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Simultaneous VLLE data correlation for ternary systems: Modification of the NRTL equation for improved calculations.

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Abstract

Simultaneous correlation of vapour-liquid-liquid equilibrium (VLLE) data is hardly ever attempted in literature with one common set of parameters for all the equilibrium regions present in the systems. It is common practice to obtain different sets of parameters for VLE, LLE and VLLE regions when experimental equilibrium data for ternary systems are fitted with a given model (e.g. an activity coefficient model for the liquid phase). Besides, when dealing with the correlation of VLE for ternary systems, it is quite frequent to obtain different sets of parameters for each one of the three binary subsystems from those obtained when exclusively binary VLE data are correlated. In the present work, the simultaneous correlation of all the equilibrium regions in the ternary VLL system is attempted. The objective function and the restrictions of the system are clearly presented. In addition, a simple modification of the NRTL equation for the Gibbs energy of mixing (G^M) is proposed including a ternary term and a binary correction based on the Wohl equation. This modification has significantly improved the quality of the results obtained in the simultaneous correlation of different equilibrium regions.

Keywords: vapour-liquid-liquid equilibrium, VLLE, VLE, NRTL model, simultaneous correlation.

Introduction

In order to perform the optimal design and simulation of separation processes in the chemical industry, the robust and realistic calculation of phase equilibria (requiring previous correlation of experimental data) appears as a challenging problem. However, there is a widely accepted feeling respecting the models used to calculate phase equilibrium data that these models work fairly well for binary VLE, and their ability decreases for ternary VLE, ternary LLE, ternary VLLE and especially for systems strongly departing from the ideal behaviour. NRTL [1] and similar equations for the liquid phase excess Gibbs free energy has shown severe limitations to simultaneously represent VLE and VLLE data [2-5]. Additionally, the correlation provided by these types of equations for ternary systems, as shown in the Data collection of DECHEMA Data Series [6] may be acceptable when dealing only with the ternary data but yield poorer results when attempting the simultaneous correlation of the ternary and the binary data. Therefore, it seems to be probed that the simultaneous correlation of different phase equilibrium regions, or even different thermodynamic properties, requires more flexible models than the classical ones. For instance, J. Ortega et al. [7] proposed an empirical parametric model for the simultaneous correlation of different properties of a binary solution: VLE data and some excess properties such as h^E, V^E and $C_p{}^E$. This model has a polynomial form with the advantage that its degree of flexibility, and thus the number of parameters can be selected according to the necessity of each case.

There are different reasons for the poor correlation results obtained in many cases, ranging from the lack of flexibility of the classical activity coefficient models, the quality and consistency of the experimental data, as well as the calculation procedures and the objective functions used. In this respect, it is very important to ensure that reliable equilibrium calculations are run and the necessary conditions to be fulfilled are satisfied. Otherwise, useless parameters could be obtained leading to mistaken calculations. Obviously, all these aspects are of paramount importance and can produce highly adverse consequences when developing models to represent the data as well as when applying such models to unit operation design or industrial process simulations.

The performance of the classical activity coefficient models can be significantly improved by the use of simple additional correction terms, based on the analysis of the behaviour of the Gibbs energy of mixture (G^M) function. Previous works have shown that the analysis of the topology of $G^{M,L}/RT$ and $G^{M,V}/RT$ for the liquid and vapour phases, respectively, provides a valuable insight into the causes of the drawbacks of the classical thermodynamic models [8-11], and allows coherent modifications of the equations capable of overcoming many of them to be suggested. In these papers, the

NRTL model was selected as a representative model of the classical activity coefficient equations because, among the equations for the excess Gibbs energy, it is considered as that which offers the best balance between simplicity, reliability and applicability to numerous mixtures [12].

From an industrial point of view, there are an important number of water + alcohol + solvent (hydrocarbons) systems where the accurate description of vapour-liquid equilibrium (VLE) and vapour-liquid-liquid equilibrium (VLLE) plays a crucial role, taking into account that purification steps are among the most energy and cost consuming. For instance, in the fuel and biofuel industry or chemicals and polymers production, these kinds of water + alcohol + solvent mixtures with a VLLE behaviour have to be purified by using different techniques, such as azeotropic distillation, liquid–liquid extraction, extractive distillation, adsorption, pervaporation, etc. [13-16].

The goals of the present work are the following:

1) Describe the objective function to be used when attempting the simultaneous correlation of all the equilibrium regions VL and VLL, in a VLLE system, with the same set of parameters, and the restrictions of the calculation strategy.
2) Test a simple modification in the expression of NRTL of the excess Gibbs energy for the simultaneous correlation of ternary VLLE data (i.e. all the equilibrium regions VL and VLL with the same set of parameters values).
3) Show the influence of the experimental data quality.

The results obtained are discussed and compared with those obtained by the classical NRTL equation.

Proposed procedure and modification of the NRTL equation

Fig. 1 shows, in a 3D triangular prism (the temperature in the vertical axis versus composition in the base of the prism), the qualitative equilibrium surfaces for all the equilibrium regions present in VLLE azeotropic systems including a binary heterogeneous azeotrope, two binary homogeneous azeotropes, and a ternary heterogeneous azeotrope. These systems present complex phase equilibrium behaviour. The existence of a ternary heterogeneous azeotrope point produces a vapour equilibrium curve in equilibrium with two liquids that present a minimum at the temperature of the azeotropic point. Thus, at temperatures below the ternary heterogeneous azeotrope, the system presents regions of one liquid (L) and two liquids (LL) in equilibrium. At temperatures between the binary heterogeneous azeotrope (components 1-2) and the plait point, it is possible to observe the existence of the corresponding VLLE tie-triangles. The system presents up to 8 different equilibrium regions: one vapour (V), one liquid (L), as well as a two-LL, VL and VLL regions as shown in Fig. 1. Two sectional isothermal planes have been selected at temperatures between the binary and the ternary azeotropes. The sections intercepted are separated from the main figure in order to clarify the qualitative behaviour of the system in this complicated region. The slide has been further separated apart into the different individual equilibrium regions, clearly showing the existence of the following: L, L_1-L_2 (between the plait point and the ternary heterogeneous azeotrope point), L_1-L_2-V, L_1-V, L_2-V, homogeneous V, L_1-L_2-V and L_1-L_2 (between the homogeneous and heterogeneous azeotrope points).

Inspection of Fig. 1 allows the conclusion to be drawn that correlation of this type of system is a difficult task involving the use of an adequate model and objective functions, as well as experimental data exhibiting low dispersion and systematically covering all the equilibrium regions.

In the present work, a new simple modification of the NRTL equation is proposed including a ternary term and a binary correction based on the Wohl equation. This modification can significantly improve the quality of the simultaneous correlation obtained using the NRTL model, thus allowing a more accurate representation of the vapour (y) vs. liquid (x) compositions and the temperature (T) or pressure (P) vs. x and y compositions at constant P or T, respectively, in all the equilibrium regions (VL and VLL), as well as the liquid composition of the two liquid phases in equilibrium with the vapour phase (i.e.: on the vapour line) in the VLL region. The modified $G^{M,L}/RT$ function is the following:

$$\frac{G^{M,L}}{RT}=\frac{G^{M,Lideal}}{RT}+\frac{G^{E,L}}{RT}=\frac{G^{M,Lideal}}{RT}+\frac{G^{E,L,NRTL}}{RT}+\frac{G^{E,L,add}}{RT} \qquad (1)$$

where the ideal contribution of the Gibbs energy of mixing is

$$\frac{G^{M,Lideal}}{RT}=\sum_{i=1}^{3} x_i \cdot \ln x_i \qquad (2)$$

the classical term for the excess Gibbs energy according to the NRTL model is

$$\frac{G^{E,L,NRTL}}{RT} = x_1 \cdot x_2 \cdot \left(\frac{\tau_{21} G_{21}}{x_1 + G_{21} x_2 + G_{31} x_3} + \frac{\tau_{12} G_{12}}{G_{12} x_1 + x_2 + G_{32} x_3} \right) + x_1 \cdot x_3 \cdot \left(\frac{\tau_{31} G_{31}}{x_1 + G_{21} x_2 + G_{31} x_3} + \frac{\tau_{13} G_{13}}{G_{13} x_1 + G_{23} x_3 + x_3} \right) + \\ + x_2 \cdot x_3 \cdot \left(\frac{\tau_{32} G_{32}}{G_{12} x_1 + x_2 + G_{32} x_3} + \frac{\tau_{23} G_{23}}{G_{13} x_1 + G_{23} x_2 + x_3} \right) \tag{3}$$

and the additional term suggested in the present work is the following

$$\frac{G^{E,L,add}}{RT} = x_1 \cdot x_2 \cdot x_3 \cdot \frac{t_1 \cdot x_1 + t_2 \cdot x_2 + t_3 \cdot x_3}{1 + t_4 \cdot x_1 \cdot x_2 \cdot x_3} + x_1 \cdot x_2 \cdot \frac{a_1 \cdot x_1 + a_2 \cdot x_2}{1 + a_3 \cdot x_1 \cdot x_2} + x_1 \cdot x_3 \cdot \frac{b_1 \cdot x_1 + b_2 \cdot x_3}{1 + b_3 \cdot x_1 \cdot x_3} + \\ + x_2 \cdot x_3 \cdot \frac{c_1 \cdot x_2 + c_2 \cdot x_3}{1 + c_3 \cdot x_2 \cdot x_3} \tag{4}$$

where t_i, a_i, b_i and c_i are fitting parameters to be obtained by correlation of experimental equilibrium data.

The activity coefficients can be obtained using the well-known expression:

$$\ln \gamma_i = \frac{G^{E,L}}{RT} + \frac{\partial G^{E,L}/RT}{\partial x_i} - \sum_{j=1}^{3} x_j \frac{\partial G^{E,L}/RT}{\partial x_j} \tag{5}$$

The additional term proposed in Eq. (4) involves two parts: the first term represents ternary contribution to the excess Gibbs energy and the other three terms are binary modifications to the NRTL equation. The ternary term will be useful for a better description of complex ternary systems that require improved flexibility of the model in the ternary region. The binary modifications will only be necessary for ternary systems that include binary subsystems presenting difficulties of correlation using the original NRTL equation. Consequently, the use of all the terms would not always be necessary and only justified by the quality of the fitting required in each case.

At this point, it is important to comment on the relevance of the objective function used in the correlation procedure for this type of complex systems with multiple equilibrium regions. The objective function should involve the equality of the fugacity of each one of the three components in all phases in equilibrium, i.e. the liquid and vapour phases for the VLE region and the two liquids and vapour phases in the VLLE region. The LL equilibrium would involve the variation of the model parameters with temperature which is out of the scope of this work. Thus, the correlation procedure determines the NRTL binary parameters (Eq. (3)) and the parameters of Eq. (4) through minimization of the following objective functions, depending on the equilibrium region:

- Homogeneous VLE region (i.e.: L_1-V and L_2-V):

$$\mathrm{O.F.}_{\mathrm{VL}} = \sum_{j=1}^{\mathrm{NVL}}\sum_{i=1}^{3}\left(\frac{\gamma_{i,j}^{\mathrm{exp}}-\gamma_{i,j}^{\mathrm{cal}}}{\gamma_{i,j}^{\mathrm{exp}}}\right)^2 \quad \text{subjected to: } \sum_{j=1}^{\mathrm{NVL}}\sum_{i=1}^{3}\left(y_{i,j}^{\mathrm{cal}}-1\right)^2 < \varepsilon \tag{6}$$

- Heterogeneous VLLE region (i.e.: L_1-L_2-V):

$$\mathrm{O.F.}_{\mathrm{total},\mathrm{VL_1L_2}} = \mathrm{O.F.}_{\gamma,\mathrm{VL_1}} + \mathrm{O.F.}_{\gamma,\mathrm{VL_2}} + \mathrm{O.F.}_{\mathrm{y},\mathrm{VL_1L_2}} + \mathrm{O.F.}_{\mathrm{x},\mathrm{L_1L_2}} \tag{7}$$

$$\mathrm{O.F.}_{\gamma,\mathrm{VL_1}} = \sum_{j=1}^{\mathrm{NVLL}}\sum_{i=1}^{3}\left(\frac{\gamma_{i,j}^{\mathrm{L_1,exp}}-\gamma_{i,j}^{\mathrm{L_1,cal}}}{\gamma_{i,j}^{\mathrm{L_1,exp}}}\right)^2 \quad \text{subjected to: } \sum_{j=1}^{NVLL}\sum_{i=1}^{3}\left(y_{i,j}^{\mathrm{L_1,cal}}-1\right)^2 < \varepsilon \tag{8}$$

$$\mathrm{O.F.}_{\gamma,\mathrm{VL_2}} = \sum_{j=1}^{\mathrm{NVLL}}\sum_{i=1}^{3}\left(\frac{\gamma_{i,j}^{\mathrm{L_2,exp}}-\gamma_{i,j}^{\mathrm{L_2,cal}}}{\gamma_{i,j}^{\mathrm{L_2,exp}}}\right)^2 \quad \text{subjected to: } \sum_{j=1}^{NVLL}\sum_{i=1}^{3}\left(y_{i,j}^{\mathrm{L_2,cal}}-1\right)^2 < \varepsilon \tag{9}$$

$$\mathrm{O.F.}_{\mathrm{x},\mathrm{L_1L_2}} = \sum_{j=1}^{\mathrm{NVLL}}\sum_{k=1}^{2}\sum_{i=1}^{3}\left(\mathrm{x}_{i,j}^{\mathrm{L}_k,\mathrm{exp}}-\mathrm{x}_{i,j}^{\mathrm{L}_k,\mathrm{cal}}\right)^2 \quad \text{subjected to: } \begin{cases} \sum_{j=1}^{NVLL}\sum_{i=1}^{3}\left(a_{i,j}^{\mathrm{L_1,cal}}-a_{i,j}^{\mathrm{L_2,cal}}\right)^2 < \varepsilon \\ \sum_{j=1}^{NVLL}\sum_{i=1}^{3}\left(y_{i,j}^{\mathrm{L_1,cal}}-y_{i,j}^{\mathrm{L_2,cal}}\right)^2 < \varepsilon \\ T_j^{bubble,L_1} = T_j^{bubble,L_2} \quad \forall \ j \in NVLL \end{cases} \tag{10}$$

where x and y represent the compositions of the corresponding liquid and vapour phases in equilibrium, and the sub-indexes j and i refer to the experimental data of the corresponding equilibrium region and the component, respectively. $y_{i,j}^{\mathrm{L_1,cal}}$ and $\mathrm{y}_{i,j}^{\mathrm{L_2,cal}}$ represent the composition of the vapour phase in equilibrium with L_1 and L_2 in the LL regions that must obviously be equal to each other, since they belong to the vapour line where the phases L_1, L_2 and V are in equilibrium. That is also the reason for the condition in Eq. (10). ε is an extremely low tolerance value. The independent variables used in the calculation algorithm are:

- Homogeneous VLE region (L_1-V and L_2-V): bubble temperatures ($\mathrm{T}_j^{\mathrm{bubble,L}} \ \forall \ \mathrm{j} \in \mathrm{NVL}$).

- Heterogeneous VLLE region (L$_1$-L$_2$-V): T_j^{bubble,L_1}; $x_{1,j}^{L_1,cal}$; $x_{2,j}^{L_1,cal}$; $x_{1,j}^{L_2,cal}$ (with: $x_{3,j}^{L_2,cal} = x_{3,j}^{L_2,\exp}$; $x_{3,j}^{L_1,cal} = 1 - x_{1,j}^{L_1,cal} - x_{2,j}^{L_1,cal}$ and $x_{2,j}^{L_2,cal} = 1 - x_{1,j}^{L_2,cal} - x_{3,j}^{L_2,\exp}$) $\forall$ $j \in \mathrm{NVLL}$.

The use of the phase stability analysis through the application of the common tangent plane criterion is necessary to ensure the consistency of the parameters obtained in all the equilibrium regions. To do that, the expression for the Gibbs energy of mixing of the vapour phase is required along with the one for the liquid phase given in Eqs. (1-4). If the vapour phase is considered as ideal, this expression is the following:

$$\frac{G^{M,Videal}}{RT} = \sum_{i=1}^{3} y_i \ln y_i + \sum_{i=1}^{3} y_i \ln \frac{P}{P_i^0} \qquad (12)$$

where P_i^0 is the vapour pressure for the i-component calculated using the Antoine equation.

Results and Discussion

The proposed modification to the NRTL equation has been used to simultaneously correlate the ternary VLLE data for the water (1) + ethanol (2) + heptane (3) system at 760 mmHg [17]. Classical activity coefficient models such as NRTL are not able to give a good representation of all the equilibrium regions for this system, using a unique set of binary interaction parameters, due to the difficulty to simultaneously represent VLE and VLLE data. Table 1 shows the binary interaction parameters A_{ij} (J/mol) obtained when these experimental data are correlated using both NRTL and the proposed modification of the NRTL equation (NRTLm). These parameters are related with the dimensionless NRTL parameters τ_{ij} by the following expression $\tau_{ij} = A_{ij}/(R \cdot T)$. Constants for the Antoine equation have also been included in Table 1.

Representations of experimental and calculated equilibrium data according to the original and the modified NRTL equations are presented in Fig. 2, showing that the proposed additional terms included in the model make possible the simultaneous correlation of all the equilibrium regions using a single set of parameters. This is especially relevant because it could allow, for instance, the design calculations required for separation processes in which this system were be involved.

Additionally, the use of 3D plots, such as those represented in Fig. 2, allows a deeper analysis of the experimental data quality showing possible data dispersion or abnormalities. Traditionally, the combination of two 2D different projections had to be used to check experimental or calculated equilibrium data for ternary systems at different T or P conditions or for quaternary systems at constant T y P (as for example the Cruickshank type projections [18] for ternary LLE). Nowadays, it is increasingly frequent to use 3D plots which can be rotated for the inspection of both the quality of the experimental data and the reliability of those calculated by correlation. For example, in Fig. 2a, it is possible to observe the existence of 3 singular points (marked with the white line) presenting distinct and unlikely behaviour with respect to the remaining experimental points, so being suspect of error. Consequently, we have repeated the correlation of the system using the NRTL and the modified NRTL models, but now removing these three problematic points and results are shown in Table 2 and represented in Fig. 3. Once these points are removed from the original data set, the quality of the correlation significantly improves especially using the modified NRTL equations. However, the real importance of this result is how three deviated points within an extensive equilibrium data set can distort so much the quality of the data correlation because of the great influence on other remote equilibrium regions of the system. This is not the case dealing with correlation of equilibrium data for more simple systems. Checking of the dispersion for experimental equilibrium data (VLE and VLLE) in systems that require 3D plots is not very common and typical 2D are not useful for these systems. The detection of dispersion or outliers is not obvious dealing with ternary systems because an experimental point cloud is obtained with serious difficulties to identify trends, mainly because in most of cases authors do not try to obtain a homogeneous distribution of the points in their experimental determinations. To compare the quality of the different correlations carried out, in Table 3 the values for the total objective function (sum of Eqs. (6) and (7)) and the deviations (average and minimum) obtained using both the NRTL and modified NRTL models are presented.

Figs. 4a and b represent a set of experimental and calculated tie-triangles for the VLLE region before and after removing the three problematic points, respectively, for the correlations using both the NRTL and the modified NRTL equations. In these figures it is observed that the NRTL model has important restrictions to represent the tie-triangles located between the heterogeneous ternary azeotrope and the ternary plait point and also the experimental vapour phase compositions of many tie-triangles. It seems that the NRTL model is not flexible enough to reproduce the tie triangle inversion that exists in this region of the experimental data. With the addition of the terms proposed to the NRTL equation, it has been possible to substantially improve the representation of the experimental VLLE region. Moreover, once the three problematic data are eliminated, the proposed modification yields a quite good representation of the experimental VLLE tie-triangles including the existing inversion previously mentioned. Specifically, the reduction in the objective function value that it is achieved by the modification proposed is of 61% for the original data set, and 93% for the reduced set of experimental data. In the last case, the objective function value could be very close to the limit imposed by the dispersion of experimental data itself.

Fig. 5 represents the experimental and calculated compositions (molar fractions) corresponding to all the vapor-liquid equilibrium data in the VLE and VLLE regions to compare the correlation results obtained with the NRTL and the modification proposed for both the original experimental data set (Fig. 5a) and the reduced experimental data set (Fig. 5b).

In order to confirm the consistency of the correlation results obtained using the proposed modification of the NRTL model according to the Gibbs minor common tangent equilibrium criteria, Fig. 6a shows the calculated liquid and vapour Gibbs energy of mixing surfaces ($G^{M,L}/RT$ and $G^{M,V}/RT$, respectively) at one constant equilibrium temperature corresponding to one specific experimental data selected in the VLLE region (T=68.93ºC). In this figure, it is possible to observe the calculated tie-triangle that connects the compositions of the three phases (VLLE) in equilibrium and how this tie-triangle corresponds to the minor tangent plane to the vapour and liquid G^M/RT surfaces. To clarify this view, Fig. 6b represents the G^M/RT surface cuts along each one of the three tie-lines forming the calculated tie-triangle (L_1-V, L_2-V and L_1-L_2 tie lines) where tangent points are more easily visualized.

In the same way, Fig. 7 presents the situation corresponding to one specific selected VLE experimental data (T=76.36ºC). In this case, the calculated tie-line represents a tangent line to both $G^{M,L}/RT$ and $G^{M,V}/RT$ surfaces. Fig. 7b shows more clearly a cut along the calculated tie-line, where it is possible to confirm that the Gibbs minor common tangent equilibrium criteria is correctly satisfied. This checking procedure has been carried out for all the calculated equilibrium data to ensure consistency of the obtained results. In addition, we have checked that the distribution of the residues, obtained as difference among the experimental and calculated VLE and VLLE data, is at random for all the correlation results presented.

Conclusions

NRTL only provides a semi-quantitative representation of the equilibrium behaviour of complex systems such as those ternary systems including one heterogeneous ternary azeotrope, when all the equilibrium regions are correlated using a unique set of parameters. Significant improvements are obtained when using the proposed additional terms that include a ternary term and other three possible contributions to increase the flexibility of the NRTL equation for the binary subsystems when necessary. The calculation algorithm should include adequate objective functions to be optimized subjected to the required restrictions. This simple modification provides the required flexibility to the model to overcome many of the classical models limitations, expanding the number and type of systems that could be correlated and, what is more important, markedly improving the correlation results obtained. This improvement might be of great interest in the optimal synthesis and design of separation processes where VLE and VLLE are present and need to be correctly reproduced with the same set of parameters. For convenience, the model is constructed “stepwise” as a sum of different contributions to the G^M function and consequently the correlations can be performed with the additional corrections that are really necessary for the required description of each system. However, for most of the ternary systems with combined VLE and VLLE regions and presence of azeotropes, as those discussed in the present paper, the simultaneous correlation of equilibrium data in all of them probably will require all the contributions proposed.

Additionally, the use of 3D plots permits the dispersion of the data to be clearly observed allowing their validation prior to the application of the correlation algorithm to obtain the parameters of the model. The use of the phase stability analysis through the application of common tangent plane criterion is necessary to assure the consistency of the parameters obtained.

Nomenclature

A_{ij}	binary interaction parameters (J/mol) for components i, j in the NRTL model
A, B, C	Parameters in the Antoine equation
C_p^E	Excess thermal capacity
G^M	Gibbs energy of mixing
h^E	Excess enthalpy
LLE	Liquid-liquid equilibrium
O.F.	Objective function
P	Total pressure
P_i^0	Vapor pressure
R	Gas constant
T	Temperature (K)
VLE	Vapor-liquid equilibriu
VLLE	Vapor-liquid-liquid equilibrium
V^E	Excess volume
x_i	Liquid molar fracion of component i

Greek symbols

α	Non-randomness NRTL factor
γ_i	Activity coefficient for component i
ε	An extremely low value
τ_{ij}	Dimensionless interaction parameter in the NRTL model

Subscripts

cal	Calculated
exp	Experimental
i, j	Components i, j

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Table 1. NRTL and modified NRTL parameters obtained for the correlation of experimental VLE and VLLE data for the water (1) + ethanol (2) + heptane (3) system at 760 mmHg ($\alpha_{i,j}$=0.3) [17]. Constants for the Antoine equation have also been included.

NRTL parameters (J/mol)							
A_{12}	2297.39	A_{13}	15327.2	A_{23}	4899.85		
A_{21}	2038.71	A_{31}	25881.7	A_{32}	3823.27		
Modified NRTL parameters (J/mol)							
A_{12}	405.853	A_{13}	9429.60	A_{23}	3585.60		
A_{21}	-6.71911	A_{31}	15525.6	A_{32}	2330.19		
Ternary interaction parameters							
t_1	0.149151	a_1	0.163049	b_1	8.154140	c_1	0.890543
t_2	0.160425	a_2	-0.424628	b_2	-0.009135	c_2	1.677112
t_3	0.164457	a_3	8.193411	b_3	0.533294	c_3	4.998920
t_4	952.9590						

	Antoine equation constants ($\log P_i^0(mmHg) = A - \frac{B}{T+C}$)		
component	A	B (ºC)	C (ºC)
1	8.07131	1730.630	233.426
2	8.11220	1592.864	226.184
3	6.89386	1264.370	216.640

Table 2. NRTL and modified NRTL parameters obtained for the correlation of reduced experimental VLE and VLLE data for the water (1) + ethanol (2) + heptane (3) system at 760 mmHg ($\alpha_{i,j}$=0.3) [17].

NRTL parameters (J/mol)							
A_{12}	1778.54	A_{13}	15896.1	A_{23}	4841.45		
A_{21}	2224.12	A_{31}	21125.7	A_{32}	3548.70		
Modified NRTL parameters (J/mol)							
A_{12}	2341.73	A_{13}	18034.4	A_{23}	9499.59		
A_{21}	2133.85	A_{31}	27650.5	A_{32}	969.733		
Ternary interaction parameters							
t_1	-0.269627	a_1	-17.37639	b_1	0.813514	c_1	-1.50508
t_2	-0.106238	a_2	-6.846643	b_2	-1.334899	c_2	1.606636
t_3	5.552816	a_3	-1.196525	b_3	48.43410	c_3	2.351793
t_4	24.10812						

Table 3. Total objective functions and deviations obtained with the NRTL and modified NRTL (mNRTL) models in the correlation of experimental VLE and VLLE data for the water (1) + ethanol (2) + heptane (3) system at 760 mmHg [17].

All experimental data					
			NRTL model (O.F.= 3.9344)		
	y_1	y_2	T (ºC)	x_1	x_2
Average deviation	0.0207	0.0383	0.9723	0.0314	0.0407
Max deviation	0.0556	0.1095	3.4021	0.1058	0.1152
			NRTLm model (O.F.= 1.5188)		
	y_1	y_2	T (ºC)	x_1	x_2
Average deviation	0.0144	0.0176	0.2492	0.0293	0.0250
Max deviation	0.0303	0.0510	1.2344	0.0991	0.0951
Reduced set of experimental data					
			NRTL model (O.F.= 3.7356)		
	y_1	y_2	T (ºC)	x_1	x_2
Average deviation	0.0205	0.0427	1.1674	0.0456	0.0428
Max deviation	0.0686	0.1227	3.9656	0.2079	0.1211
			NRTLm model (O.F.= 0.2612)		
	y1	y2	T (ºC)	x1	x2
Average deviation	0.0047	0.0069	0.1745	0.0104	0.0104
Max deviation	0.0307	0.0351	1.1475	0.0389	0.0399

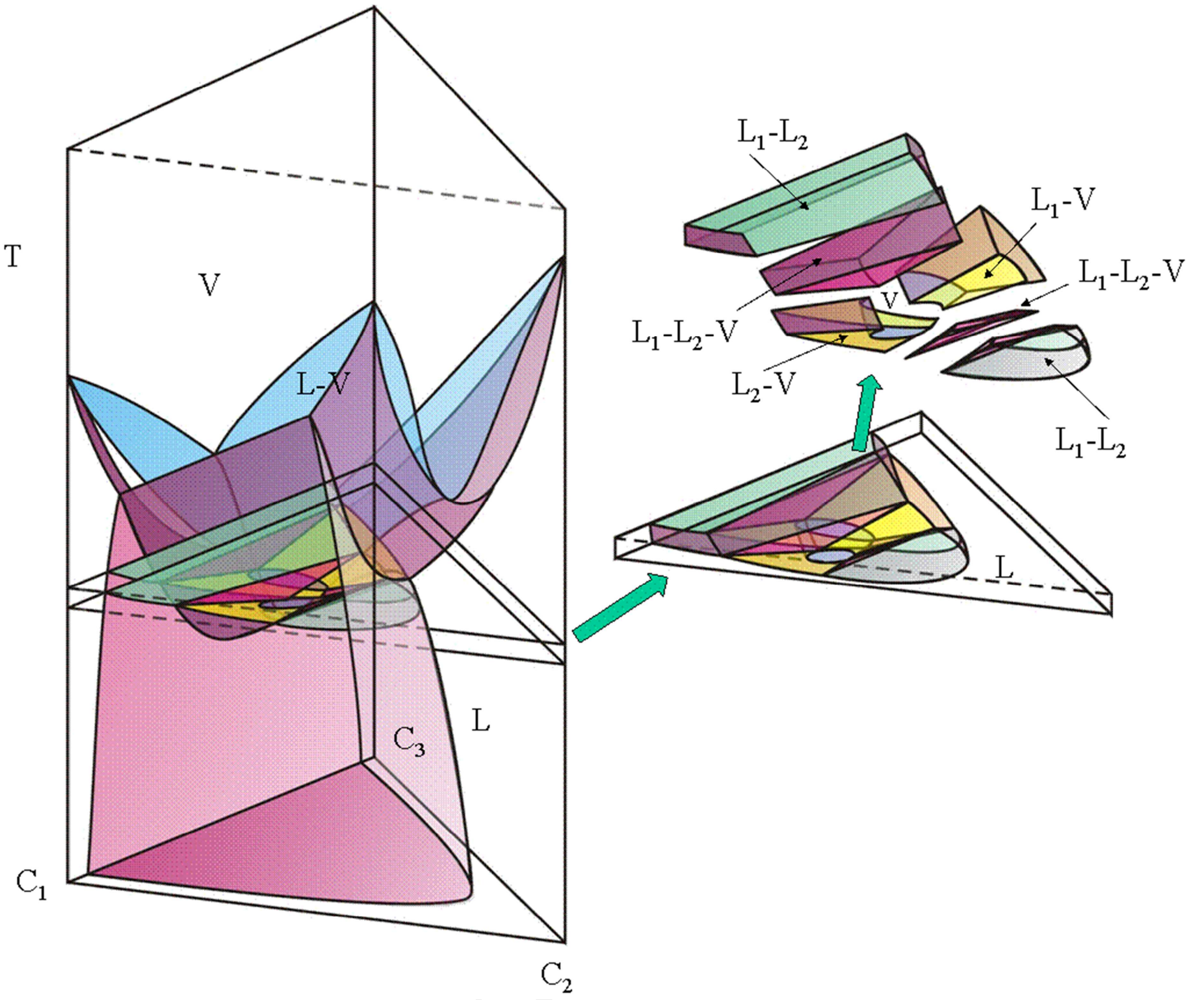

Figure 1. Qualitative representation of temperature versus composition for a ternary system of components $C_1 + C_2 + C_3$ involving two binary minimum boiling point homogeneous azeotropes (B_{13} and B_{23}) and one binary heterogeneous azeotrope (B_{12}).

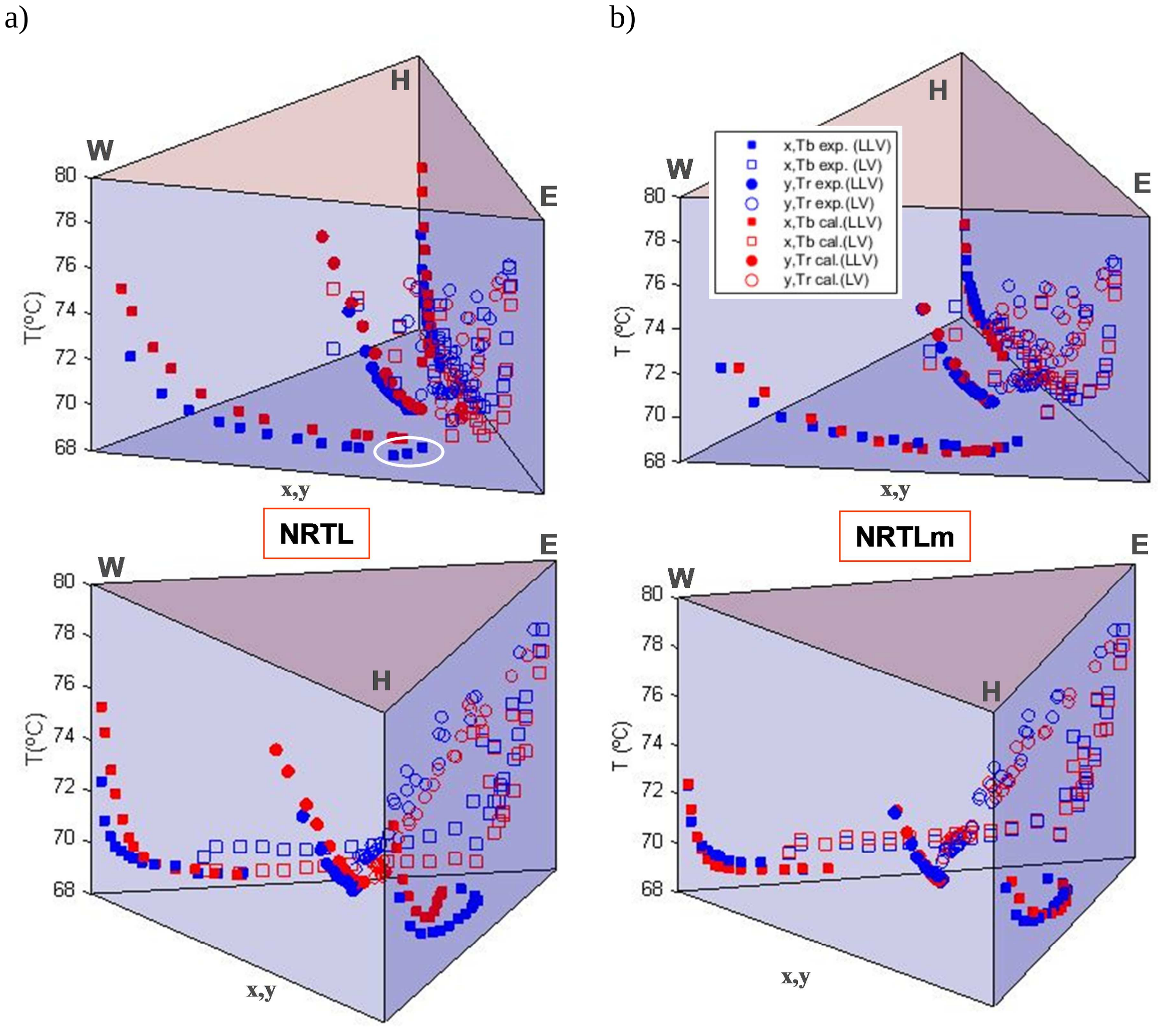

Figure 2. Different 3 D projections of experimental and calculated VLE data for the water (1) + ethanol (2) + heptane (3) ternary system at 760 mmHg [17] obtained by correlation using: a) NRTL, and b) modified NRTL models.

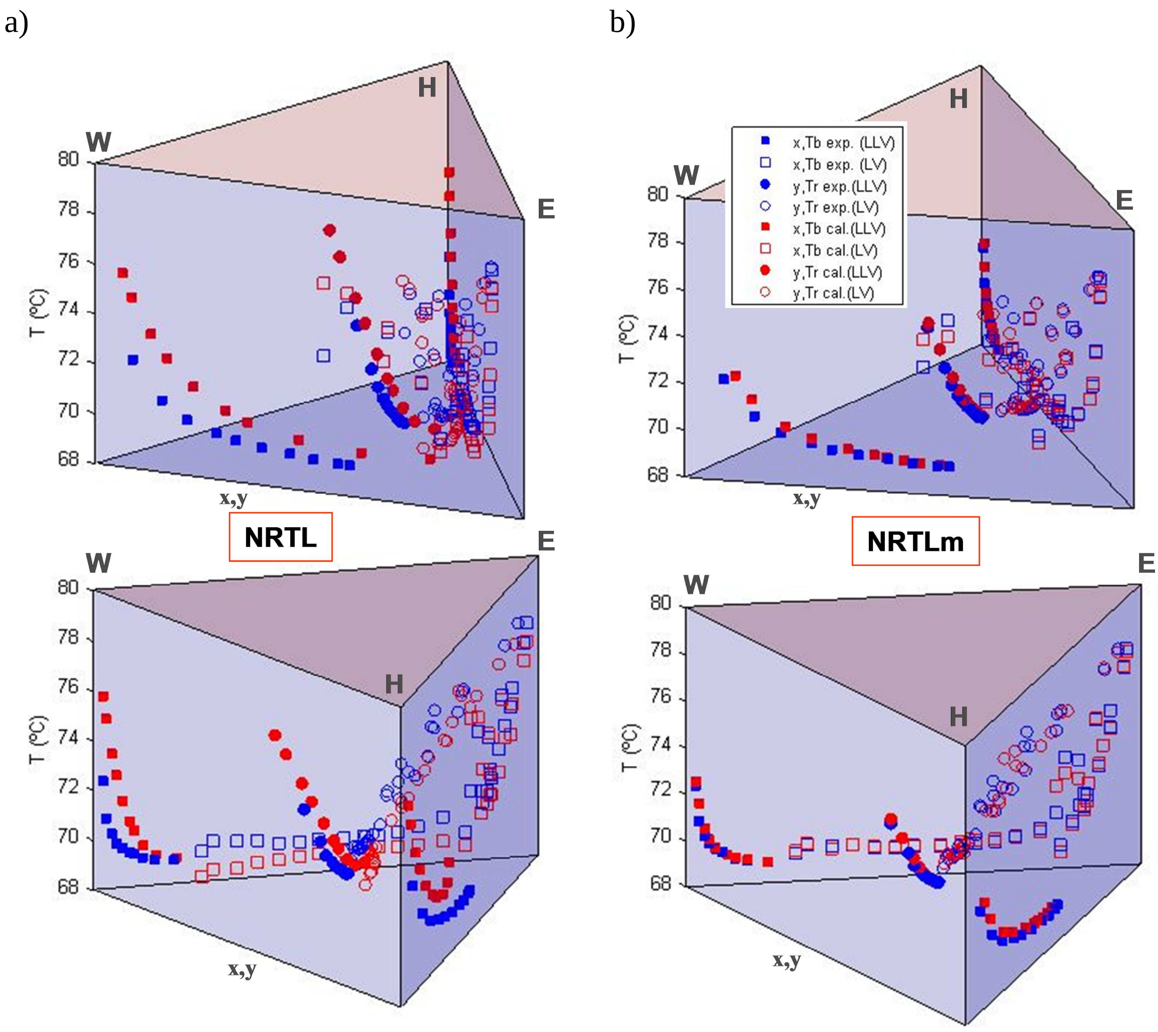

Figure 3. Different 3 D projections of experimental and calculated VLE data for the water (1) + ethanol (2) + heptane (3) ternary system at 760 mmHg [17] obtained by correlation using: a) NRTL, and b) modified NRTL models. Three experimental points presenting unlikely behaviour have been removed in the present correlation.

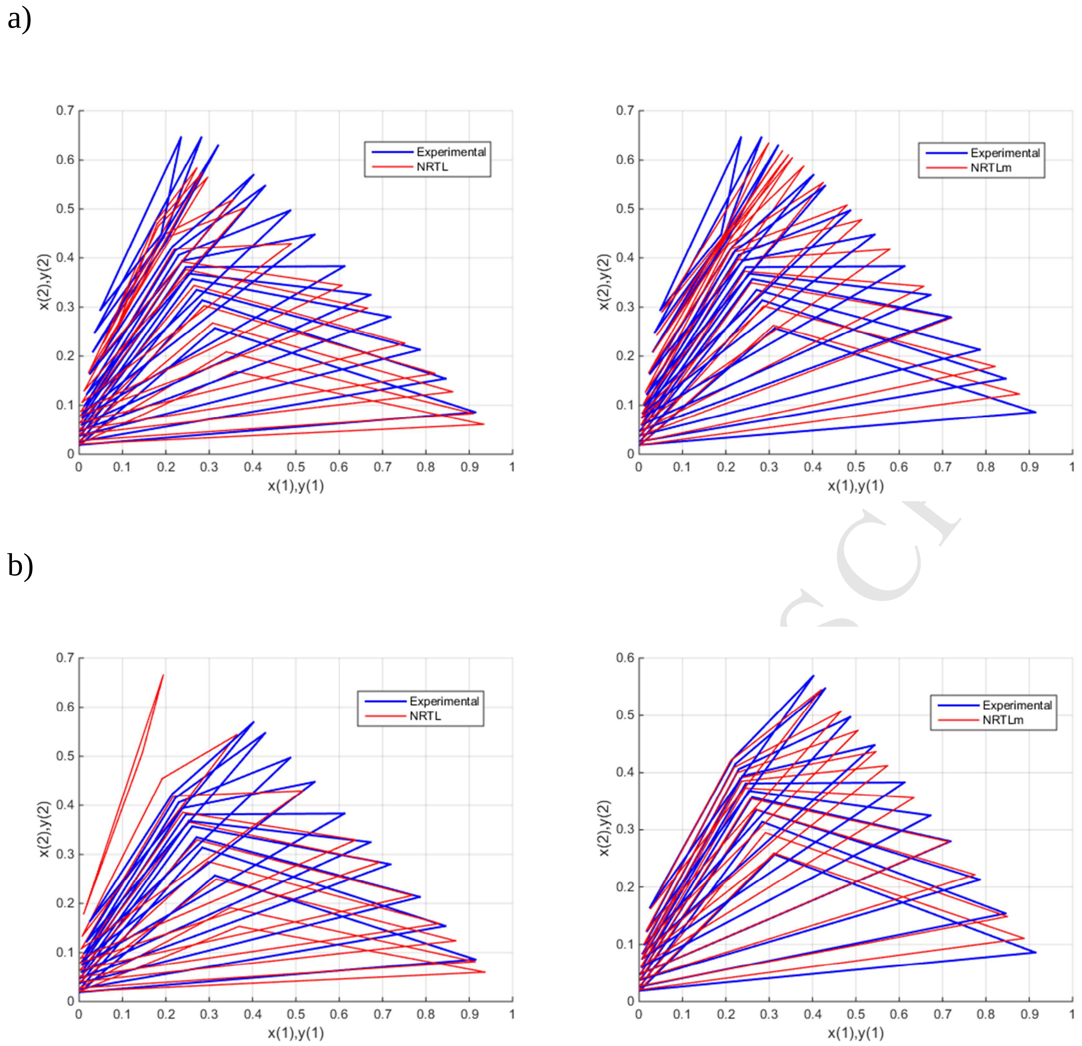

Figure 4. Experimental and calculated tie-triangles (molar fractions) for the VLLE region of the water (1) + ethanol (2) + heptane (3) ternary system at 760 mmHg [17] obtained by correlation using NRTL and modified NRTL (NRTLm) models: a) original experimental data set, and b) reduced experimental data set.

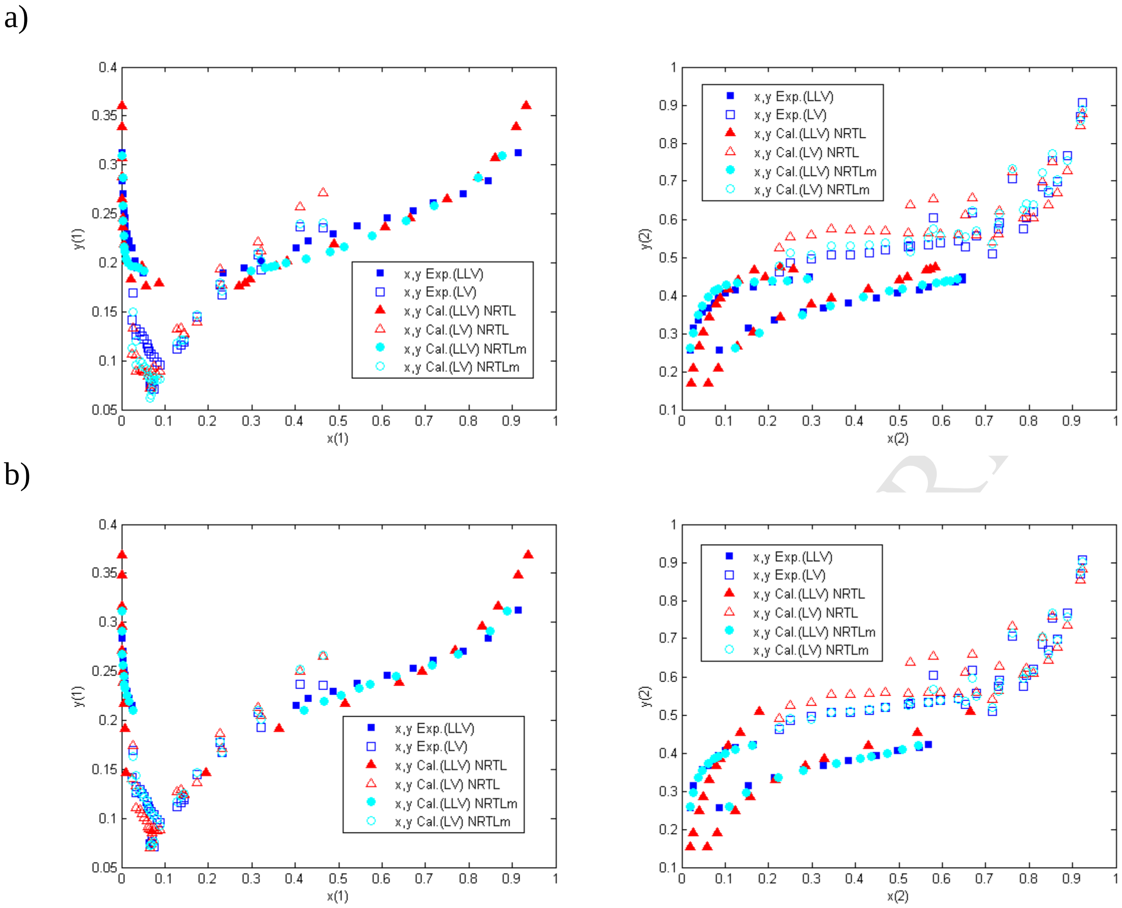

Figure 5. Experimental and calculated compositions (molar fractions) obtained by correlation of the data for the water (1) + ethanol (2) + heptane (3) ternary system at 760 mmHg [17] using NRTL and modified NRTL (NRTLm) models: a) original experimental data set, and b) reduced experimental data set.

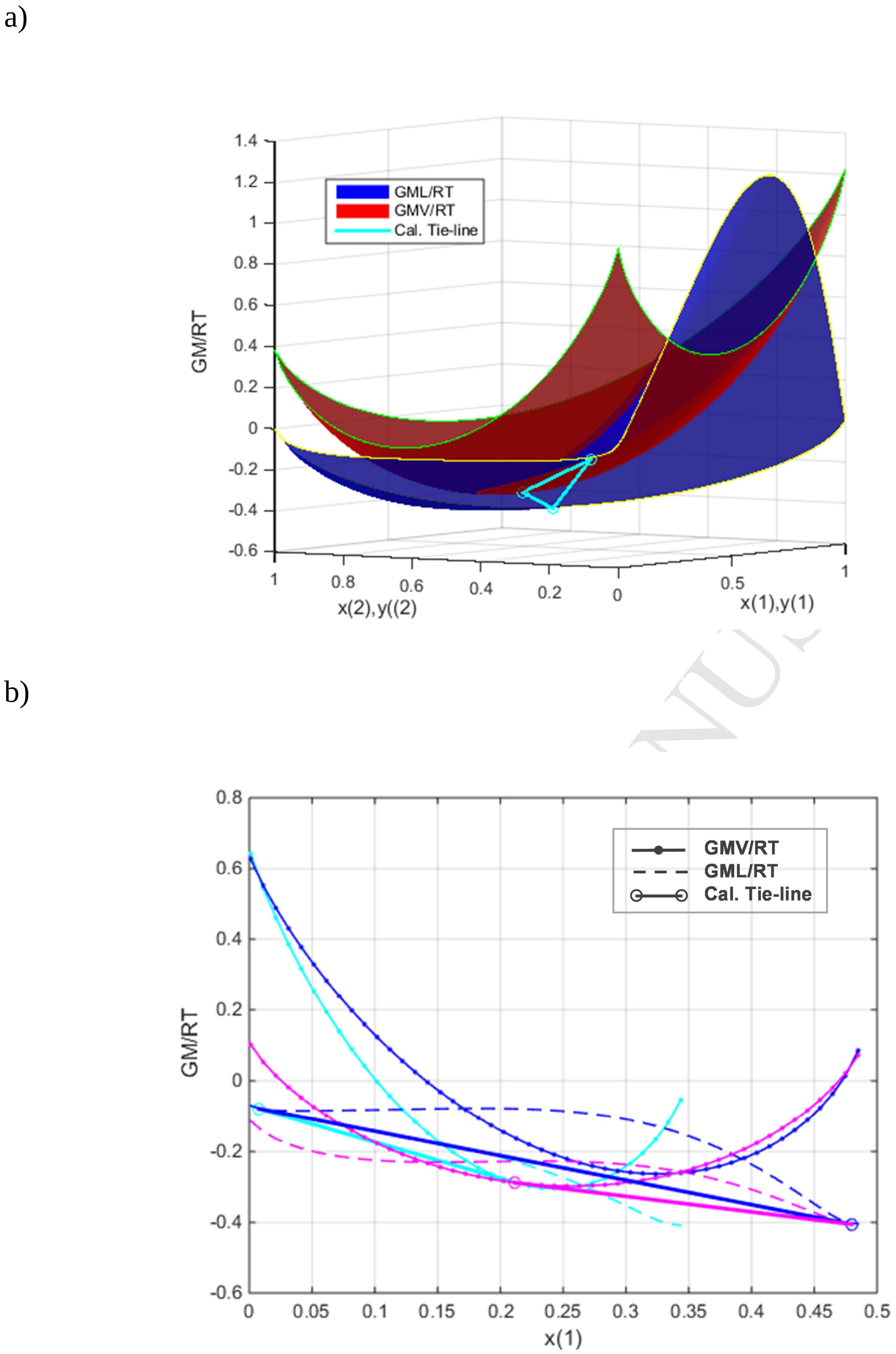

Figure 6. Verification of the Gibbs minor common tangent equilibrium criteria at conditions for the existence of VLLE: a) $G^{M,V}/RT$ and $G^{M,L}/RT$ surfaces as a function of compositions including the tie-triangle corresponding to the experimental VLLE data, and b) cuts of surfaces along the 3 tie-lines forming the calculated tie-triangle: $G^{M,L}/RT$ solid lines with points, $G^{M,V}/RT$ dashed lines and common tangent continuous lines (corresponding to the L_1-V, L_2-V and L_1-L_2 tie lines).

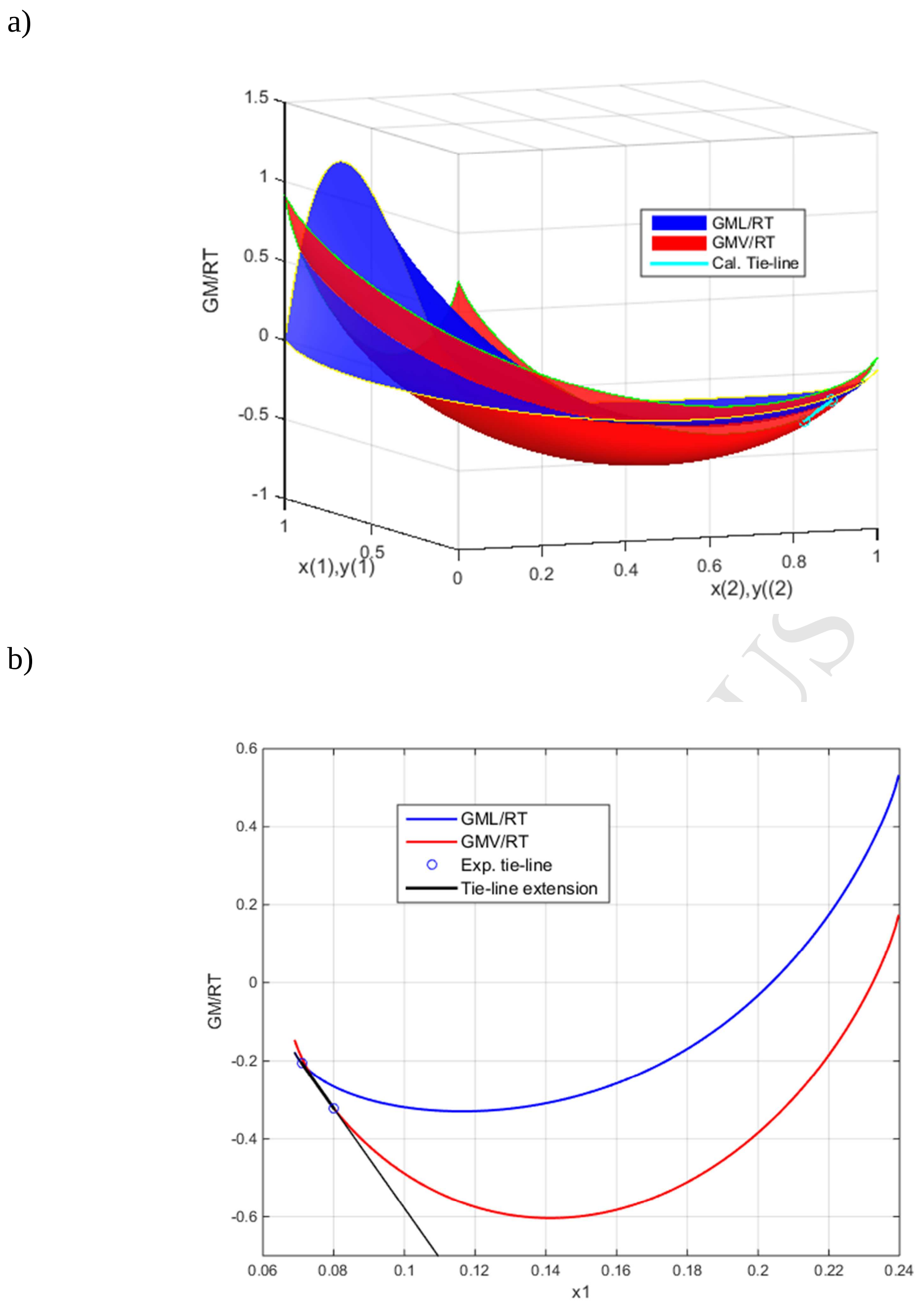

Figure 7. Verification of the Gibbs minor common tangent equilibrium criteria at conditions of one specific VLE data: a) $G^{M,V}$ and $G^{M,L}$ surfaces as a function of compositions including the tie-line corresponding to the experimental VLE data, and b) cut of the these G^{M} surfaces along the VL tie-line.