

# **ParamIni\_LL\_NRTL: Graphical User Interface (GUI) for the Selection of NRTL Initial Parameters for the Correlation of Ternary Liquid-Liquid Equilibrium Data (Type I, II, III and 0 (LL island), i.e. with 1, 2, 3 or 0 binary pairs partially miscibles)**

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## **INTRODUCTION AND USER INSTRUCTIONS\***

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**Keywords:** NRTL model, phase equilibria, experimental data correlation, LLE, initial parameters.

### **1. INTRODUCTION**

The correlation of liquid-liquid equilibrium data is still currently a problem not fully resolved, especially for complex systems such as, those involving ionic liquid (Rodríguez-Escontrela et al. 2016, Zhu et al. 2020, Zhang et al. 2020), etc., where the high nonlinearity and non-convexity of the equations involved produce convergence problems, with a strong dependence on the initialization values used of the obtained solution (Marcilla et al. 2017, Labarta et al. 2022a). To avoid this situation, for the NRTL model, we have analyzed more than 200 LLE ternary systems (including type I, II, III and 0 or island, following the Treybal classification, Figure 1) in order to obtain a good representation of the different possible binodal curves and tie triangles that this model can reproduce satisfactorily, in a wide enough interval of values of the different parameters ( $\tau_{i,j}$ ,  $\alpha_{i,j}$ ). All these systems have been parametrized regarding the main characteristics of the corresponding LLE, such as the number of binary subsystems partially miscible, the size and middle point of the binary tie-lines, the slope of the tie-lines, the location of the plate point (Marcilla et al. 2012), etc.

With this parametrization, we have created a database and a new graphical user interface, GUI (Labarta et al. 2022b-d) that allows loading a set of liquid-liquid experimental data to obtain, using optimization algorithms and machine learning techniques, a consistent set of initial NRTL parameters that predicts a parametrized LLE near the experimental one. This set of parameters can be used now in any correlation data algorithm (using the corresponding equilibrium condition: isoactivity, minimum of the global Gibbs energy of mixing, or the Gibbs energy of mixing minor common tangent plane) to obtain the final rigorous solution (Marcilla et al. 2011).

We believe that the present work can help researchers, professionals and students, in the task of correlating experimental liquid-liquid equilibrium data, in order to obtain consistent binary interaction parameters, taking into account that the correct calculation of the phase equilibrium is a key point in the optimal (efficient and sustainable) design of the corresponding processes and equipment.

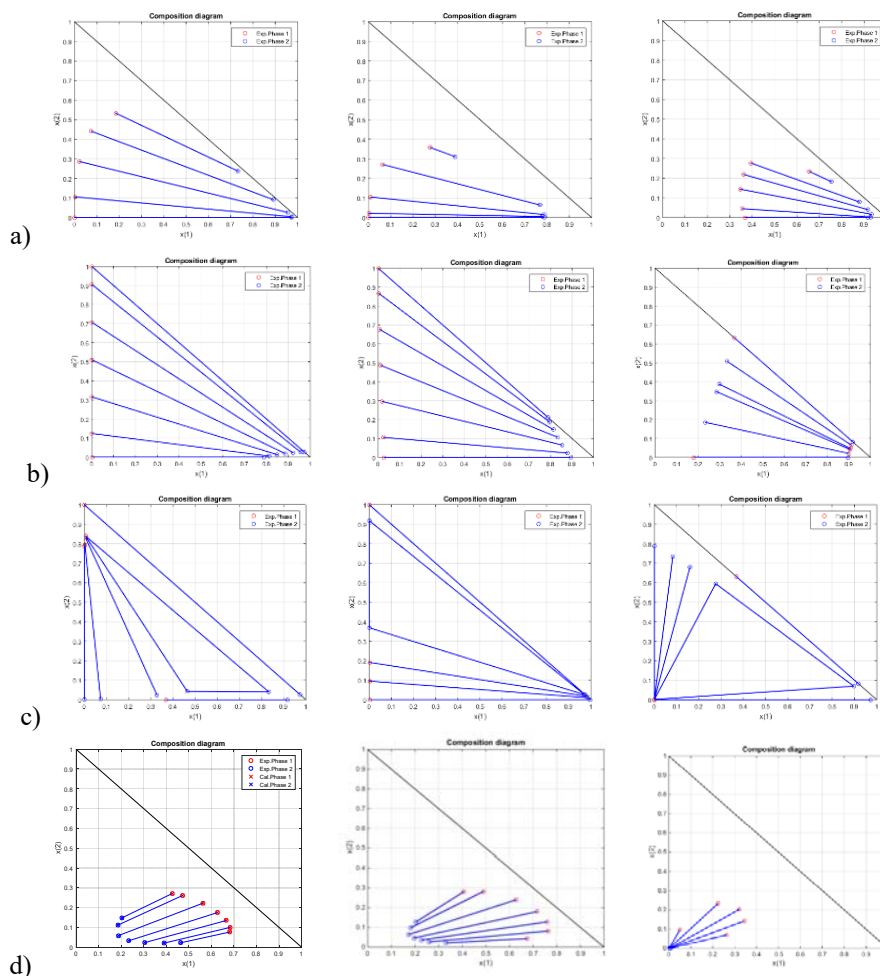


Figure 1. Examples of different LLE behaviors: a) Type I with only one binary partially miscible, b) Type II with two binaries partially miscible, c) Type III with three binaries partially miscible and a tie-triangle, d) Type 0 without binaries partially miscible but with an internal region of two liquids partially miscible.

## 2. DOWNLOAD INSTRUCTIONS

1. Download the file to your computer in a known folder: [ParamIni\\_LL\\_NRTL.zip](#)
2. Unzip the file

## 3. BEFORE USING THE GUI ParamIni\_LL\_NRTL

1. In order to use this GUI it is necessary to have an excel file with an adequate structure for each type of LLE (I, II, III or 0) system, with the following information corresponding to the system under study. It is essential to respect the correct structure of the excel file. It is possible to use the different files Data\_Example*i*\_Ti.xls included, as a draft for others similar case studies (see **Appendix A: Structure of the excel data file**):
  - a. Values of  $T^{(*)}$  and P for the corresponding LLE system.
  - b.  $G^{\text{Excess}}(\text{L})/RT$  Model selection variable: 1 (NRTL model)
  - c. The total number of experimental tie-lines ( $N_t$ ) (max. value: 40).

- d. Experimental molar fractions
- e. Specific information depending on the type of system (such as plate point or tie triangle)

#### 4. CLASIC $G^M$ MODELS RESUME

➤  $G^{Mixture}/RT = G^{Ideal}/RT + G^{Excess}/RT = \sum x_i \cdot \ln(x_i) + G^E/RT$

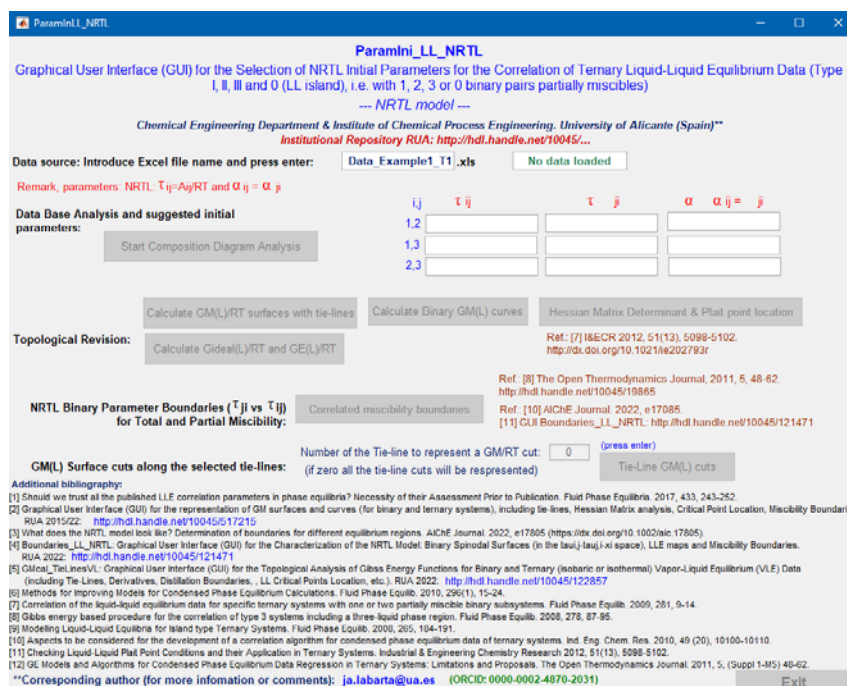
NRTL model:

$$\frac{G^E}{RT} = \sum_{i=1}^C x_i \cdot \frac{\sum_{j=1}^C \tau_{j,i} \cdot G_{j,i} \cdot x_j}{\sum_{k=1}^C G_{k,i} \cdot x_k}; \text{ with } \tau_{j,i} (\text{dimensionless}) = \frac{A_{j,i}}{RT}; G_{j,i} = \exp(-\alpha_{j,i} \cdot \tau_{j,i}); A_{i,i}=0$$

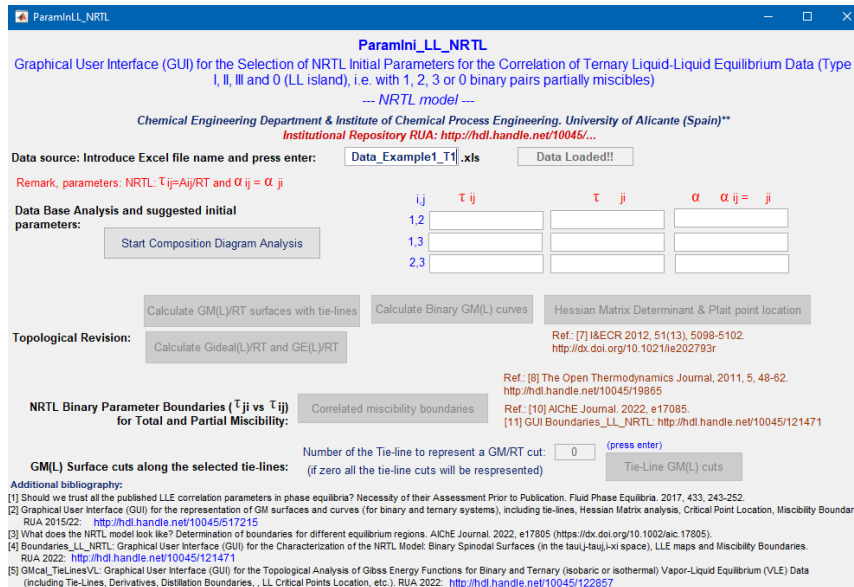
and  $\alpha_{i,j} = \alpha_{j,i}$

#### 5. USING THE GUI ParamIni\_LL\_NRTL

1. Open Matlab software
2. Once in MatLab, select the folder where the file **ParamIni\_LL\_NRTL.zip** was unzipped as “current folder”.
3. Localize and execute the file **ParamIni\_LL\_NRTL.p** from the MatLab Command Window (i.e.: writing **ParamIni\_LL\_NRTL** in the Command Window, and pressing enter)

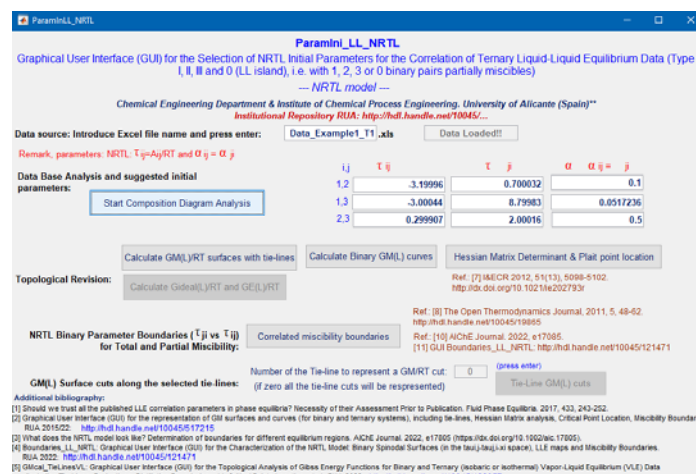
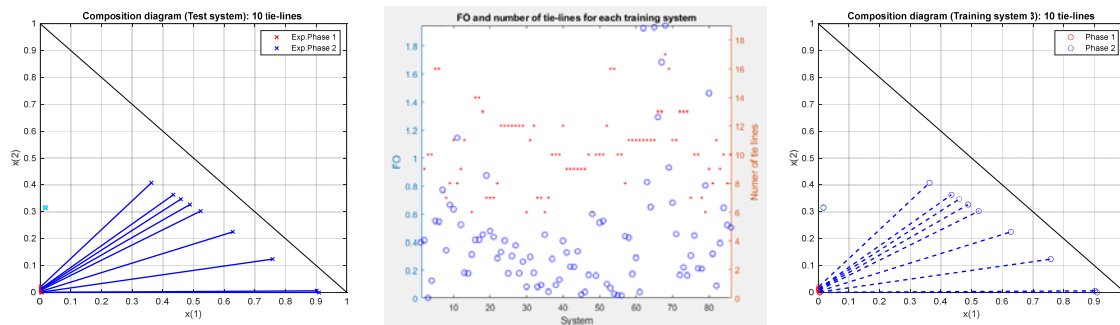


4. At this moment only the windows of the excel file name is active. Introduce the name of the excel data file corresponding to the system under study type 1, 2, 3, or 0 (e.g. Data\_Example1\_T1) and press enter. Please wait a moment for the data load process.



5. Now it is possible to start with the database analysis in order to obtain a consistent set of initial guest NRTL parameters for the correlation of the LLE under study by using the corresponding push buttons.

Once this analysis finish, the suggested set of initial NRTL parameters appears. Additionally, three figures are shown: the ternary composition diagram (in molar fractions) of the system under study, a revision of the results regarding the system analysed, and the ternary composition diagram of the system included in the database with the biggest percentage of similitude (taking into account the parametrization done to characterize the corresponding LLE and solubility curves).



6. At this point it is possible to check the consistency of the suggested parameters by analyzing the topology of the calculated Gibbs Energy of Mixing Function [1,2], the calculated plait point [3], and the corresponding miscibility boundaries of the NRTL model [4-6], by pushing the push buttons:

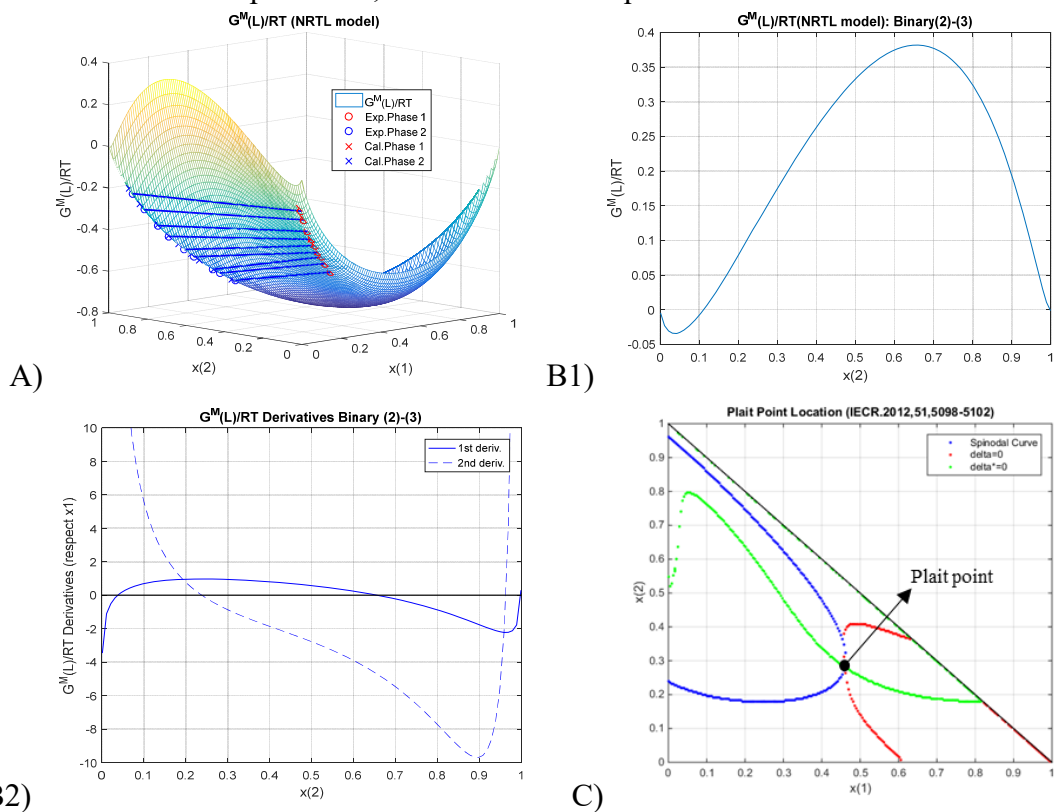
A)  $G^M(L)/RT$  surface (calculated with the model and parameters defined), including also the experimental tie-lines (included in the excel file loaded).

B) Calculated Binary  $G^M(L)$  curves, including 1<sup>st</sup> and 2<sup>nd</sup> derivatives (to facilitate the topological analysis).

C) Hessian matrix determinant ( $\sigma$ ), spinodal curve ( $\sigma=0$ ), and Plait point visual location using additionally  $\delta$  and  $\delta^*$  matrix determinants, which have to be also equal to zero:

$$\sigma = \begin{vmatrix} \frac{\partial^2 G^M}{\partial x_1^2} & \frac{\partial^2 G^M}{\partial x_1 \partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial x_2^2} \end{vmatrix} = 0; \delta = \begin{vmatrix} \frac{\partial \sigma}{\partial x_1} & \frac{\partial \sigma}{\partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial x_2^2} \end{vmatrix} = 0; \delta^* = \begin{vmatrix} \frac{\partial \sigma}{\partial x_2} & \frac{\partial \sigma}{\partial x_1} \\ \frac{\partial^2 G^M}{\partial x_1 \partial x_2} & \frac{\partial^2 G^M}{\partial x_1^2} \end{vmatrix} = 0$$

D) Correlated NRTL binary Miscibility Boundaries (e.g. for Total and Partial Miscibility):  $\tau_{j,i}$  vs  $\tau_{i,j}$  (for  $\alpha_{ij}=0.2$ ) and for  $\alpha_{ij}$  between 0 and 0.95). The obtained  $\tau_{i,j}$  binary parameters are also represented, to check their adequate location.



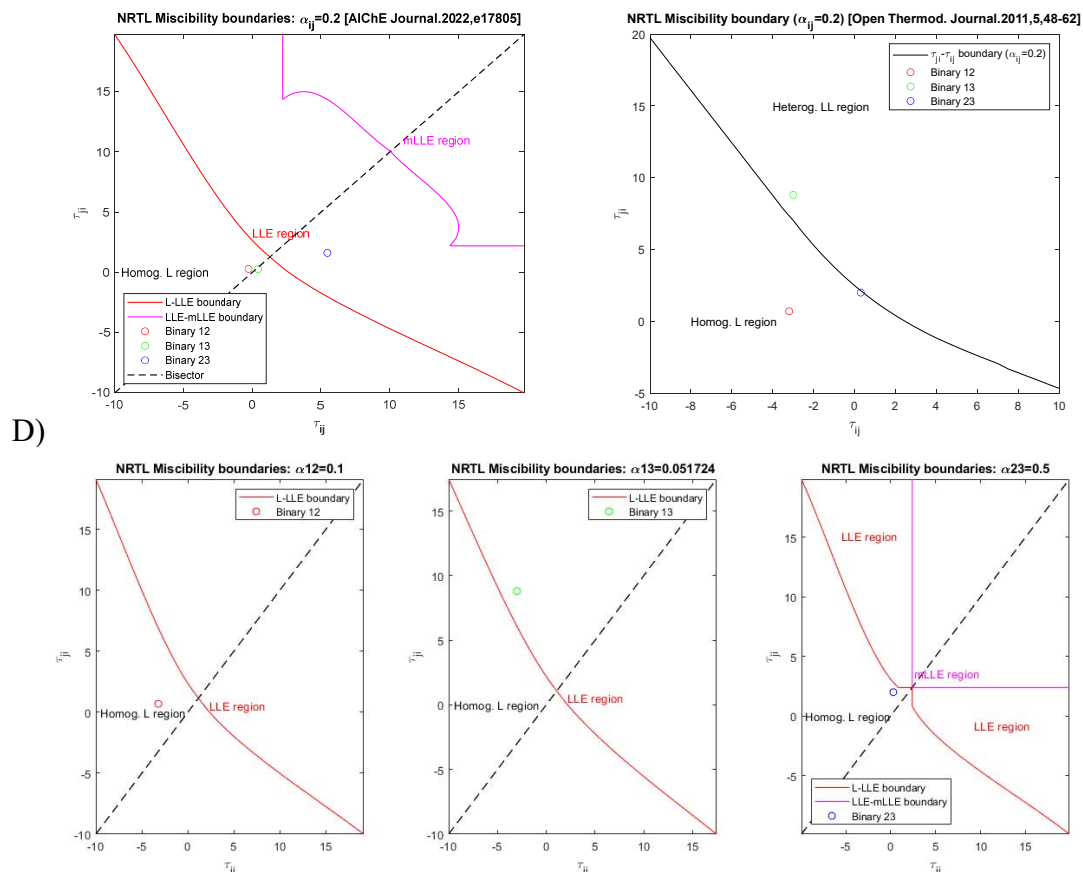


Figure 2. Examples of different diagrams for the topological analysis of NRTL parameters.

7. Once the  $G^M(L)/RT$  surface (A) is calculated, two more options are active:

**ParamIni\_LL\_NRTL**  
 Graphical User Interface (GUI) for the Selection of NRTL Initial Parameters for the Correlation of Ternary Liquid-Liquid Equilibrium Data (Type I, II, III and 0 (LL island), i.e. with 1, 2, 3 or 0 binary pairs partially miscibles)  
 --- NRTL model ---  
 Chemical Engineering Department & Institute of Chemical Process Engineering, University of Alicante (Spain)\*\*  
 Institutional Repository RUA: <http://hdl.handle.net/10045/...>

Data source: Introduce Excel file name and press enter:  Data Loaded!!!

Remark, parameters: NRTL:  $\tau_{ij}=A_{ij}/RT$  and  $\alpha_{ij} = \alpha_{ji}$

i,j	$\tau_{ij}$	$\tau_{ji}$	$\alpha_{ij} = \alpha_{ji}$
1,2	-3.19996	0.700032	0.1
1,3	-3.00044	8.79983	0.0517236
2,3	0.299907	2.00016	0.5

Buttons: Start Composition Diagram Analysis, Calculate GM(L)/RT surfaces with tie-lines, Calculate Binary GM(L) curves, Hessian Matrix Determinant & Plait point location, Calculate Gideal(L)/RT and GE(L)/RT, Correlated miscibility boundaries

Topological Revision: Calculate Gideal(L)/RT and GE(L)/RT

NRTL Binary Parameter Boundaries ( $\tau_{ji}$  vs  $\tau_{ij}$ ) for Total and Partial Miscibility: Correlated miscibility boundaries

GM(L) Surface cuts along the selected tie-lines: (if zero all the tie-line cuts will be represented) Number of the Tie-line to represent a GM/RT cut:  Tie-Line GM(L) cuts

Additional bibliography:  
 [1] Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. Fluid Phase Equilibria. 2017, 433, 243-252.  
 [2] Graphical User Interface (GUI) for the representation of GM surfaces and curves (for binary and ternary systems), including tie-lines, Hessian Matrix analysis, Critical Point Location, Miscibility Boundaries RUA 2015/22: <http://hdl.handle.net/10045/517215>  
 [3] What does the NRTL model look like? Determination of boundaries for different equilibrium regions. AIChE Journal. 2022, e17805 (<https://dx.doi.org/10.1002/aic.17805>).  
 [4] Boundaries\_LL\_NRTL: Graphical User Interface (GUI) for the Characterization of the NRTL Model: Binary Spinodal Surfaces (in the tau<sub>ij</sub>-tau<sub>ji</sub>-x<sub>i</sub> space), LLE maps and Miscibility Boundaries. RUA 2022: <http://hdl.handle.net/10045/121471>  
 [5] GMcal\_TieLinesVL, Graphical User Interface (GUI) for the Topological Analysis of Gibbs Energy Functions for Binary and Ternary (isobaric or isothermal) Vapor-Liquid Equilibrium (VLE) Data (including Tie-Lines, Derivatives, Distillation Boundaries, ... LL Critical Points Location, etc.). RUA 2022: <http://hdl.handle.net/10045/122857>

E)  $G^{Ideal}(L)/RT$  and  $G^E(L)/RT$  surfaces (ideal and excess contributions of the  $G^M(L)/RT$  function calculated with the suggested NRTL: Push button.

F)  $G^M(L)/RT$  surface cuts along the selected Experimental Tie-Lines. In this case, the ordinal number corresponding to a tie-line (from 0 to  $N_t$ ) has to be introduced (the value 0 will select the representation of the different cuts along all the experimental tie-lines). Then **press enter**. After that, push the button “Tie Line  $G^M(L)$ ” to represent the  $G^M(L)/RT$  surface cut is active and can be used.

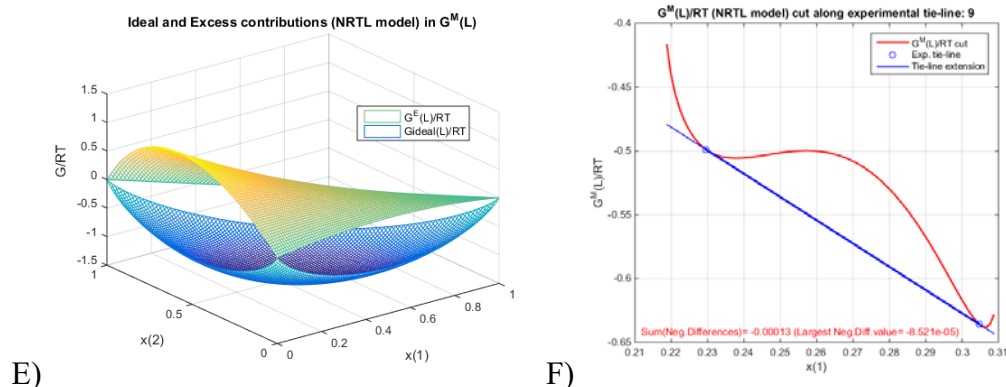


Figure 3. Different diagrams: Ideal and Excess contribution, and  $G^M(L)/RT$  cut along an exp. tie-line.

When the number of the Tie Line is different from 0, two additional figures are also generated in ternary systems to facilitate and complete the visual analysis (Figures 4). On one hand, a new 3D figure representing the complete  $G^M(L)/RT$  surface (in modified units for drawing horizontal the tangent planes for the selected tie line, to facilitate the viewing and the coherence of the results). This figure includes the selected tie-line and the tangent planes at both extremes of the corresponding experimental (Figure 4.a1). The second figure represents additionally the difference between  $(G^M(L)/RT)_{Surface(model)}$  and  $(G^M(L)/RT)_{tangent\ plane}$  in the whole range of compositions, including the way along the tie line cut and the tangent planes at its both extremes (see Figure 4.a2). Evidently, this difference in the equilibrium compositions should be equal to zero.

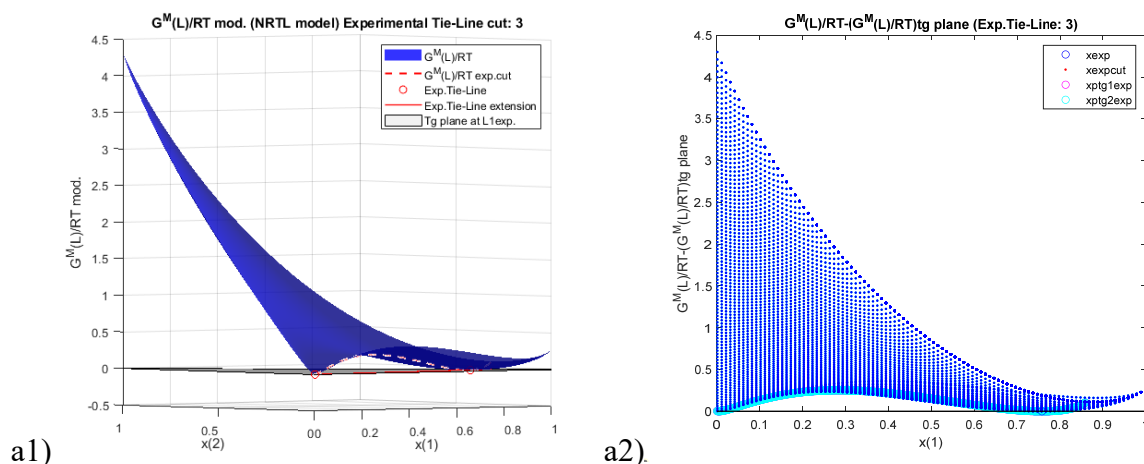



Figure 4. Complete  $G^M(L)/RT$  surface including the selected tie-line and the tangent planes at both extremes of the experimental tie-line. Remark: the values of the  $G^M(L)/RT$  surface have been modified to draw horizontal tangent planes to facilitate the viewing.

In order to complement this visual analysis in a rigorous way, the summation of all the negative differences  $[(G^M(L)/RT)_{Surface(model)} - (G^M(L)/RT)_{tangent\ plane}]$ , and the largest negative difference, for each tie line (and the global for all the tie lines) are also calculated and showed in the Command

Windows of MatLab (Figure 5). This calculation is carried out in the cut along the tie lines and additionally in ternary systems, in the whole range of composition. Obviously, these summations should be zero for totally consistent parameters with the expected experimental behaviour.



```
Command Window

Cut along exp. Tie Line 1: Sum(Neg.Differences)= 0 (Largest Neg.Diff.value= 0)
CONSISTENT parameters along this exp. cut

Cut along cal. Tie Line 1: Sum(Neg.Differences)= 0 (Largest Neg.Diff.value= 0)
CONSISTENT parameters along this cal. cut
>>> Tangent Plane at Tie Line cal.1: Sum(Neg.Differences)= -0.00097828 (Largest(Neg.Diff.value)= -0.00071431)

Cut along exp. Tie Line 2: Sum(Neg.Differences)= 0 (Largest Neg.Diff.value= 0)
CONSISTENT parameters along this exp. cut

Cut along cal. Tie Line 2: Sum(Neg.Differences)= 0 (Largest Neg.Diff.value= 0)
CONSISTENT parameters along this cal. cut
>>> Tangent Plane at Tie Line cal.2: Sum(Neg.Differences)= -0.0014636 (Largest(Neg.Diff.value)= -0.00073019)

...

Cut along exp. Tie Line 8: Sum(Neg.Differences)= -8.382e-05 (Largest Neg.Diff.value= -8.382e-05)

Cut along cal. Tie Line 8: Sum(Neg.Differences)= 0 (Largest Neg.Diff.value= 0)
CONSISTENT parameters along this cal. cut
>>> Tangent Plane at Tie Line cal.8: Sum(Neg.Differences)= -0.0035389 (Largest(Neg.Diff.value)= -0.00060293)

Cut along exp. Tie Line 9: Sum(Neg.Differences)= -0.00012998 (Largest Neg.Diff.value= -8.5209e-05)

Cut along cal. Tie Line 9: Sum(Neg.Differences)= 0 (Largest Neg.Diff.value= 0)
CONSISTENT parameters along this cal. cut
>>> Tangent Plane at Tie Line cal.9: Sum(Neg.Differences)= -0.00089197 (Largest(Neg.Diff.value)= -0.00023245)

--> TOTAL Sum(Neg.Differences) along all exp. cuts= -0.005024 (Largest Neg.Diff.value= -0.0017592)

----> TOTAL Sum(Neg.Differences) along all cal. cuts= 0 (Largest Neg.Diff.value= 0)
CONSISTENT PARAMETERS ALONG ALL CAL. CUTS

>>>>> TOTAL Sum(Neg.Differences) along all Tangent Planes at cal. Tie Lines= -0.18865 (Largest Neg.Diff.value= -0.0047468)

fx >>
```

Figure 5. Example of the additional information that appears at the Command Window after pushing the "Tie-Line GM(L) cuts" button.

Finally, a new excel file for other ternary case of study can be loaded to start again, or exit to the applications by using the exit push button.

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(ORCID : <http://orcid.org/0000-0002-4870-2031>)

**REMARK: IF YOU WANT TO RECEIVE A NOTIFICATION WITH POSSIBLE UPDATES OF THIS GUI. PLEASE SENT AN E-MAIL TO: [ja.labarta@ua.es](mailto:ja.labarta@ua.es)**

## ACKNOWLEDGMENTS

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## APPENDIX A: STRUCTURE OF THE EXCEL DATA FILE FOR THE ParamIni\_LL\_NRTL GUI

It is essential to respect the correct structure of the excel file. It is possible to use the file Data\_ExampleI\_Ti.xls included as a draft for other case studies or systems. (Note that this structure is totally compatible with the excel test files for the GUI GMcal\_TieLinesLL: <http://hdl.handle.net/10045/51725>).

- 1.- The active sheet of the excel file has to call it: **Example**
- 2.- The different data needed for the calculations and graphical representations has to be located in the following concrete cells of the active excel sheet. **It is important to remark that for type 1 systems, the binary 13 has to be the binary partially miscible, and for type 2 systems, the binary subsystems that have to be partially miscible are de 13 and 23:**

Variable	Concrete cell location in the active (loaded) excel sheet
Pressure (atm)	B2
T(°C) <sup>(*)</sup>	B3
Total number of experimental tie-lines (Nt≤40) <sup>(**)</sup>	B4
<b>Model Used: (1: NRTL)</b>	B5
<b>Treybal type: (0, 1, 2 or 3)</b>	B6
<b>For Treybal type 1 systems: Plait point location</b>	---
Molar fraction component 1	Q24
Molar fraction component 2	R24
Molar fraction component 3	S24
<b>For Treybal type 3 systems: Tie triangle or Plait points location (x1 increasing order)</b>	---
Molar fraction component 1 (lowest)	Q24
Molar fraction component 2	R24
Molar fraction component 3	S24
Molar fraction component 1 (intermediate)	Q25
Molar fraction component 2	R25
Molar fraction component 3	S25
Molar fraction component 1 (higher)	Q26
Molar fraction component 2	R26
Molar fraction component 3	S26
<b>For Treybal type 0 systems: Plait points (x1 increasing order)</b>	---
Molar fraction component 1 (lowest)	Q24
Molar fraction component 2	R24
Molar fraction component 3	S24
Molar fraction component 1 (higher)	Q25
Molar fraction component 2	R25
Molar fraction component 3	S25

<b>EXPERIMENTAL TIE-LINES*</b>	
Molar fraction component 1 in Phase 1	A10:A50
Molar fraction component 2 in Phase 1	B10:B50
Molar fraction component 3 in Phase 1	C10:C50
Molar fraction component 1 in Phase 2	D10:D50
Molar fraction component 2 in Phase 2	E10:E50
Molar fraction component 3 in Phase 2	F10:F50

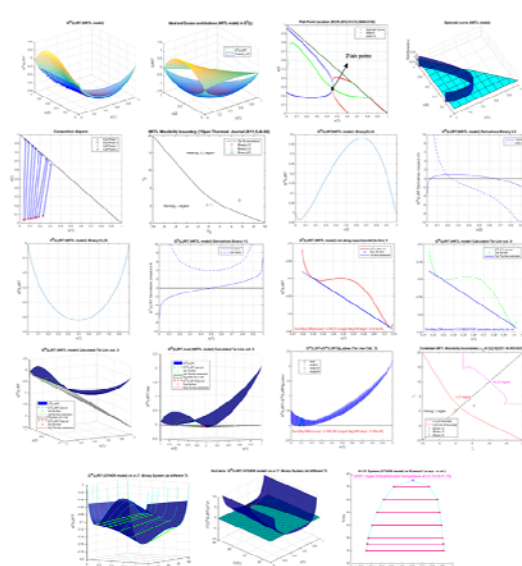
**(\*\*) Initially, the maximum value of the total number of tie-lines admitted is: 40.**

**List of test files included (Data Examplei\_Ti.xls.xls)**

- **Data\_Example1\_T1.xls.xls:** LLE ternary system (Type 1).
- **Data\_Example2\_T2.xls.xls:** LLE ternary system (Type 2).
- **Data\_Example3\_T3.xls.xls:** LLE ternary system (Type 3).
- **Data\_Example4\_T0.xls.xls:** LLE ternary system (Type 0).

## References

- I. Rodríguez-Escontrela, A. Arce, A. Soto, A. Marcilla, M.M. Olaya, J.A. Labarta, 2016, Correlation of Three-Liquid-Phase Equilibria involving Ionic Liquids. *Phys. Chem. Chem. Phys.* 2016; 18: 21610-21617.
- Z. Zhu, Y. Xu, T. Feng, N. Wang, K. Liu, H. Fan, J.A. Labarta, Y. Wang, J. Gao, L. Wang. Measurement and correlation of Liquid - Liquid equilibria of three imidazolium ionic liquids with acetone and cyclohexane. *J. Mol. Liq.* 2020; 298: 111947-111962.
- L. Zhang, X. Bing, Z. Cui, J.A. Labarta, D. Xu, J. Gao, S. Zhou, Y. Wang, 2021, Multiscale Exploration and Experimental Insights into Separating Neutral Heterocyclic Nitrogen Compounds Using [emim][NO<sub>3</sub>] as an Extractant, *ACS Sustainable Chem. Eng.* 2020, 8, 14, 5662-5673.
- A. Marcilla, J.A. Labarta, M.M Olaya, 2017, Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication, *Fluid Phase Equilibria.* 433, 243-252. (<http://dx.doi.org/10.1016/j.fluid.2016.11.009>). [RUA: http://hdl.handle.net/10045/66521](http://hdl.handle.net/10045/66521).
- J.A. Labarta, M.M. Olaya, A. Marcilla, 2022a, What does the NRTL model look like? Determination of boundaries for different fluid phase equilibrium regions, *AIChE Journal*, e17805. <https://dx.doi.org/10.1002/aic.17805>.
- A. Marcilla, M.D. Serrano, J.A. Labarta, M.M. Olaya, 2012, Checking Liquid-Liquid Critical Point Conditions and their Application in Ternary Systems. *Industrial & Engineering Chemistry Research*, 51(13), 5098-5102. <http://dx.doi.org/10.1021/ie202793r>.
- J.A. Labarta, M.M. Olaya, A. Marcilla, 2022b, **GMcal\_TieLinesLL**: Graphical User Interface (GUI) for Topological Analysis of Calculated  $G^M$  Surfaces and Curves, including Tie-Lines, Hessian Matrix, Spinodal Curve, Plait Point Location, Miscibility Boundaries, etc. for Binary and Ternary Liquid-Liquid Equilibrium (LLE) Data. *Institutional Repository (RUA) 2015-2022*. Publicly available online at: <http://hdl.handle.net/10045/51725>. (Including a **Thermodynamic Review**).



- J.A. Labarta, M.M. Olaya, A. Marcilla, 2022c, **Boundaries\_LL\_NRTL**: Graphical User Interface (GUI) for the characterization of the NRTL model: Binary Spinodal Surfaces (in the  $\tau_{i,j}-\tau_{j,i}-x_i$  space), **LLE maps and Miscibility Boundaries**, *Institutional Repository of the University of Alicante*, <http://hdl.handle.net/10045/121471>.

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**Boundaries\_LL\_NRTL**  
 Boundaries\_LL\_NRTL: Graphical User Interface (GUI) for the Characterization of the NRTL Model: Binary Spinodal Surfaces (in the  $T_{ij}$ ,  $x_i$  space), LLE Maps and Miscibility Boundaries  
 Chemical Engineering Department & Institute of Chemical Process Engineering, University of Alicante (Spain)\*\*  
 Institutional Repository RUA: <http://hdl.handle.net/10045/121471>

Visualization of pre-calculated binary spinodal surfaces, LLE maps and miscibility boundaries for the NRTL model ( $\alpha_{ij}$  from 0 to 0.95):  
  $\alpha_{ij}=0$    $\alpha_{ij}=0.10$    $\alpha_{ij}=0.20$    $\alpha_{ij}=0.30$    $\alpha_{ij}=0.40$    $\alpha_{ij}=0.50$    $\alpha_{ij}=0.60$    $\alpha_{ij}=0.70$    $\alpha_{ij}=0.80$    $\alpha_{ij}=0.90$   
  $\alpha_{ij}=0.05$    $\alpha_{ij}=0.15$    $\alpha_{ij}=0.25$    $\alpha_{ij}=0.35$    $\alpha_{ij}=0.45$    $\alpha_{ij}=0.55$    $\alpha_{ij}=0.65$    $\alpha_{ij}=0.75$    $\alpha_{ij}=0.85$    $\alpha_{ij}=0.95$

Calculation of a specific NRTL binary spinodal surface and LLE maps (by discrete scanning):  
 $T_{ij}$  limits +/-: 10 Number of  $T_{ij}$  points: 100 Number of  $x_i$  points: 15000  
 $\alpha_{ij}$  value: 0.2 Map Calculation Grid of individual gM curves

Representation of correlated miscibility boundaries for the NRTL model: (Ref.: [10] AIChE Journal, 2022, e17085)

LLE	k	t(1,k)	t(2,k)	t(3,k)	t(4,k)	f(LLE)	p(1)	p(2)	p(3)	p(4)
0	0.611382	144.834	586.0999	9.89155	(0.4 + $\alpha_{ij}$ < 0.95)	a(q)	0.17018	0.94122	-15.0026	7.41426
					(0 < $\alpha_{ij}$ < 0.4)	b(q)	1.10745	0.38618	6.61230	0.99112
1	11.0599	-7.61358	2.79799	0.94847	c(q)	0.80617	0.08518	0.30456	0.54404	
2	-18.9354	46.0735	-37.9100	19.6231	(0.4 + $\alpha_{ij}$ < 0.95)	d(q)	-1.25689	-2.15482	-2.86603	-11.2090
mLLE 3	-712.144	789.320	-297.731	44.5860	(0.15 < $\alpha_{ij}$ < 0.43)	e(q)	0.45992	1.95455	3.08991	3.68998

Correlated boundaries evolution: LLE Boundaries LLE/mLLE Boundaries  
 Additional bibliography:  
 [1] Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. Fluid Phase Equilibria, 2017, 433, 243-252.  
 [2] Gmcal\_TieLinesLL: Graphical User Interface (GUI) for the Topological Analysis of Calculated GM Surfaces and Curves, including Tie-Lines, Hessian Matrix, Spinodal Curve, Plat Point Location, etc. for Binary and Ternary Liquid-Liquid Equilibrium (LLE) Data (RUA 2015/22). <http://hdl.handle.net/10045/91726>.  
 [3] GE Models and Algorithms for Condensed Phase Equilibrium Data Regression in Ternary Systems. Limitations and Proposals. The Open Thermodynamics Journal, 2011, 5, (Suppl 1-MS) 48-62  
 [4] Methods for Improving Models for Condensed Phase Equilibrium Calculations. Fluid Phase Equilib. 2019, 296(1), 15-24.  
 [5] Correlation of the liquid-liquid equilibria for aprotic ternary systems with one or two partially miscible binary subsystems. Fluid Phase Equilib. 2009, 281, 9-14.  
 [6] Gibbs energy based procedure for the correlation of type 3 systems including a three-liquid phase region. Fluid Phase Equilib. 2008, 278, 87-95.  
 [7] Modeling Liquid-Liquid Equilibria for Island-type Ternary Systems. Fluid Phase Equilib. 2008, 295, 104-109.  
 [8] Aspects to be considered for the development of a correlation algorithm for condensed phase equilibrium data of ternary systems. Ind. Eng. Chem. Res. 2010, 49, (20), 10100-10110.  
 [9] Checking Liquid-Liquid Critical Point Conditions and their Application in Ternary Systems. Industrial & Engineering Chemistry Research 2012, 51(13), 5098-5102.  
 [10] What does the NRTL model look like? Determination of boundaries for different equilibrium regions. AIChE Journal, 2022, e17085 (<https://doi.org/10.1002/aic.17805>).  
 [11] Gmcal\_TieLinesVL: Graphical User Interface (GUI) for the Topological Analysis of Gibbs Energy Functions for Binary and Ternary (isobaric or isothermal) Vapor-Liquid Equilibrium (VLE) Data (including Tie-Lines, Derivatives, Distillation Boundaries, etc.) (RUA 2022). <http://hdl.handle.net/10045/122857>.  
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J.A. Labarta, M.M. Olaya, A. Marcilla, 2022d, **Gmcal\_TieLinesVL: Graphical User Interface (GUI) for the Topological Analysis of Experimental and Calculated  $G^M$  Functions for Binary and Ternary (isobaric or isothermal) Vapor-Liquid Equilibrium (VLE) data (including Tie-Lines, Derivatives, Distillation Boundaries, LL Critical Points Location, etc.)**, Institutional Repository of the University of Alicante, <http://hdl.handle.net/10045/122857>.

**Gmcal\_TieLinesVL (v.2.2): TOPOLOGICAL ANALYSIS OF VAPOR-LIQUID EQUILIBRIUM DATA AND CORRELATIONS**  
 Graphical User Interface (GUI) for the Representation of Experimental and Calculated GM Functions for Binary and Ternary (isobaric or isothermal) Vapor-Liquid Equilibrium (VLE or VLLE) data (including Tie-Lines, Derivatives, Distillation Boundaries, LL Critical Points, etc.)  
 --- using NRTL, UNIQUAC or an alternative model ---  
 Chemical Engineering Department & Institute of Chemical Process Engineering, University of Alicante (Spain)\*\*  
 Institutional Repository RUA: <http://hdl.handle.net/10045/122857>

Data source: Introduce Excel file name and press enter: exampleVLIsoP\_test2.xls Data Loaded!!

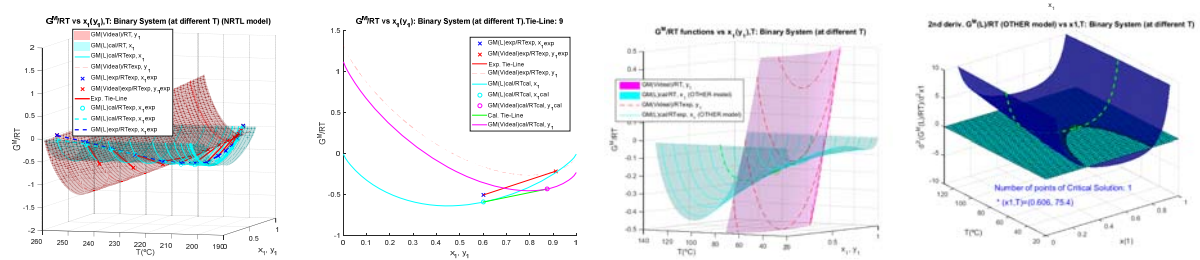
Remark, parameters: NRTL:  $A_{ij}$  (K) and  $\alpha_{ij} = \alpha_j$ ; UNIQUAC:  $A_{ij}$  (K),  $n_i$ ,  $q_i$  and  $Z$

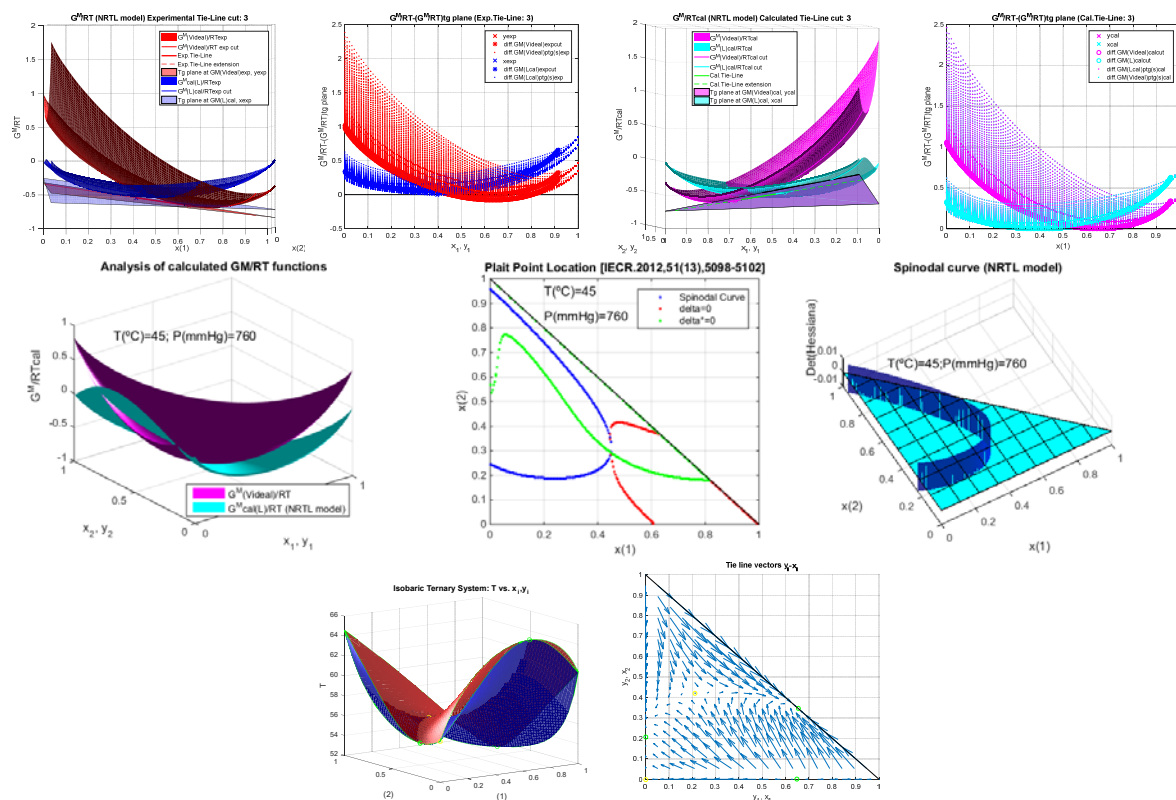
Graphical and topological analysis: GMRT values at VL Tie-Lines GMRT functions: 3D representations and LL Critical Points Analysis (interval)  
 Comparatives of GMRT and  $d(\text{GMRT})/dx_1$  calculated with models and with the experimental data Ref.: [8, 9]  
 Equilibrium Diagrams (data) Ternary Tie-Lines Map and 3D Txy Equilibrium Diagram (calculated) Ref.: [10, 11]

NRTL Binary Parameter Boundaries ( $T_{ij}$  vs  $T_{ij}$ ) for Total and Partial Miscibility:  
 Correlated miscibility boundaries Ref.: [5] The Open Thermodynamics Journal, 2011, 5, 48-62. <http://hdl.handle.net/10045/19885>  
 Ref.: [6] AIChE Journal, 2022, e17085. <https://doi.org/10.1002/aic.17805>  
 [7] GUI Boundaries\_LL\_NRTL: <http://hdl.handle.net/10045/121471>

GMRT functions along selected tie-line: Number of the Tie-line to represent: 3 (press enter)  
 (if zero all tie-lines will be represented) Tie-Line GMRT curves

Additional bibliography:  
 [1] Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. Fluid Phase Equilibria, 2017, 433, 243-252.  
 [2] Gmcal\_TieLinesLL: Graphical User Interface (GUI) for the Topological Analysis of Calculated GM Surfaces and Curves, including Tie-Lines, Hessian Matrix, Spinodal Curve, Plat Point Location, etc. for Binary and Ternary Liquid-Liquid Equilibrium (LLE) Data (RUA 2015/22). <http://hdl.handle.net/10045/91726>.  
 [3] The unavoidable necessity of considering temperature dependence of the liquid Gibbs energy of mixing for certain VLE data correlations Fluid Phase Equilibria, 2018, 473, 17-31.  
 [4] Procedure for the correlation of normal appearance VLE data, where the classical models dramatically fail with no apparent reason. Fluid Phase Equilibria, 2019, 493, 88-101.  
 [5] GE Models and Algorithms for Condensed Phase Equilibrium Data Regression in Ternary Systems. Limitations and Proposals. The Open Thermodynamics Journal, 2011, 5, 48-62.  
 [6] What does the NRTL model look like? Determination of boundaries for different fluid phase equilibrium regions. AIChE Journal, 2022, e17085 (<https://doi.org/10.1002/aic.17805>).  
 [7] Boundaries\_LL\_NRTL: Graphical User Interface (GUI) for the Characterization of the NRTL Model: Binary Spinodal Surfaces (in the  $T_{ij}$ ,  $x_i$  space), LLE maps and Miscibility Boundaries. (RUA 2022). <http://hdl.handle.net/10045/121471>  
 [8] Checking Liquid-Liquid Critical Point Conditions and their Application in Ternary Systems. Industrial & Engineering Chemistry Research, 2012, 51(13), 5098-5102.  
 [9] LLE data correlation using NRTL model for different types of binary systems. UCST, LCST and closed miscibility loops. Industrial & Engineering Chemistry Research, 2020, 59(17), 8469-8479.  
 [10] Approximate Calculation of Distillation Boundaries for Ternary Azeotropic Systems. Ind. Eng. Chem. Res., 2011, 50(12), 7452-7456.  
 [11] Numerical Determination of Distillation Boundaries for Multicomponent Homogeneous and Heterogeneous Azeotropic Systems. Computer Aided Chemical Engineering, 2010, 28(C), 643-648.  
 \*\*Corresponding author (for more information or comments): [ja.labarta@ua.es](mailto:ja.labarta@ua.es) (ORCID: 0000-0002-4870-2031)





A. Marcilla, J.A. Labarta, M.D. Serrano, M.M. Olaya, 2011, GE Models and Algorithms for Condensed Phase Equilibrium Data Regression in Ternary Systems: Limitations and Proposals. The Open Thermodynamics Journal, 5 (Suppl 1-M5), 48-62. <http://dx.doi.org/10.2174/1874396X01105010048>.

### Additional bibliography:

- [1] Vicente-Martínez, M.; Labarta, J.A. Análisis topológico del modelo NRTL en sistemas binarios y ternarios para caracterizar la tipología de los sistemas líquido-líquido que predice en función de los valores de los parámetros de interacción binaria. Institutional Repository of the University of Alicante (RUA) 2021. Available at: <http://hdl.handle.net/10045/117665>.
- [2] Olaya, M.M.; Ibarra, I.; Labarta, J.A.; Serrano, M.D.; Marcilla, A. Computing Liquid-Liquid Phase Equilibria: An exercise to understand the nature of false solutions and how to avoid them. Chemical Engineering Education **2007**, 41(3), 218-224. Institutional Repository RUA: <http://hdl.handle.net/10045/14277>.
- [3] Marcilla, A.; Labarta J.A.; Serrano, M.D.; Olaya, M.M. Pitfalls on computing liquid-liquid phase equilibria using the k-value method. 11<sup>th</sup> Mediterranean Congress of Chemical Engineering. EXPOQUIMIA **2008**. Institutional Repository RUA: <http://hdl.handle.net/10045/26610>.
- [4] Marcilla, A.; Labarta, J.A.; Olaya, M.M.; Serrano, M.D. Simultaneous correlation of liquid-liquid, liquid-solid, and liquid-liquid-solid equilibrium data for water + organic solvent + salt ternary systems: hydrated solid phase formation. *Ind. Eng. Chem. Res.* **2008**, 47, 2100-2108. <http://dx.doi.org/10.1021/ie071290w>.
- [5] Reyes, J.A.; Conesa, J.A.; Marcilla, A.; Olaya, M.M. Solid-Liquid Equilibrium Thermodynamics: checking stability in multiphase systems using Gibbs Energy Function. *Ind. Eng. Chem. Res.* **2001**; 40: 902-907. <http://dx.doi.org/10.1021/ie000435v>.

- [6] Olaya, M.M.; Marcilla, A.; Serrano, M.D.; Botella, A.; Labarta, J.A. Simultaneous Correlation of LL, LS and LLS Equilibrium Data for Water + Organic Solvent + Salt Ternary Systems. Anhydrous Solid Phase. *Ind. Eng. Chem. Res.* **2007**, 46(21), 7030-7037. <http://dx.doi.org/10.1021/ie0705610>.
- [7] Marcilla, A.; Olaya, M.M.; Serrano, M.D.; Labarta, J.A. Methods for Improving Models for Condensed Phase Equilibrium Calculations. *Fluid Phase Equilib.* **2010**, 296(1), 15-24. <http://dx.doi.org/10.1016/j.fluid.2009.12.026> (<http://hdl.handle.net/10045/13314>).
- [8] Labarta, J.A.; Olaya, M.M.; Velasco, R.; Serrano, M.D.; Marcilla, A. Correlation of the liquid-liquid equilibrium data for specific ternary systems with one or two partially miscible binary subsystems. *Fluid Phase Equilib.* **2009**, 281, 9-14. <http://dx.doi.org/10.1016/j.fluid.2008.12.002> (<http://hdl.handle.net/10045/24683>).
- [9] Marcilla, A.; Olaya, M.M.; Serrano, M.D.; Velasco, R.; Labarta, J.A. Gibbs energy based procedure for the correlation of type 3 systems including a three-liquid phase region. *Fluid Phase Equilib.* **2008**, 278, 87-95. <http://dx.doi.org/10.1016/j.fluid.2009.04.005> (<http://hdl.handle.net/10045/13315>).
- [10] Olaya, M.M.; Labarta, J.A.; Velasco, R.; Ibarra, I.; Marcilla, A. Modelling Liquid-Liquid Equilibria for Island type Ternary Systems. *Fluid Phase Equilib.* **2008**, 265, 184-191. <http://dx.doi.org/10.1016/j.fluid.2007.12.010> (<http://hdl.handle.net/10045/24681>).
- [11] Marcilla, A.; Olaya, M.M.; Serrano, M.D.; Labarta, J.A. Aspects to be considered for the development of a correlation algorithm for condensed phase equilibrium data of ternary systems. *Ind. Eng. Chem. Res.* **2010**, 49 (20), 10100-10110. <http://dx.doi.org/10.1021/ie1010383>.
- [12] Olaya, M.M.; Labarta, J.A.; Serrano, M.D.; Marcilla, A. Vapor-Liquid Equilibria using the Gibbs Energy and the Common Tangent Plane Criterion. *Chemical Engineering Education.* **2010**, 44(3), 236-244. Institutional Repository RUA: <http://hdl.handle.net/10045/24677>.
- [13] Marcilla, A.; Labarta J.A; Olaya, M.M. Gibbs energy of mixing function: topological analysis in azeotropic systems. 27<sup>th</sup> European Symposium on Applied Thermodynamics ESAT **2014**. Institutional Repository RUA: <http://hdl.handle.net/10045/42249>.
- [14] Labarta, J.A.; Olaya, M.M.; Marcilla, A. Mapping Binary Liquid-Vapor or Liquid-Liquid-Vapor Equilibria Regions, including the Different Azeotropic Behaviours, as a Function of the NRTL Binary Parameters. 13th Mediterranean Congress of Chemical Engineering. **2014**. Institutional Repository RUA: <http://hdl.handle.net/10045/42248>.
- [15] Marcilla, A.; Labarta, J.A.; Olaya, M.M. Phase Equilibrium Correlation. Regarding the full consistency of the thermodynamics. 10th World Congress of Chemical Engineering. Barcelona (SPAIN), 1st-5th October, **2017**. RUA: <http://hdl.handle.net/10045/70035>.
- [16] Olaya, M.M.; Carbonell-Hermida, P.; Trives, M.; Labarta, J.A.; Marcilla, A. LLE data correlation using NRTL model for different types of binary systems: UCST, LCST and closed miscibility loops. *Industrial & Engineering Chemistry Research.* **2020**, 59(17), 8469-8479. <https://doi.org/10.1021/acs.iecr.0c00141>.
- [17] Marcilla, A.; Olaya, M.M.; Labarta, J.A. Ensuring that Correlation Parameters for Liquid-Liquid Equilibrium Produce the Right Results (Guest Editorial by editor-in-chief Joan Brennecke). *Journal of Chemical & Engineering Data.* **2018**, 63(5), 1133-11114 (<https://dx.doi.org/10.1021/acs.jced.8b00260>).