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Robust program for LLSE data correlation of ternary systems

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Abstract

The existing commercial software packages (like Dechema Data Preparation Package (DPP) and the regression utilities of Chemical Engineering simulators like Chemcad) have been widely used and their extensive capabilities are well-known. Nevertheless, and as long as LLE calculations is concerned, they have been designed for the simplest equilibrium behaviour. For example, for ternary systems it is only possible the correlation of type 1 and type 2 LLE data. None of these applications allows for the correlation of type 0 LLE, type 3 LLLE or type 4 LLSE systems. To enable a possible extension of such software, a robust calculation algorithm to compute phase equilibria among condensed phases for all these more complicated behaviours has been developed.

1. Introduction

Existing software packages like DPP (Dechema) or utilities of equilibrium calculation of simulators like Chemcad (Chemstations) have multiple capabilities. Nevertheless, due to the complex nature of phase equilibria for certain ternary systems, they are restricted to type 1 and 2 ternary systems (LLE) and do not have the capability to correlate type 0 LLE systems, type 3 LLLE systems or type 4 LLSE systems.

Besides, these tools do not allow finding out about their internal procedure details. It is only possible to change some of their parameters (iteration limits, definition of deviation, etc.) and most of them can only be used with the classical models (NRTL, UNIQUAC) . Chemcad does not permit the implementation of any model modifications and DPP allows the utilization of user-defined models but, it is restricted to type 1 and 2 ternary systems. These programs, in case of lack of convergency during correlation of LLE data, which frequently occurs, do not permit to find out if it is due to the initial set of parameters proposed, to a lack of capability of the model itself, to an algorithm error or to a problem of the numerical method used. This information, though, would be really valuable to improve the regression process and to guarantee that the result obtained is the best possibility that the chosen model can provide. In a previous work, some important problems related to the correlation of type 1 ternary systems were discussed [1].

To overcome all these limitations, a robust calculation algorithm to compute phase equilibria among condensed phases of ternary systems (LLE, LLLE, LLSE, etc.) has been developed to avoid inconsistencies along the phase equilibrium calculations, to test new models and to improve the correlation results. Figure 1 shows an schematized flow chart of this program. Its

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main characteristics and advantages are highligthed in the next sections. It must be noticed that the program has been developed for ternary systems, but the same algorithm could be extended to four or more components.

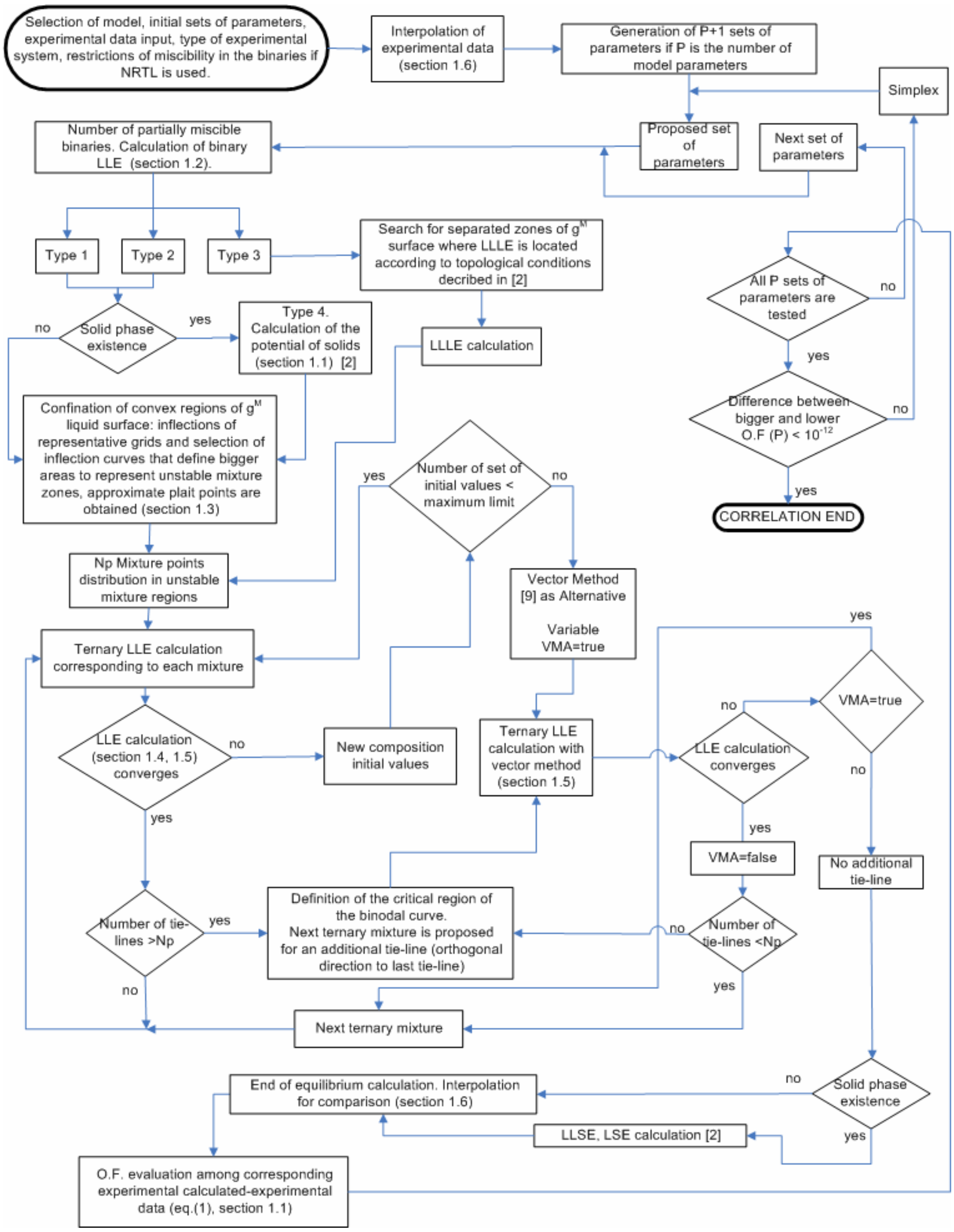

***Figure 1**. Flow chart of the simultaneous equilibrium calculation algorithm generalized to type 1, 2, 3 and 4 ternary systems. More details for most of the intermediate steps are developed in the corresponding sections in this paper, as indicated in this figure.*

2. Program scope and novelties

The program scope comprises the data correlation of equilibrium among condensed phases for ternary systems: LLE, LSE, LLSE, LShE, LLShE and LSShE; being L=liquid, S=solid and Sh=hydrated solid.

2.1. Simultaneous correlation for all the equilibrium regions.

According to the flow chart in Figure 1, the parameters of whatever classical or user-defined models are obtained via simultaneous correlation of the equilibrium data for all the regions present for the system at constant T and P. The main advantage of simultaneous correlation is that the parameters obtained can be used in any composition region of the diagram.

The reference state for all the components of the system to calculate the Gibbs energy of mixing (g^M) is the pure liquid component at the same T and P of the system:

- When the system only contains liquid phases, the Gibbs energy for the liquid mixtures g^M is formulated by the selected model. According to restrictions of miscibility (section 1.2) of the three binary subsystems, LLE (and LLLE if appropriate) regions are calculated according to the flow chart in Figure 1. The special case of type 3 ternary systems (with LLLE tie-triangle) correlation is included with an algorithm based on geometric aspects related to the g^M [2].

- If solid phases are present, the Gibbs energy for the anhydrous solid (g^S) is calculated as the chemical potential change from the pure liquid to the pure solid at the system T and P conditions, using a thermodynamic cycle [3]. If hydrated solids (Sh) are present, their Gibbs energy of formation with respect to the reference state (hypothetical subcooled molten salt and liquid water) is calculated using a resemblance of salt hydration to gas adsorption on solid surfaces (BET multilayer gas adsorption model) as it is propossed by Zeng and Voigt [4].

The optimization of the parameters to be calculated via simultaneous correlation of the equilibrium data for all the regions of the system LLE, LSE, LLSE, LShE, LLShE, LSShE is carried out with the Simplex Flexible method defining the objective function (eq.(1)) as the minimization of the sum of the differences between *comparable* calculated and experimental molar fractions. The explanation of the criterium of comparison, that is novelty of this work and presents important advantages, is dealt in section 1.6. The O.F. is generally expressed as the sum of two contributions: LLE region ($O.F_{LL}$), and the regions where a solid (anhydrous or hydrated) is present in the equilibrium ($O.F_{LS}$):

$$O.F. = O.F_{LL} + O.F_{LS} = \min\left\{ \sum_{n=1}^{nLL} \sum_{i=1}^{3} \sum_{P=1}^{Np} \left[\left(x_{i,n,P}\right)_{exp} - \left(x_{i,n,P}\right)_{cal} \right]^2 + \sum_{n=1}^{nLS} \sum_{i=1}^{3} \left[\left(x_{i,n,L}\right)_{exp} - \left(x_{i,n,L}\right)_{cal} \right]^2 \right\} \tag{1}$$

where $x_{i,n,P}$ is the molar fraction of component i in phase P for the LL tie-line n and and $x_{i,n,L}$ is the molar fraction of component i in the liquid phase L of LS tie-line n; nLL and nLS denote the number of tie-lines in the LL and LS regions, respectively; subscripts exp and cal respectively denote the experimental and calculated equilibrium data. For the correlation of tie-triangle data, we consider them to be divided into three pairs of conjugated compositions.

2.2. Total or partial miscibility restrictions.

In the proposed program, inconsistent behaviours are avoided restricting parameters to total or partial miscibility of each binary subsystem, according to the type of the experimental system to be correlated (Treybal classification). The procedure avoids the comparison of experimental equilibrium data with calculated ones defined by a set of parameters that, despite describing accurately certain equilibrium region, could be inconsistent with the miscibility behaviour of the binary subsystems included in the multicomponent system [5]. A boundary between the two zones of the binary interaction parameter values was defined for the NRTL model that separates the total (L) and partial (LL) miscibility behaviour [6]. That boundary defines a restriction which guarantees that NRTL binary parameter values always correspond to the imposed miscibility behaviour. When a different model is used, splitting is tested for the three binary systems and the proposed set of parameters is used when their behaviour is consistent with the experimental data. Dechema database [7] does not take care of these considerations when regressing experimental data and this sometimes leads to incoherent results, for example, a type 2 ternary system is correlated with binary NRTL parameters that give three partially miscible (type 3) binary subsystems (Dechema Vol. 2, page 71) or a type 1 ternary system is correlated with binary parameters that give two partially miscible (type 2) binary subsystems (Vol. 2, page 436).

2.3. LLE restriction to concave regions

The separation between convex and concave regions of the g^M ternary surface are calculated approximately in the program for each parameter iteration. So, the equilibrium compositions to be calculated can be restricted to concave regions to avoid trivial and multiple solution problems and the necessity of using very good initial values for the parameters [8].

The optimum direction for searching inflections would be the one defined by each tie-line. In this case the curve of inflections would coincide with the binodal curve at the plait point. Since the slope of the tie-lines is not known in advance, six different grids are defined to guarantee a complete study of the g^M surface. Those grids are explored by following these representative directions (constant x_1, x_2, x_3, x_3/x_2, x_1/x_2, x_1/x_3). Each one of them defines g^M sections where pairs of inflection points, that define changes of curvature, are searched. The selected grid, whose directions are closer to the slopes of tie-lines, is the one that provides a curve of inflection points comprising a greater convex area.

Unstable mixture compositions are homogeneously distributed in each convex area following the line defined by the middle point of each pair of inflections. LLE is searched for each unstable mixture, restricting the composition zones where the conjugated LLE phases must be located outside the inflection points curve. Fig. 2 shows an example of an iteration during the regression process, still far from an adequate fitting, that illustrates the detection of inflections on the surface by three grids (constant x_2, x_1/x_2, x_3/x_2), being that at constant x_2 the one that comprises a greater convex area. Mixture points homogeneously distributed together with calculated tie-lines, for the given set of parameters, are represented. More data shown in the same figure will be described in sections 1.5 and 1.6.

2.4. Minimum tangent plane equilibrium condition.

The K-value method, which imposes equality of chemical potentials as equilibrium condition, is frequently used to formulate phase equilibria conditions. Nevertheless, it was proved in a previous work [9] that this method can result in multiple solutions that seem to satisfy the isofugacity condition, being local Gibbs energy minima. The phase equilibria conditions used in the proposed program are based on the common tangent plane criterium, which avoid multiple solutions often encountered by the K-value method. Such a procedure simultaneously solves orthogonal derivatives, the tangent plane equations, and the mass balances [8,10].

Newton-Raphson is the numerical method used to solve all the phase equilibria conditions. This method is strongly dependent on initial guesses, and the non-linearity of the equations complicates the convergency of the method to a great extent. Special attention is paid to these difficulties: initial parameters are chosen to be coherent with the system behaviour (1.2), trivial solutions are not allowed (1.3) and different sets of initial values are tested if the method fails to converge for a maximum number of iterations. Besides, an alternative “guided” method (section 1.5.) for calculating ternary LLE is implemented to overcome convergence failures.

The Complex Step Derivative Approximation Technique [11] is used to precisely generalize numerical first and second derivatives in the Newton-Raphson method to solve the tangent plane equations, avoiding the necessity to program extensive analytical expresions.

2.5. Vector method used as alternative for calculation and for the accurate definition of the critical region of the binodal curve.

The vector method [9] is used as an alternative to overcome possible convergency failures during LLE calculations even when, for different sets of initial values, the resolution of tangent plane conditions still fails. This method is also used to accurately define the binodal curve close to the plait point. Once the equilibrium is calculated for all ternary mixtures homogeneousy distributed in the approximate unstable region (1.3), more mixture points are proposed moving slightly, following an orthogonal direction, from the last calculated ternary tie-line. The vector method is repeatedly used for mixtures proposed using the same criterium until failure of convergence is produced.

2.6. Different criterium of comparison between calculated and experimental data.

The phase equilibrium data correlation procedure to obtain the values for the parameters of a model requires the comparison between some experimental and calculated equilibrium data using the objective function defined by eq.(1).

Unlike LVE calculations, where the phase splitting occurs in all the composition region, in the LLE only a restricted composition area for two liquid phases exist (tie-lines region). The location and size of the calculated LLE region depend on the values for the parameters of the model in each iteration and, therefore, can be very far of the experimental one when the process is starting or when the model is not very adequate for that system.

The selection of the criteria used to define the calculated tie-line that is comparable with each experimental one in the objective function is very important because inconsistent situations can occur. Some of the criteria used to calculate equivalent LLE data have been: the tie-line that passes through the mixture point obtained as the middle point of the experimental tie-line, or the tie-line with a molar fraction of one component in one phase set as the experimental one. These two criteria can give situations, depending on the parameters values in a given iteration, where the program is trying to find the calculated LL equilibrium in homogeneous areas of composition, for example when the calculated LLE region is smaller or it is too displaced from the experimental one. Fig. 2 shows a situation of an iteration during a regression process, still far from an appropriate fitting, where any trial with x_2>0.45 will not converge. This fact causes convergence failures that can prevent a convenient correlation result.

To avoid this important limitation we have included in the algorithm proposed a new and robust criterion for the comparison of the experimental and calculated data. For a given set of parameters, among all calculated tie-lines (section 1.3 and 1.5) for each convex region, a representative number of them is homogeneously obtained by interpolation. A corresponding set of interpolated experimental data is also obtained so that both sets can be orderly compared to obtain the O.F. (eq. (1)). Experimental, calculated and interpolated data, for the specified set of parameters, are represented in Figure 2.

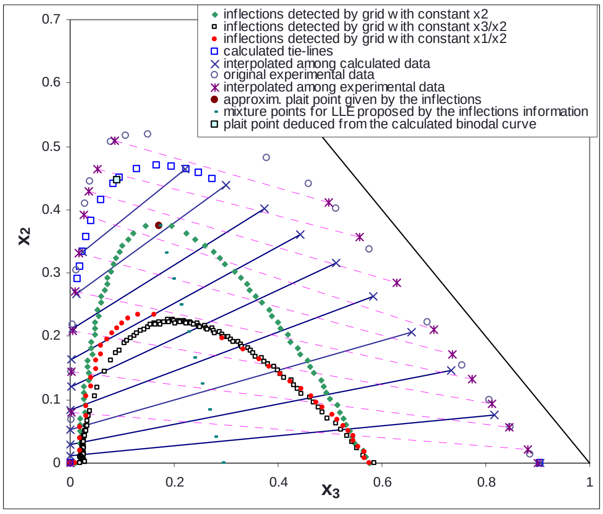

***Figure 2**. Intermediate step of correlation for a ternary type 1 experimental system [7], still far from an appropriate fitting. NRTL binary parameters being tested are: A_{12}=-50, A_{21}=-300, A_{13}=2887.02, A_{31}=-182.37, A_{23}=-50, A_{32}=-1000, α_{12}=0.1, α_{13}=0.12, α_{23}=0.1, T=25ºC. Inflections are found with grids corresponding to constant x_2, x_1/x_2 and x_3/x_2 directions. Original and interpolated experimental and calculated data are represented.*

3. Conclusions

A robust calculation algorithm to simultaneously compute the phase equilibria between condensed phases of ternary systems, has been developed to overcome the lack of flexibility of the existing software dealing with equilibrium among condensed phases, to avoid inconsistencies in the phase equilibrium calculations, to improve the correlation results obtained with the classical models and to test new more capable ones.

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