

LIQUID-LIQUID EQUILIBRIUM DATA CORRELATION: PREDICTING A ROBUST AND CONSISTENT SET OF INITIAL NRTL PARAMETERS. Graphical User Interface (GUI): ParamIni_LL_NRTL



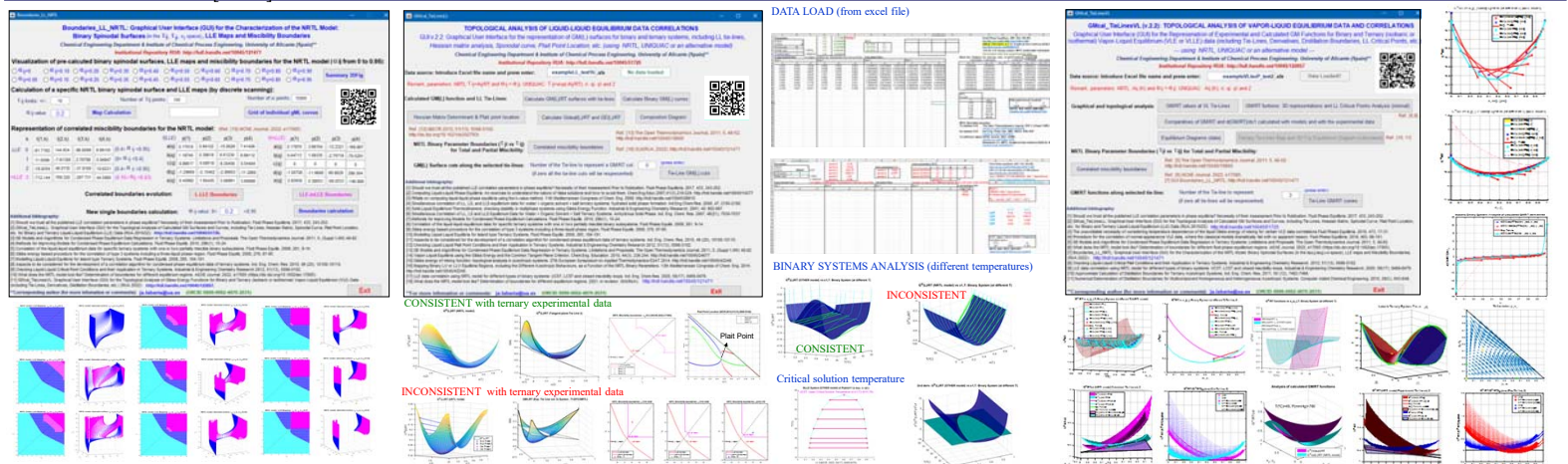
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Introduction: Problem Statement and Previous Helping Tools (for teaching and research) <http://hdl.handle.net/10045/130017>

The synthesis and design of separation processes require the use of models to represent the phase equilibrium data, which involves the previous correlation of the experimental equilibrium data to obtain the values of the corresponding parameters, which have to be consistent with the experimental behavior [1-3]. The correlation of liquid-liquid equilibrium data is still currently a challenging problem not fully resolved [4-11], especially for complex systems such as those involving for instance ionic liquids [12-14], biodiesel [15], 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. At this point, it is also important to remark that parameters of thermodynamic models (such as NRTL and UNIQUAC) that are inconsistent with the experimental behavior that is intended to be correlated can be found in the literature as it has been pointed out previously [1-2,16].

Different tools have been developed to help researchers, professionals, and students that have to deal with phase equilibrium correlation to avoid the intrinsic convergence difficulties of these calculations, reduce the search space, and/or confirm the consistency of the obtained results (interaction parameters) in the whole range of composition. For instance, the Graphical User Interface (GUI) **Boundaries_LL_NRTL** [17,4] allows the visualization of the different LL equilibrium regions and **miscibility boundaries** that present the **NRTL model** in the binary interaction parameters space. The modeling as constraints of these boundaries helps to reduce significantly the search space of the unknown parameters in the correlation process [4]. Other GUIs such as **GMcal_TieLinesLL** [18,1] or **GMcal_TieLinesLV** [19,6-7] allow **checking the consistency** of the parameter obtained in the correlation of binary and ternary LLE or (isobaric or isothermal) LVE experimental data, respectively, by analyzing the topology of the corresponding Gibbs Energy of mixing functions (calculated with NRTL, UNIQUAC or any other alternative model) and its consistency with the equilibrium of the system under study. These tools include also, in the case of the LLE, the analysis of the Hessian matrix, Spinodal curve, and critical point location, and in the case of the LVE, additionally the analysis of the necessity of an additional dependence with the temperature or pressure of the binary interaction parameters, and also the possible existence of distillation boundaries [20-22].



Methodology, LLE database and ParamIni_LL_NRTL GUI

The NRTL model has been analyzed through more than 200 LLE ternary systems (including type I, II, III, and 0 or island, following the Treybal classification) to obtain a good representation of the different possible LLE (i.e. binodal curves, tie triangles, etc.) that this model can reproduce satisfactorily, in a wide enough interval of values of the different parameters (τ_{ij} , α_{ij}). The next figures show different examples of the results obtained in this scanning of the NRTL model, where it is possible to observe several systems with differences in the number of binary subsystems partially miscible, in the size of the LLE region, and even presenting different possibilities of LLE tie-triangles.

The **equilibrium regions** of all these systems have been **parametrized** regarding the main characteristics of the corresponding LLE depending on the classification of the system:

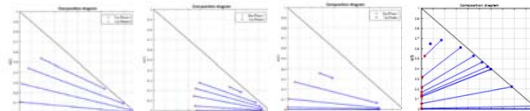
- > **Systems type 1** (with only one binary subsystem partially miscible). In this case, the location and extension of the equilibrium LL regions have been characterized by 5 parameters:
 - Size and average composition of the binary partially miscible (2 parameters)
 - Composition of the plait point (2 parameters)
 - Average slope of the experimental ternary tie lines (1 parameter)
- > **Systems type 2** (with two binary subsystems partially miscible). 6+4 parameters:
 - Size and average composition of the two partially miscible binaries (4 parameters)
 - Maximum size and average slope of the experimental ternary tie lines (2 parameters)
 - Composition of the two plait points, if exit (4 additional parameters)
- > **Systems type 3** (with three binary subsystems partially miscible). 12 parameters:
 - Size and average composition of the three partially miscible binaries (6 parameters)
 - Composition of the three points that configure the tie triangle, or the composition of the different plait points, if exit (6 parameters)
- > **Systems type 0** (with no binary subsystems partially miscible). 8 parameters:
 - Average composition of all the tie lines (2 parameters)
 - Average and maximum size of the tie lines (2 parameters)
 - Composition of the two plait points (4 parameters)

With this parametrization, we have created a database and a new graphical user interface **ParamIni_LL_NRTL** [23] that allows loading a set of liquid-liquid experimental data, to obtain, by comparison with the different elements of the database, a **consistent set of initial NRTL parameters** that predicts the parametrized LLE nearest the experimental one. The topology of the Gibbs Energy of mixing function regarding the behavior of the experimental data studied can be also checked, in order to evaluate the goodness of the binary interaction parameters suggested as an initial point in the corresponding correlation data algorithm.

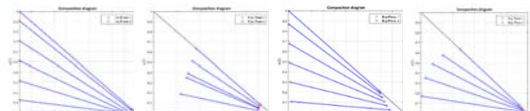
The suggested set of the binary interaction parameters can be used now in any correlation data algorithm (using the corresponding equilibrium condition: isoactivity, minimum of the global Gibbs energy of mixing, or the Gibbs energy of mixing minor common tangent plane) to obtain the final rigorous solution [5,24].

The intention is to periodically update the database with more systems, and also to include the UNIQUAC model, 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.

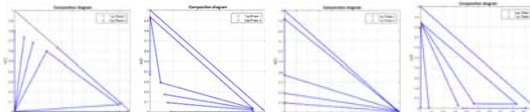
EXAMPLES OF TYPE 1 SYSTEMS:



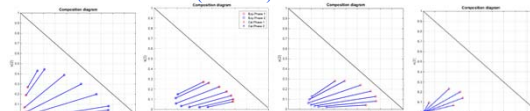
EXAMPLES OF TYPE 2 SYSTEMS:



EXAMPLES OF TYPE 3 SYSTEMS:



EXAMPLES OF TYPE 3 (ISLAND) SYSTEMS:



ACKNOWLEDGEMENTS This project has received funding from the Ministry of Science and Innovation from Spain, under the project PID2021-124139NB-C21: SUS4Energy, 2022/00666/001 (AEI).

References

