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Comments & Replies

Comments on Liquid−Liquid Equilibrium Data Regression

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The aim of this letter is to remark on the importance of the rigorous fulfillment of the isoactivity criterion when tie-lines are calculated during the correlation of experimental liquid−liquid equilibrium (LLE) data, which seeks the optimum set of binary parameters for the model used to formulate the activity coefficients (i.e., NRTL, UNIQUAC, ...). As will be presented below, we have found some papers and also one process simulation software package where an inconsistent procedure for LLE regression is used that leads to apparent solutions which are not tie-lines (i.e., with different activities in each phase wrongly assumed to be at equilibrium) and lie very far from the true values.

The equilibrium condition states the equality of chemical potentials for each component in all phases present, which translates into the equality of activities (the isoactivity criterion) whenever all phases are in the same aggregation state at constant temperature and pressure. In the case of LLE, the following equation must be satisfied

$$a_i^{\mathrm{I}} = a_i^{\mathrm{II}} \quad \text{or} \quad \gamma_i^{\mathrm{I}} \cdot x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} \cdot x_i^{\mathrm{II}} \tag{1}$$

where a_i^P, γ_i^P, and x_i^P are the activity, activity coefficient, and mole fraction of component *i* in phase *P* (I and II denote liquid phases), respectively.

The representation of the dimensionless Gibbs energy of mixing ($g^{\mathrm{M}} = G^{\mathrm{M}}/RT$) versus composition defines a curve/surface/hypersurface, depending on the number of components in the system, i.e., two, three, or more components. Gibbs proved that a necessary and sufficient condition for absolute stability of a mixture (M) at a fixed temperature, pressure, and overall composition is that the Gibbs energy of mixing (g^{M}) curve/surface/hypersurface at no point lies below the line/plane/hyperplane tangent to the surface at a given overall composition (x_i). A more modern explanation and derivation of this condition was given in other references.[1,2]

Figure 1a shows a qualitative representation of the g^{M} curve versus composition for a partially miscible pair, where x_1^{I} and x_1^{II} are the equilibrium compositions (common tangent line). Figure 1b shows a qualitative representation of a typical triangular phase diagram (top face) and the Gibbs energy of mixing surface for a type 1 (Treybal classification) ternary system, where the LLE tie-lines correspond to the two conjugated points having a common tangent plane to the g^{M} surface. If a cross-section of the g^{M} surface through one of the tie-lines is examined, the g^{M} line between the equilibrium compositions must be tangent to the curve at the equilibrium points to satisfy the minor tangent plane criteria, in a way similar to that shown in Figure 1a for a binary system.

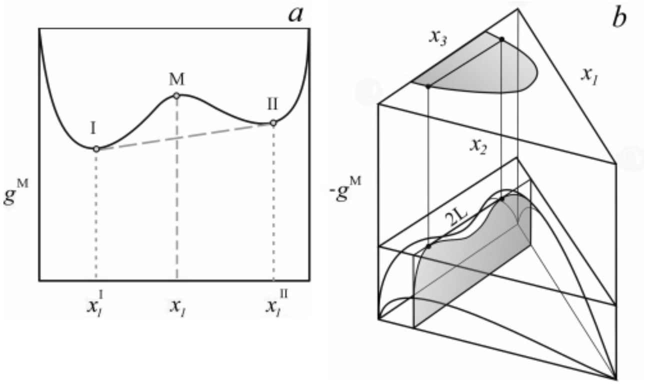

Figure 1. Qualitative representation of the dimensionless Gibbs energy of mixing (g^{M}) function versus composition for (a) a binary system and (b) a ternary system.

Therefore, LLE calculations can be carried out using the necessary but not sufficient isoactivity criteria or the necessary and sufficient minor common tangent condition. If the first criterion is used, a stability test must be performed to check that a stable and not a metastable solution has been calculated. The isoactivity criterion is in practice the most frequently used equilibrium condition in LLE calculations.

For example, the procedure used in the Liquid−Liquid Equilibrium Data Collection DECHEMA Chemistry Data Series,[3] which is applied by many authors to make equilibrium data regressions, considers the following objective functions. The activity objective function (OF(*a*))

$$\mathrm{OF}(a) = \sum_j \sum_i (a_{ij}^{\mathrm{I}} - a_{ij}^{\mathrm{II}})^2 \tag{2}$$

The concentration objective function (OF(*x*))

$$\mathrm{OF}(x) = \sum_j \min \sum_i [[(x_{ij} - x_{ij}^{\mathrm{calcd}})^2]^{\mathrm{I}} + [(x_{ij} - x_{ij}^{\mathrm{calcd}})^2]^{\mathrm{II}}] \tag{3}$$

where *i* refers to each component and *j* refers to the tie-line.

They start the parameter estimation using OF(*a*) since this requires no qualified guess of the parameters. After convergence, they shift to the OF(*x*) which is in agreement with the goal of fitting the experimental concentrations.

We would like to emphasize two very important points:

(1) The OF(*a*) with experimental mole fractions may only be used as a simplification in the first steps of the regression procedure. However, it must be pointed out that, for a given set of parameters, this condition will not give *real* equilibrium compositions for the model used, unless the calculated and experimental compositions accidentally coincide.

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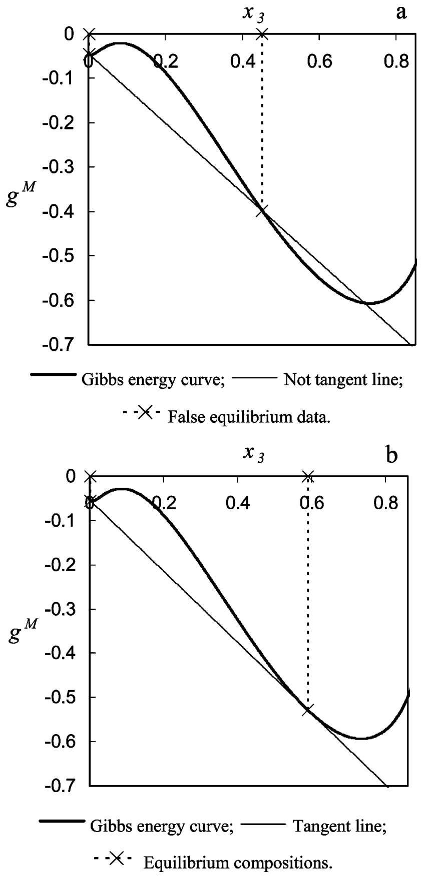

Figure 2. Dimensionless Gibbs energy of mixing (g^M) versus composition (molar fraction) (a) on a false published tie-line[10] and (b) on a true tie-line that fulfills the minor common tangent criterion.

(2) The calculated mole fractions x_{ij}^{calcd} in OF(x) must be those obtained when solving the equation OF(a) = 0 for a given set of parameters and where the experimental compositions x_{ij} should *not* be introduced to calculate the activity coefficients.

Therefore, although at the beginning of the correlation procedure OF(a) can be used in the following form

$$\text{OF}(a) = \min \sum_j \sum_i (\gamma_{ij}^{\text{I}}(x_{ij}^{\text{I}})\cdot x_{ij}^{\text{I}} - \gamma_{ij}^{\text{II}}(x_{ij}^{\text{II}})\cdot x_{ij}^{\text{II}})^2 \qquad (4)$$

where $\gamma_{ij}^{P}(x_{ij}^{P})$ denotes that the activity coefficients γ_{ij}^{P} are calculated as a function of the experimental mole fractions x_{ij}^{P} (i = component, P = I or II liquid phases, j = tie-line) and OF(a) cannot be zero (unless purely by chance), the calculation procedure must finish using the following equation

$$\text{OF}(a) = \sum_j \sum_i (\gamma_{ij}^{\text{I}}(x_{ij}^{\text{calcd,I}})\cdot x_{ij}^{\text{calcd,I}} - \gamma_{ij}^{\text{II}}(x_{ij}^{\text{calcd,II}})\cdot x_{ij}^{\text{calcd,II}})^2 = 0 \qquad (5)$$

to obtain the calculated compositions x_{ij}^{calcd} for each set of parameters. Such calculated compositions, which solve eq 5, are those to be compared with the experimental ones in OF(x). That is, the optimization method must determine the best set of parameters for the model that minimize the composition deviations of eq 3 between calculated and experimental data, but where the x_{ij}^{calcd} are real equilibrium compositions. This condition is satisfied by solving eq 2, which must be equal to zero (minimum is not enough), as is indicated in eq 5. Therefore, the two objective functions (eqs 2 and 3) are not comparable at all. The isoactivity condition is a requirement (necessary condition) that must be imposed to obtain calculated compositions for a given set of parameters and therefore must be zero or extremely small. However, the composition objective function would only decrease as far as the model is capable of reproducing the experimental behavior, a condition that depends on many factors, such as the quality of the experimental data or the capability of the model to reproduce the desired behavior, among others. For many published LLE data regressions, the OF(x) value is usually not small enough. Therefore, it is not an acceptable practice to promote a decrease in the OF(x) value by "relaxing" the isoactivity requirement OF(a) for the calculated tie-lines because:

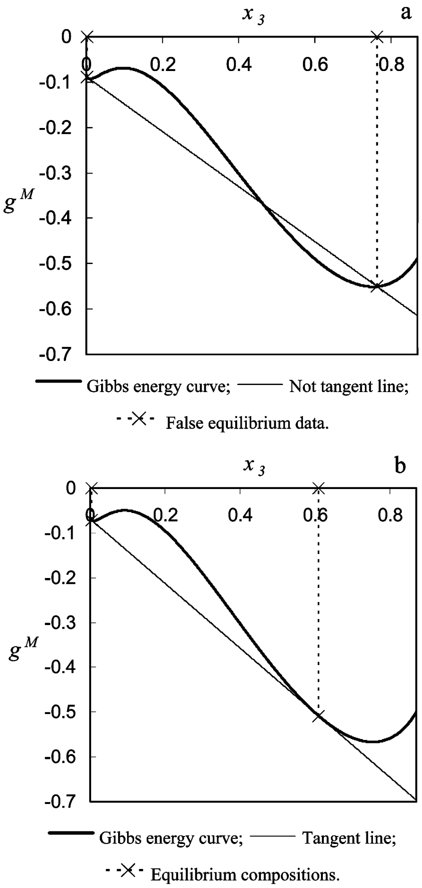

Figure 3. Dimensionless Gibbs energy of mixing (g^M) versus composition (molar fraction) (a) on a false published tie-line[7] and (b) on a true tie-line that fulfills the minor common tangent criterion.

(1) The calculated compositions would not be the real tie-lines corresponding to the model and the binary parameters obtained, which is inconsistent.

(2) When the regressed parameters are used to calculate LLE data, the tie-lines obtained would be different from those obtained in the regression.

(3) The calculated parameter values set (i.e., NRTL, UNIQUAC, ..., parameters) would probably be improved if the true calculated equilibrium compositions are compared with the experimental ones.

Despite the fact that the above-stated ideas are widely known, the acceptance of simplifications during regression calculations is surprisingly common. Many authors do not give details about their equilibrium calculation steps, and in some cases, it has even been found that published calculated compositions given as a result of the correlation are not real equilibrium compositions (eq 2 is not fulfilled). If simplifications are made during correlations and isoactivity is not strictly required or checked, the calculated compositions obtained may not be *real equilib-*

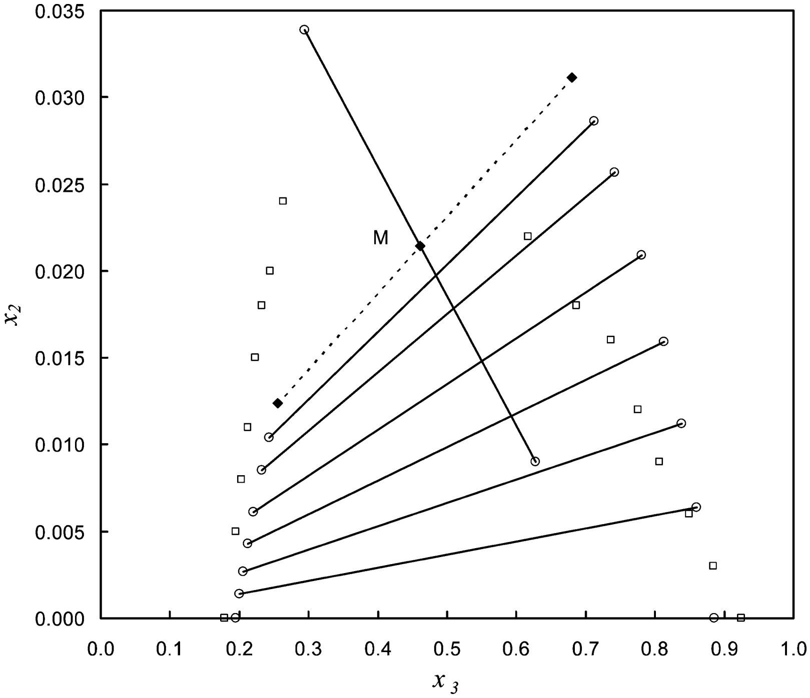

Figure 4. LLE data for the ternary system methanol (1) + diphenyl amine (2) + cyclohexane (3) at 25 °C. Experimental and calculated data (ChemCAD regression) together with the re-calculated tie-line obtained with the Flash Unit for the global mixture M (in mole fractions). □, experimental data; −○−, tie-lines (ChemCAD regression); --◆--, LLE flash unit; ◆, global mixture for LLE flash unit.

Table 1. False Tie-Lines and Their Equivalent True Tie-Lines (Obtained Using the Midpoint of the False Tie-Line as the Mixture Point), Including the OF(*a*) Values[a]

		phase I		phase II		
tie-line reference		x_1	x_3	x_1	x_3	OF(a)
10	false published tie-line	0.98857	0.00225	0.48139	0.45200	0.05372
	true tie-line	0.98595	0.00240	0.33029	0.58949	$5.38 \cdot 10^{-9}$
7	false published tie-line	0.9810	0.0019	0.1690	0.7637	0.3716
	true tie-line	0.98370	0.00372	0.32999	0.61005	$4.77 \cdot 10^{-9}$

[a] In mole fractions.

rium compositions; the accuracy of the regression is distorted; and neither standard deviation nor any other data fit indicator obtained is valuable.

After we discovered some published papers where this inconsistency appeared, a bibliographic search was carried out to determine the frequency of this inadequate procedure. To make this verification, it was necessary that the papers included not only the values for the activity coefficient model parameters but also the calculated compositions. This requirement noticeably decreased the number of articles available for checking. We had not intended to find all the papers with this kind of inconsistency but only to check those encountered with all the information required. The *Journal of Chemical & Engineering Data* and *Fluid Phase Equilibria* were used as sources of information, and a total of seven papers were checked.[4−10]

Only in two of the seven papers reviewed[8,9] did all the calculated tie-lines fulfill the Gibbs energy minor common tangent criterion. In the other four papers,[4,6,7,10] more than 35 % of the calculated tie-lines were thermodynamically inconsistent. One paper[5] had only incorrectly calculated tie-lines. To quantify the consequences of this inconsistent practice, the deviation between the falsely calculated tie-lines published in the reviewed papers and the true ones was calculated. To do that, the isoactivity criterion was rigorously applied to calculate true LLE compositions, obtaining deviations as high as 28 % in component mole fraction, which obviously cannot be neglected.

The following two examples (two incorrectly calculated tie-lines) corresponding to different papers and authors (Figures 2 and 3) are used to illustrate the above discussion. In these figures, the dimensionless Gibbs energy of mixing curve is plotted against x_3 on the cross-section that contains the incorrectly calculated tie-line. Also, the straight line that connects the g^M values of the wrong LLE compositions has been graphically represented. Such a line must be tangent to the Gibbs energy curve at both conjugated equilibrium points, according to the necessary and sufficient equilibrium condition of the minor common tangent plane.[11] However, it can be observed in Figures 2a and 3a that the line which connects the calculated tie-line is secant and therefore is not a true tie-line. Consequently, the corresponding OF(a) is not small enough to consider the equilibrium requirement to be fulfilled (Table 1). To check the difference between the correctly calculated tie-lines and the incorrect published ones having the same parameters, the isoactivity criterion was rigorously applied to the mixture defined by the midpoint of the line given by the published conjugated compositions. The g^M versus x_3 cross-sections obtained for the two previous examples are represented in Figures 2b and 3b, where the lines connecting the conjugated phases have also been represented. It can be seen that calculated tie-lines are now tangent to the Gibbs energy curve as is required by the equilibrium condition and also that the values for the activity objective function (OF(a)) are extremely small, indicating isoactivity. All incorrect conjugated compositions and

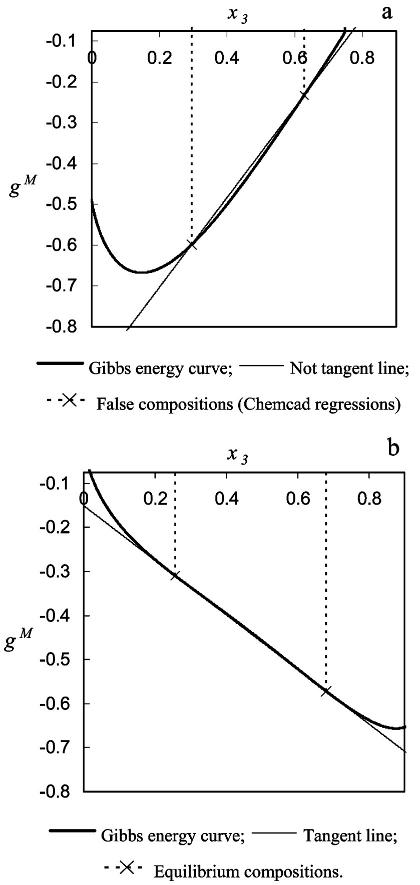

Figure 5. LLE phase splitting for the global mixture M: (a) incorrect tie-line (ChemCAD regression) and (b) correct tie-line (ChemCAD Flash Unit) (in mole fractions).

correctly calculated tie-lines together with OF(a) values for the two examples are arranged in Table 1.

All these frequent inconsistencies in the LLE data regression may be caused by inconsistent use of the equilibrium requirement together with the experimental and calculated mole fraction comparison and demonstrate the evident absence of stability verification. The application of the results obtained using this inconsistent practice is obviously unproductive.

On the other hand, apart from correlation results published, a widely used commercial process simulator such as ChemCAD (Chemstations Inc.)[12] has been tested as far as equilibrium calculations are concerned. It includes phase equilibrium calculation strategies that are capable of overcoming the most important difficulties encountered when dealing with equilibrium calculations, but unfortunately, it does not include details about its internal procedures. It has been proved that globally stable solutions are always found using the Flash Unit with LLVS option. However, the Binary Interaction Parameter (BIP) regression tool does not work properly in some cases: when some LLE ternary systems were regressed, certain calculated tie-lines were obtained that do not satisfy the equilibrium conditions, although the program guarantees convergence. If those "incorrect" tie-lines are recalculated running an LLE flash and using the midpoint of the incorrect conjugated phases as the input mixture, a correct tie-line is obtained.

In Figure 4, the ternary system methanol (1) + diphenyl amine (2) + cyclohexane (3) at 25 °C is shown as an example to illustrate this inconsistency. In this figure, the experimental data for this system are represented together with a convergent regression result given by the ChemCAD Regression Tool using NRTL to formulate the activity coefficients. The binary parameters obtained are: $A_{12} = 973.66$, $A_{21} = -1186.80$, $A_{13} = 296.54$, $A_{31} = 575.61$, $A_{23} = -1038.90$, $A_{32} = -912.45$ ($\alpha = 0.2$). The upper calculated tie-line is obviously incorrect. If the dimensionless Gibbs energy (G^M/RT) given by NRTL is represented along the last incorrect ternary tie-line given by ChemCAD, the minimum common tangent criterion is not satisfied: the compositions of the incorrect tie-line do not have the lowest global energy and therefore do not represent a stable solution (Figure 5a). The same representation for the recalculated tie-line shows that the minimum common tangent criterion is now satisfied (Figure 5b). The midpoint M ($x_1 = 0.51765$, $x_2 = 0.02145$, $x_3 = 0.4609$) of the incorrect tie-line obtained in the regression of the LLE data has been used as input for a splitting calculation in ChemCAD's Flash Unit to recalculate the tie-line, obtaining the correct result that fulfills the isoactivity and stability criteria (Figure 5b).

Phase equilibria calculation is a complex matter which involves overcoming many pitfalls. In the LLE regressions, the calculated compositions must be real equilibrium compositions and, therefore, must satisfy the isoactivity condition, although they may be very different from the experimental data. For any set of parameters involved in the regression procedure, the equilibrium compositions must be calculated to compare them with experimental ones. Besides, a global stability test must be used to guarantee the stability of the solution.

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