Article

# Analysis of Vapor−Liquid Equilibrium in Ternary Systems for an Adequate Planning of Their Experimental Determination and Correlation

Antonio Marcilla, Inés Oliver, Liam Moncur, Paloma Carbonell-Hermida, and María del Mar Olaya*

Cite This: https://doi.org/10.1021/acs.jced.3c00712

Read Online

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

**ABSTRACT:** Experimental vapor−liquid equilibrium (VLE) data, and the activity coefficient model parameters obtained by their correlation, are frequently used in separation processes design. The inspection of this information for ternary systems has revealed some problems that are not widely known and could lead to serious mistakes. A small sampling of ten ternary systems, with VLE data sets at constant pressure, arbitrarily selected has been considered to illustrate these problems. The experimental VLE data and the NRTL model parameters for these systems have been taken from different sources, one database and two commercial simulation packages. A MATLAB code has been developed to prepare 3D graphs where the $T/x$ and $T/y$ surfaces calculated by the activity coefficient model (NRTL) are represented along with the experimental VLE data. The results of the analysis of this small sample are very worrying. In fact, half of the selected systems present severe inconsistences between the experimental VLE data and the $T/x,y$ surfaces calculated using the correlation results published or implemented in the simulation software. These inconsistences are of different natures, but the most notable is the existence of parameter sets that do not correlate at all the VLE behavior of the system that they supposedly represent. These irregularities may occur only in the ternary region, only in the binary subsystems, or, in some cases, in both. These problems go frequently unnoticed for different reasons. As discussed in this work, the typical 2D graphs and deviations in $T$ or $P$ and vapor composition are not enough in some cases so as to have an adequate idea of both the quality of the data and the suitability of the model to represent them. This is particularly true when considering, as is strongly advisable, the complete set of data, i.e. the ternary and binary VLE data simultaneously. Some recommendations are presented in this work to overcome the problems detected both when planning the experimental design to determine VLE data and to correlate them with a model.
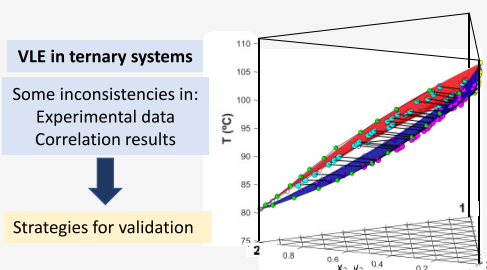
## 1. INTRODUCTION

The availability of phase equilibrium data is of paramount importance for designing separation processes in chemical industry. This importance has been recognized by the scientific and engineering community decades ago, resulting in a significant number of researchers devoted to the experimental determination of phase equilibrium data under different temperature ($T$) and pressure ($P$) conditions; the development of models of a different nature (i.e., activity coefficient models, equations of state) to represent, correlate, and calculate equilibrium data; the proposal of calculation algorithms to solve the related problems; and the compilation of all existing data and its implementation in the simulation packages used by engineers, among other issues.

Regarding vapor−liquid (VL), liquid−liquid (LL), and vapor−liquid−liquid (VLL) equilibria, different approaches have been applied to obtain models capable of representing the fugacity or activity coefficients. Starting with empirical activity coefficient models for the liquid phase, passing to local composition models and equation of states (EOS) to the last models based on molecular simulations, a large number of

equations have been published in literature. They may have different advantages and disadvantages, but in their application to mixtures, a common feature is that all of them require some experimental equilibrium data to calculate their characteristic constants by correlation of such data. Thus, the quality of the experimental equilibrium data and the reliability of the model parameters obtained in their correlation are compulsory to obtain confident results in the design and simulation of separation processes.

In previous works, the lack of flexibility to correlate certain types of phase equilibrium behaviors, including both LLE and VLE, has been discussed,[1−4] and also the lack of reliability of certain published parameters that may lead to inexistant equilibrium regions, false solutions, and other problems of a

different nature.[5,6] Since commercial databases of model parameters used by the simulation software include many of these problematic or inconsistent parameters, severe problems may arise when working with the corresponding systems. Consequently, it would be very convenient to use additional tools to validate the equilibrium data, and the model parameters obtained, prior to entering them into any database.

Considering VLE in binary systems, though the way of reporting the experimental and calculated equilibrium data may be improved, it may be easy to have an idea of the experimental data quality, its degree of dispersion, and the reliability of the model parameters obtained. Nevertheless, when working with VLE in ternary systems, the situation is not as easy since it is more difficult, from the usual way of reporting the data, to have a reference to quantify the dispersion of the experimental equilibrium data and the quality of their fitting.

Additionally, when obtaining VLE data in ternary systems, it is a common practice to attempt the correlation of ternary equilibrium data exclusively, instead of carrying out the simultaneous correlation of ternary and binary VLE data. Consequently, the parameters obtained may provide a poor representation of the VLE in the binary subsystems included in the ternary system, as well as in those regions where no experimental equilibrium data have been obtained. Additionally, as it is very well-known, all models have severe limitations for representing certain equilibrium behaviors.

Thus, the objective of the present work is to review the way VLE data for ternary systems are reported and fitted by models, as well as the associated problems and inconsistences, to enable a clear analysis of the quality of these data and to suggest procedures to improve it. With this aim, a short sampling exercise has been carried out using VLE data for ten ternary systems randomly chosen from the DECHEMA database.[7,8] Later the study has been extended to some of the most popular simulation packages such as Aspen Plus[9] and CHEMCAD[10] with the objective of checking the model parameters included in them for the ten ternary systems selected and the possible problems that could arise associated with the VLE calculations.

We would like to remark that nothing in this work is really new, that some of these problems have been discussed in previous papers (e.g., in ref 11), and also that many researchers obtain experimentally excellent VLE data and provide checked model parameters that adequately reproduce the phase equilibrium behavior in all of the composition domains of ternary systems. Nevertheless, our previous experience, and the results of this short sampling exercise, has encouraged us to write this work that may be considered as a wake-up call, in order to correct the problematic situation detected in a non-negligible number of cases, with the ultimate goal of obtaining more representative VLE experimental data and model parameters for process design and simulation.

## 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

**2.1. How VLE Data Are Usually Reported.** There may be different way to report VLE data. A good example, very well-known for those working with phase equilibrium data, is the excellent DECHEMA Data Collection.[12] This database is one of the most used references for searching phase equilibrium data, in general, and VLE in particular, and is used in commercial simulation and design packages. The volumes devoted to binary VLE data typically present the following: the components and conditions of the experiments (i.e., constant temperature or pressure); the literature reference of the data; the Antoine

**Table 1. Ternary Systems Selected for Inspection of the Experimental and Calculated VLE Data at Atmospheric Pressure**

| System | Components |
|---|---|
| S1 | heptane (1) + cyclohexane (2) + toluene (3) |
| S2 | hexane (1) + benzene (2) + toluene (3) |
| S3 | hexane (1) + benzene (2) + chlorobenzene (3) |
| S4 | hexane (1) + benzene (2) + p-xylene (3) |
| S5 | hexane (1) + methylcyclopentane (2) + benzene (3) |
| S6 | hexane (1) + 1-hexene (2) + 1,2,3-trichloropropane (3) |
| S7 | hyclohexane (1) + cyclohexene (2) + 1,2-dichloroethane (3) |
| S8 | benzene (1) + cyclohexane (2) + toluene (3) |
| S9 | isoprene (1) + 2-methyl-2-butene (2) + acetonitrile (3) |
| S10 | isoprene (1) + 2-methyl-2-butene (2) + cyclopentadiene (3) |

constants for the pure component vapor pressures; the pass/no pass of certain thermodynamic consistency tests (object of some discussion[13−17]); the tables with the experimental equilibrium data; the corresponding parameters as well as the differences in $T$ (or $P$) and in the vapor mole fraction ($y$), provided by the different models used to correlate the experimental VLE data; finally, the $y/x$ graph where the experimental vapor and liquid mole fractions in equilibrium are plotted together with the $y/x$ curve obtained by the activity coefficient model providing the best correlation (i.e., that providing the lower deviations).

This way of reporting the VLE data for binary systems allows, in a quick view of the $y/x$ graph, to get a certain idea of the data dispersion and the quality of the fitting, although it should be complemented with the $T/x,y$ or the $P/x,y$ diagram (experimental and provided by the selected model) to have the complete information on such data.

The situation with VLE for ternary systems is rather different, partly due to a single graph does not allow a clear image of the dispersion of the data but mainly because other problems are present. The way the ternary VLE data are presented in the DECHEMA Data Collection,[12] and in many other references, includes a 2D triangular graph where the experimental VLE tie lines are reported. No reference to singular points (azeotropes) is usually explicitly specified. Besides, these singular data, and those for the three binary subsystems included in the ternary system, are not usually included in the correlation of the ternary VLE data. Besides, the experimental VLE data sets do not always cover all of the composition domain. This way of measuring, presenting, and fitting experimental VLE data seems quite incomplete and could lead to inconsistent parameters as it will be shown in this work. No idea about the dispersion of the experimental data or the quality of their correlation can be easily obtained from such representation. Obviously, low mean and maximum deviations in $T$ (or $P$) and $y$ (mole fraction) should suggest a good correlation, but this is not always true because additional problems may arise. In the present work, some examples of such problems are presented and discussed, some of them being the consequence of the common practice of correlating exclusively ternary VLE data, not including the VLE data for the three binary subsystems that compose the ternary system. Thus, it could be possible to obtain low deviations between the experimental and calculated equilibrium data in the ternary region, but the model parameters obtained predict VLE for the binary subsystems very differently from the real (experimental) ones. Furthermore, if the ternary VLE data do not cover all of the equilibrium domain, inexistant equilibrium regions may be also predicted by the parameters.
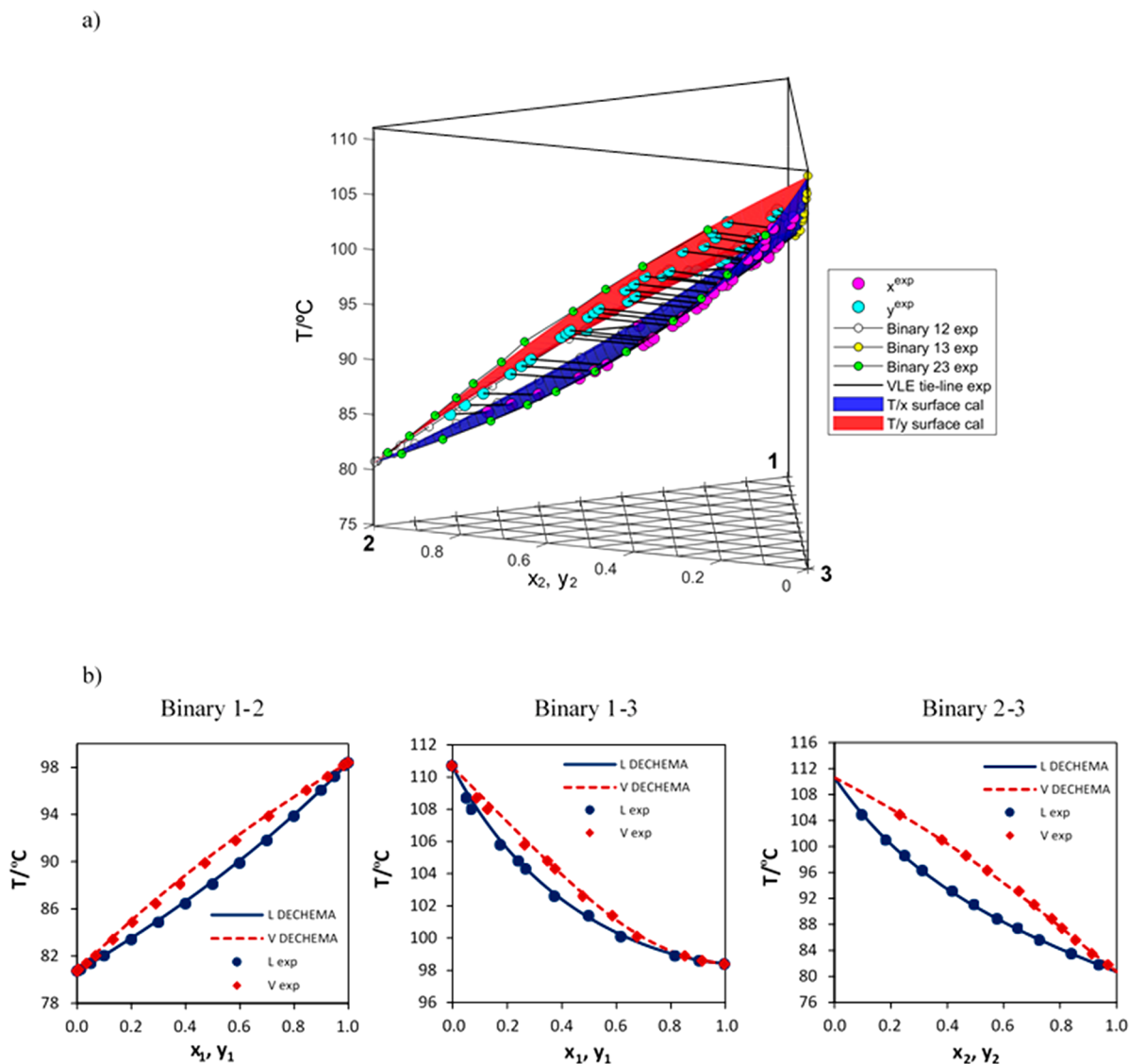
a)



b)



**Figure 1.** VLE $T/x,y$ diagram for system S1 showing the calculated surfaces and curves using the NRTL parameters published in DECHEMA for the ternary system:[7] (a) ternary system and (b) binary subsystems.

**2.2. Suggested Validation Procedure.** Obviously, the problematic situation that has been previously presented seems to need an improvement. The quality of the data, and that of the corresponding correlation parameters, should be checked before they are published and included in any data bank. Thus, the following steps are suggested to analyze the data reported in a different way (other similar ones could be used with the same objective):

1. Plot the experimental VLE data for the ternary system in a 3D $T/x,y$ or $P/x,y$ graph susceptible of being rotated.
2. Calculate the $T/x,y$ or $P/x,y$ data by the activity coefficient model selected and the parameters obtained in the correlation of the experimental VLE data in all of the composition domain, *including the binary subsystems*.
3. If not measured, try to locate the experimental VLE data for the three binary subsystems included in the ternary system under the same $T$ or $P$ conditions, as well as possible singular points as azeotropes (homogeneous or heterogeneous).
4. Calculate the boiling points ($T$ or $P$) of the pure components using, e.g., the Antoine constants.

5. Plot all these data in the same 3D graph and analyze the results.

This procedure provides a reference to judge the dispersion of the experimental data, the quality of the correlation, the compatibility of the ternary correlation with the binary VLE data, and to get a clear idea if such data (experimental VLE data and model parameters) could be validated to be included in a data bank. If not, other measures should be taken as explained later.

Some additional procedures to verify the mathematical modeling adequacy have already been proposed, as the construction of a projection of the temperature surface, i.e. an isothermal−isobar diagram, or characteristic lines of constant distribution coefficients or relative volatilities on the composition triangle.[11]

**2.3. Systems, Model, and Parameters Selected.** In the present section, the suggested procedure has been applied to analyze a sampling of ten ternary systems (Table 1) with VLE data sets at constant pressure (760 mmHg). The experimental VLE data for these systems have been taken from DECHEMA Data Collection (Vol. I Part 6a and Vol. I Part 6c).[7,8] Three
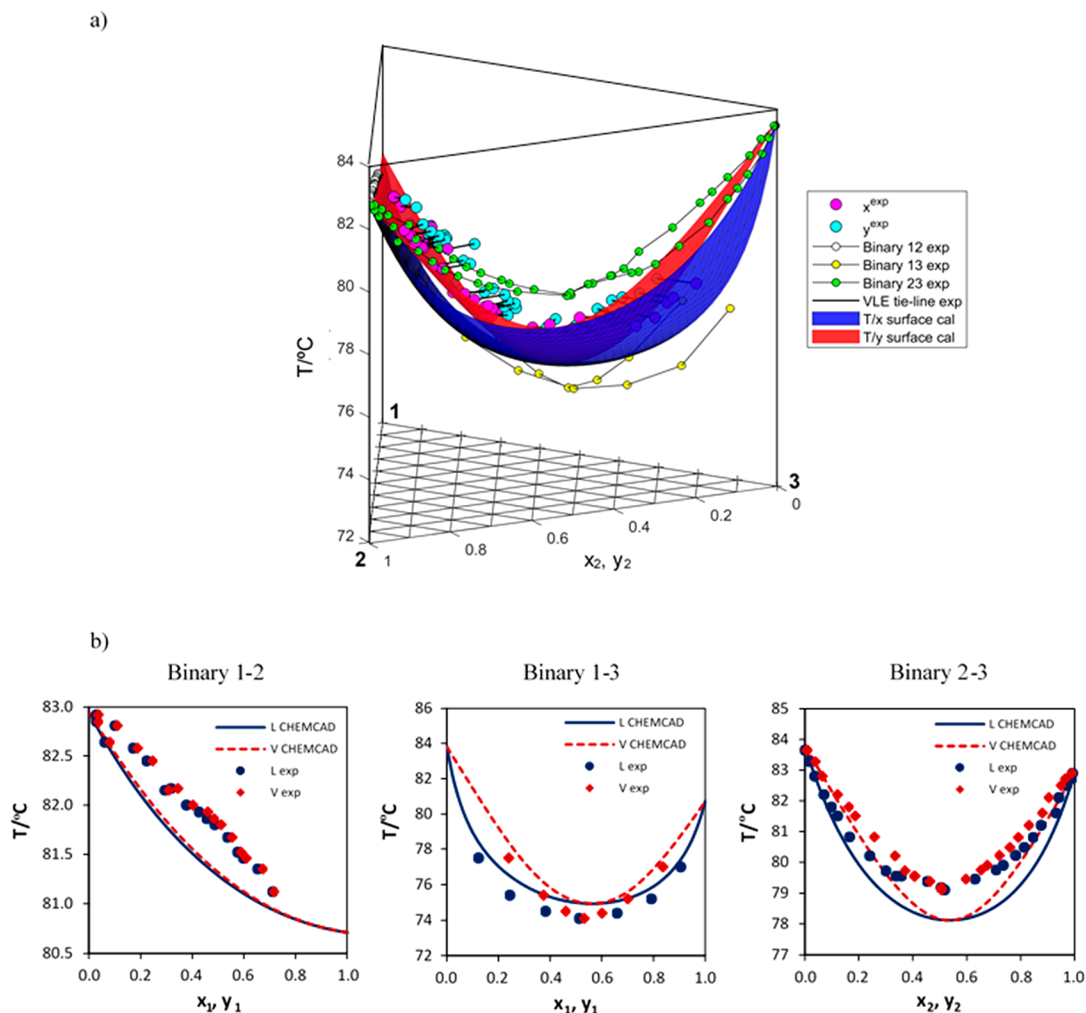
c

**Figure 2.** VLE $T/x,y$ diagram for system S7 showing the calculated surfaces and curves using the NRTL parameters implemented in CHEMCAD:[10] (a) ternary system and (b) binary subsystems.

different sources for the model parameters of these systems have been analyzed: DECHEMA Data Collection, and two process simulators, Aspen Plus and CHEMCAD. The comparison between different activity coefficient models (Wilson, NRTL, and UNIQUAC) presented in the first of these sources demonstrated that the one providing the best correlation results in most cases was NRTL (eqs 1−3). Thus, the NRTL model was chosen for this study, also for the analysis of the parameters included in the two simulation packages. However, it would be taken into account that the activity coefficient model used is not relevant for the discussion presented in this work, because similar conclusions would be obtained using any other classical activity coefficient model. The equations for the NRTL model are the following:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{\sum_k G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_r \tau_{rj} G_{rj} x_r}{\sum_k G_{kj} x_k} \right) \quad (1)$$

$$\tau_{ij}/\text{dimensionless} = a_{ij} + \frac{b_{ij}}{T} \quad (2)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (3)$$

where $\gamma_i$ is the activity coefficient of component $i$; $\tau_{ij}$ (dimensionless), $a_{ij}$ (dimensionless), and $b_{ij}/K$ are the binary

interaction parameters of the model; $x_i$ represents the mole fraction of component $i$; $\alpha_{ij}$ is the nonrandomness parameter; and $T$ is the temperature in K.

The NRTL parameters that the three data sources provide for the ten ternary systems are summarized in Table S1 (Supporting Information). In this table, two different parameter sets appear for the DECHEMA database, those obtained from VLE data correlation of the ternary system and those from VLE data correlation of the binary subsystems. In the two simulation packages, Aspen Plus and CHEMCAD, only one set of NRTL binary interaction parameters appears for each pair of compounds, independently of the type of mixture (binary, ternary or multicomponent) in which they are going to be used.

Moreover, a MATLAB[18] code has been developed to prepare 3D graphs, susceptible to being rotated, in which the equilibrium temperature (vertical axis) is represented versus the liquid ($x$) and vapor ($y$) compositions (mole fractions) in a prism of triangular basis. In this domain, the experimental VLE tie lines are represented along with the $T/x$ and $T/y$ surfaces calculated by the activity coefficient model (NRTL) using the parameters reported and the corresponding MATLAB code. These surfaces provide a *certain* reference to evaluate the dispersion of the experimental data, as well as the quality of their fitting. Basically, the code performs bubble point calculations. First, a square mesh is created (each side corresponding to $x_1$ and $x_2$ mole
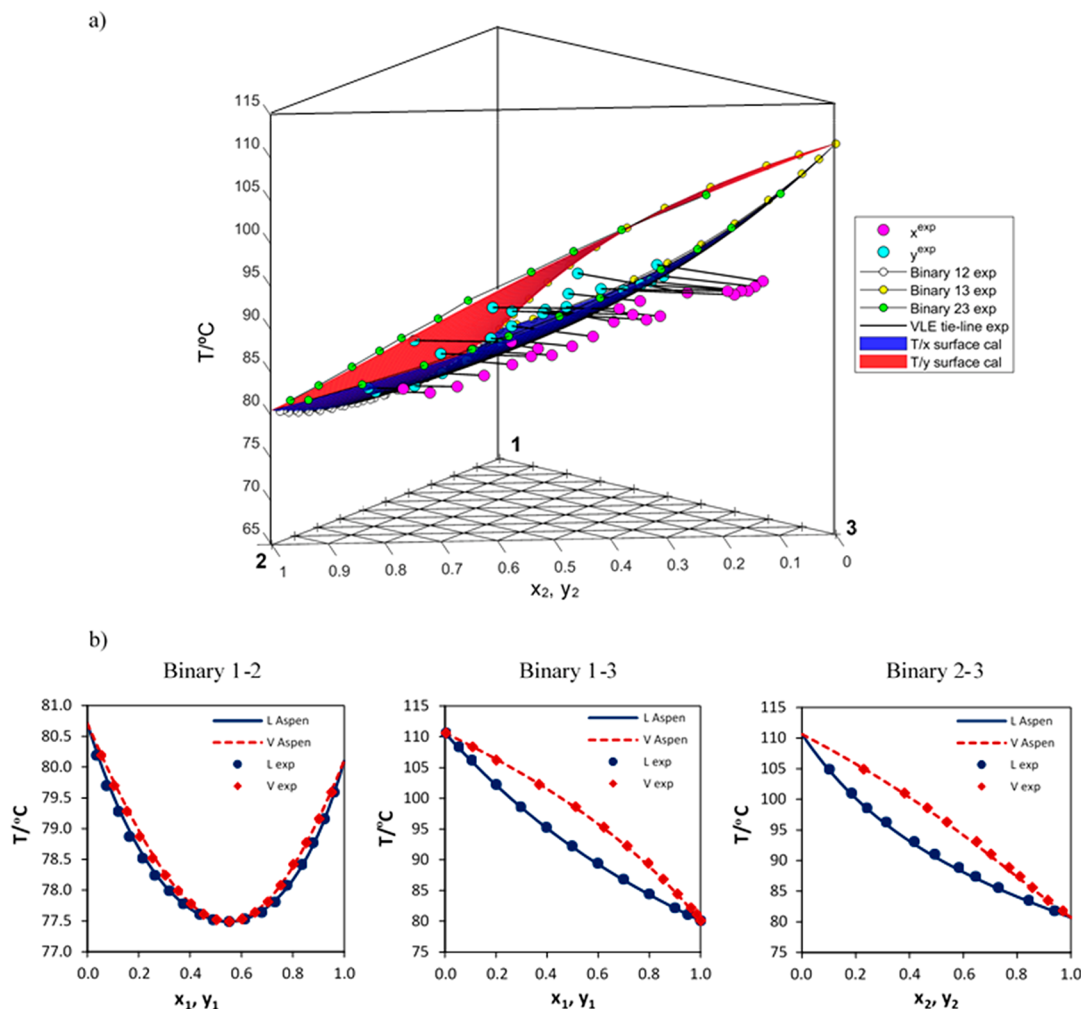
**Figure 3.** VLE $T/x,y$ diagram for system S8 showing the calculated surfaces and curves using the NRTL parameters implemented in Aspen Plus:[9] (a) ternary system and (b) binary subsystems.

fractions) and from it, by using trigonometric transformations, an equilateral triangular mesh is obtained. Bubble temperature calculations are then performed to calculate the VLE of the system. This requires a function file in which the variable to optimize is the bubble temperature ($T_b$) and an initial guess of this variable in the main file. The objective function is the fulfilment of the mass balance in the vapor phase. The MATLAB code performs this calculation for each point of the mesh and once each $T_b$ is obtained, the vapor composition is determined, thus obtaining the points that will form the calculated $T/x$ and $T/y$ surfaces.

Besides, the experimental VLE data for the three binary subsystems included in each ternary system have also been located[7,8,19,20] and represented along with those calculated using the different sets of NRTL parameters obtained by correlation of the ternary VLE data, with the aim of checking their compatibility.

## 3. RESULTS AND DISCUSSION

3D graphs using the MATLAB code previously described have been generated for the ten ternary systems selected using the NRTL parameter sets included in the three sources previously cited. After analyzing these figures, it is concluded that for five of the ten ternary systems (S1−S5) acceptable correlation results are obtained regardless of the source of the parameters, although

some improvements could be possible in some cases. However, for the other five systems (S6−S10), which represent half of the sample size, very questionable results of different natures are present, i.e., experimental data scattering, prediction of inexistent equilibrium regions, and high discrepancy between the experimental VLE for the binary subsystems and those calculated using the ternary parameters, among others.

Next, some examples are presented to illustrate these statements. As an example of one system providing acceptable results of the ternary VLE data, system S1 is shown in Figure 1. Figure 1a shows a view of the 3D $T/x,y$ graph calculated using the NRTL parameters from DECHEMA database along with the experimental VLE data.[7,8] The rotation of this figure allows to confirm an acceptable agreement between the calculated surfaces for the vapor and liquid phases and the experimental points. Figure 1b shows the three binary subsystems of the S1 ternary system. It is observed that the experimental VLE data and those calculated using the NRTL parameters obtained from the ternary VLE data correlation are compatible with each other. For systems S2 to S5 quite similar conclusions were obtained as, in principle, it would be expected for all systems.

In contrast, Figures 2, 3 and 4 show three examples of systems (S7, S8 and S10) whose NRTL parameter sets, accessible through CHEMCAD and Aspen Plus simulation software, and DECHEMA database, respectively, provide very poor and
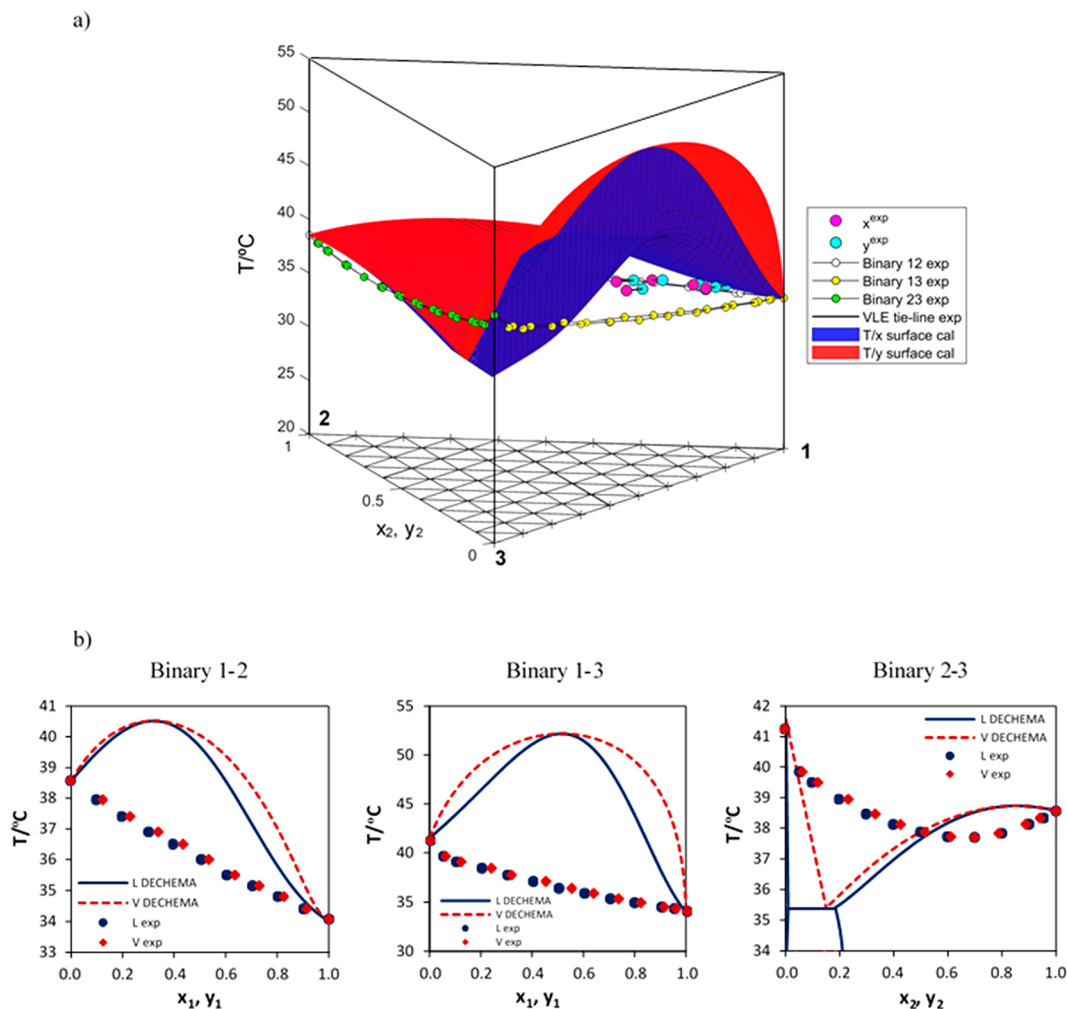
**Figure 4.** VLE $T/x,y$ diagram for system S10 showing the calculated surfaces and curves using the NRTL parameters published in DECHEMA for the ternary system:[7] (a) ternary system and (b) binary subsystems.

inconsistent results. Figure 2a shows that the NRTL parameter set available in CHEMCAD provides calculated $T/x,y$ liquid and vapor surfaces that are very far from the compositions of the liquid and vapor phases in equilibrium. The representation also shows that the deviations between experimental and calculated equilibrium data are not randomly distributed as it would be desirable. Almost all experimental equilibrium points are "out" and far of the calculated surfaces, invalidating this correlation result. In Figure 2b the deviations between the calculated and experimental VLE data in the three binary subsystems of the S7 system are shown, which are also not correctly represented by the parameters. In the example represented in Figure 3, the experimental VLE data for system S8, are represented along with the NRTL parameters that, for this system, are implemented in Aspen Plus software. These parameters adequately represent the VLE for the three binary subsystems, as shown in Figure 3b. However, the VLE behavior in the ternary region is wrongly represented by the parameters (Figure 3a). In the last selected example, the experimental VLE data for the S10 system have been represented along with those calculated using the NRTL parameter set given in DECHEMA database. In this case, the differences between experimental and calculated equilibrium data are particularly high, to the point that the parameters do not represent at all the ternary VLE data nor the binary subsystems. The calculated 1−2 and 1−3 binaries present a maximum

boiling point azeotrope each and the binary 2−3 a heterogeneous azeotrope that are not present in the experimental VLE behavior. So, not only the deviations in temperature and composition become very high, but also the *type* of behavior can be very different.

Beyond the specific examples selected to be represented in the previous figures, the deviations between the experimental VLE data and those obtained using the NRTL parameters have been calculated for all cases. These deviations (eqs 4 and 5) include mean and maximum (max) differences in temperature ($\Delta T$) and in vapor mole fraction ($\Delta y_i$):

$$\Delta T = |T^{exp} - T^{cal}| \tag{4}$$

$$\Delta y_i = |y_i^{exp} - y_i^{cal}| \tag{5}$$

The calculated deviation values for all selected systems are summarized in Table S2, for the ternary composition region, and in Tables S3−S5, for the binary subsystems using the NRTL parameter sets from the DECHEMA database, Aspen Plus, and CHEMCAD, respectively. They have also been represented in Figures 5 and 6 for the ternary systems S1−S10 and for their corresponding binary subsystems, respectively. Considering exclusively the ternary region of the systems, the maximum values of mean $\Delta T$ have been obtained for the S8 system with parameters from CHEMCAD (4.38 °C) and Aspen Plus (3.71
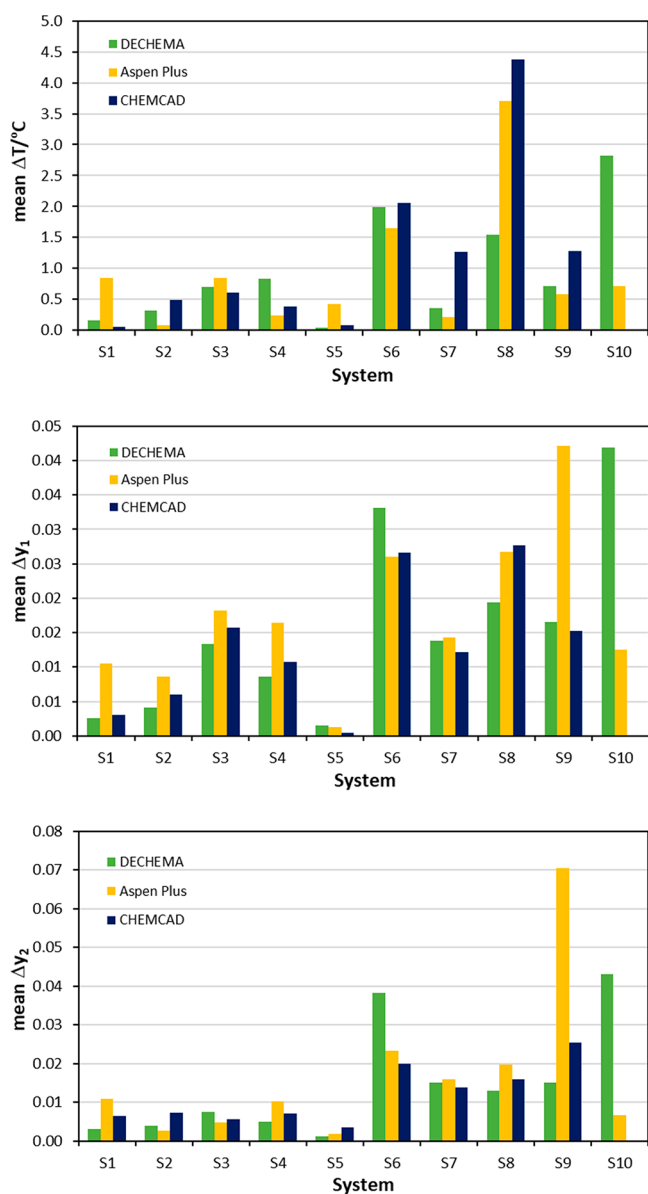
**Figure 5.** Mean deviations in temperature ($\Delta T$) and mole fraction ($\Delta y_i$) between the experimental and calculated (NRTL) VLE data for the selected ternary systems (S1−S10). Sources for the parameters: DECHEMA, Aspen Plus, and CHEMCAD.

°C) followed by S10 (2.82 °C) using the parameters from DECHEMA. For system S10 there is not results from CHEMCAD because the NRTL parameters for one of the binary subsystems (2−3) were not available. The maximum values of the mean $\Delta y_1$ have been obtained for S9 from Aspen Plus (0.0421) and S10 from DECHEMA (0.0419). For mean $\Delta y_2$, the maximum values are obtained for S9 with parameters from Aspen Plus (0.0705) and for S10 (0.0431) and S8 (0.0383) from DECHEMA. With regard to the binary subsystems included in the ternary systems S1−S10, deviations are generally lower using parameters from the process simulation software than from the databank with NRTL parameters obtained from ternary VLE data, as would be expected if binary interaction parameters implemented in process simulation software have been obtained from binary VLE data. To highlight some data, mean deviations in temperature are higher than 2 °C for some binary subsystem in S4, S6, S8, and S10 ternary systems. On the

other hand, mean deviations in mole fraction are higher than 0.03 for S4, S6, S8, and S10 systems. For the S9 system it was not possible to find experimental VLE data for the binary subsystems 1−3 and 2−3 in DECHEMA database, so deviations for S9 could not be calculated using this source for the parameters.

Obviously, the use of parameters that present these types of problems for process design and simulation would have serious consequences on the results. However, although this problem has been previously discussed in literature (e.g., in ref 11) seems to go unnoticed in many cases, in part because the numerical values for deviations can be insufficient (or not sufficiently striking) to qualify the correlation results. Besides, there may be a widespread tendency of taking for granted that data and parameters, published or implemented in a software, are necessarily valid, unless explicitly stated otherwise. These worrying results advise the necessity of planning a strategy to validate the published VLE data and parameters for ternary systems, as well as to determine new ones, since not all data and parameters being published, or included in the simulation packages, have been adequately checked from this point of view. The results obtained in this work confirm some of the conclusions presented in the work by Frolkova et al.[11]

As has been shown, one of the reasons leading to the problematic situations that are present in ternary VLE data determination and correlation is the fact of not including VLE data for the binary subsystems, along with the fact that many papers report ternary VLE data in restricted regions of the composition domain, not covering it systematically. It would be convenient that these two aspects were considered and corrected when planning the experimental design. Nevertheless, the second aspect, i.e., trying to systematically cover all of the composition domain of the ternary mixture, may be not an easy task since it requires a previous knowledge of the expected VLE behavior of the system. Thus, it would be convenient to try to get a close idea of such equilibrium behavior before starting the experiments. This recommendation has been translated to the following procedure that could be applied in the experimental determination and correlation of ternary VLE data:

1. Determine experimentally, or locate in the literature, the boiling points of the pure components and the VLE data of the three binary subsystems involved in the ternary system.
2. Pay especial attention to the singular points (i.e., homogeneous or heterogeneous azeotropes) that could be present in the system.
3. Correlate the VLE data for the three binary subsystems and calculate (predict) the ternary VLE diagram with the model parameters obtained in the binary data correlation.
4. Calculate, with this same set of parameters, adequate isothermal (isobaric) sectional planes and study, in each of them, the existence of ternary azeotropes and distillation boundaries.
5. With all of the previous information, plan the experimental design to systematically cover all phase equilibrium regions and all of the composition domain.
6. Correlate simultaneously the pure components, binary and ternary VLE data of the system at constant pressure (or temperature).
7. Plot all of the data together, along with the $T/x$ and $T/y$ (or $P/x$ and $P/y$) surfaces calculated by the activity coefficient model using the parameters obtained in the previous step.
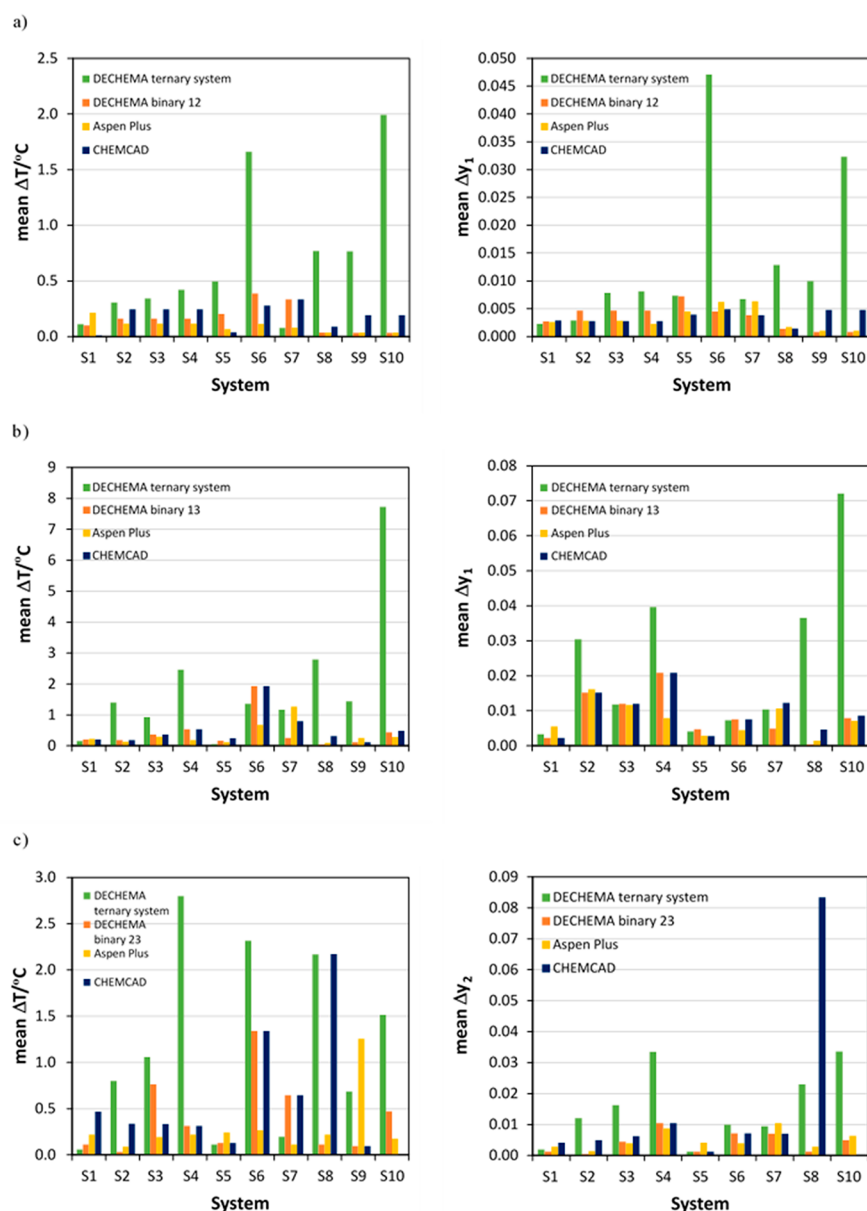
**Figure 6.** Mean deviations in temperature ($\Delta T$) and mole fraction ($\Delta y_i$) between the experimental and calculated (NRTL) VLE data for the selected ternary systems (S1−S10): (a) binary 1−2, (b) binary 1−3, and (c) binary 2−3. Model parameter sources: DECHEMA, Aspen Plus, and CHEMCAD.

8. Analyze the dispersion of the experimental VLE data and the quality of the correlation.

9. If required, repeat those VLE data that could be necessary until a reasonable dispersion is obtained.

10. Once confident with the VLE data, if the correlation result is not satisfactory with any of the classical activity coefficient models, would be possible to try some modifications, such as including the temperature or pressure dependence of the parameters as well as ternary terms or association contributions in the excess Gibbs free energy.

By following a procedure of this type, the incidence of problematic VLE data and inconsistent parameters as those detected in the preliminary sampling exercise would be significantly reduced.

The general ideas presented in this work could be extended to systems with a higher number of components (e.g., quaternary

systems). Besides, these ideas do not depend on the specific model used to represent the activity coefficient; i.e., the same cautions should be taken for all of them.

## 4. CONCLUSIONS

The analysis of the experimental VLE data and the correlation results (NRTL) for a small sample of ten ternary systems from different sources, one databank and two process simulation software, all of them very valuable tools commonly used by chemical engineers, shows that half of the systems present questionable results of a different nature. These problems, which may lead to dramatic errors when attempting design calculations, are not new. However, they are much more frequent and serious than usually thought, as shown in the examples discussed in the present work. One of these problems is that, in some cases, the experimental VLE data for ternary systems do not cover systematically all of the ternary

composition domain and consequently the parameters obtained from their fitting are only valid in a restricted area of compositions, without any specific warning about it. A particular case of this is the publication of parameters obtained from correlation of ternary VLE data that do not include data of the three binary subsystems. These parameters usually produce nonacceptable VLE results in the corresponding binary subsystems. In some cases, not even the ternary VLE data are adequately represented by the parameters supposedly obtained from their correlation and published as such. All of these problems seem to go unnoticed for different reasons. One of them could be that graphical representations are not so frequent, or not complete, for ternary VLE. Besides, the numerical values for deviations (in temperature or pressure, and composition) could be insufficient, in some cases, to qualify the correlation results. Moreover, it is generally thought that data and parameters, published or implemented in a software, are necessarily valid, without restrictions, for any calculation where they were required. The results obtained from this analysis warn of the necessity of planning a strategy to validate the published VLE data and parameters for ternary systems, as well as that to determine new ones. Some recommendations are presented in this work to overcome the problems discussed, almost all of them already known but frequently ignored. Among them, it could be highlighted that only reliable VLE data sets should be fitted by a model and, in the specific case of ternary VLE, these data should be combined with binary and pure components data for their simultaneous correlation, to obtain a parameter set representative of the VLE behavior *in all of the composition domain*.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.3c00712.

Supplementary Tables S1−S5 (published NRTL parameters; temperature and mole fraction deviations) and Figures S1 and S2 (VLE $T/x,y$ diagrams) (PDF)

## AUTHOR INFORMATION

### Corresponding Author

**María del Mar Olaya** − *Institute of Chemical Process Engineering and Department of Chemical Engineering, University of Alicante, 03080 Alicante, Spain;* orcid.org/0000-0001-8068-9562; Email: maria.olaya@ua.es

### Authors

**Antonio Marcilla** − *Institute of Chemical Process Engineering and Department of Chemical Engineering, University of Alicante, 03080 Alicante, Spain*

**Inés Oliver** − *Institute of Chemical Process Engineering, University of Alicante, 03080 Alicante, Spain*

**Liam Moncur** − *Faculty of Engineering, University of Strathclyde, Glasgow, Scotland G1 1XQ, United Kingdom*

**Paloma Carbonell-Hermida** − *Institute of Chemical Process Engineering, University of Alicante, 03080 Alicante, Spain;* orcid.org/0000-0001-9046-9678

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jced.3c00712

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

## NOMENCLATURE

$a_{ij}$, $b_{ij}$  binary interaction parameters of the NRTL model
LLE  liquid−liquid equilibrium
P  pressure (Pa or kPa)
T  temperature (K or °C)
$T_b$  bubble temperature (K or °C)
VLE  vapor−liquid equilibrium
VLLE  vapor−liquid−liquid equilibrium
$x_i$  mole fraction of component $i$ in liquid phase
$y_i$  mole fraction of component $i$ in vapor phase

### Greek Symbols

$\alpha_{ij}$  nonrandomness parameter of the NRTL model
$\Delta$  deviation
$\gamma_i$  activity coefficient of component $i$
$\tau_{ij}$  binary interaction parameter of the NRTL model (dimensionless)

### Superscripts

cal  calculated
exp  experimental

### Subscripts

b  referred to bubble temperature
i, j, k, r  components

## REFERENCES

(1) Marcilla, A.; Olaya, M. M.; Reyes-Labarta, J. A.; Carbonell-Hermida, P. Procedure for the correlation of normal appearance VLE data, where the classical models dramatically fail with no apparent reason. *Fluid Phase Equilib.* **2019**, *493*, 88−101.

(2) Marcilla, A.; Olaya, M. M.; Reyes-Labarta, J. A. The unavoidable necessity of considering temperature dependence of the liquid Gibbs energy of mixing for certain VLE data correlations. *Fluid Phase Equilib.* **2018**, *473*, 17−31.

(3) Marcilla Gomis, A.; Reyes-Labarta, J. A.; Serrano Cayuelas, M. D.; Olaya López, M. M. GE Models and Algorithms for Condensed Phase Equilibrium Data Regression in Ternary Systems: Limitations and Proposals. *Open Thermodynamics Journal* **2011**, *5*, 48−62.

(4) Marcilla, A.; Olaya, M. M.; Serrano, M. D.; Reyes-Labarta, J. A. Methods for improving models for condensed phase equilibrium calculations. *Fluid Phase Equilib.* **2010**, *296*, 15−24.

(5) Marcilla, A.; Olaya, M. M.; Reyes-Labarta, J. A. Ensuring That Correlation Parameters for Liquid-Liquid Equilibrium Produce the Right Results. *J. Chem. Eng. Data* **2018**, *63*, 1133−1134.

(6) Marcilla, A.; Reyes-Labarta, J. A.; Olaya, M. M. Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication. *Fluid Phase Equilib.* **2017**, *433*, 243−252.

(7) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-liquid Equilibrium Data Collection: Aliphatic Hydrocarbons C4-C6*; Chemistry Data Series, Vol. *I*, Part 6a; DECHEMA: Frankfurt, Germany, 1997.

(8) Gmehling, J.; Onken, U.; Kolbe, B. *Vapor-liquid Equilibrium Data Collection: Aliphatic Hydrocarbons (Supplement 1)*; Chemistry Data Series, Vol. *I*, Part 6c; DECHEMA: Frankfurt, Germany, 1983.

(9) *ASPEN-PLUS: Chemical Process Optimization Software*. Version 12.2; Aspen Technology: Cambridge, MA, release 2021.

(10) *CHEMCAD: Chemical Process Engineering Software*. Version 8.1.1.17611; Chemstations: Houston, TX, release 2023.

(11) Frolkova, A. V.; Fertikova, V. G.; Rytova, E. V.; Frolkova, A. K. Evaluation of the adequacy of phase equilibria modeling based on various sets of experimental data. *Fine Chem. Technol.* **2022**, *16*, 457−464.

(12) *Vapor-liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA, Frankfurt, Germany.

(13) Herington, E. F. G. A Thermodynamic Test for the Internal Consistency of Experimental Data on Volatility Ratios. *Nature* **1947**, *160*, 610−611.

(14) Redlich, O.; Kister, A. T. Algebraic representations of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(15) Herington, E. F. G. Test for the consistency of experimental isobaric vapor-liquid equilibrium data. *J. Inst. Pet* **1951**, *37*, 457−470.

(16) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-Liquid Equilibrium: Part. I. An Appraisal of Data Reduction Methods. *AIChe J.* **1973**, *19*, 238−244.

(17) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapour-Liquid Equilibria Using UNIFAC, A Group-Contribution Method*; Elsevier: Amsterdam, 1977. DOI: 10.1016/B978-0-444-41621-6.X5001-7.

(18) *MATLAB*, Release 2023a (R2023a); The MathWorks: Natick, MA,2023.

(19) Gmehling, J.; Onken, U. *Vapor-liquid Equilibrium Data Collection: Aliphatic Hydrocarbons C4-C30*; Chemistry Data Series, Vol. *I*, Part 6d (in conjunction with Part 6e): DECHEMA: Frankfurt, Germany, 1999.

(20) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-liquid Equilibrium Data Collection: Aromatic Hydrocarbons*; Chemistry Data Series, Vol. *I*, Part 7; DECHEMA: Frankfurt, Germany, 1997.