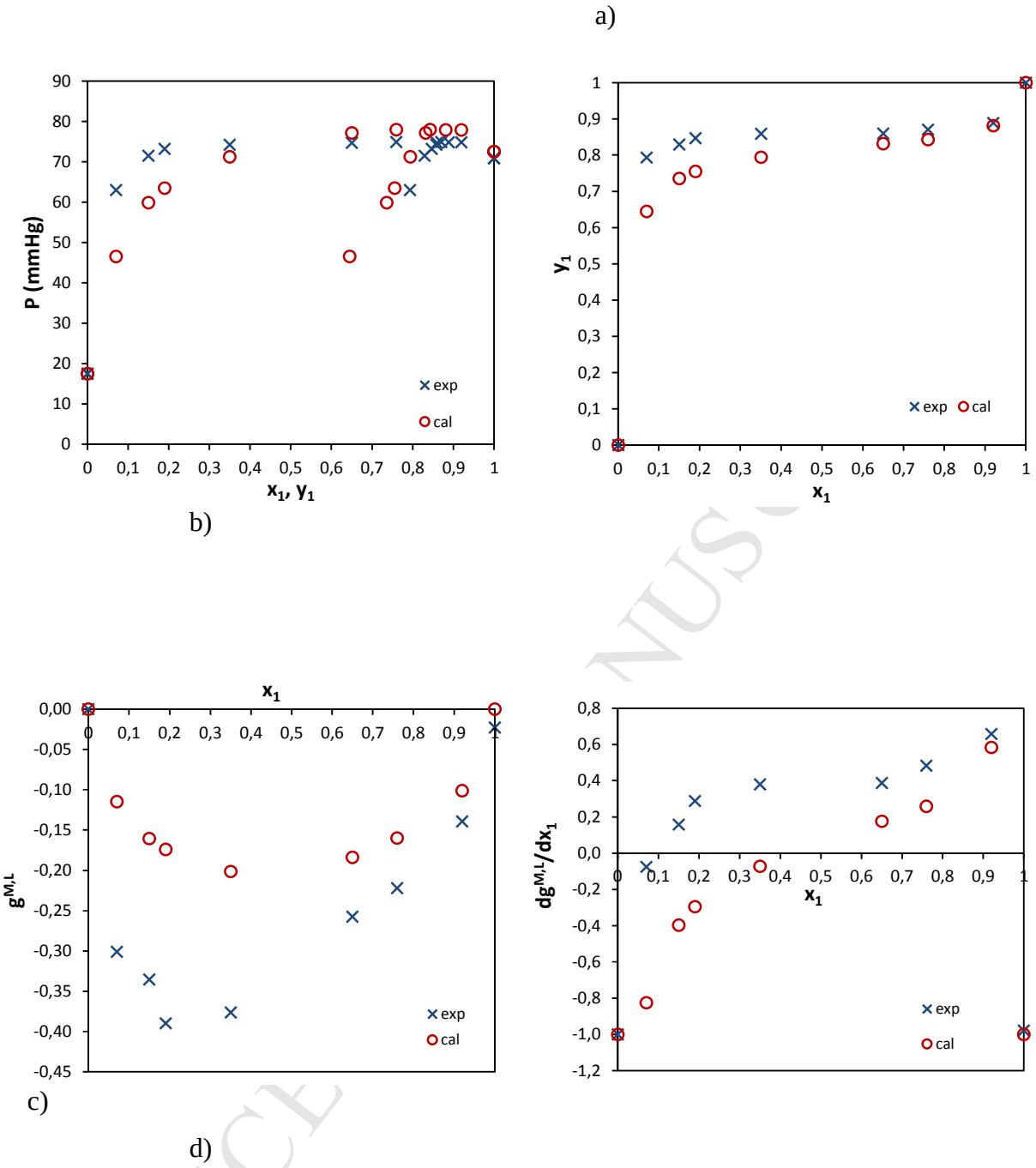

Fig. 3. Experimental data and correlation results using the NRTL model for example 4: (a) P vs. x,y, (b) y vs. x, (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1. Parameters are given in Table 1(a) [8].

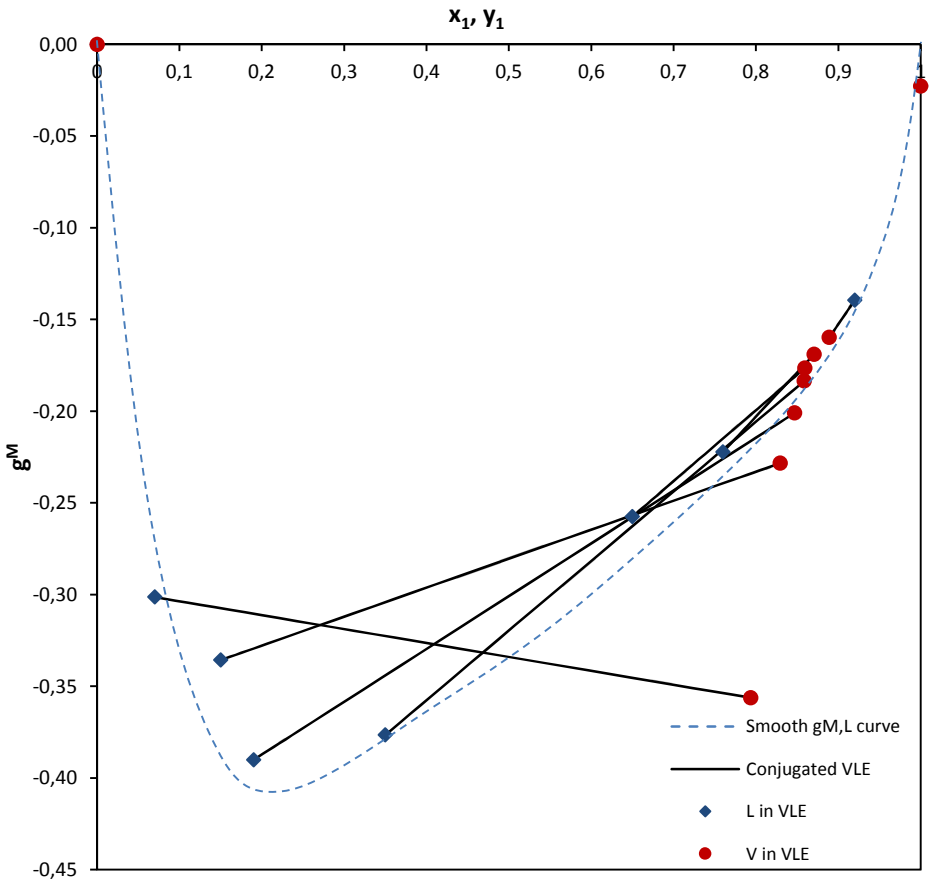

Fig. 4. Representation of the straight lines that connect the conjugated VLE phases for example 4 and are tangent to the $g^{M,V}$ curves (ideal vapor). A smooth curve for $g^{M,L}$ passing through all the L phases has been included.

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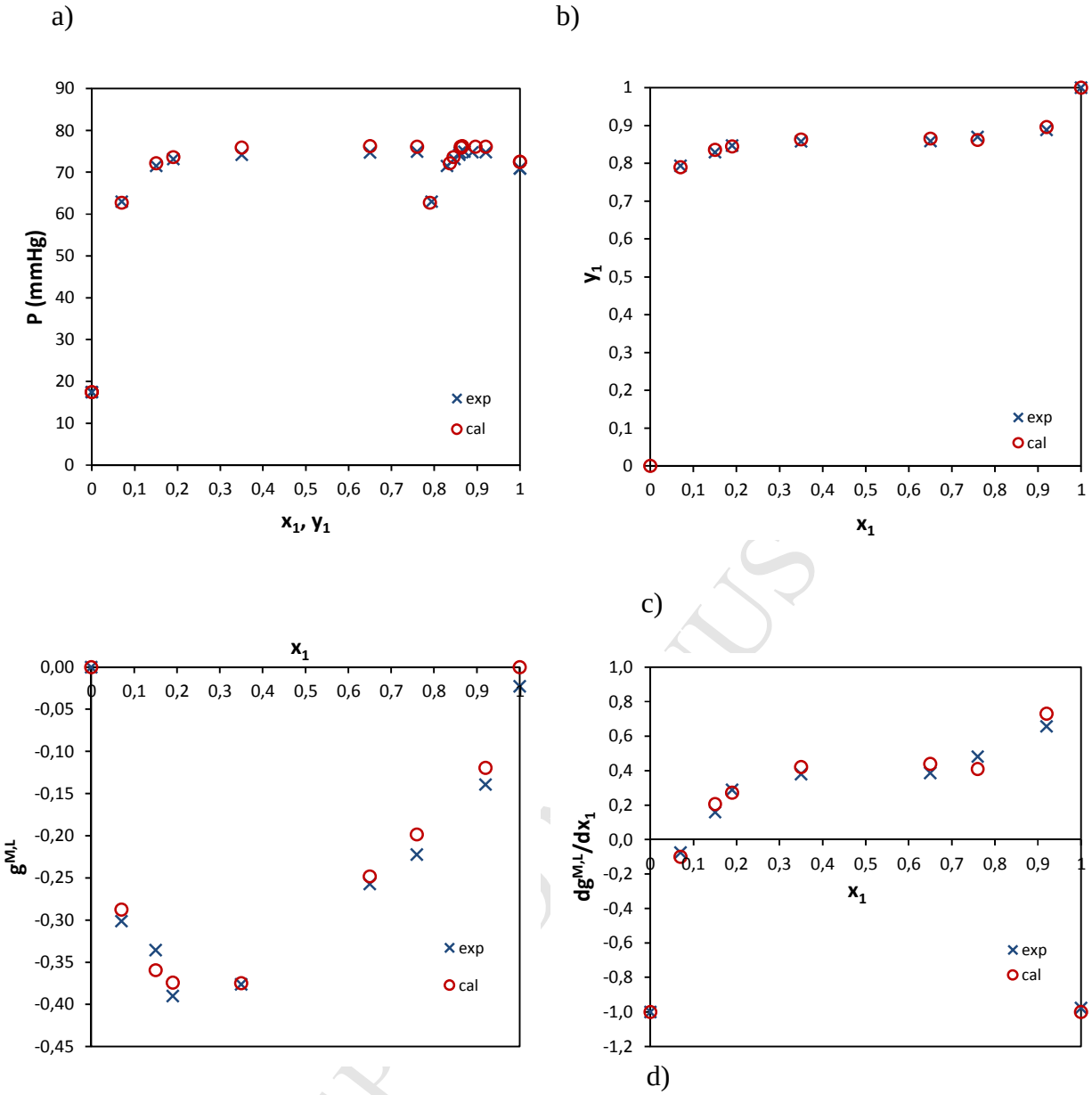
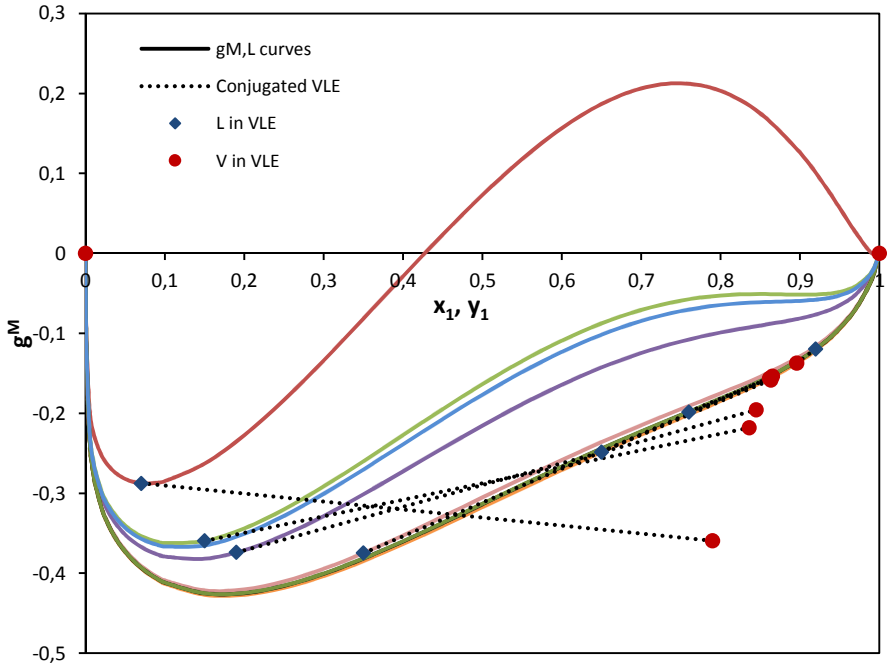


Fig. 5. Experimental data and correlation results using the NRTL f(P) model for example 4: (a) P vs. x,y, (b) y vs. x, (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1. Parameters are given in Table 1(b).

a)



b)

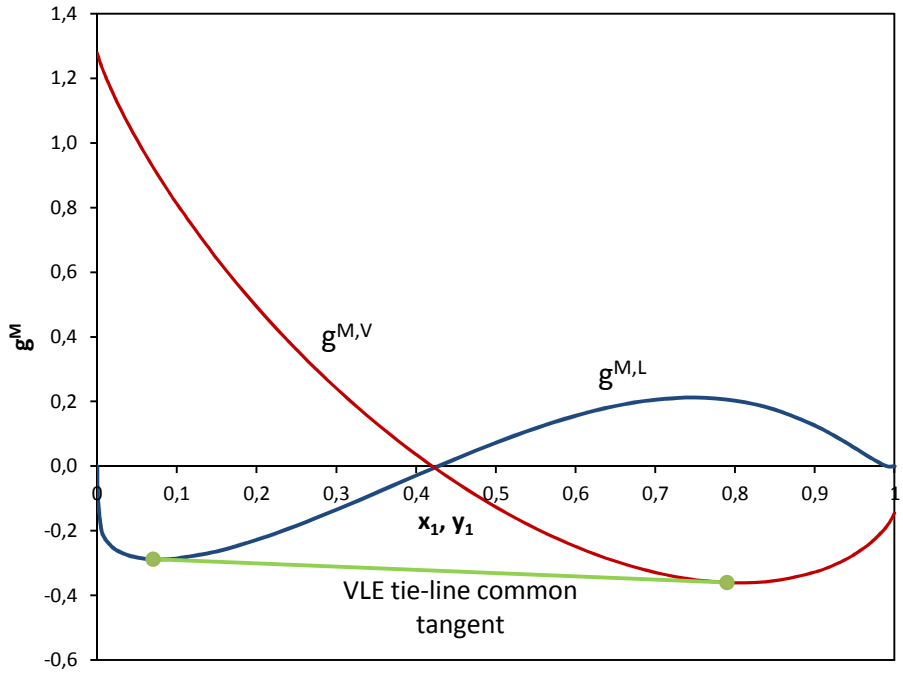


Fig. 6. Representation of the straight lines that connect the conjugated VLE phases for example 4 and calculated $g^{M,L}$ curves using the NRTL f(P) model, b) $g^{M,L}$ and $g^{M,V}$ curves showing the VLE Gibbs common tangent criterion at P=62.8 mmHg. Parameters are given in Table 1(b).

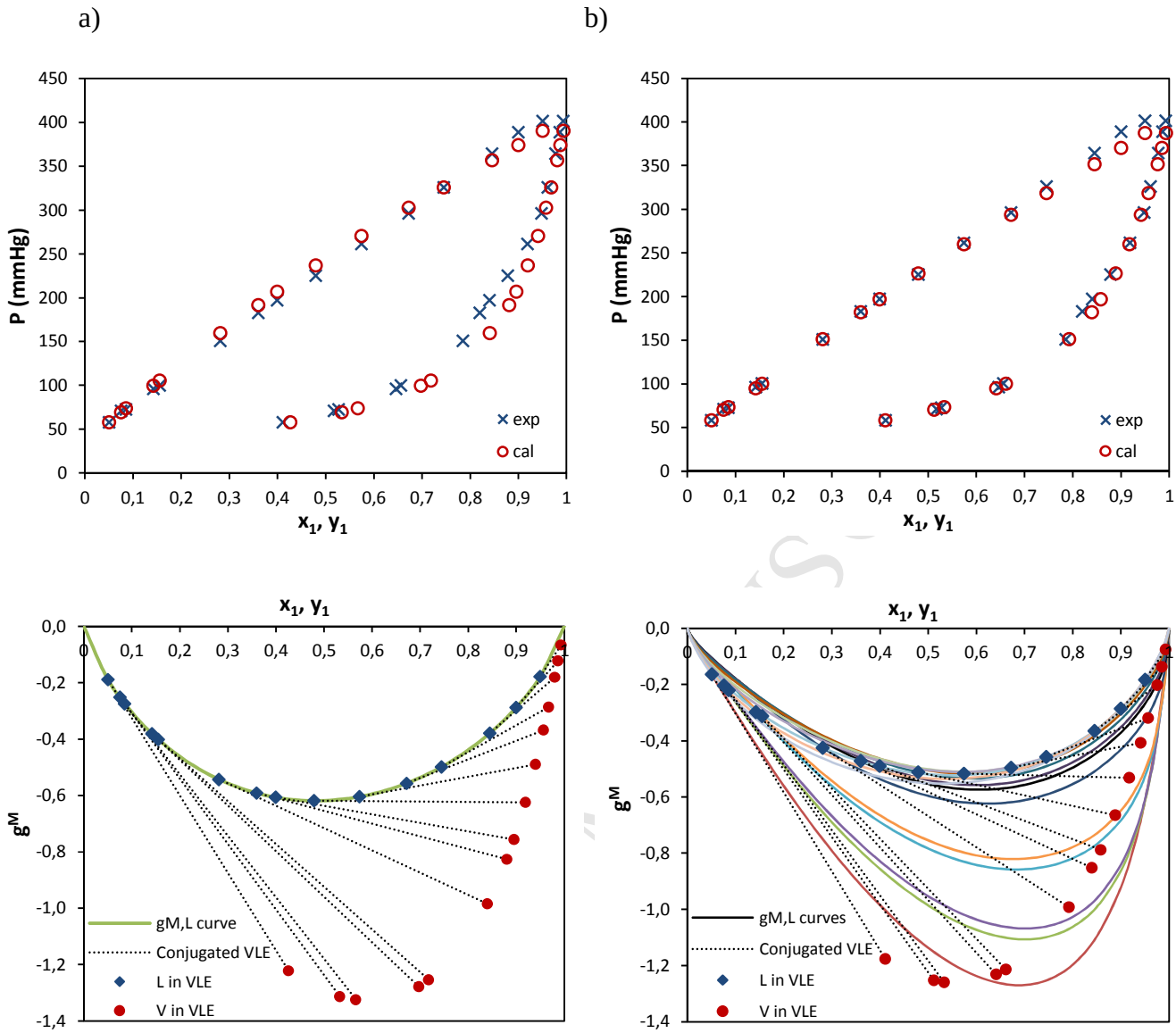


Fig. 7. Experimental and calculated VLE data for example 5, represented in P vs x,y and g^{M} vs x,y graphs to show the VLE tie-lines and the $g^{M,L}$ curves generated by the model: a) NRTL [10], and b) NRTL f(P)

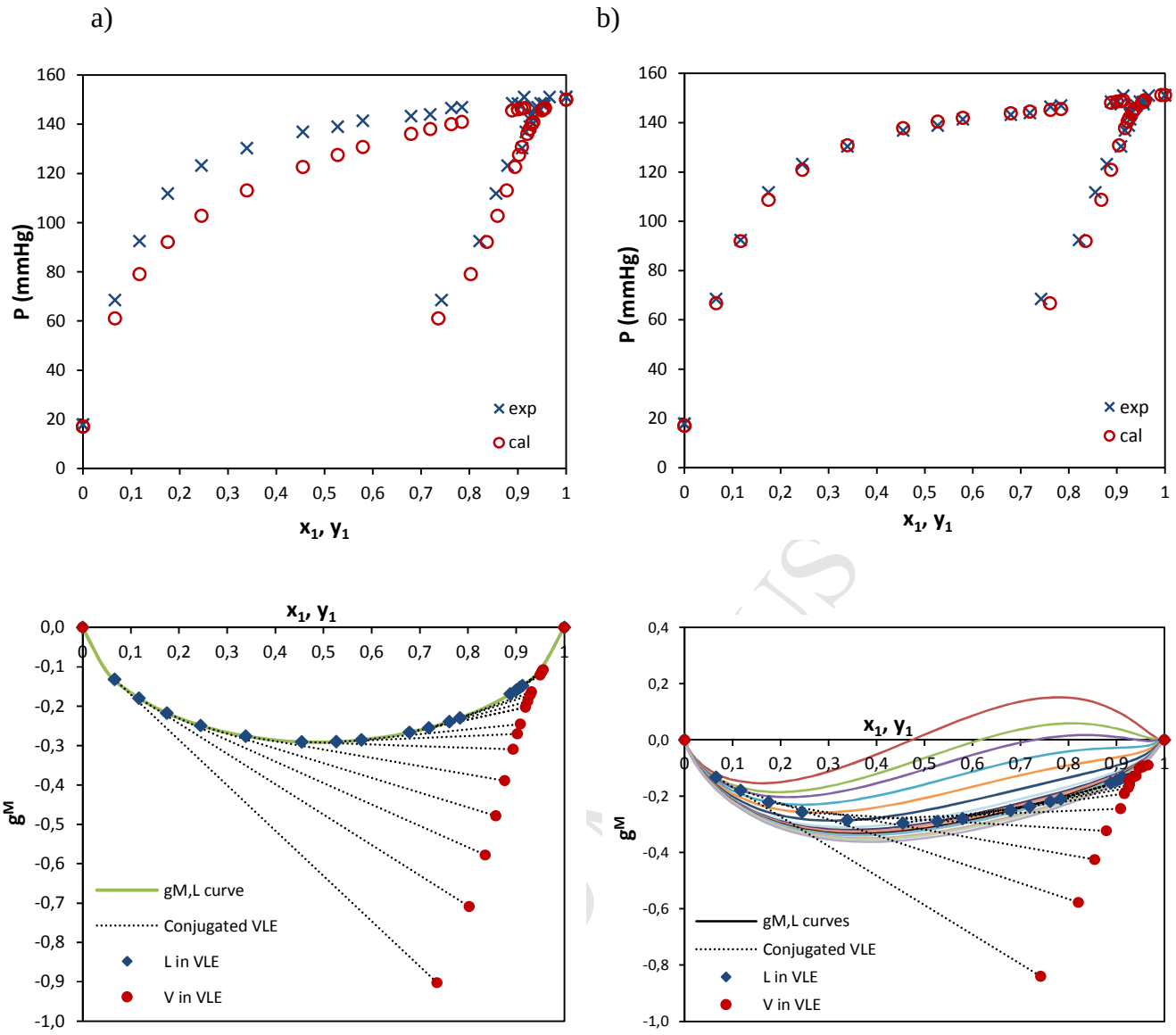


Fig. 8. Experimental and calculated VLE data for example 6, represented in P vs x,y andgM vs x,y graphs to show the VLE tie-lines and the gM,L curves generated by the model: a) NRTL [11], and b) NRTL f(P)

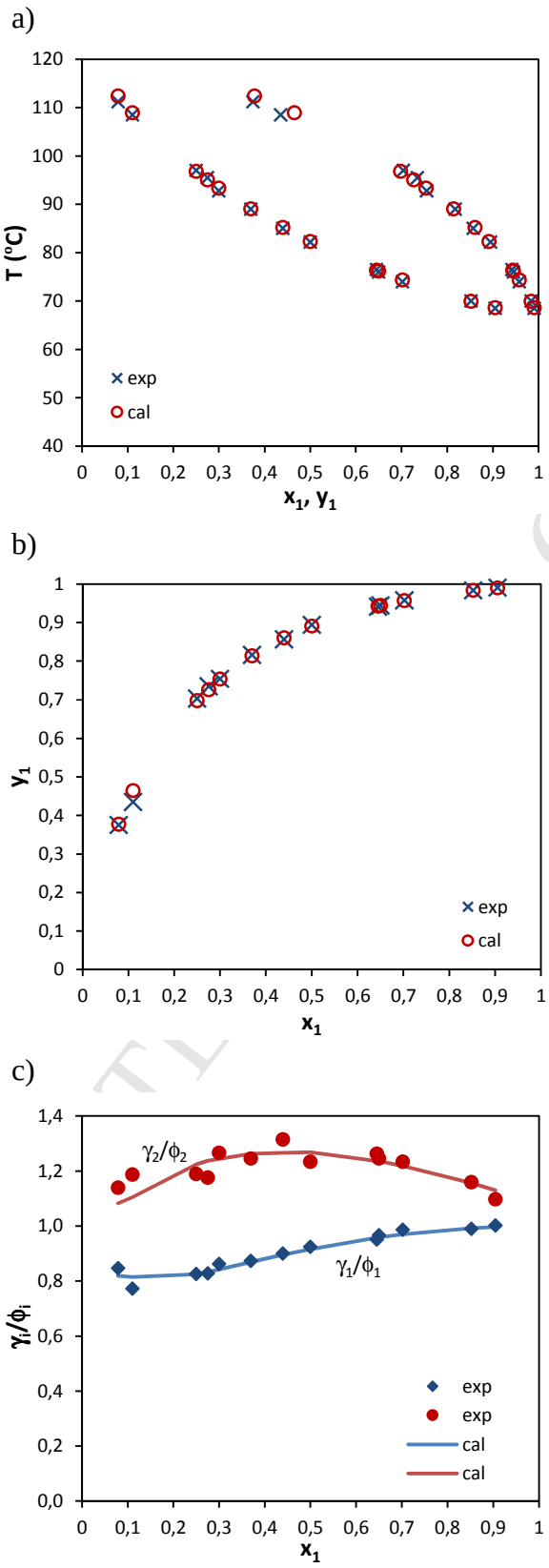
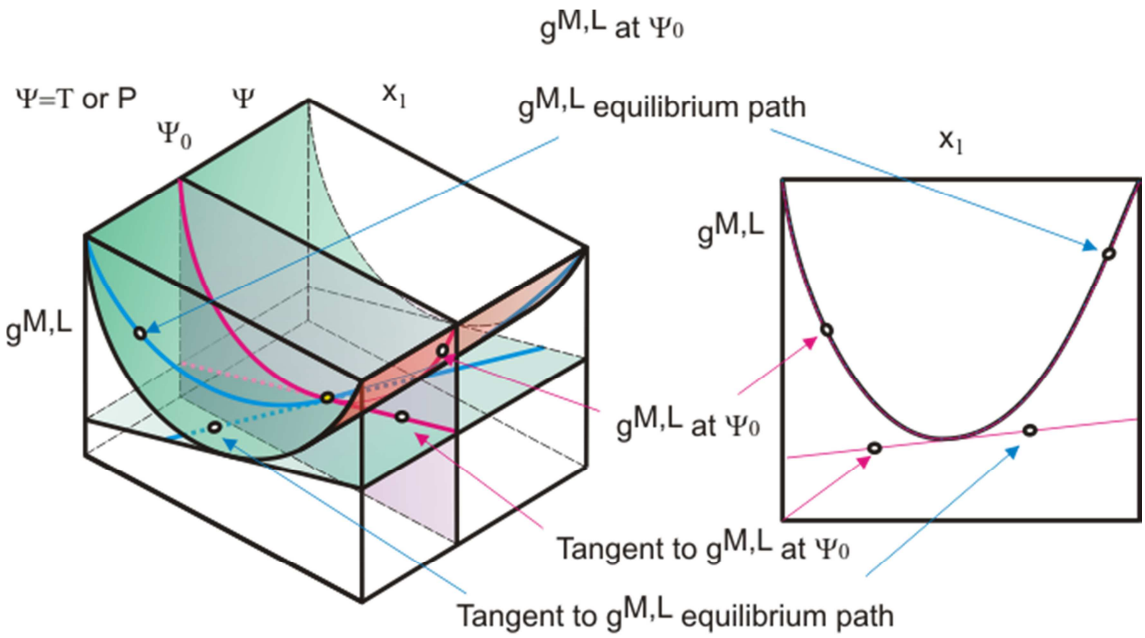


Fig. 9. Experimental data and correlation results using the NRTL f(T) model with non-ideal vapor phase (Wilson type equation) for the water (1) + n,n-dimethylacetamide (2) system at 200 mmHg: (a) T vs. x,y, (b) y vs. x, (c) γ/φ. Parameters are given in Table 4(b).

a)



b)

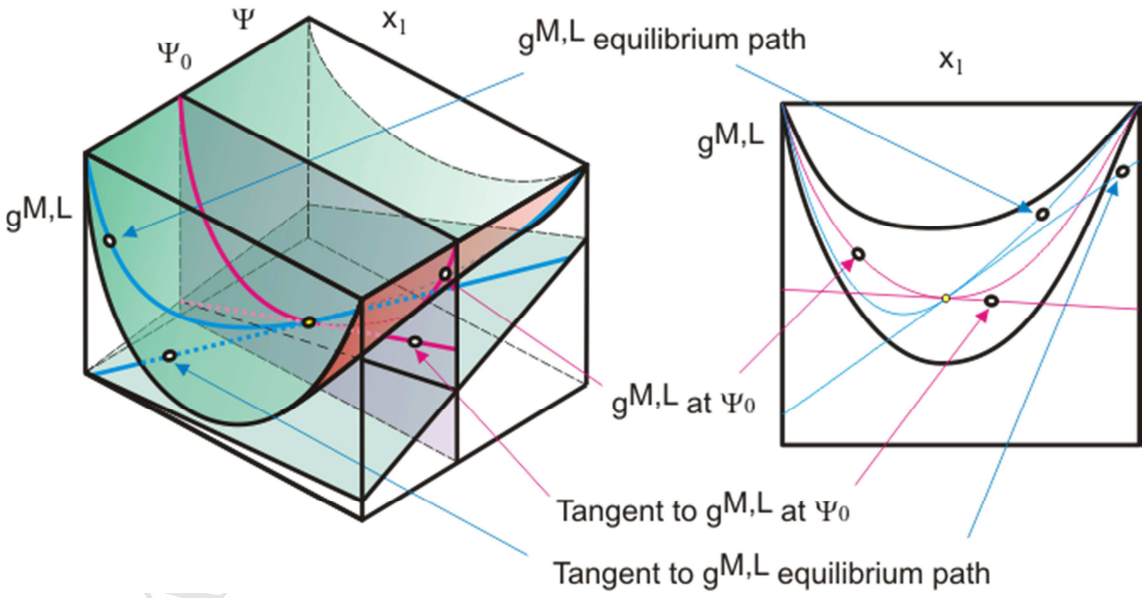
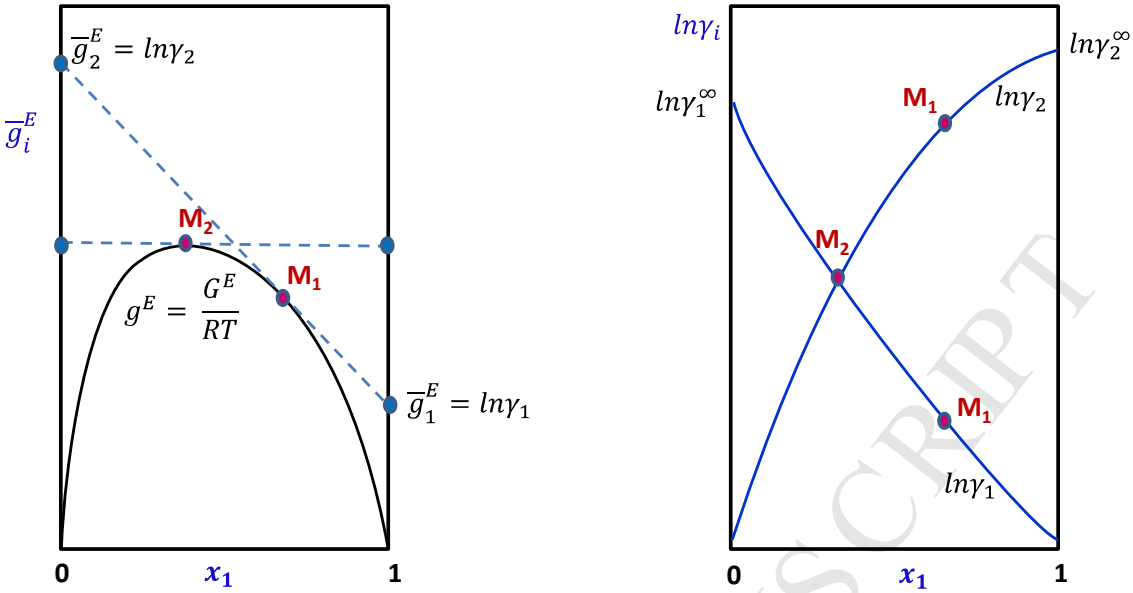


Fig. 10. Schematic representation of the Gibbs energy of mixing function for the liquid phase ($g^{M,L}$) for different behaviour of experimental VLE data sets: a) Group 1 with negligible dependence on ψ, and b) Group 2 with a substantial dependence on ψ (ψ = T (isobaric data) or P (isothermal data))

a)



b)

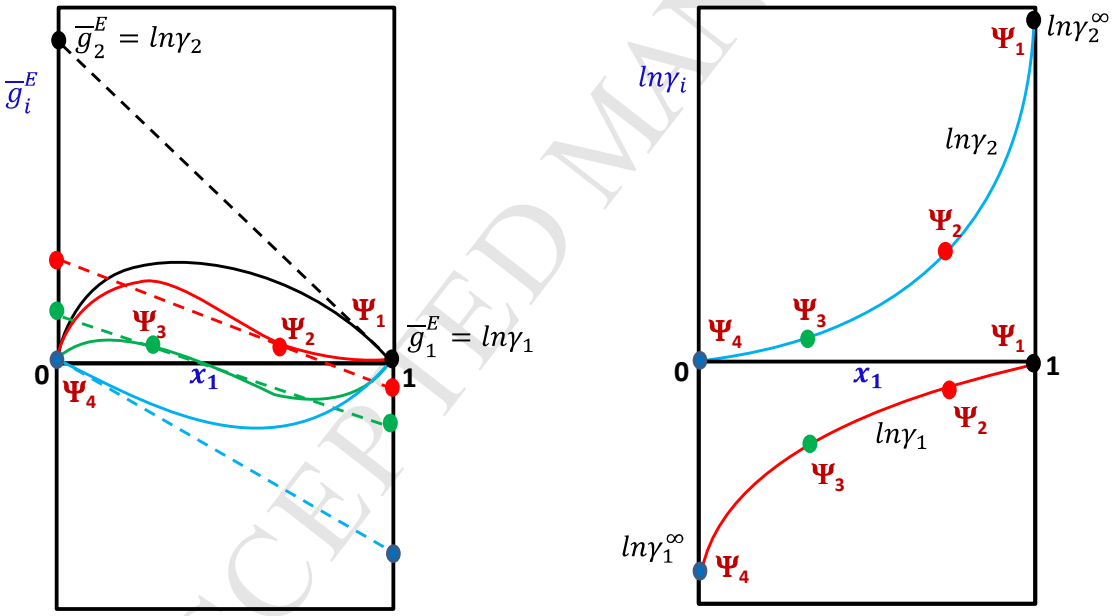


Fig. 11. Schematic representation of the activity coefficient curves (ln γ_i) for the components of a binary system: a) when $g^{M,L}$ function do not depend (or have a weak dependency) on Ψ, and b) when $g^{M,L}$ markedly depend on Ψ.

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Table 1

Correlation results of the experimental VLE data for example 4 using the NRTL model: a) with constant parameters (NRTL) [8], and b) with parameters dependent on pressure (NRTL f(P)). The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	1133.67	890.574	0.5296			
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.893	5.68	16.48	0.0511	0.1485	
(b) NRTL f(P)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	44.4118	0.873161	-6.87589	-0.158597	0.147648	0
21	-452.753	-2.59140	77.1902	-0.566901	-0.039320	0
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.0145	0.972	1.735	0.0044	0.0086	

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Table 2

Correlation results of the experimental VLE data for example 5 using the NRTL model: a) with constant parameters (NRTL) [10], and b) with parameters dependent on pressure (NRTL f(P)). The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	835.626	-461.593	0.2749			
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.649	6.65	14.7	0.0293	0.0620	
(b) NRTL f(P)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	41.6503	65.5484	-13.1781	-0.039177	-0.171954	0
21	1.21027	-31.3570	0.699303	-0.011635	0.681666	0
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.0638	4.22	18.8	0.0061	0.019	

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Table 3

Correlation results of the experimental VLE data for example 6 using the NRTL model: a) with constant parameters (NRTL) [11], and b) with parameters dependent on pressure (NRTL f(P)). The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	847.988	780.622	0.6421			
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.396	8.52	20.5	0.0112	0.0318	
(b) NRTL f(P)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	46.9449	243.191	-3.38461	0.046585	0.199393	0
21	-7.85728	52.2899	2.52101	-0.027135	-0.577396	0
	O.F(γ)	mean ΔP (mmHg)	max ΔP (mmHg)	mean Δy_1	max Δy_1	
	0.102	1.10	3.18	0.0053	0.0186	

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Table 4

Correlation results of the experimental VLE data for water (1) + n,n-dimethylacetamide (2) at 200 mmHg using the NRTL model: a) with constant parameters (NRTL) [12], and b) with parameters dependent on temperature (NRTL f(T)) and non-ideal vapor phase. The objective function calculated by Eq. (6) and the mean and maximum deviations in P and y_1 have been included.

(a) NRTL						
	A_{12} (cal/mol)	A_{21} (cal/mol)	α_{12}			
	3.0940	-53.8757	0.3024			
	O.F(γ)	mean ΔT (ºC)	max ΔT (ºC)	mean Δy_1	max Δy_1	
	0.898	0.770	1.986	0.0374	0.0941	
(b) NRTL f(T) and non-ideal vapor phase (Wilson)						
ij	a_{ij}	b_{ij} (mmHg)	c_{ij}	d_{ij} ($mmHg^{-1}$)	e_{ij}	f_{ij} ($mmHg^{-1}$)
12	-0.001587	697.900	-0.804139	0.008289	0.2	0
21	-0.080572	153.715	0.018984	-0.002705	0.2	0
	A_{ij} (Wilson)					
12	0.794					
21	1.779					
	O.F(γ)	mean ΔT (ºC)	max ΔT (ºC)	mean Δy_1	max Δy_1	
	0.020	0.317	1.202	0.0047	0.0299	

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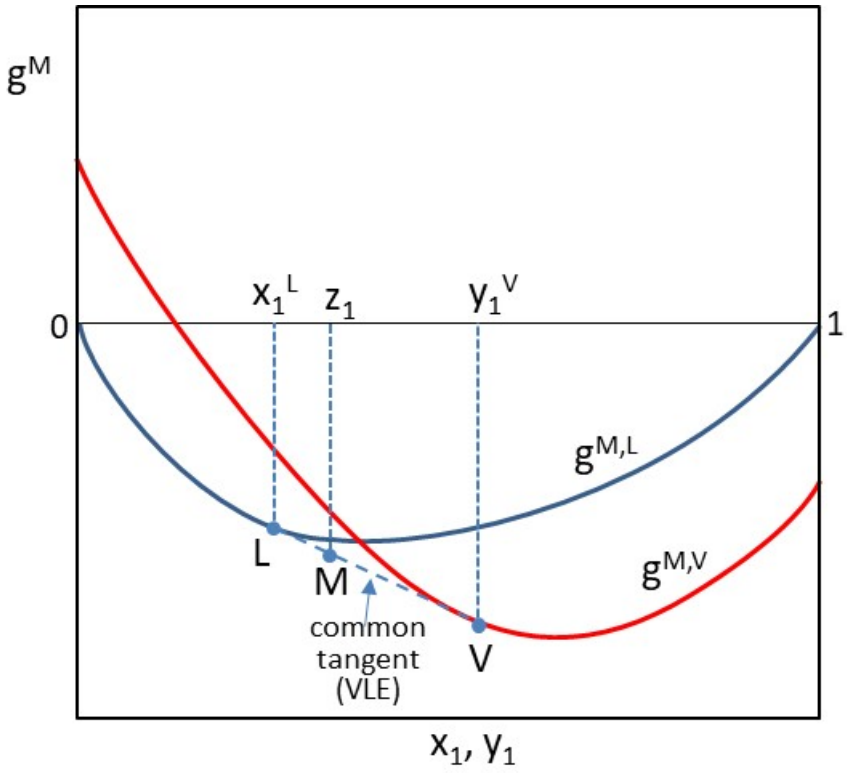

Fig. 1. Qualitative representation of the Gibbs minor common tangent equilibrium criterion applied to VLE of a binary system at some specific T and P.

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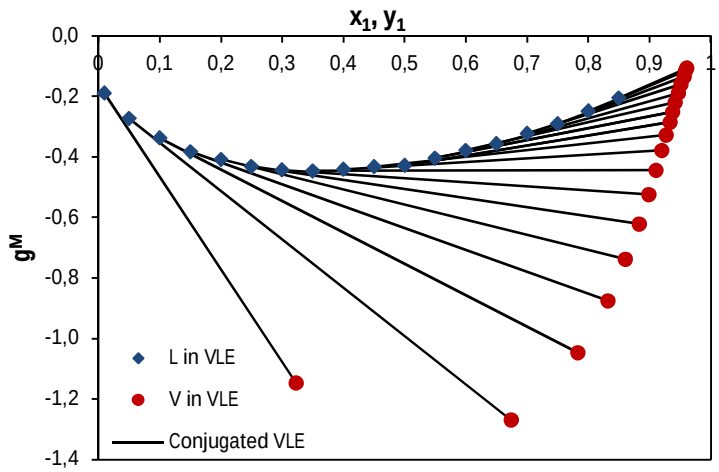
a)



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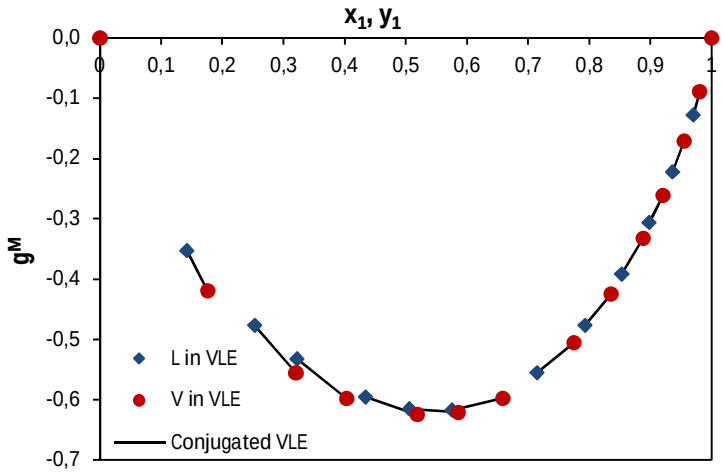

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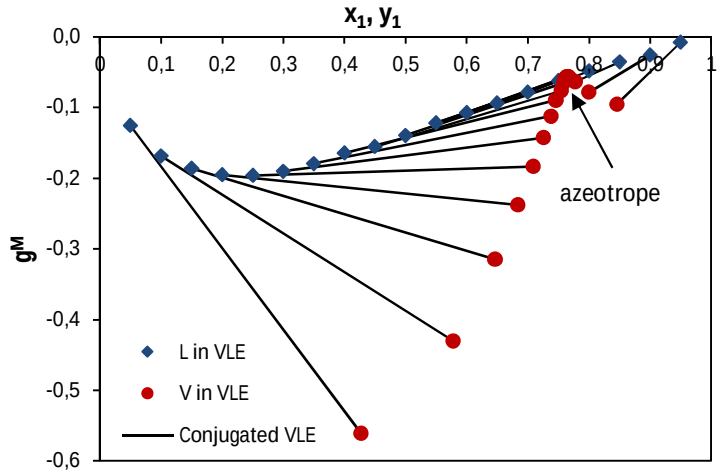

Fig. 2. Representation of the straight lines that connect the conjugated VLE phases and are tangent to the $g^{M,V}$ curves (ideal gas) for systems that do not require P-dependence in the $g^{M,L}$ function: a) example 1, b) example 2, and c) example 3.

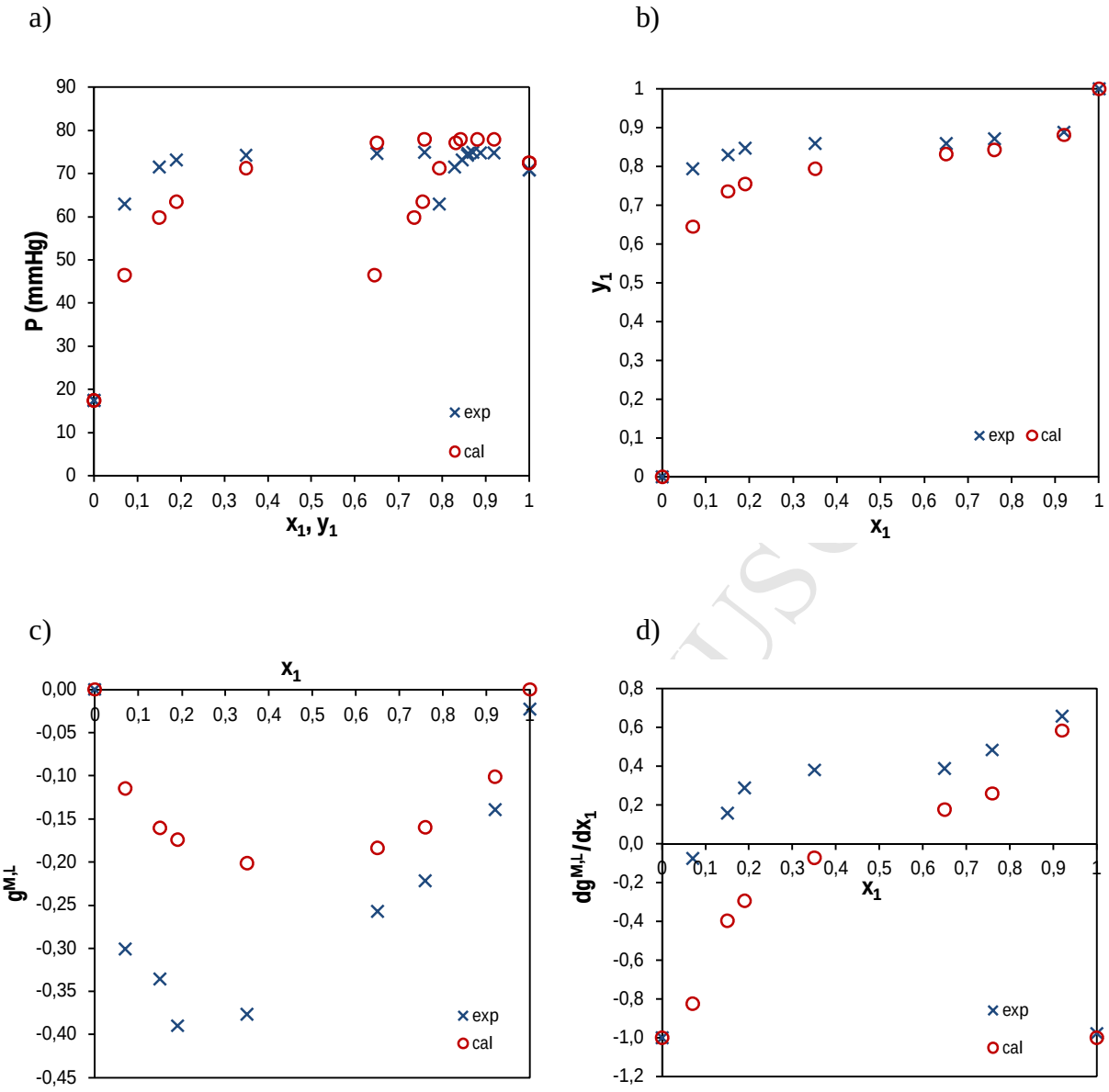

Fig. 3. Experimental data and correlation results using the NRTL model for example 4: (a) P vs. x,y, (b) y vs. x, (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1. Parameters are given in Table 1(a) [8].

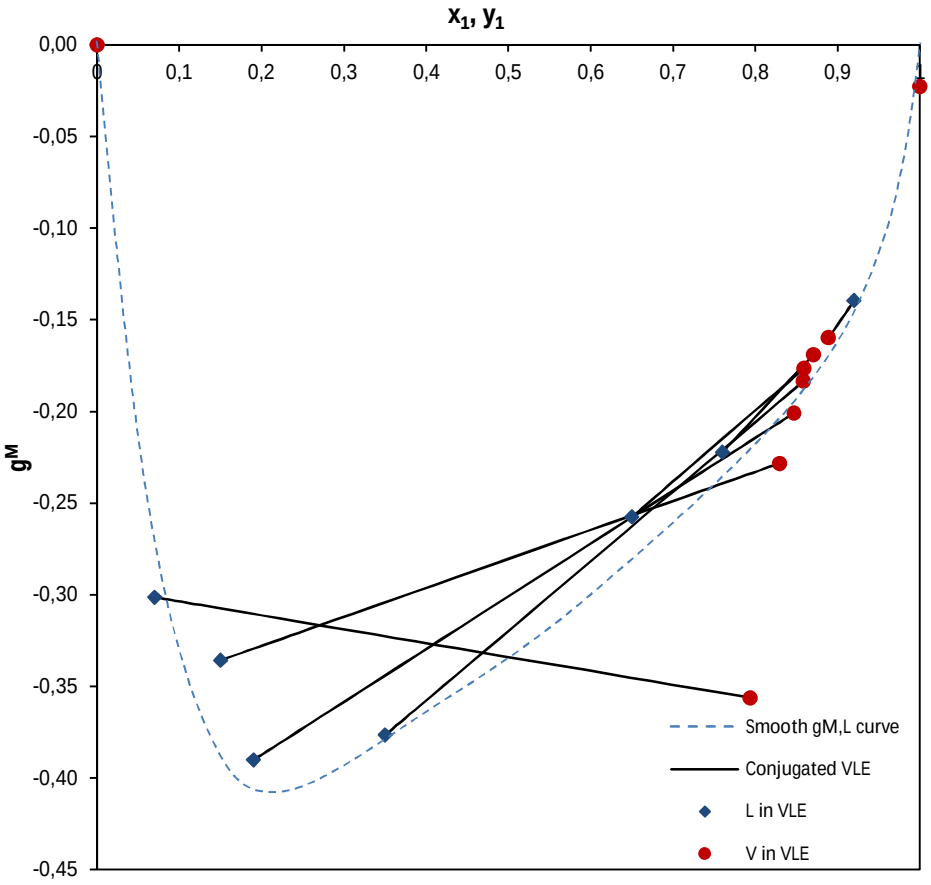

Fig. 4. Representation of the straight lines that connect the conjugated VLE phases for example 4 and are tangent to the $g^{M,V}$ curves (ideal vapor). A smooth curve for $g^{M,L}$ passing through all the L phases has been included.

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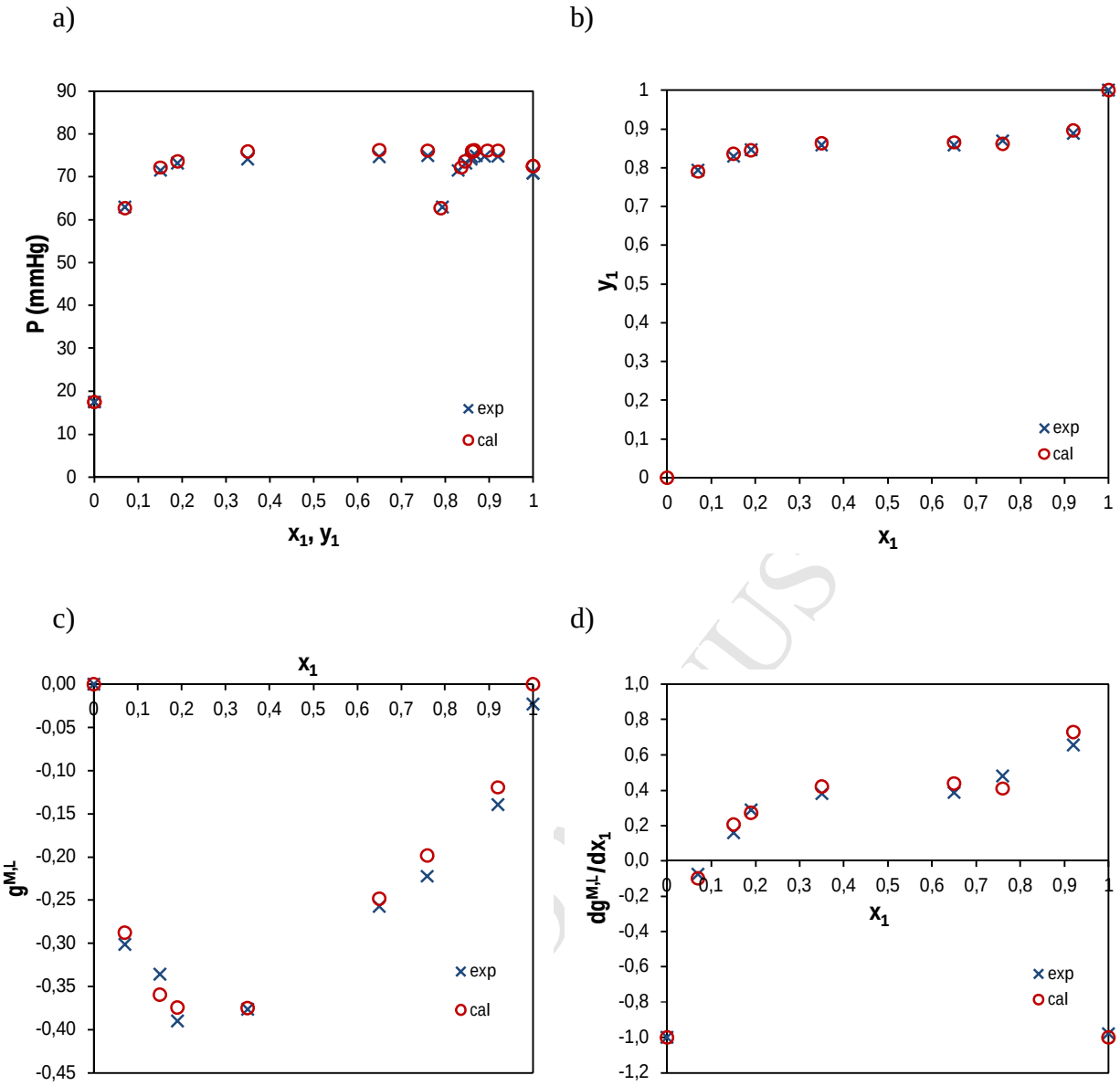
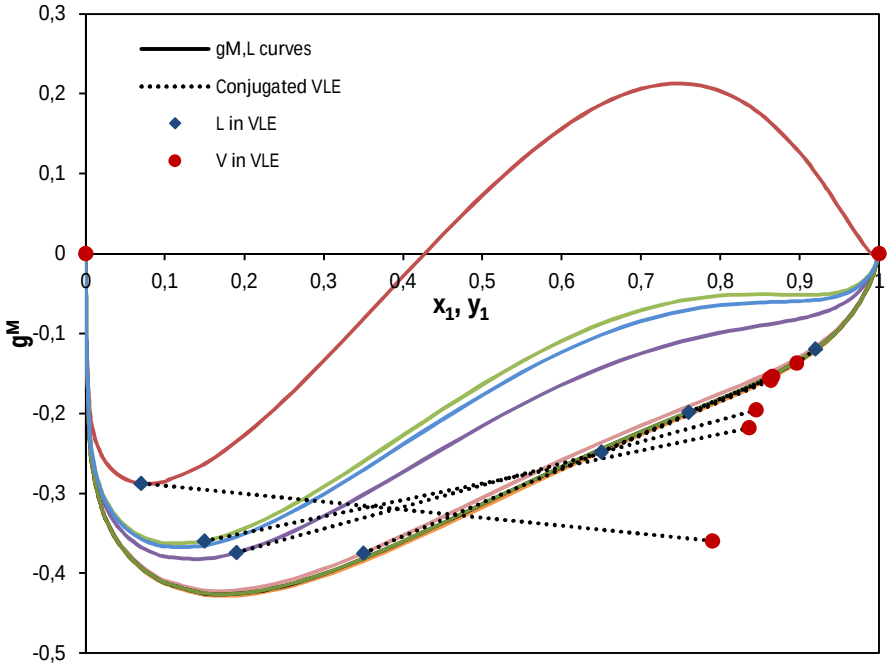


Fig. 5. Experimental data and correlation results using the NRTL f(P) model for example 4: (a) P vs. x,y, (b) y vs. x, (c) $g^{M,L}$ vs. x_1 and (d) slope values for the tangent line to the $g^{M,L}$ curve vs. x_1. Parameters are given in Table 1(b).

a)



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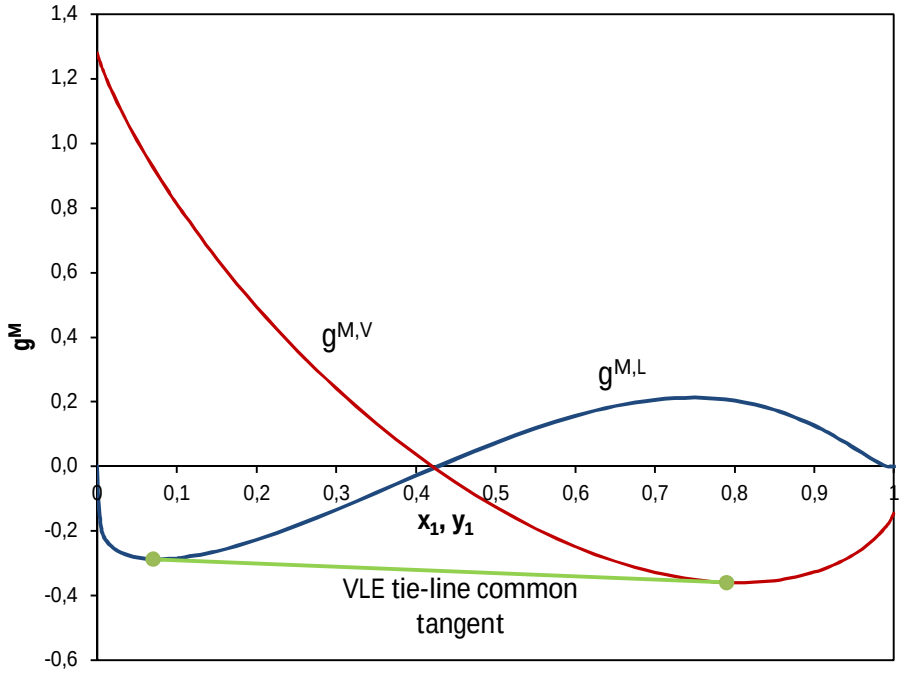


Fig. 6. Representation of the straight lines that connect the conjugated VLE phases for example 4 and calculated $g^{M,L}$ curves using the NRTL f(P) model, b) $g^{M,L}$ and $g^{M,V}$ curves showing the VLE Gibbs common tangent criterion at P=62.8 mmHg. Parameters are given in Table 1(b).

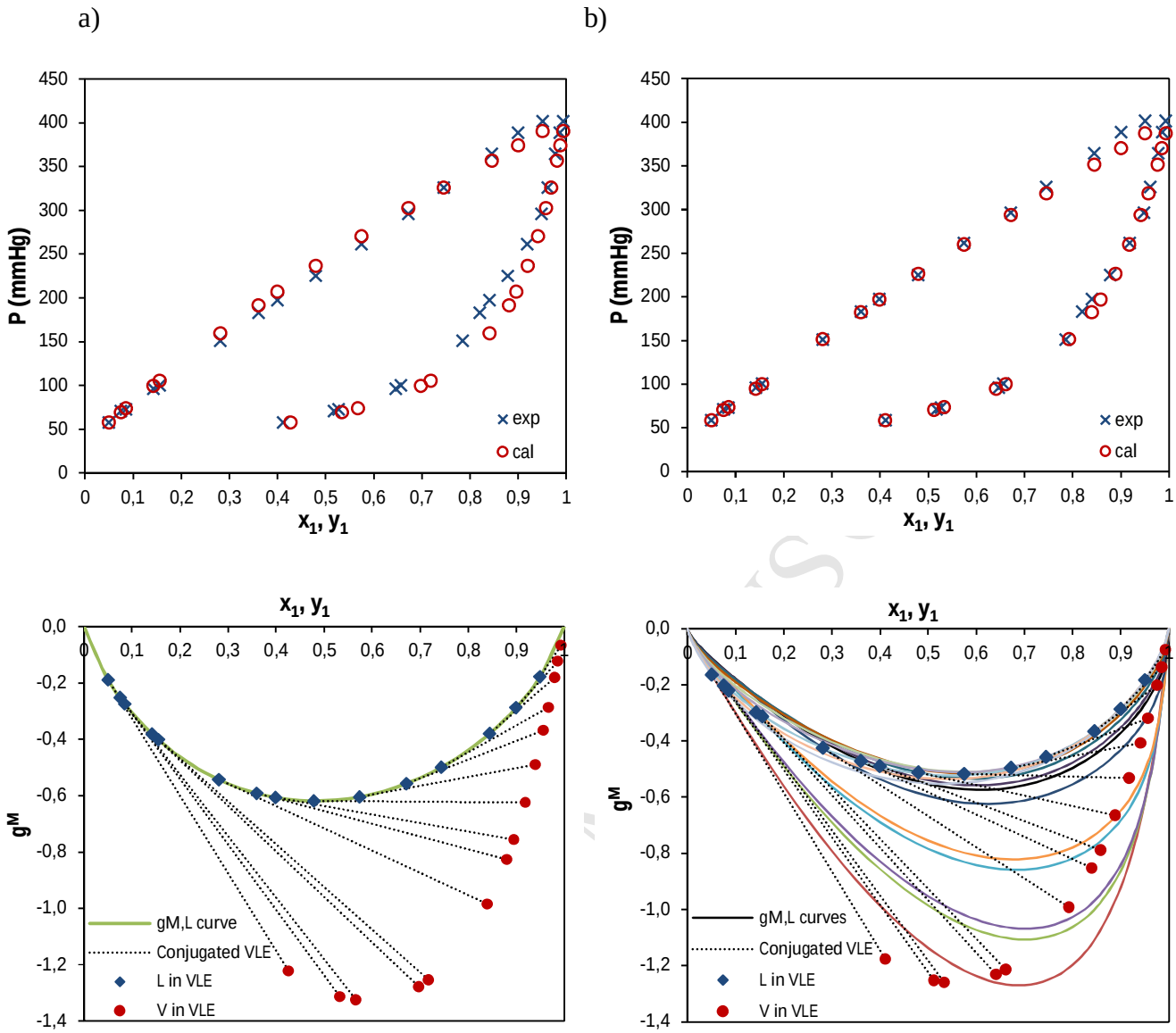


Fig. 7. Experimental and calculated VLE data for example 5, represented in P vs x,y and g^M vs x,y graphs to show the VLE tie-lines and the $g^{M,L}$ curves generated by the model: a) NRTL [10], and b) NRTL f(P)

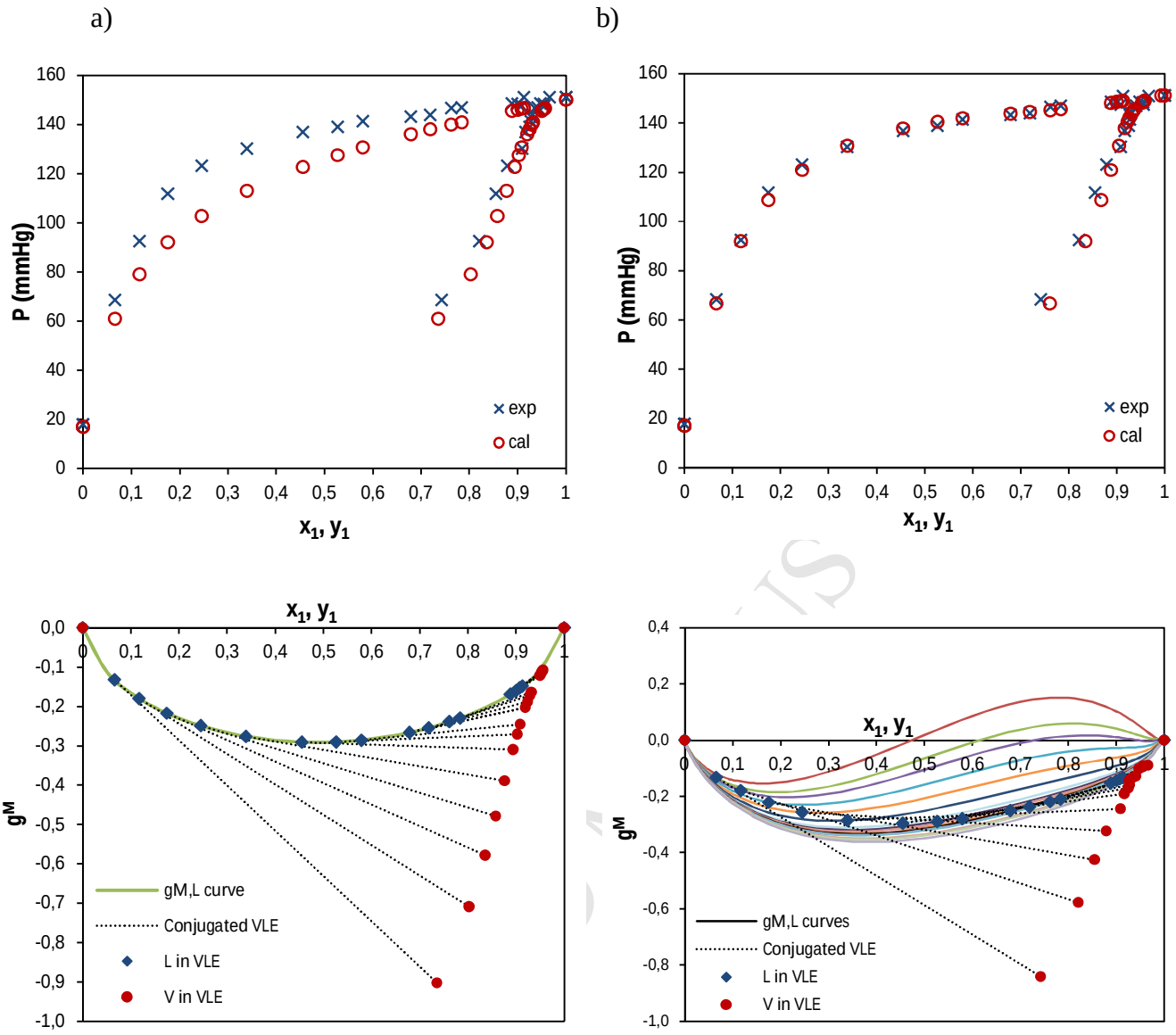


Fig. 8. Experimental and calculated VLE data for example 6, represented in P vs x,y andgM vs x,y graphs to show the VLE tie-lines and the gM,L curves generated by the model: a) NRTL [11], and b) NRTL f(P)

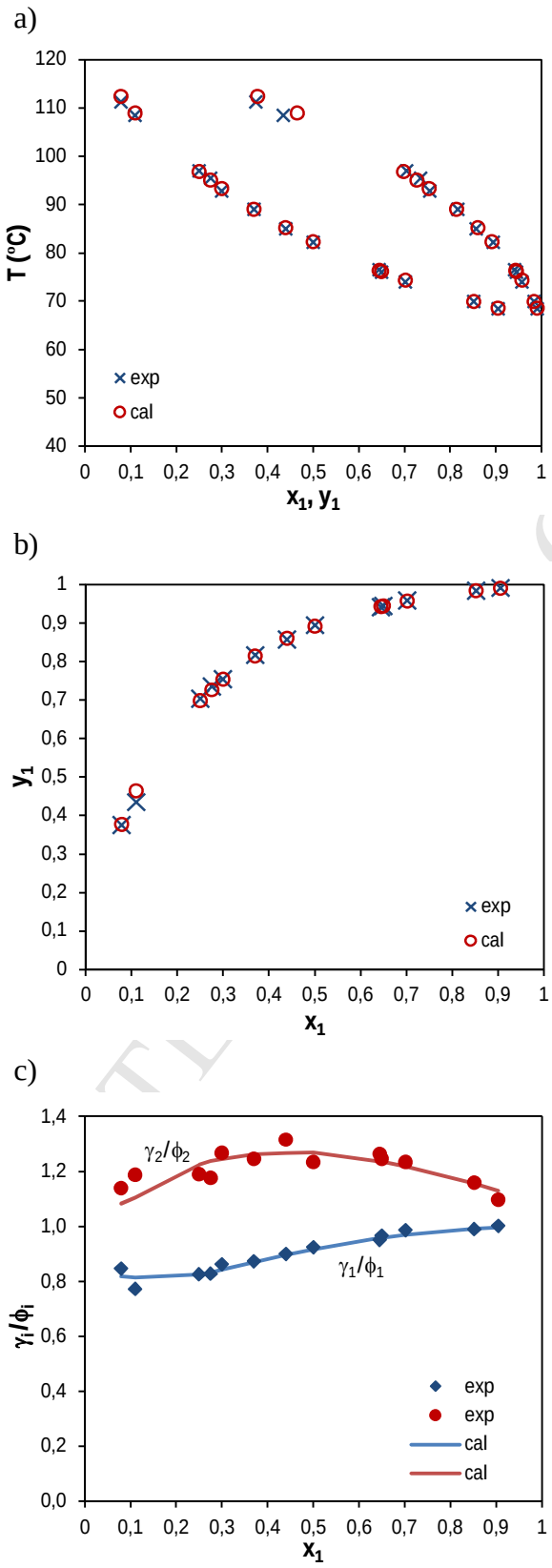
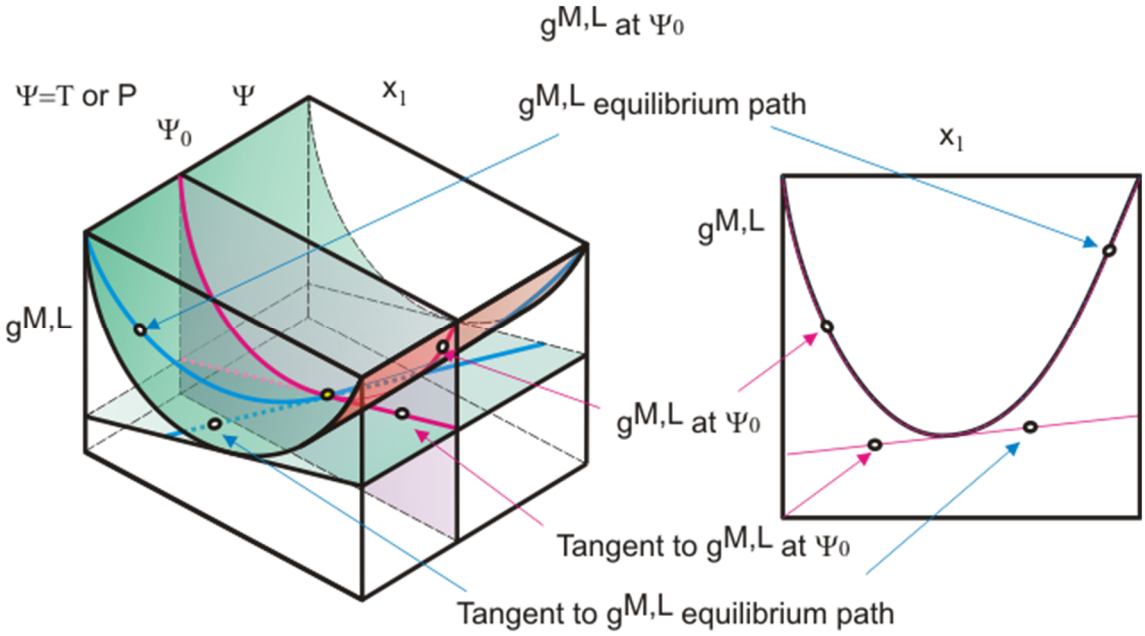


Fig. 9. Experimental data and correlation results using the NRTL f(T) model with non-ideal vapor phase (Wilson type equation) for the water (1) + n,n-dimethylacetamide (2) system at 200 mmHg: (a) T vs. x,y, (b) y vs. x, (c) γ/φ. Parameters are given in Table 4(b).

a)



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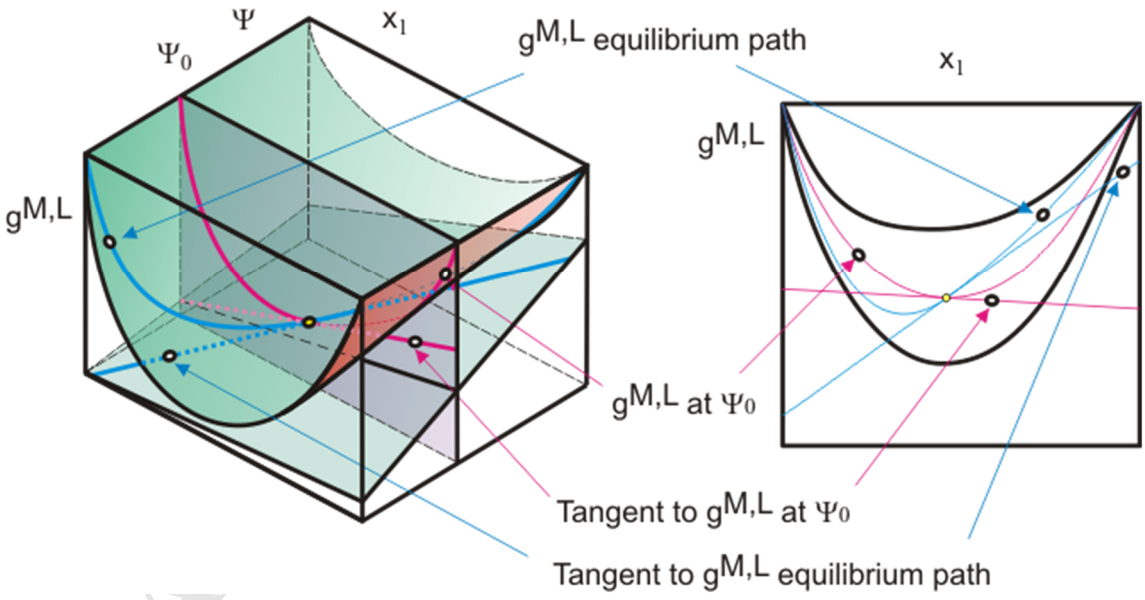
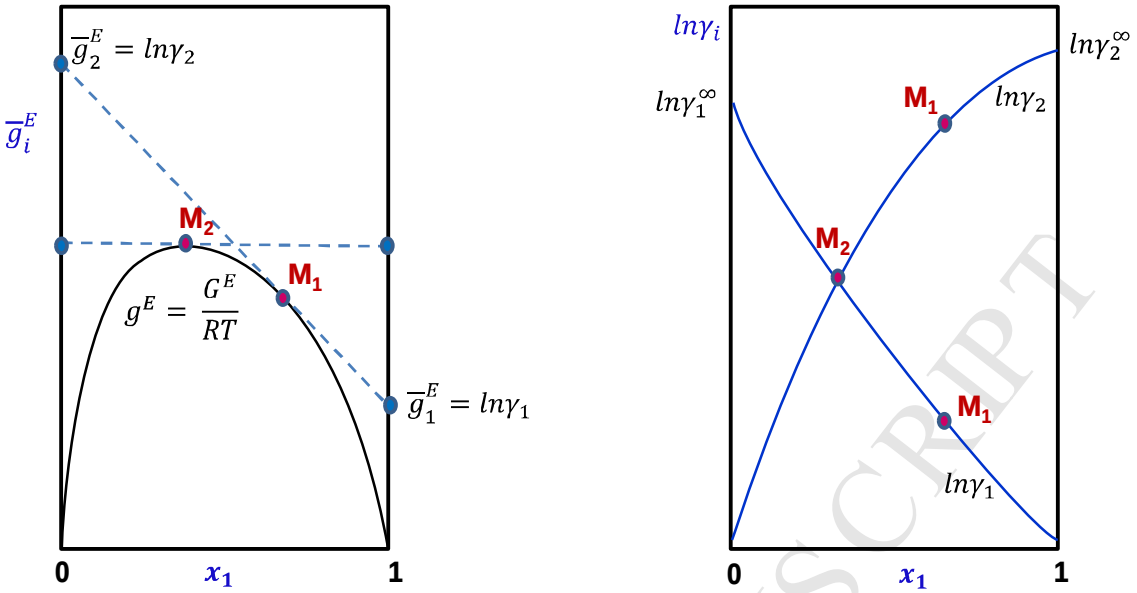


Fig. 10. Schematic representation of the Gibbs energy of mixing function for the liquid phase ($g^{M,L}$) for different behaviour of experimental VLE data sets: a) Group 1 with negligible dependence on ψ, and b) Group 2 with a substantial dependence on ψ (ψ = T (isobaric data) or P (isothermal data))

a)



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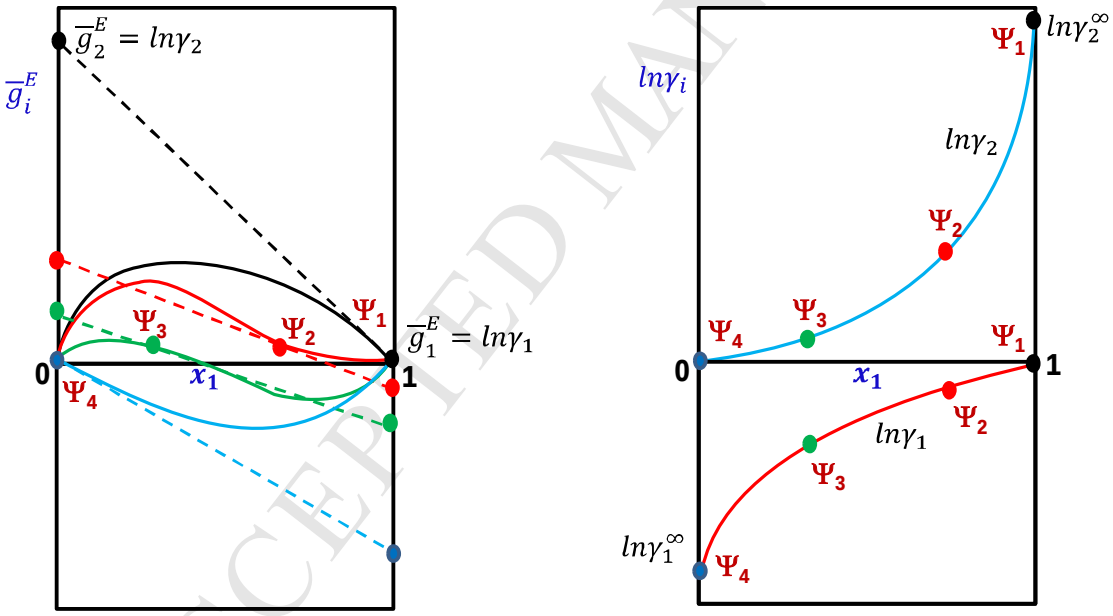

Fig. 11. Schematic representation of the activity coefficient curves (ln γ_i) for the components of a binary system: a) when $g^{M,L}$ function do not depend (or have a weak dependency) on Ψ, and b) when $g^{M,L}$ markedly depend on Ψ.

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