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# Identification of UNIQUAC Binary Interaction Parameters in Liquid-Liquid Equilibrium

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## Abstract

An algorithm is presented for the estimation of the UNIQUAC interaction parameters for liquid-liquid equilibrium of ternary systems. The algorithm is based on two optimization levels. In the inner level the algorithm performs the minimization of an objective function based on the isoactivity conditions. The outer level aims to minimize the error between calculated and experimental compositions. The Common Tangent Plane condition is checked at the end to guarantee a thermodynamically consistent representation of the phase behavior of ternary liquid systems.

The algorithm is challenged with a historical Type 1 ternary liquid-liquid equilibrium system from the seminal study of Anderson and Prausnitz in which the authors showed the limitations of the original UNIQUAC model and justified its amendment in the modified UNIQUAC model. The present algorithm makes available single temperature and temperature-dependent interaction parameters enabling accurate and thermodynamically correct description of the experimental data with the original UNIQUAC model, therefore without the need of any model modification. This outcome does not change when the interaction parameters from the binary partially miscible constituent pair are first regressed and kept constant during the estimation of the remaining parameters on ternary equilibrium data. This investigation confirms that a model cannot be judged if the correctness of the model parameters has not been proved first.

**Keywords:** parameter regression; activity coefficient models; common tangent plane; excess Gibbs free energy; stability criterion; UNIQUAC.

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## 1. Introduction

UNIQUAC [1] and NRTL [2] are the most popular excess Gibbs free energy models for the description of liquid phase equilibria. These local composition thermodynamic models contain adjustable binary interaction parameters which can show an in-built temperature dependency. In addition, these models can theoretically predict the phase equilibrium of multicomponent systems only by using the interaction parameters of all the constituent pairs [3,4]. Therefore, if binary experimental data of the constituent pairs are available and the model parameters are regressed on these data, the model has to return a correct multicomponent phase equilibrium. However, in practice parameters regressed only on binary equilibrium data usually provide unreliable multicomponent equilibrium, especially in Liquid-Liquid Equilibrium (LLE) [5].

In many cases, it is difficult to state if inconsistent phase equilibria are due to limitations of the thermodynamic models or inaccuracy of the model parameters. Marcilla et al. [6,7] pointed out that in LLE of binary and ternary systems, local composition models often give both qualitative (prediction of non-existent multi-phase splits and spurious liquid splits) and quantitative errors (calculated compositions different from experimental tie-lines and metastable solutions) because of the model parameters and the algorithms adopted for their regression. In this regard it is understood that when all the necessary and sufficient conditions for phase equilibrium are fulfilled, only global optimization algorithms should be applied to the objective functions [8–10]. In fact, only in this case it is more likely that the mismatch between model and experiments is due to the limitations of the models and not to unreliable model parameters.

Different studies highlighted the inadequacy of model parameters for LLE which were estimated with commercial software or internally-developed algorithms. In particular, the correlation tools available in the DECHEMA Data Preparation Package [11], ChemCAD [12] and Aspen Plus [13] in a number of cases provide inaccurate description of the phase behavior of complex ternary liquid systems [14].

Anderson and Prausnitz [15] highlighted the disagreement of model and experimental LLE data for some Type 1 [16] ternary systems. In [15], the UNIQUAC parameters were fitted only on phase equilibrium data of the binary subsystems resulting in large deviations between ternary experimental and calculated equilibrium. A more accurate LLE description was obtained using a modified version of the UNIQUAC model [17] and adjusting the parameters by regressing them with experimental LLE data of the ternary systems, in addition to binary experimental data. However, it is uncertain if the poor results for LLE of ternary systems were because of the limitations of the original UNIQUAC model or because of inappropriate interaction parameters.

Therefore, a robust strategy to check and prove the quality of the parameters calculated from experimental data is needed before these can be released or before declaring a model as inadequate.

Common approaches include constrained parameter regression such as a check of the isoactivity condition. Algorithms that include this condition are the method based on Maximum Likelihood principle developed by Britt and Luecke [18], the algorithm proposed by Sørensen et al. [19] and the parameter estimation procedure based on the k-value method, presented by Gmehling et al. [20].

Despite the compliance with the isoactivity condition, it has been shown that the aforementioned qualitative and quantitative inconsistencies can still be present [6,7]. This drawback is rooted in the fact that the equality of the chemical potential is necessary but not sufficient condition for phase equilibrium. These algorithms are likely to converge to a local minimum of the objective function with no guarantees that the solution represents a global minimum of the Gibbs free energy. Therefore, the local and global methods adopted to minimize these objective functions must be adequately tuned. In addition, in many cases, a phase stability test is carried out a-posteriori [21]. However, if the phase stability test is not completely fulfilled, it is not clear how to proceed for finding consistent results.

The most reliable algorithms for parameter computation are those including steps for the minimization of the Gibbs free energy or for the Common Tangent Plane (CTP) condition [22,23],

also expressed as minimization of the Tangent Plane Distance Function (TPDF), as originally proposed graphically by Gibbs [24]. As shown in Fig. 1 for the LLE of a binary system, necessary and sufficient condition for the stability of the phases at constant temperature and pressure is that the Gibbs free energy curve, surface or hyper-surface of mixing ( $\Delta g_{\text{mix}}(x)$ ) lies completely above the tangent line, plane or hyper-plane at the equilibrium compositions of all phases for binary, ternary or multicomponent systems, respectively, in the entire range of compositions.

The Tangent Plane Distance Function (TPDF) is:

$$\begin{aligned} \text{TPDF}(x, x_{\text{calc}}^k, \tau_{ij}, \tau_{ji}) = & \Delta g_{\text{mix}}(x, \tau_{ij}, \tau_{ji}) - (\Delta g_{\text{mix}}(x_{\text{calc}}^k, \tau_{ij}, \tau_{ji})) \\ & + \sum_{i=1}^{n'} \left. \frac{\delta \Delta g_{\text{mix}}}{\delta x_i} \right|_{x_{\text{calc}}^k, \tau_{ij}, \tau_{ji}} (x_i - x_{i,\text{calc}}^k) \end{aligned} \quad (1)$$

where  $x_i$  is the mole fraction of the  $i$ -th component,  $x_{i,\text{calc}}^k$  is the calculated equilibrium mole fraction for  $i$ -th component of the  $k$ -th phase,  $\tau_{ij}$  and  $\tau_{ji}$  are the dimensionless binary interaction parameters, and  $n'$  is the number of independent components. To ensure the stability of the phases, the TPDF must be never negative and its global minimum must be zero, corresponding to the points of tangency. The equations of the Gibbs free energy of mixing from the UNIQUAC model are reported in Appendix A.

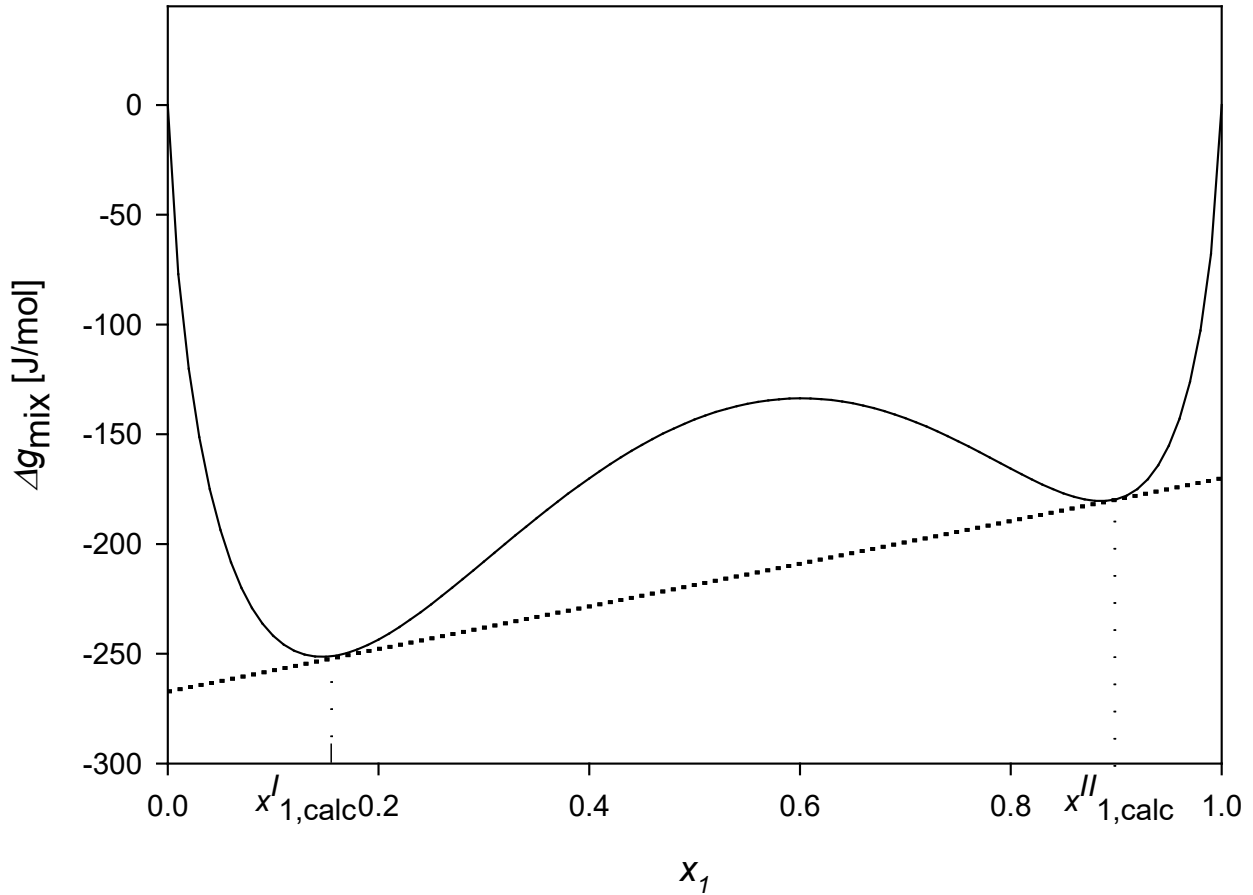


Figure 1.  $\Delta g_{\text{mix}}(x, \tau_{ij}, \tau_{ji})$  for a partially miscible binary liquid system (solid line). The dotted line is the tangent line at the equilibrium compositions of all phases

$(\Delta g_{\text{mix}}(x_{1,\text{calc}}^k, \tau_{ij}, \tau_{ji}) + \left. \frac{\delta \Delta g_{\text{mix}}}{\delta x_1} \right|_{x_{1,\text{calc}}^k, \tau_{ij}, \tau_{ji}} (x_1 - x_{1,\text{calc}}^k))$ .  $x_{1,\text{calc}}^I$  and  $x_{1,\text{calc}}^{II}$  are the compositions of one component in the two coexisting phases at equilibrium.

Since  $\Delta g_{\text{mix}}(x, \tau_{ij}, \tau_{ji})$  is calculated by strongly non-linear models, such as UNIQUAC, the minimization of TPDF is not a trivial task. In recent years, because of the notable developments in computational techniques to solve nonlinear and nonconvex global optimization problems, different algorithms for the model parameter estimation, which include the CTP criterion were proposed:

- Simoni et al. [25] proposed an algorithm for the interaction parameter evaluation of LLE of binary systems at a specific temperature that is based on the interval-Newton method. This method finds all the roots for the model parameters from the isoactivity equations, considering

the temperature and the experimental mole fractions as known. By checking the minimization of the TPDF, the obtained multiple solutions are distinguished between stable and unstable solutions. However, the algorithm was developed to fit the parameters on LLE data of binary systems at a specific temperature. Therefore, a modification of the algorithm is needed for multicomponent multi-temperature data.

- The algorithm from Mitsos et al. [9] and Bollas et al. [10] is based on bilevel programming where an optimization problem (outer level) is hierarchically embedded in another one (inner level). The algorithm was applied to NRTL model for LLE of binary systems and to NRTL, UNIQUAC and Wilson [26] models for VLE of binary systems. In particular, the outer level deals with the minimization of the errors on the compositions while the inner level ensures the minimization of the Gibbs free energy by matching the CTP criterion. Moreover, additional conditions to exclude the presence of spurious phase splits and unreal multi-phase splits were provided. The algorithm for LLE parameter estimation was implemented in the tool BOARPET (Bilevel Optimization Algorithm for Rigorous and Robust Parameter Estimation in Thermodynamics) presented by Glass et al. [27]. Bilevel optimization ensures thermodynamically consistent parameters and is able to capture the temperature dependence of the parameters. However, powerful bilevel algorithms that are able to solve strongly non-linear system of equations are necessary [28,29]. The algorithm can in principle be applied for LLE and VLE parameter estimation of multicomponent systems but, to the best of our knowledge, this was not tried and reported in the open scientific literature.

Recently, Diaz et al. [30] presented a simplified algorithm to estimate NRTL interaction parameters for LLE of ternary systems based on the problem formulation stated by Mitsos et al. [9]. This algorithm aims at providing consistent model parameters by simultaneously ensuring the CTP criterion and the minimization of the deviations between the calculated and experimental compositions. However, the algorithm was only used to estimate single temperature NRTL interaction parameter from ternary LLE data.

- Santori et al. [31] proposed an algorithm for the computation of the UNIQUAC model interaction parameters for LLE of binary systems, also based on a bilevel problem approach. This algorithm involves basic optimization algorithms and the  $(\mu+\lambda)$ -Evolution Strategy optimization algorithm [32,33] that ensure both the minimization of the deviations between the calculated and experimental compositions and the matching of the CTP criterion by means of the variation of the experimental compositions. In particular, both single temperature parameters and temperature-dependent parameters were calculated that provided a consistent representation for LLE of the studied binary systems. However, the algorithm was not applied to multicomponent systems.
- Marcilla et al. [5,14,34] proposed different algorithms for the evaluation of the interaction parameters of the NRTL model to represent the liquid phase equilibrium, i.e. LLE, Liquid-Liquid-Liquid Equilibrium (LLLE), of different types of ternary systems. These algorithms include conditions based on topological information on the Gibbs free energy mixing. In particular, a procedure based on the plait point condition for ternary binodal curve [35] was adopted in order to ensure the representation of the correct type of ternary system and the real phase behavior of the binary subsystems. However, these algorithms present complex and iterative calculations, therefore they can be time consuming when nonlinear models such as the UNIQUAC model are used.

This study shows how to accurately evaluate the UNIQUAC [1] interaction parameters for LLE of ternary systems by extending and improving the algorithm of Santori et al. [31]. The presented approach can be applied to any thermodynamic model for LLE and Vapor-Liquid-Liquid Equilibrium (VLLE) [2,36,37].

The developed algorithm is applied to the exemplar case of the Type 1 Methanol (1) + Benzene (2) + n-Heptane (3) LLE ternary system. In the original study of Anderson and Prausnitz [15], where the UNIQUAC model was used for the first time for LLE, this ternary system was used as justification for the formulation of a modified UNIQUAC model. We demonstrate that there is no



need for any modification of the UNIQUAC model and all the mismatch between model and data is originated by the model interaction parameters. In fact, we show that the original UNIQUAC model can provide accurate LLE results when its parameters are regressed with the proposed algorithm. Finally, we prove that the model is appropriate for the ternary system also when the parameters are assessed from the LLE data of the partially miscible constituent pair.

## 2. Algorithm

The proposed algorithm for the UNIQUAC model interaction parameter estimation can be applied to different single temperature experimental liquid-liquid (LL) tie-lines or multi-temperature experimental LL tie-lines of ternary systems at a fixed pressure. The algorithm includes two separate nested iteration loops and the possibility to vary the experimental mole fractions in a predefined range depending on the accuracy of the experimental data. The algorithm is reasonably fast; in all single temperature and temperature-dependent parameter estimations reported in this study, the computational time for a complete iteration has never taken longer than 120 s and 240 s, respectively.

The algorithm flowchart is reported in Fig. 2 showing the steps to estimate the UNIQUAC parameters of Type 1 ternary systems. However, the algorithm can in principle be adopted for different and more complex types of ternary systems.

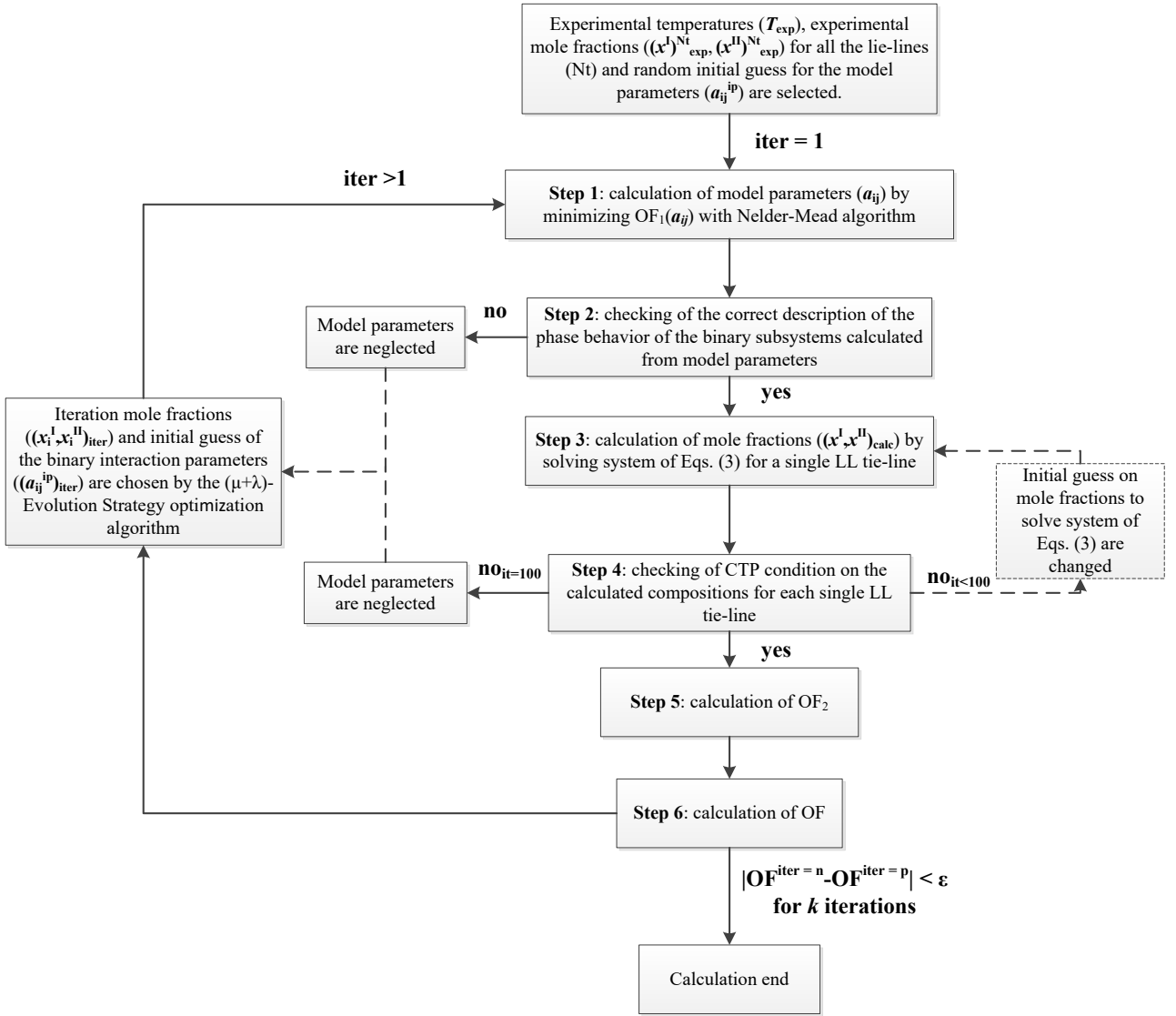


Figure 2. Flow chart of the algorithm for the estimation of the UNIQUAC binary interaction parameters for Type 1 LLE ternary systems. Detailed explanations of the calculation steps are provided in the text (algorithm description).  $\varepsilon$  is a chosen small value (e.g.  $10^{-3}$ ).

The inputs consist of the sets of experimental mole fractions at equilibrium and the experimental temperatures. The algorithm steps are the following:

1. A first optimization problem is solved following the Nelder-Mead algorithm [38] to estimate the single temperature or the temperature-dependent binary interaction parameters of the UNIQUAC model for the three constituent pairs  $(a_{12}, a_{21}, a_{13}, a_{31}, a_{23}, a_{32})$ , from the experimental data and considering random initial guess for the parameters. This step corresponds to the inner loop. The interaction parameters resulting from this step will be

adopted in the outer loop. The objective function  $OF_1$  of the inner loop includes the isoactivity conditions and is solved using the experimental compositions, in the first iteration (indicated as iter =1 in Fig. 2), and the experimental temperatures.  $OF_1$  is:

$$OF_1 = \sum_{n=1}^{Nt} \sum_{i=1}^3 \left| x_{i,\text{exp}}^{\text{I}} \gamma_i^{\text{I}}(T_{\text{exp}}, x_{\text{exp}}^{\text{I}}, a_{ij}, a_{ji}) - x_{i,\text{exp}}^{\text{II}} \gamma_i^{\text{II}}(T_{\text{exp}}, x_{\text{exp}}^{\text{II}}, a_{ij}, a_{ji}) \right| \quad (2)$$

where  $Nt$  is the number of LL tie-lines available at a fixed temperature or for all the studied temperatures,  $T_{\text{exp}}$  is the experimental temperature,  $x_{i,\text{exp}}^k$  is the experimental mole fraction of the  $i$ -th component for  $k$ -th phase ( $k = \text{I}, \text{II}$ ),  $\gamma_i^k$  is the activity coefficient of the  $i$ -th component for  $k$ -th phase and  $a_{ij}$  and  $a_{ji}$  are binary interaction parameters [K]. Therefore, the given values of  $OF_1$  are  $T_{\text{exp}}$  and  $x_{\text{exp}}^k$ . Unknowns are  $a_{ij}$  and  $a_{ji}$ .

2. The correct description of the phase behavior of the binary subsystems calculated from the parameters of step 1 is checked at fixed temperature through the analysis of the  $\Delta g_{\text{mix}}$  curves. In the specific case of Type 1 ternary systems, the algorithm checks the presence of one minimum in the  $\Delta g_{\text{mix}}$  curve for the miscible binary subsystems, then checks that the  $\Delta g_{\text{mix}}$  curve does not have inflection points. The  $\Delta g_{\text{mix}}$  curve for the partially miscible subsystems should show a CTP. If the calculated parameters do not accurately respect these conditions, they are discarded and the computation is started again by changing the experimental mole fractions within their experimental uncertainty and the initial guess of the interaction parameters.
3. The binary interaction parameters are used in the calculation of the mole fractions by solving the isoactivity conditions and the mass balance for a single LL tie-line. For Type 1 ternary systems, this system is:

$$\begin{cases} x_{1,\text{calc}}^{\text{I}} \gamma_1^{\text{I}}(T_{\text{exp}}, x_{\text{calc}}^{\text{I}}, a_{ij}, a_{ji}) = x_{1,\text{calc}}^{\text{II}} \gamma_1^{\text{II}}(T_{\text{exp}}, x_{\text{calc}}^{\text{II}}, a_{ij}, a_{ji}) \\ x_{2,\text{calc}}^{\text{I}} \gamma_2^{\text{I}}(T_{\text{exp}}, x_{\text{calc}}^{\text{I}}, a_{ij}, a_{ji}) = x_{2,\text{calc}}^{\text{II}} \gamma_2^{\text{II}}(T_{\text{exp}}, x_{\text{calc}}^{\text{II}}, a_{ij}, a_{ji}) \\ x_{3,\text{calc}}^{\text{I}} \gamma_3^{\text{I}}(T_{\text{exp}}, x_{\text{calc}}^{\text{I}}, a_{ij}, a_{ji}) = x_{3,\text{calc}}^{\text{II}} \gamma_3^{\text{II}}(T_{\text{exp}}, x_{\text{calc}}^{\text{II}}, a_{ij}, a_{ji}) \\ z_{1,\text{exp}} = \beta x_{1,\text{calc}}^{\text{I}} + (1 - \beta) x_{1,\text{calc}}^{\text{II}} \\ z_{2,\text{exp}} = \beta x_{2,\text{calc}}^{\text{I}} + (1 - \beta) x_{2,\text{calc}}^{\text{II}} \end{cases} \quad (3)$$

where  $x_{i,\text{calc}}^k$  is the calculated equilibrium mole fraction of the  $i$ -th component for  $k$ -th phase,  $z_{i,\text{exp}} = n_{i,\text{exp}}/n_{\text{tot}}$  is the overall experimental mole fraction of the  $i$ -th component in the system,  $n_{i,\text{exp}} = x_{i,\text{exp}}^{\text{I}} n_{i,\text{exp}}^{\text{I}} + x_{i,\text{exp}}^{\text{II}} n_{i,\text{exp}}^{\text{II}}$  is the overall number of moles of the  $i$ -th component in the system,  $n_{i,\text{exp}}^{\text{I}}$  and  $n_{i,\text{exp}}^{\text{II}}$  are the number of moles of the  $i$ -th component in liquid phase I and liquid phase II, respectively,  $n_{\text{tot}} = \sum n_{i,\text{exp}}$  is the total number of moles of the system (for the sake of simplicity the system is composed of 1 mole per phase), and  $\beta$  is the mole fraction of the overall liquid in phase I. Since the mole fraction balances ( $\sum x_{i,\text{calc}}^{\text{I}} = 1$ ,  $\sum x_{i,\text{calc}}^{\text{II}} = 1$ , and  $\sum z_{i,\text{exp}} = 1$ ), the system of Eqs. (3) has 5 equations in 5 independent variables ( $x_{1,\text{calc}}^{\text{I}}$ ,  $x_{2,\text{calc}}^{\text{I}}$ ,  $x_{1,\text{calc}}^{\text{II}}$ ,  $x_{2,\text{calc}}^{\text{II}}$ ,  $\beta$ ). Therefore, the given values in Eqs. (3) are  $T_{\text{exp}}$ ,  $z_{i,\text{exp}}$ ,  $x_{3,\text{calc}}^{\text{I}}$ ,  $x_{3,\text{calc}}^{\text{II}}$ ,  $a_{ij}$  and  $a_{ji}$ . Unknowns are  $x_{1,\text{calc}}^{\text{I}}$ ,  $x_{2,\text{calc}}^{\text{I}}$ ,  $x_{1,\text{calc}}^{\text{II}}$ ,  $x_{2,\text{calc}}^{\text{II}}$ ,  $\beta$ . The equation system is solved for each LL tie-line using a quasi-Newton method [39] and multi-start approach.

4. To avoid possible unreliable solutions of system of Eqs. (3), a stability test is performed using the CTP condition on the calculated compositions for each single LL tie-line. If the CTP condition is not met, the step 3 is repeated by changing the initial guess on mole fractions until the CTP is met. In case the CTP condition is not matched after a sufficiently high number of iterations (e.g. 100 iterations as reported in Fig. 2), the calculated binary interaction parameters are discarded, since it is likely they show incorrect LLE for the studied ternary system, even though their consistency for the binary subsystems is fulfilled. In this case, the calculation is started again by adopting a new set of experimental compositions within the experimental uncertainty and initial guess of the binary interaction parameters.

5. When the mole fractions calculated for each tie-line meet the CTP criterion, these compositions are used to evaluate a second objective function  $OF_2$ :

$$OF_2 = \sum_{n=1}^{N_t} \sum_{k=1}^{nPh} \sum_{i=1}^3 (|x_{i,\text{exp}}^k - x_{i,\text{calc}}^k| + |x_{i,\text{iter}}^k - x_{i,\text{calc}}^k| + |x_{i,\text{exp}}^k - x_{i,\text{iter}}^k|) \quad (4)$$

where  $nPh$  is the number of coexisting liquid phases in the system ( $nPh = I, II$  for a Type 1 ternary system),  $x_{i,\text{iter}}^k$  is a iteration mole fraction of the  $i$ -th component for  $k$ -th phase and its choice is described in the next step. All the variables in Eq. 4 are known, so this step consists only of the calculation of  $OF_2$ .

6. To obtain interaction parameters providing an accurate description of LLE, the whole steps from 1 to 5 are repeated by changing the experimental mole fractions in a range defined by their uncertainties and centered on the experimental values. The new values of iteration mole fractions ( $x_{\text{iter}}$  in step 5) are chosen by using a  $(\mu+\lambda)$ -Evolution Strategy optimization algorithm [32,33] that operates on the following objective function:

$$OF = \sqrt{OF_1 + OF_2} \quad (5)$$

where  $OF_1$  and  $OF_2$  are calculated in the previous steps. From the second iteration,  $x_{\text{iter}}$  are used in steps 1 and 3 instead of the experimental  $x_{\text{exp}}$ . Moreover, in order to improve the convergence of the algorithm, the initial guess of the binary interaction parameters used in step 1 and indicated as  $(a_{ij}^{\text{ip}})_{\text{iter}}$  in Fig. 2, are changed according to  $(\mu+\lambda)$ -Evolution Strategy optimization algorithm. In particular, even when unfeasible results are obtained in the first iterations, this optimization algorithm can continue the calculation by changing  $x_{\text{iter}}$  and

$(a_{ij}^{ip})_{iter}$  in the predefined ranges until consistent solutions are reached. As shown in Fig. 3, the calculation ends when the lowest value of OF does not change significantly after several successive iterations.

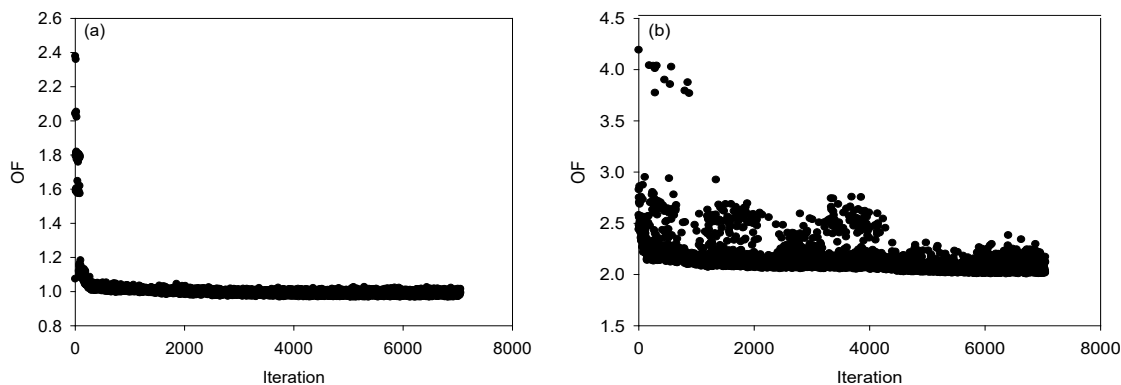


Figure 3. OF trends during the estimation of the UNIQUAC parameters from single temperature (a) and multi-temperature (b) LLE ternary data.

The algorithm above can be used adapted to the estimation of the UNIQUAC interaction parameters for LLE of binary systems by applying some straightforward simplifications. The two objective functions ( $OF_1$  and  $OF_2$ ) have to be modified because of the different number of components in liquid binary systems. In the same way, the system of non-linear equations (3) simplifies to a system of 2 equations in 2 independent variables ( $x^I, x^{II}$ ). Finally, Step 2 is not needed. In agreement with the original algorithm for LLE of binary systems [31], if the algorithm is applied to single temperature experimental compositions of binary systems, the procedure ends after the evaluation of  $OF_2$  and the results are usually correct. This allows to skip the iterative procedure based on the  $(\mu+\lambda)$  - Evolution Strategy algorithm. The described algorithm for LLE for binary systems takes an average of 5 s to converge. An open software that contains an implementation of the algorithm for single temperature LLE data of binary systems is provided as supplementary material. This software is a source which can be freely used for research and teaching to estimate reliable UNIQUAC parameters from binary LLE data.

In conclusion, the proposed algorithm provides UNIQUAC model parameters that give a thermodynamically consistent description for LLE of ternary systems since the parameter consistency for the ternary system and for binary constituent pairs is checked. Moreover, the algorithm has the

aim to provide the model parameters that minimize the deviations between experimental and calculated compositions by varying the experimental mole fractions in a predefined range defined by their uncertainties.

### 3. Results and Discussion

The algorithm described above was used to estimate the UNIQUAC model parameters for LLE of Methanol (1) + Benzene (2) + n-Heptane (3) ternary system. This system shows a Type 1 LLE and was taken as an example from the seminal study of Anderson and Prausnitz [15] to justify the need for a modification of the newly developed UNIQUAC model.

The structural parameters of the UNIQUAC model for the Methanol (1) + Benzene (2) + n-Heptane (3) are reported in Table 1.

Table 1. Structural parameters of the UNIQUAC equations

	$r_i$	$q_i$
Methanol	1.4311	1.432
Benzene	3.1878	2.4
n – Heptane	5.1742	4.396

The prediction capability of the UNIQUAC model for LLE of the studied system with interaction parameters from binary data was first checked. However, local composition models show limited prediction capabilities of LLE of multicomponent systems equilibrium when the parameters are regressed only from binary data [5]. In particular, this class of models has severe limitations in the simultaneous correlation of LLE of ternary systems and VLE of the constituent pairs when the same set of parameters are used [40,41]. In order to overcome this drawback, modified versions of the original local composition models were proposed to simultaneously describe different phase equilibria [40,41].

#### 3.1 Phase equilibria for binary subsystems

The simplified version of the presented algorithm to estimate the UNIQUAC model

parameters for LLE was applied to single temperature experimental data of Methanol (1) + n-Heptane (2) binary system. A total of 63 LLE data for the studied binary system in a temperature range from 253.15 K to 323.15 K were selected from the DETHERM database [42] and Sorensen and Arlt [43] to evaluate the interaction parameters in a temperature range as wide as possible. The data were collected from different sources, among which the most recent source is the study of Narasigadu et al. [44], with different uncertainties, as it is possible to note in Fig. 4. Since the experimental data show scattering, the binary interaction parameters calculated from each single temperature point are consequently scattered. Nevertheless, a temperature dependence in the parameters was evident. Accordingly, data were smoothed through nonlinear regression and the correlation along with its uncertainty were then used in the application of the presented algorithm.

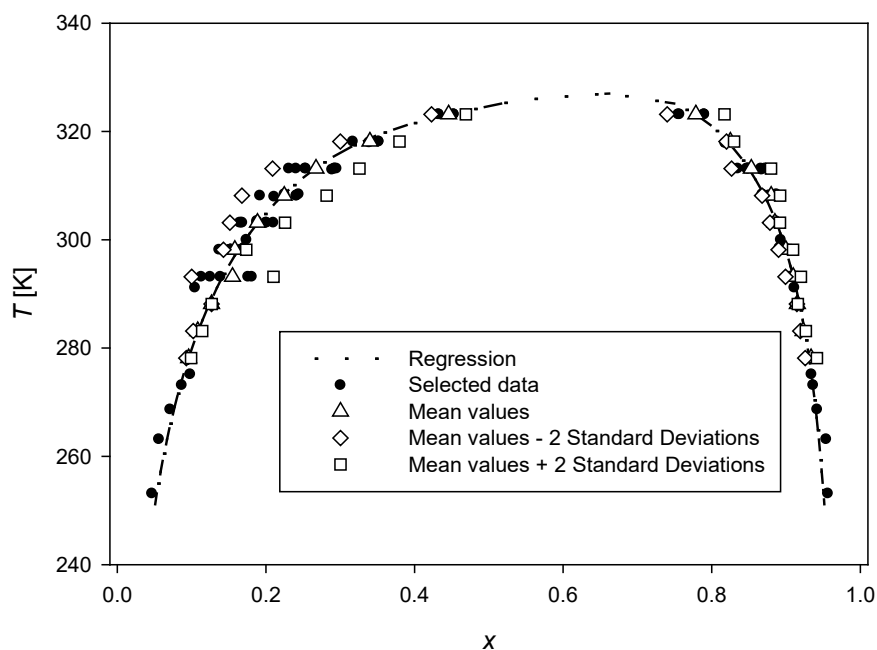


Figure 4. LLE data and regression for Methanol (1) + n-Heptane (2) across the experimental temperature range. All the collected data are sufficiently accurate showing deviations lower than twice the standard deviations from their average values.

The complete results for single temperature parameters fitted on the selected data and on the smoothed database are given as supplementary material. Table 2 reports the average errors in mole fractions  $|x_{i,\text{exp}}^k - x_{i,\text{calc}}^k|$  and isoactivity conditions  $|x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II}|$  for the selected data by using



parameters regressed on single temperature smoothed data. Table 2 shows that the parameters from the present algorithm can provide a precise description of the LLE of Methanol (1) + n-Heptane (2) binary system since low average errors in mole fractions were obtained.

Table 2. Methanol (1) + n-Heptane (2) LLE average errors in mole fractions  $|x_{i,\text{exp}}^k - x_{i,\text{calc}}^k|$  and isoactivity conditions  $|x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II}|$  from: (a) single temperature parameters from the smoothed database; (b) a-posteriori temperature-correlated\* parameters.

	$ x_{1,\text{exp}}^I - x_{1,\text{calc}}^I $	$ x_{1,\text{exp}}^{II} - x_{1,\text{calc}}^{II} $	$ x_1^I \gamma_1^I - x_1^{II} \gamma_1^{II} $	$ x_2^I \gamma_2^I - x_2^{II} \gamma_2^{II} $
(a)	$1.22 \cdot 10^{-10}$	$3.85 \cdot 10^{-10}$	$1.92 \cdot 10^{-15}$	$4.25 \cdot 10^{-15}$
(b)	$1.04 \cdot 10^{-3}$	$7.48 \cdot 10^{-3}$	$1.51 \cdot 10^{-15}$	$4.82 \cdot 10^{-15}$

\*The a-posteriori correlations are:  $a_{12} = -181.65133 + 1.732898 T - 0.00365537 T^2$  and  $a_{21} = -220.836861 + 7.23934 T - 0.01473142 T^2$

An accurate a-posteriori temperature-dependent correlation of the interaction parameters can be inferred from the trend of single temperature values. The non-linear correlations reported in Table 2 provide low composition errors and each parameter matches the CTP condition across the whole temperature range [31].

Complete results of the a-posteriori regressed interaction parameters are given in the supplementary material, while the average errors in mole fractions and isoactivity conditions are reported in Table 2. Table 2 shows that parameters from the temperature regression provide higher but still sufficiently accurate errors than those regressed on single temperatures.

Model parameters for the miscible subsystems (Methanol + Benzene and Benzene + n-Heptane) are not available since these systems do not show LLE in the conditions where the ternary data are available. At the conditions of pressure and temperature of the ternary system, only the Methanol + n-Heptane binary is partially miscible. Therefore, only in this case, the interaction parameters fitted on LLE data of the binary subsystem can be used. The missing interaction parameters could be assessed from VLE data. However, the binary interaction parameters estimated from VLE data do not show a monotonic temperature dependence, making impossible their eventual extrapolation in the region where the liquid binary systems are completely miscible. For instance, as shown in Fig. 5, the UNIQUAC model parameters estimated from experimental VLE data of Benzene

(1) + n-Heptane (2) show oscillations at the upper and lower temperatures.

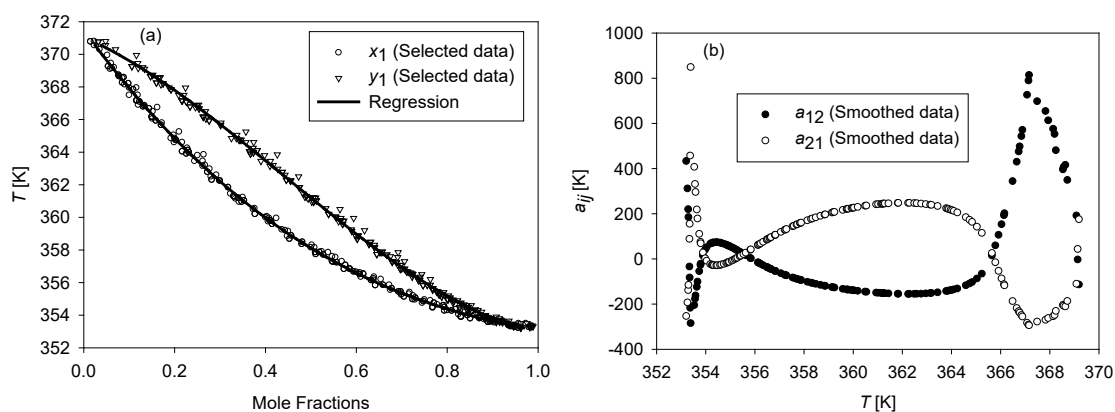


Figure 5. Experimental VLE data (a) and calculated binary interaction parameters of UNIQUAC model (b) for Benzene (1) + n-Heptane (2). The interaction parameters are calculated by smoothing 262 experimental data from DETHERM database [42]. To ensure the consistency, the regression algorithm is an adapted version of the one proposed for LLE of binary systems [31], where equation model approximations are identical to those in Bollas et al. [10].

### 3.2 Liquid-Liquid Equilibrium for Methanol + Benzene + n-Heptane system

The proposed algorithm was used to evaluate the binary interaction parameters of UNIQUAC model for LLE of Methanol (1) + Benzene (2) + n-Heptane (3) Type 1 ternary systems on a total of 24 experimental LLE data of Table 3. Among the data used, those at 305.95 K were studied by Anderson and Prausnitz [15] to show the application of the UNIQUAC model to LLE. For the data at 293.15 K, García-Flores et al. [45] proposed a set of interaction parameters for the original UNIQUAC model.

Table 3. Experimental LLE data of Methanol (1) + Benzene (2) + n-Heptane (3) system from DETHERM database [42].

$T$ [K]	Original Source	N. points
286.95	[46]	6
293.15	[45]	5
298.15	[47]	8
305.95	[46]	5
Total	-	24

The UNIQUAC model parameters for LLE of the studied ternary system were calculated adopting four different approaches:

1. All the UNIQUAC model binary interaction parameters were determined using the experimental data of the ternary system at fixed temperature.
2. At the studied temperatures, the binary interaction parameters of Methanol (1) + n-Heptane (3) system were kept constant to the values calculated from the a-posteriori parameter regression of the partially miscible binary system. Since thermodynamically consistent binary interaction parameters calculated from the binary LLE are used, parameter consistency check of the partially miscible subsystem implemented in the algorithm of Fig. 2 for LLE of the ternary systems is redundant. In addition,  $a_{23}$  was set as a function of the remaining interaction parameters, according to the linear dependence among parameters already demonstrated elsewhere [3,48]. Therefore, only the values of 3 independent binary interaction parameters ( $a_{12}$ ,  $a_{21}$ ,  $a_{32}$ ) were obtained from the ternary experimental data of Methanol (1) + Benzene (2) + n-Heptane (3) system.
3. All the temperature-dependent UNIQUAC model parameters were estimated from multi-temperature experimental LLE data of the ternary system. In particular, the algorithm was used to find the best coefficients ( $a_{ij}^A$ ,  $a_{ij}^B$ ,  $a_{ij}^C$ ,  $a_{ji}^A$ ,  $a_{ji}^B$  and  $a_{ji}^C$ ) of nonlinear temperature-dependent correlations of the parameters, expressed as  $a_{ij} = a_{ij}^A + a_{ij}^B T + a_{ij}^C T^2$  and  $a_{ji} = a_{ji}^A + a_{ji}^B T + a_{ji}^C$ . The coefficient values are reported in Table 6. In this case, predefined bounds on coefficient values help to speed up the convergence. These bounds were defined on the basis of the parameter values obtained for the single temperature study.
4. The coefficients of the temperature-dependent parameter correlations ( $a_{13}^A$ ,  $a_{31}^A$ ,  $a_{13}^B$ ,  $a_{31}^B$ ,  $a_{13}^C$ , and  $a_{31}^C$ ) of Methanol (1) + n-Heptane (3) system were kept constant to the coefficients from the a-posteriori parameter regression. In addition,  $a_{23}$  was set as a function of the remaining interaction parameters. Therefore, only the coefficients of the correlations of  $a_{12}$ ,  $a_{21}$ , and  $a_{32}$  were

evaluated from the multi-temperature experimental LLE data of the ternary system.  $a_{ij}^A$ ,  $a_{ij}^B$ ,  $a_{ij}^C$ ,  $a_{ji}^A$ ,  $a_{ji}^B$  and  $a_{ji}^C$  are reported in Table 7.

The UNIQUAC binary interaction parameters calculated for the four approaches at the studied temperatures, along with the values of the objective functions defined by Eqs.(2), (4), and (5), are reported in Table 4, 5, 6, and 7. More detailed results are given as supplementary material.

As shown in Fig. 6, the approaches 3 and 4 that adopt temperature-dependent parameters, always provide slightly higher errors on compositions than the approaches that focus on single temperatures independently. However, the results from approaches 3 and 4 still remain sufficiently accurate. The drawback of the temperature-dependent approach consists of the number of coefficients to be estimated from multi-temperature data (between 12 and 18), the different origin of the data and accordingly their different experimental uncertainty.

To avoid incorrect results, it is not recommended to extrapolate the calculated temperature-dependent correlations to describe different phase equilibria such as the VLE of the binary subsystems. In fact, there are limiting temperatures beyond which the correlations are not applicable.

Table 4. Calculated binary interaction parameters of Methanol (1) + Benzene (2) + n-Heptane (3) system and objective function values for approach 1.

$T$ [K]	$a_{12}$ [K]	$a_{21}$ [K]	$a_{13}$ [K]	$a_{31}$ [K]	$a_{23}$ [K]	$a_{32}$ [K]	$OF_1$	$OF_2$	$OF$
286.95	-121.42	183.67	7.04	709.79	-218.55	133.76	0.08	0.59	0.82
293.15	-87.13	501.44	17.68	631.64	-232.51	338.95	0.02	0.25	0.51
298.15	-56.20	139.68	0.36	648.29	233.28	-268.19	0.03	0.25	0.53
305.95	-394.82	618.49	8.71	648.21	-313.28	152.48	0.05	0.53	0.76
Tot.	-	-	-	-	-	-	0.18	1.62	1.34

Table 5. Calculated binary interaction parameters of Methanol (1) + Benzene (2) + n-Heptane (3) system and objective function values for approach 2.

$T$ [K]	$a_{12}$ [K]	$a_{21}$ [K]	$a_{13}$ [K]	$a_{31}$ [K]	$a_{23}$ [K]	$a_{32}$ [K]	$OF_1$	$OF_2$	$OF$
286.95	-227.92	215.34	14.62	643.50	-193.10	-7.46	0.05	0.87	0.96
293.15	-335.14	221.45	12.22	635.40	-186.84	-120.25	0.06	0.42	0.70
298.15	69.87	167.46	10.07	628.05	-183.68	336.52	0.04	0.65	0.83
305.95	-290.43	203.52	6.37	615.10	-184.43	-69.65	0.06	0.92	0.99
Tot.	-	-	-	-	-	-	0.21	2.87	1.75

Table 6. Calculated temperature-dependent\* binary interaction parameters of Methanol (1) + Benzene (2) + n-Heptane (3) system and objective function values for approach 3.

$T$ [K]	$a_{12}$ [K]	$a_{21}$ [K]	$a_{13}$ [K]	$a_{31}$ [K]	$a_{23}$ [K]	$a_{32}$ [K]	$OF_1$	$OF_2$	$OF$
286.95	-311.90	193.07	9.07	652.63	-179.41	-149.55	0.18	0.95	1.06
293.15	-326.01	197.71	3.87	648.41	-162.23	-159.81	0.08	0.57	0.80
298.15	-337.62	201.51	-0.56	644.30	-147.57	-168.24	0.11	0.86	0.98
305.95	-356.13	207.56	-7.88	636.63	-123.27	-181.68	0.09	1.19	1.13
Tot.	-	-	-	-	-	-	0.46	3.57	2.01

\*The correlations are:  $a_{12} = -2.4426 + 0.0933279 T - 0.00408352 T^2$ ,  $a_{21} = 74.0387 + 0.0885467 T + 0.00113702 T^2$ ,  $a_{13} = -99.9663 + 1.57332 T - 0.00415867 T^2$ ,  $a_{31} = -214.502 + 6.64597 T - 0.0126297 T^2$ ,  $a_{23} = 231.231 - 5.54453 T + 0.0143352 T^2$ ,  $a_{32} = 83.365 + 0.0128506 T - 0.00287352 T^2$

Table 7. Calculated temperature-dependent\* binary interaction parameters of Methanol (1) + Benzene (2) + n-Heptane (3) system and objective function values for approach 4.

$T$ [K]	$a_{12}$ [K]	$a_{21}$ [K]	$a_{13}$ [K]	$a_{31}$ [K]	$a_{23}$ [K]	$a_{32}$ [K]	$OF_1$	$OF_2$	$OF$
286.95	-355.41	202.63	14.62	643.50	-217.37	-146.52	0.22	1.07	1.14
293.15	-371.60	207.20	12.22	635.40	-201.18	-156.79	0.12	0.54	0.81
298.15	-384.91	210.95	10.07	628.05	-187.34	-165.23	0.26	1.65	1.38
305.95	-406.16	216.92	6.37	615.10	-164.33	-178.68	0.15	0.97	1.06
Tot.	-	-	-	-	-	-	0.74	4.23	2.23

\*The correlations are:  $a_{12} = -2.31397 + 0.120533 T - 0.00470829 T^2$ ,  $a_{21} = 91.5787 + 0.0442946 T + 0.00119428 T^2$ ,  $a_{13} = -181.65133 + 1.732898 T - 0.00365537 T^2$  and  $a_{31} = -220.836861 + 7.23934 T - 0.01473142 T^2$ ,  $a_{23} = 221.232 - 5.57982 T + 0.0141186 T^2$ ,  $a_{32} = 88.1535 + 0.00285856 T - 0.00285998 T^2$

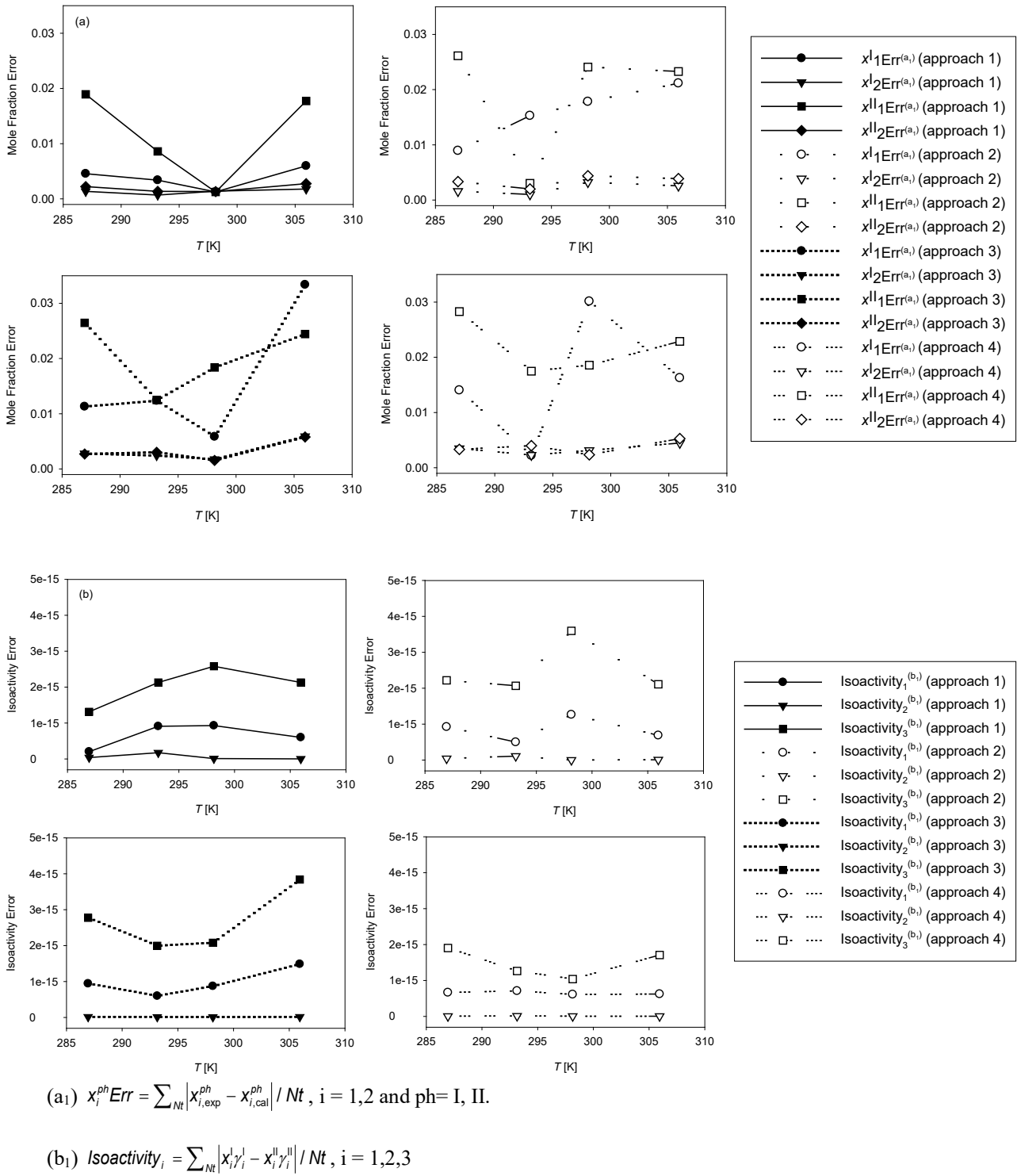


Figure 6. (a) Mole fraction errors and (b) isoactivity errors for Methanol (1) + Benzene (2) + n-Heptane (3) system against temperature.

Despite what shown in the original study of Anderson and Prausnitz [15], no modification of the original UNIQUAC model is needed in the LLE of the studied ternary system. In fact, with the

right set of thermodynamically consistent interaction parameters, the original UNIQUAC model provides an excellent fit of the data. This outcome is illustrated in Table 8 and in Fig. 7 where the experimental LLE data at 305.95 K are compared against the LLE calculated using the original UNIQUAC with the presented interaction parameters, the modified UNIQUAC with interaction parameters given by Anderson and Prausnitz [15] and the modified UNIQUAC with model parameters available in Honeywell's UniSim<sup>®</sup> Design Suite ( $a_{12} = -112.9$  K,  $a_{21} = 1287$  K,  $a_{13} = 17.91$  K,  $a_{31} = 1360$  K,  $a_{23} = -21.09$  K and  $a_{32} = 105.7$  K). In this last case, as shown in Table 8 and in Fig. 7, the calculated LLE has still large deviations from the experimental data, similar to those of the original UNIQUAC model with parameters from Anderson and Prausnitz [15]. This case is particularly worrying since UniSim<sup>®</sup> is routinely used for process design in the oil and gas sector.

Table 8. Average errors in mole fractions  $|x_{i,\text{exp}}^k - x_{i,\text{calc}}^k|$  and isoactivity conditions  $|x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II}|$  for the original UNIQUAC model with interaction parameters from approach 1 (a), approach 2 (b), approach 3 (c) and approach 4 (d), the modified UNIQUAC with interaction parameters given by Anderson and Prausnitz [15] (e) and the modified UNIQUAC with model parameters available in Honeywell's UniSim<sup>®</sup> Design Suite (f) for LLE of Methanol (1) + Benzene (2) + n-Heptane (3) system at 305.95 K.

	$ x_{1,\text{exp}}^I - x_{1,\text{calc}}^I $	$ x_{1,\text{exp}}^{II} - x_{1,\text{calc}}^{II} $	$ x_{2,\text{exp}}^I - x_{2,\text{calc}}^I $	$ x_{2,\text{exp}}^{II} - x_{2,\text{calc}}^{II} $	$ x_1^I \gamma_1^I - x_1^{II} \gamma_1^{II} $	$ x_2^I \gamma_2^I - x_2^{II} \gamma_2^{II} $	$ x_3^I \gamma_3^I - x_3^{II} \gamma_3^{II} $
(a)	$5.98 \cdot 10^{-3}$	$1.78 \cdot 10^{-3}$	$1.77 \cdot 10^{-2}$	$2.76 \cdot 10^{-3}$	$6.00 \cdot 10^{-16}$	$3.73 \cdot 10^{-18}$	$2.13 \cdot 10^{-15}$
(b)	$2.12 \cdot 10^{-2}$	$2.56 \cdot 10^{-3}$	$2.33 \cdot 10^{-2}$	$3.86 \cdot 10^{-3}$	$6.88 \cdot 10^{-16}$	$9.71 \cdot 10^{-18}$	$2.11 \cdot 10^{-15}$
(c)	$1.23 \cdot 10^{-2}$	$2.42 \cdot 10^{-3}$	$1.25 \cdot 10^{-2}$	$3.01 \cdot 10^{-3}$	$1.49 \cdot 10^{-15}$	$1.60 \cdot 10^{-17}$	$3.84 \cdot 10^{-15}$
(d)	$2.21 \cdot 10^{-3}$	$2.29 \cdot 10^{-3}$	$1.75 \cdot 10^{-2}$	$3.98 \cdot 10^{-3}$	$6.22 \cdot 10^{-16}$	$5.51 \cdot 10^{-18}$	$1.71 \cdot 10^{-15}$
(e)	$1.57 \cdot 10^{-2}$	$6.72 \cdot 10^{-3}$	$1.43 \cdot 10^{-2}$	$1.96 \cdot 10^{-2}$	$7.55 \cdot 10^{-16}$	$2.82 \cdot 10^{-16}$	$2.89 \cdot 10^{-15}$
(f)	$9.28 \cdot 10^{-2}$	$8.15 \cdot 10^{-2}$	$7.09 \cdot 10^{-2}$	$9.67 \cdot 10^{-2}$	$5.77 \cdot 10^{-16}$	$4.94 \cdot 10^{-16}$	$2.24 \cdot 10^{-16}$



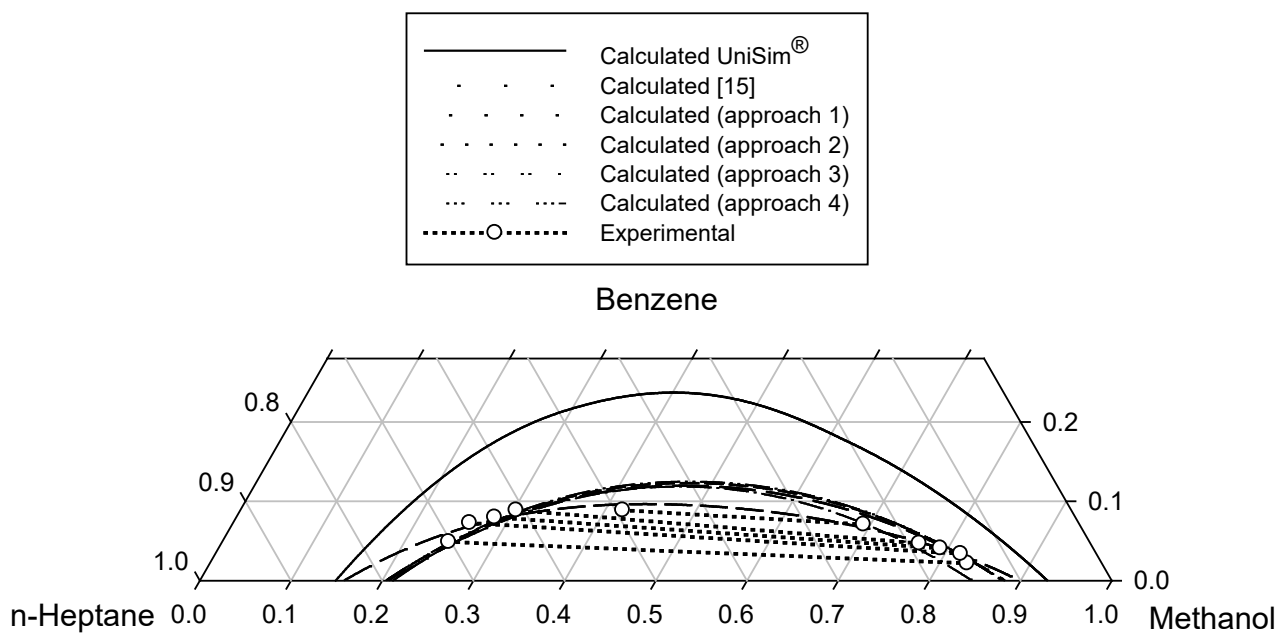


Figure 7. Experimental and calculated (UNIQUAC model, modified UNIQUAC with interaction parameters proposed by Anderson and Prausnitz [15], modified UNIQUAC with interaction parameters available in Honeywell's UniSim<sup>®</sup> Design Suite) LLE tie-lines of Methanol (1) + Benzene (2) + n-Heptane (3) system at 305.95 K.

It is worth noting that the original UNIQUAC model is able to correlate the liquid phase behavior of this ternary system using interaction parameters fitted only on binary LLE data of the partially miscible constituent binary pair. Therefore, in this case, the possibility to set the binary interaction parameters of the partially miscible binary pair before starting the regression allowed to reduce the calculation complexity and ensure at the same time accurate results. This aspect was especially valuable for the estimation of temperature-dependent interaction parameters. However, as also shown in Fig. 8, the interaction parameters calculated with the different approaches are still different. Consequently, different sets of interaction parameters can correlate the same set of experimental ternary LLE data with close errors. Furthermore, it can be noted from Fig. 8 that linear correlations can provide sufficiently accurate descriptions of the temperature dependency of the parameters. However, nonlinear temperature-dependent UNIQUAC parameters were chosen to ensure no influence of the fitting error on the results and conclusions.

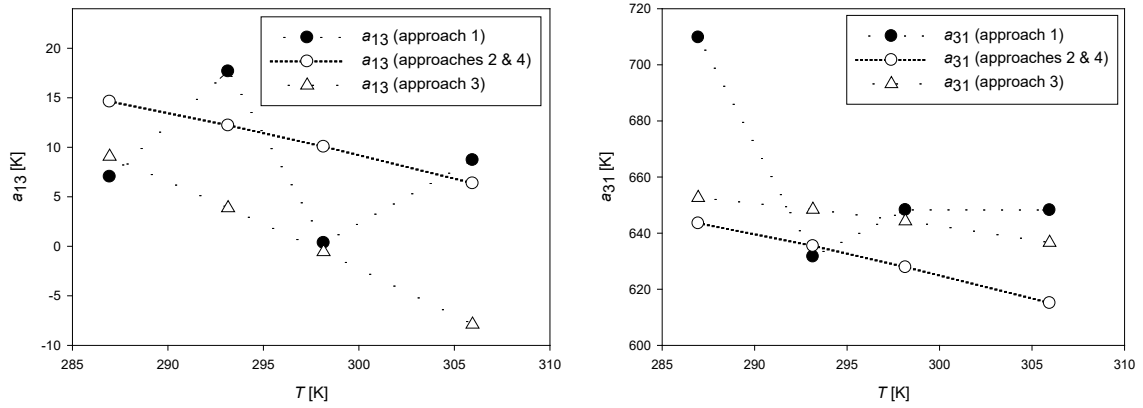


Figure 8. Trends of the parameters  $a_{13}$  and  $a_{31}$  for Methanol (1) – Benzene (2) – n-Heptane (3) system against temperature.

The results given by the UNIQUAC model parameters calculated in this work were compared with the LLE representation obtained with the interaction parameters presented in García-Flores et al. [45]. In García-Flores et al. [45], the model parameters of Methanol + n-Heptane system were evaluated from the binary equilibrium data ( $a_{13} = 20.829$  K and  $a_{31} = 607.14$  K), while the remaining four parameters were estimated from ternary equilibrium data ( $a_{12} = -104.37$  K,  $a_{21} = 1155.2$  K,  $a_{23} = -233.82$  K and  $a_{32} = 376.36$  K). Fig. 9 shows the experimental tie-lines of the studied ternary system at 293.15 K and the compositions calculated with the three different sets of interaction parameters. This figure indicates that all five parameter sets ensure low mole fraction errors at this temperature.

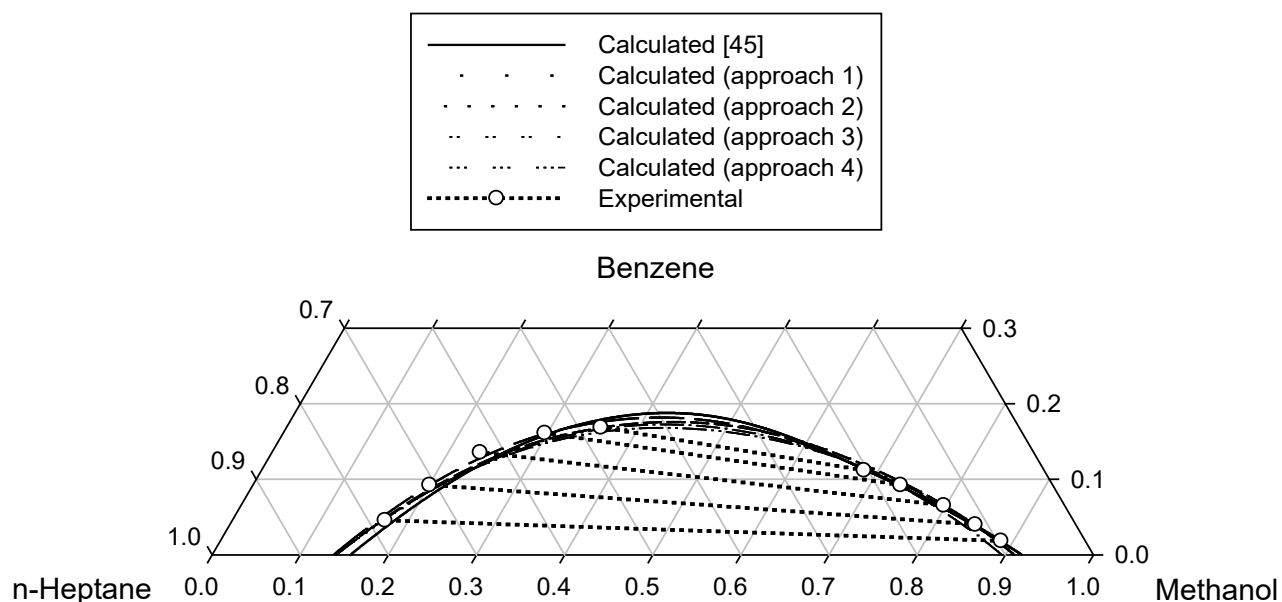


Figure 9. Experimental and calculated (UNIQUAC model) LLE tie-lines of Methanol (1) + Benzene (2) +n-Heptane (3) system at 293.15 K.

However, a comparison between the parameters proposed in this study and in García-Flores et al. [45] is needed. As pointed out by Marcilla et al. [7], a reliable tool to judge the parameters is the plate point condition check for the ternary binodal curve [14,35]. This condition consists of the calculation of the solutions of the determinants of the Hessian matrix of  $\Delta g_{\text{mix}}$ , ( $\sigma$ ) and of an additional matrix ( $\delta$ ) being simultaneously equal to zero that define the plait point location and the inflection points curve ( $\sigma = 0$ ).

Fig. 10 (a) shows that the model parameters calculated by the proposed algorithm respect the plate point condition for ternary binodal curve. The shaded areas in Fig. 10 (a) represent the stable composition coexisting regions from the set of UNIQUAC parameters calculated with approach 2 at 293.15 K. These regions correspond to the real coexisting compositions regions for LLE of the studied ternary system. Instead, as visible in Fig. 10 (b), the model parameters given in García-Flores et al. [45] do not fulfill this condition. It was observed that these interaction parameters respect the CTP condition for the calculated mole fractions, but wrongly describe the phase behavior of Methanol (1) + Benzene (2) as partially miscible.

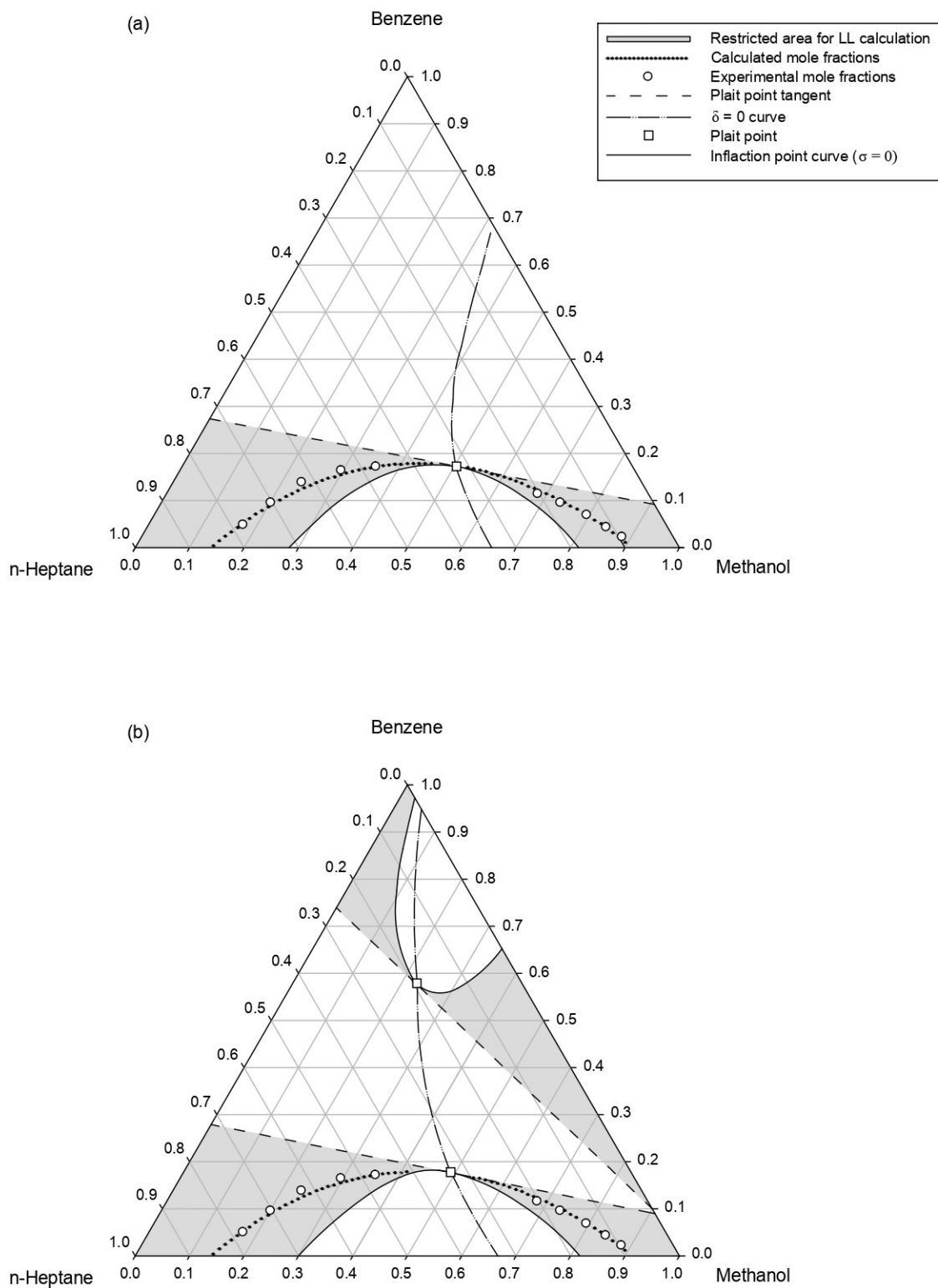


Figure 10. Plait point location for ternary binodal curve provided by the UNIQUAC model parameters for approach 2 (a) and by the interaction parameters proposed by García-Flores et al. [45] (b) at 293.15 K.

## Conclusions

An algorithm for the calculation of thermodynamically consistent single temperature and temperature-dependent parameters of the UNIQUAC model for Type 1 LLE ternary systems was proposed. The algorithm includes specific conditions, such as the stability check in terms of Common Tangent Plane criterion, to ensure that the calculated binary interaction parameters provide an accurate and consistent description of the phase behavior of the liquid systems in all the composition regions at a fixed temperature. In particular, the proposed algorithm was challenged on a popular Type 1 LLE ternary system, namely Methanol (1) + Benzene (2) + n-Heptane (3), which was investigated by Prausnitz and Anderson in their original study on the application of the UNIQUAC model to LLE. This ternary system gave them justification for the modification of the original UNIQUAC model in the modified UNIQUAC model. Furthermore, the system is still wrongly reproduced by the Honeywell's UniSim® Design Suite process simulator. Accurate results were obtained, proving that the original UNIQUAC model with appropriate interaction parameters can describe excellently the studied Type 1 ternary system.

Moreover, it was proved that when the present algorithm is first applied to the binary LLE subsystems to obtain interaction parameters and the same parameters are then used on the ternary LLE without further reeving them, the UNIQUAC model can still provide an accurate representation of the ternary LLE.

### **Free software for the UNIQUAC parameters regression from binary LLE data**

A software that implements the algorithm described for single temperature LLE data of binary systems is provided as supplementary material. The software is free for research and teaching.

## Nomenclature

### Latin symbols

$\Delta g_{\text{mix}}$	Gibbs free energy of mixing [J/mol];
$x_i$	Mole fraction of $i$ -th component;
$a_{ij}, a_{ji}$	Binary interaction parameters of the UNIQUAC model [K];
$a^A_{ij}, a^B_{ij}, a^C_{ij}, a^A_{ji}, a^B_{ji}, a^C_{ji}$	Coefficients of the temperature-dependent correlations of the UNIQUAC parameters;
$a_{ij}^{\text{ip}}, a_{ji}^{\text{ip}}$	Initial points of binary interaction parameters [K];
$l$	Parameter of UNIQUAC model;
$n$	Number of components;
$n_i$	Overall number of moles of $i$ -th component;
$n_{\text{tot}}$	Total number of moles of the system;
$n'$	Number of independent components;
$T$	Temperature;
$R$	Universal gas constant;
$r$	Volume structural parameter of UNIQUAC model;
$q$	Surface area structural parameter of UNIQUAC model;
$nPh$	Number of phases;
$Nt$	Number of experimental LL tie-lines;
$z$	Parameter of UNIQUAC model;
$z_i$	Overall experimental mole fraction of $i$ -th component;

### Greek Symbols

$\gamma_i$	Activity coefficient of $i$ -th component;
$\beta$	Mole fraction of the overall liquid in phase I;
$\sigma$	Determinant of Hessian matrix of $\Delta g_{\text{mix}}$ ;
$\delta$	Determinant of additional matrix for plait point condition;
$\phi_i$	Segment (or volume) fraction of the $i$ -th component;
$\theta_i$	Area fraction of the $i$ -th component;
$\tau_{ij}, \tau_{ji}$	Dimensionless binary interaction parameters of UNIQUAC model;

### Acronyms

CTP	Common Tangent Plane;
LLE	Liquid-Liquid Equilibrium;
LLLE	Liquid-Liquid-Liquid Equilibrium;
OF	Objective Function;
TPDF	Tangent Plane Distance Function;
VLE	Vapor-Liquid Equilibrium;
VLLE	Vapor-Liquid-Liquid Equilibrium;

### Subscripts/Superscripts

I	Phase 1;
II	Phase 2;
calc	Calculated;
exp	Experimental;
iter	Iterative;
comb	Combinatorial;
res	Residual;

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## Appendix A. Gibbs free energy of mixing calculated with UNIQUAC model

For a multicomponent liquid system, the Gibbs free energy of mixing ( $\Delta g_{\text{mix}}$ ) is equal to:

$$\frac{\Delta g_{\text{mix}}}{RT} = \sum_{i=1}^n (x_i \ln x_i) + \sum_{i=1}^n (x_i \ln \gamma_i) \quad (6)$$

where  $R$  is universal gas constant,  $T$  is the temperature, and  $n$  is the number of the components of the system. The activity coefficient modelled by the UNIQUAC model is defined as:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \quad (7)$$

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^n x_j l_j \quad (8)$$

$$\ln \gamma_i^{\text{res}} = q_i \left[ 1 - \ln \left( \sum_{j=1}^n \theta_j \tau_{ji} \right) - \sum_{j=1}^n \frac{\theta_j \tau_{ij}}{\sum_{k=1}^n \theta_k \tau_{kj}} \right] \quad (9)$$

where  $\gamma_i^{\text{comb}}$  is the combinatorial part of the activity coefficient of the  $i$ -th component,  $\gamma_i^{\text{res}}$  is the residual part of the activity coefficient of the  $i$ -th component,  $\phi_i = x_i r_i / \sum x_j r_j$  is the segment (or volume) fraction of the  $i$ -th component,  $r_i$  is the volume structural parameter of the  $i$ -th component,  $\theta_i = x_i q_i / \sum x_j q_j$  is the area fraction of the  $i$ -th component,  $q_i$  is the surface area structural parameter of

the  $i$ -th component,  $z$  is the average coordination number (usually equal to 10),  $l_i = (r_i - q_j) z/2 - (r_i - 1)$ , and  $\tau_{ij} = \exp(-a_{ij}/T)$  and  $\tau_{ji} = \exp(-a_{ji}/T)$  are the dimensionless binary interaction parameters that contains the binary interaction parameters [K]. The values of the structural parameters ( $r_i$  and  $q_i$ ) of the compounds studied in this work are reported in Table 1.



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