Calculation of ternary liquid-liquid equilibrium data using arc-length continuation

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Abstract
Liquid-liquid extraction is an important separation technique used in several chemical engineering processes. When experimental data are unavailable, reliable prediction of liquid-liquid equilibrium (LLE) data is essential for the optimal design of these processes. This paper describes a new methodology based on the application of the arc-length continuation numerical technique in order to compute LLE data using non-random two liquid or universal quasi-chemical activity coefficient models. This technique is straightforward to implement in MATHEMATICA®. In addition, the arc-length method avoids the main disadvantage of root finding methods, such as Newton’s method, for which the convergence often depends on the proper choice of an initial guess. Another advantage of the proposed approach, based on arc-length continuation, is that all LLE data are generated in one single calculation. Several case studies, involving the three main types of ternary systems (ie, Type I, II and 0), illustrate the proposed method. For type I, we study the following three ternary systems: (1) water-ethanol-benzene, (2) 5-hydroxymethylfurfural-1-butanol-water, and (3) methanol-benzene-water. We have selected, for type II systems, the following mixtures: (1) isobutyl alcohol-cyclohexane-water, (2) methanol-cyclohexane-water, and (3) 4-methyl-2-pentanone-2-butanol-water. For type 0 systems, we have chosen a mixture composed of DMSO-THF-water. Finally, for each case, our predicted results are benchmarked against the corresponding experimental data.

KEYWORDS
arc-length continuation, liquid-liquid equilibrium data, Mathematica®, NRTL and UNIQUAC models

1 INTRODUCTION

Liquid-liquid extraction is an important separation technique utilized in many industrial processes. Examples include treatment of lubricating oil, separation of organic aliphatic acids from aromatic hydrocarbons, extraction of phenols,
sulfonic acids, amines, metal salts and inorganic acids, as well preparation of pesticides\textsuperscript{1,2} and many processes of the pharmaceutical industry (eg, production of penicillin\textsuperscript{3}).

The design of an efficient extraction process requires accurate Liquid-Liquid Equilibrium (LLE) data. The cost and effort required to collect these experimental data, encourages scientists to develop new theoretical methods for their prediction. For an in-depth treatment of the experimental procedures and the related theory on LLE, the readers can refer to References 4–6. It should however be noted that it is complicated to calculate LLE in three-component and more complex liquid mixtures and that even by using binary interaction parameters the prediction of ternary mixture equilibrium may lead to inaccurate bimodal curves and tie lines. The reason is that the activities of the components in the liquid phases have to reproduce correctly composition as well as temperature effects.\textsuperscript{7} The Non-Random Two Liquid (NRTL)\textsuperscript{8} and Universal Quasi-Chemical (UNIQUAC)\textsuperscript{9} models are commonly used in order to predict the activity coefficients. They are applicable to any multi-component system, assuming that local compositions for the system can be described by relationships similar to those for binary systems.\textsuperscript{10} The required binary interaction parameters for the models are obtained via regression from experimental LLE data.\textsuperscript{7,11-13}

The procedure used to predict LLE data, for ternary mixtures, involves solving a group of iso/activity equations under mass/mole balance constraints. The objective of the present paper is to describe a new method to solve this problem. The proposed approach is based on arc-length continuation. This method has been applied to solve various chemical engineering problems.\textsuperscript{14-18} Although the complex homotopic continuation method was utilized for problems related to LLE,\textsuperscript{19,20} to the best of our knowledge, the simpler arc-length continuation technique has not been applied to LLE data computations.

In the present paper we start by describing the proposed method used to generate LLE data and the two thermodynamics models used for the calculations. The subsequent section is dedicated to illustration of the application of the arc-length approach for the prediction of binodal curves and tie lines LLE data for several different ternary mixtures. The calculated data are compared with the bibliographical reported experimental data. In cases where binary interaction parameters are missing, they are deduced by regression of the experimental data using numerical optimization.

2 | THE PROPOSED COMPUTATIONAL METHOD

2.1 | Governing equations

Consider 1 mol of a heterogeneous two-phase liquid mixture involving three chemical species (a solvent, a diluent, and a solute) with the corresponding overall molar composition: \(z_1, z_2,\) and \(z_3\).

At fixed temperature \(T\) and pressure \(P\), the chemical equilibrium implies the equality of the activity \(a_i = x_i \gamma_i\) of any component \(i\) in both phases (‘\(\prime\)’ and ‘\(\prime\)’):

\[
x'_i \gamma'_i = x''_i \gamma''_i \text{ for } i = 1..3
\]

where \(x_i\) denotes the mole fraction and \(\gamma_i\), the activity coefficient.

In the present paper, two thermodynamic approaches are applied for the evaluation of \(\gamma_i\), NRTL and UNIQUAC models.

According to NRTL model\textsuperscript{7,21-23} the activity coefficient \(\gamma_i\) of component \(i\) in a liquid phase mixture writes:

\[
\ln \gamma_i = \frac{\sum_{j=1}^{3} \tau_{ij} G_{ij} x_j}{\sum_{j=1}^{3} G_{ij} x_j} + \sum_{j=1}^{3} \left[ \frac{x_j G_{ij}}{\sum_{k=1}^{3} G_{jk} x_k} \left( \tau_{ij} - \frac{\sum_{k=1}^{N3} \tau_{kj} G_{kj} x_k}{\sum_{k=1}^{N3} G_{kj} x_k} \right) \right]
\]

when \(\Delta g_{ij}\) denotes the interaction parameter between components \(i\) and \(j\), and \(a_{ij}\), the non-randomness parameter \((a_{ij} = a_{ji})\). \(\tau_{ij}\) in Equation (2) is defined as

\[
\tau_{ij} = \frac{\Delta g_{ij}}{T}
\]
with $\Delta g_{ii} = 0$, and hence $\tau_{ii} = 0$, and $G_{ij}$, as

$$G_{ij} = e^{-\alpha_{ij} \tau_{ij}}$$

In the UNIQUAC model,\textsuperscript{7,21-23} the activity coefficient $\gamma_i$ is written as the product of a combinatorial contribution $\gamma_i^C$ and a residual contribution, $\gamma_i^R$, or equivalently.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$  \hfill (3)

The combinatorial part depends on the geometrical properties of the mixture components, for example, for component $i$, on the relative van der Waals surface area $q_i$ and the relative van der Waals volume $r_i$. In the mixture, the individual volumetric characteristics are expressed as

$$V_i = \frac{r_i}{\sum_{j=1}^{3} r_j x_j}$$

and the surface characteristics as

$$F_i = \frac{q_i}{\sum_{j=1}^{3} q_j x_j}$$

The combinatorial contribution $\gamma_i^C$ is then

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i}\right)$$  \hfill (4)

The residual part of the activity coefficient expresses the energetic interactions between the components in the considered phase,

$$\ln \gamma_i^R = q_i \left(1 - \ln \frac{\sum_{j=1}^{3} \tau_{ij} q_j x_j}{\sum_{j=1}^{3} q_j x_j} - \sum_{j=1}^{3} \frac{\tau_{ij} q_j x_j}{\sum_{k=1}^{3} \tau_{ik} q_k x_k}\right)$$  \hfill (5)

with

$$\tau_{ij} = e^{-\Delta u_{ij}/T}$$

where $\Delta u_{ij}$ stands for the binary interaction parameter between components $i$ and $j$, with $\Delta u_{ii} = 0$ and hence, $\tau_{ii} = 1$.

Considering the summation rule $\left(\sum_{i=1}^{3} x'_i = 1\right)$ and $\sum_{i=1}^{3} x''_i = 1$ and denoting by $K_i$ the ratio of the activity coefficients of component $i$ in the two phases,

$$K_i = \frac{\gamma_i'}{\gamma_i''}, \quad i = 1.3$$  \hfill (6)

and by $\phi$ the amount of phase \textsuperscript{('')}, we can write for the mole composition of phase \textsuperscript{('')}

$$x'_1 = \frac{z_1}{1 + (K_1 - 1)\phi}$$

$$x'_2 = \frac{z_2}{1 + (K_2 - 1)\phi}$$

$$x'_3 = 1 - x'_1 - x'_2 = \frac{z_3}{1 + (K_3 - 1)\phi} = \frac{1 - z_1 - z_2}{1 + (K_3 - 1)\phi}$$  \hfill (7)
The problem now is to calculate for fixed temperature, pressure, and overall molar composition \((z_1, z_2, \text{ and } z_3)\) of the two-phase mixture the compositions in both phases. To solve this system of three algebraic equations in three unknowns \((x'_1, x'_2, \text{ and } \varphi)\), numerous classical algorithms are available. In a previous work, a method to solve this problem with the help of the built-in MATHEMATICA© command FindRoot\textsuperscript{24} was presented. However, FindRoot, similar to other iterative methods based on either the secant or Newton’s methods, requires a good initial guess. It is quite difficult to provide a good initial guess in certain cases, particularly when the objective, as it is in the present paper, is not to calculate just one equilibrium situation, but also to predict complete bimodal curves as well as tie lines.

We think that the following presented new approach based on the arc-length continuation technique is more suitable for such repetitive calculations. In particular, this method circumvents the problem of finding good start values for each new calculation.

2.2 The arc-length continuation method

Consider a system of nonlinear algebraic equations in \(N\) unknowns \((u_1, u_2, \ldots, u_N)\), which in vector representation writes

\[ f(u; \alpha) = 0 \]  

(8)

And where \(\alpha\) is a parameter on which the solution of this system depends. \(u\) and \(f\) are vectors with the respective components \(f = (f_1, f_2, \ldots, f_N)\) and \(u = (u_1, u_2, \ldots, u_N)\). In order to obtain a solution for this system, the value of \(\alpha\) has to be set. Finding the solution of such system as a continuous function of \(\alpha\) is challenging due to the nonlinearity of the system and the eventual existence of multiple roots. However, the parametric methods help obtaining the solution as function of the continuous varying parameter \(\alpha\). One such approach is the arc-length continuation method. The unknown variable and the parameter \(\alpha\) are set as a function of the arc-length, represented by the symbol \(s\) in the following.

Let us assume that the solution \(u\) is an analytic function of \(\alpha\) (ie, continuous and differentiable). Let us further suppose that for a particular value of \(\alpha\), \(\alpha = \alpha_0\), the system has a solution \(u_0\), that is,

\[ f(u_0; \alpha_0) = 0 \]  

(9)

In this case, a neighboring solution \(u = u(\alpha)\) can be calculated starting from \(u_0 = u(\alpha_0)\) by constructing a Taylor expansion about \(u_0\). For a multi-value function of \(\alpha\), the solution can be parameterized in term of arc-length \(s\) on the solution curve for convenience. Therefore, we can write:

\[ u = u(s), \alpha = \alpha(s) \]  

(10)

So that Equation (8) becomes

\[ f(u(s), \alpha(s)) = 0 \]  

(11)

To solve the system of equations (11), an additional relation is needed. The appropriate auxiliary equation is given by the definition of the arc-length:

\[ \frac{du}{ds} \frac{du}{ds} + \left( \frac{d\alpha}{ds} \right)^2 = 1 \]  

(12)

The equations set (11) and (12) is now a differential algebraic equations (DAE) system. In this article, we solve it using the built-in MATHEMATICA© command NDSolve. Alternatively, one can discretize Equation (12) and solve the algebraic system (11) and (12) again with the built-in MATHEMATICA© function FindRoot in combination with the continuation procedure NestList, in which every found solution is used as starting point for the next equilibrium calculation.
### 2.3 Application of the method

The computational procedure for the proposed method begins by setting up the DAE system for a fixed value of the temperature $T$. For practical purposes, we choose to solve the following set of equations.

\[
\begin{align*}
    x'_1(s) - \frac{z_1}{1 + (K_1(s) - 1)\varphi(s)} &= 0 \\
    x'_2(s) - \frac{z_2(s)}{1 + (K_2(s) - 1)\varphi(s)} &= 0 \\
    x''_1(s) - \frac{K_1(s)z_1}{1 + (K_1(s) - 1)\varphi(s)} &= 0 \\
    x''_2(s) - \frac{K_2(s)z_2(s)}{1 + (K_2(s) - 1)\varphi(s)} &= 0 \\
    \sum_{i=1}^{3} (K_i(s) - 1) - \frac{K_i(s)z_i}{1 + (K_i(s) - 1)\varphi(s)} &= 0 \\
\end{align*}
\]

For an arbitrary value of $z_1$, a particular solution $u_0 = (x'_1, x'_2, x''_1, x''_2, \varphi_0)$ of the set of algebraic equations (the first five equations) of system (13) is found for a chosen value of $z_2$, that is, $z_2 = z_2(s = 0)$ using the MATHEMATICA© functions FindRoot or alternatively FindMinimum. This particular solution together with the initialization of the derivatives in the last equation of the set (13) are used as initial conditions for the resolution of the DAE system.

### 3 Illustrations and Discussion

Liquid ternary mixtures can roughly be classified in three types based on the number of miscible component pairs. In the type I systems, also called closed systems, observed for about 75% of the LLE, only one binary pair shows a miscibility gap, generally solvent and diluent, while the solvent and solute are completely miscible. Such systems exhibit a plait or critical point where both liquid phases have the same composition.

In the Type II, also called open systems, the solvent is partially miscible with the two other components. Such systems exhibit no plait points. This behavior is encountered in about 20% of all cases. The third type, labeled Type 0, is less frequently observed but interesting as although all three component pairs (diluent-solute, solute-solvent, diluent-solvent) are miscible, there exists a composition region where the homogeneous liquid splits in two partially miscible liquid phases. In the LLE diagram, this system is represented by a heterogeneous island enclosed by an otherwise homogeneous three-component phase. The Type 0 systems exhibit two plait points, which limit the tie lines on both sides, bottom and top, of the island. At plait points, the composition of the two phases become identical and hence further separation is impossible. Various other LLE cases are also observed in practice but in the following, we will consider only the three most encountered cases.

#### 3.1 Water-ethanol-benzene

As first illustration we propose to calculate the LLE data for the ternary system benzene-ethanol-water at (25°C, 1 bar) using the UNIQUAC model. Application of such equilibrium diagram includes heterogeneous azeotropic distillation to obtain anhydrous ethanol using benzene as an entrainer (eg, the three column Kubierschky system). The ternary saturation curve is of Type I. The UNIQUAC parameters are given in Table 1.

The obtained binodal curve is depicted in Figure 1 (red curve) together with literature two-phase equilibrium data (blue dots) as well as several reported tie lines. Calculated and experimental plait points (red and magenta dots, respectively) are also represented. Note the very good agreement between the predicted data by the new method and their corresponding experimental values. This good concordance is also observed for the tie lines as Table 2 shows and Figure 2 graphically illustrates.
### Table 1: UNIQUAC parameters of the system water-ethanol-benzene

| $i/j$ | $r_i$ | $q_i$ | $\Delta u_{ij}$(K) |
|---|---|---|---|
| 1 | Water | 0.92 | 1.4 | 0 | 526.02 | 309.64 |
| 2 | Ethanol | 2.1055 | 1.972 | −318.06 | 0 | −91.532 |
| 3 | Benzene | 3.1878 | 2.4 | 1325.1 | 302.57 | 0 |

![Figure 1](image)  
**Figure 1** Calculated binodal curve (red line) and experimental data (blue dots) for the system Water-Ethanol-Benzene (1 bar, 25°C)

#### 3.2 5-Hydroxymethylfurfural (5-HMF)-1-butanol-water

5-Hydroxymethylfurfural is an important biomass product. Its synthesis in homogenous catalytic micro-reactors involves an in-situ extraction step from the aqueous reaction mixture using low boiling point organic solvents such as 1-butanol, iso-butanol, 4-methyl-2-pentanone (MIBK), and so on. We treat in the following the 1-butanol case. The NRTL model is applied for the calculation of the liquid-liquid two-phase equilibrium. The binary interaction parameters are taken from Reference 27. For a pressure of 1 bar and at 313.15 K, the ternary equilibrium curve is of type I.

The calculated solubility curve is depicted in Figure 3 (red curve) together with the available bibliographical equilibrium data (blue dots) and the corresponding tie lines. The proposed numerical procedure enables to generate the totality of the bimodal curve using the reported NRTL parameters. The comparison between calculated and experimental equilibrium solubility data shows that the former are quite accurately predicted. We notice also a good concordance between calculated and experimental tie lines as Table 3 shows and Figure 4 graphically illustrates.

#### 3.3 Methanol-benzene-water

For this system, also a type I bimodal curve at 20°C and 1 bar, a rich databank of equilibrium data is available, but no NRTL or UNIQUAC parameters. Regression of the tie line data using the numerical technique of Particle Swarm Optimization (PSO) yields the missing UNIQUAC binary interaction parameters. The goodness of the fit was measured by calculating the root-mean-squared deviation (RMSD) which was equal to 0.831%. As Figure 5 shows, the generated solubility curve is in very good agreement with the bibliographical data as well as the plait points. Further, the experimental distribution data of methanol are accurately represented by the calculated distribution curve (Figure 6). Table 4 shows that the difference between calculated and reported methanol equilibrium composition in both phases is fairly low.
**TABLE 2** Equilibrium ethanol molar composition in aqueous ($x'_1$) and organic ($x''_1$) phase in comparison with calculated data ($x''_{1,c}$)

| $x'_1$ | $x''_1$ | $x''_{1,c}$ | $|x''_1 - x''_{1,c}|$ |
|--------|---------|-------------|-----------------|
| 0.0308 | 0.0996  | 0.0748      | 0.0248          |
| 0.0332 | 0.0797  | 0.0809      | 0.0017          |
| 0.0523 | 0.1484  | 0.1263      | 0.0221          |
| 0.0576 | 0.1496  | 0.1379      | 0.0103          |
| 0.0586 | 0.1298  | 0.1400      | 0.0103          |
| 0.0725 | 0.1821  | 0.1684      | 0.0137          |
| 0.0733 | 0.1849  | 0.1700      | 0.0149          |
| 0.0856 | 0.1819  | 0.1930      | 0.0111          |
| 0.0912 | 0.1813  | 0.2029      | 0.0216          |
| 0.1171 | 0.2398  | 0.2446      | 0.0048          |
| 0.1192 | 0.2453  | 0.2477      | 0.0024          |
| 0.1294 | 0.2354  | 0.2623      | 0.0270          |
| 0.132  | 0.2626  | 0.2659      | 0.0033          |
| 0.1334 | 0.2407  | 0.2679      | 0.0272          |
| 0.1609 | 0.2789  | 0.3026      | 0.0237          |
| 0.1894 | 0.3173  | 0.3334      | 0.0161          |
| 0.2034 | 0.3539  | 0.3468      | 0.0071          |
| 0.2244 | 0.3551  | 0.3649      | 0.0098          |
| 0.2452 | 0.3884  | 0.3805      | 0.0079          |
| 0.2622 | 0.3938  | 0.3917      | 0.0021          |
| 0.2934 | 0.4106  | 0.4085      | 0.0021          |
| 0.3162 | 0.415   | 0.4175      | 0.0025          |
| 0.3247 | 0.4156  | 0.4201      | 0.0045          |
| 0.3309 | 0.4177  | 0.4217      | 0.0040          |
| 0.3309 | 0.4177  | 0.4217      | 0.0040          |
| 0.3914 | 0.3914  | 0.4230      | 0.0316          |
| 0.3930 | 0.3930  | 0.4226      | 0.0296          |

**FIGURE 2** Equilibrium distribution diagram of ethanol between aqueous and organic phases (1 bar, 25°C). Blue: calculated curve, red dots: experimental data. 

![Equilibrium distribution diagram](image)
FIGURE 3  Calculated binodal solubility curve (red line) and experimental data (blue dots)\textsuperscript{27} for the system 5-HMF-1-butanol-water (1 bar, 40°C). Dashed lines: tie lines

TABLE 3  Equilibrium 5-HMF composition (mass fraction) in aqueous ($\xi_1'$) and organic ($\xi_1''$) phase in comparison with calculated data ($\xi_1'''$)

| $\xi_1'$ | $\xi_1''$ | $\xi_1'''$ | $|\xi_1'' - \xi_1''|$
|----------|----------|----------|----------------|
| 0.019    | 0.007    | 0.006    | 0.001         |
| 0.041    | 0.016    | 0.013    | 0.003         |
| 0.078    | 0.039    | 0.030    | 0.009         |
| 0.122    | 0.059    | 0.056    | 0.003         |
| 0.154    | 0.081    | 0.081    | 0.000         |
| 0.183    | 0.109    | 0.108    | 0.001         |

FIGURE 4  Equilibrium distribution curve of 5-HMF (molar fraction) between aqueous and organic phases (1 bar, 40°C). Blue: calculated curve, red dots: experimental data

3.4  Isobutyl alcohol-cyclohexane-water

As first illustration of type II solubility curve of a ternary liquid system, we treat the case of isobutyl alcohol-cyclohexane-water. LLE of this system is needed for example in the recovery process of isobutyl alcohol from wastewater using cyclohexane as entrainer.\textsuperscript{30} At 25°C (and 1 bar), diluent (water) and solvent (cyclohexane) are practically immiscible, but the binary mixture of diluent and solute (isobutyl alcohol) exhibits also a large miscibility gap.

For this ternary equilibrium, experimental data are available\textsuperscript{26} but binary interaction parameters are missing. The numerical PSO procedure is used to deduce the UNIQUAC parameters basing on the equilibrium compositions of the coexisting phases (tie lines). The RMSD was equal to 0.354%, which indicates the goodness of the fit. The generated
**Figure 5** Calculated binodal solubility curve (red line) and experimental data (blue dots) for the system methanol-benzene-water (1 bar, 20°C). Dashed lines: experimental tie lines.  

**Figure 6** Distribution diagram of methanol between organic and aqueous phases (1 bar, 20°C). Blue: calculated curve, red dots: experimental data.  

**Table 4** Equilibrium methanol composition in aqueous and organic phase in comparison with calculated data

| $x_1'$ | $x_1''$ | $x_{lc}'$ | $|x_1'' - x_{lc}'|$ |
|-------|--------|--------|----------------|
| 0.0000 | 0.0000 | 0.0000 | 0.0000         |
| 0.0192 | 0.1538 | 0.2008 | 0.0470         |
| 0.0450 | 0.3498 | 0.3831 | 0.0333         |
| 0.0674 | 0.4814 | 0.4791 | 0.0022         |
| 0.1145 | 0.5972 | 0.5840 | 0.0132         |
| 0.1775 | 0.6320 | 0.6255 | 0.0065         |
| 0.4410 | 0.4410 | 0.4491 | 0.0081         |

bimodal curve as well as the tie lines are in almost perfect agreement with the experimental data (Figure 7). The difference between calculated and experimental composition of the solute in the aqueous phase are, as Table 5 displays, very low.

### 3.5 Methanol-cyclohexane-water

The bimodal solubility curve of this ternary mixture exhibits two miscibility gaps at 25°C and 1 bar. Solvent and diluent are immiscible, solute and solvent only partially miscible while diluent and solvent are totally miscible.
Experimental solubility diagram and tie lines with their calculated counterparts are depicted in Figure 8. Theoretical curve and tie lines are generated using the UNIQUAC model with interaction binary parameters deduced by PSO regression of the experimental tie lines data. The RMSD was equal to 0.297%.

We notice that calculated and experimental solubility are in very good concordance. The distribution of the alcohol between the organic phase and the aqueous phase is also accurately predicted as Table 6 demonstrates.

### 3.6 4-Methyl-2-pentanone (MIBK)-2-butanol-water

The miscibility bimodal curve of the system MIBK-2-butanol-water at 20°C (1 bar) shows a solubility gap for the binary solvent (MIBK)/diluent (water) and another gap for the binary solute/diluent (2-butanol/water), while solute and solvent are totally miscible. Figure 9 depicts the experimental tie lines data and the generated binodal curve basing on the UNIQUAC parameters from Reference 31. The RMSD between experimental and calculated tie line compositions (Table 7) is 0.61.
**FIGURE 8** Calculated binodal solubility curve (red line) and experimental data (blue dots)\(^2\)\(^6\) for the system methanol-cyclohexane-water (1 bar, 25°C). Dashed blue lines: experimental tie lines, red line segments: calculated tie lines\(^2\)\(^6\)

**TABLE 6** Calculated equilibrium methanol composition in aqueous and organic phases in comparison with experimental data

| \(x'_1\) | \(x''_1\) | \(x'''_1\) | \(|x''_1 - x'''_1|\) |
|---------|---------|---------|----------------|
| 0.0006  | 0.100   | 0.100   | 0.0004         |
| 0.0019  | 0.242   | 0.243   | 0.0012         |
| 0.0047  | 0.369   | 0.371   | 0.0020         |
| 0.0064  | 0.529   | 0.530   | 0.0007         |
| 0.0097  | 0.719   | 0.717   | 0.0016         |
| 0.0276  | 0.828   | 0.819   | 0.0087         |
| 0.0567  | 0.843   | 0.850   | 0.0065         |

**FIGURE 9** Calculated binodal solubility curve (red line) and experimental data (blue dots)\(^3\)\(^1\) for the system 2-butanol-MIBK-water (1 bar, 20°C). Dashed blue lines: experimental tie lines

**3.7 | DMSO-THF-water**

The ternary liquid system dimethyl-sulfoxide/tetra-hydrofuran/water exhibits at 20°C and 1 bar a closed binodal curve.\(^3\)\(^2\) In the ternary miscibility diagram, the heterogeneous two-phase region is enclosed in a homogenous liquid phase. This island type LLE, type O in the Treybal classification,\(^6\) although not very frequent, is interesting, as all three binaries of the considered ternary system are completely miscible.
TABLE 7  Calculated equilibrium 2-butanol composition in aqueous and organic phases in comparison with experimental data

| $x'_1$ | $x''_1$ | $x''_{L_2}$ | $|x''_1 - x''_{L_2}|$ |
|----------|----------|-------------|---------------------|
| 0.000    | 0.000    | 0.000       | 0.000               |
| 0.045    | 0.004    | 0.001       | 0.003               |
| 0.106    | 0.010    | 0.004       | 0.006               |
| 0.164    | 0.014    | 0.007       | 0.007               |
| 0.205    | 0.016    | 0.009       | 0.007               |
| 0.253    | 0.020    | 0.013       | 0.007               |
| 0.289    | 0.023    | 0.017       | 0.006               |
| 0.313    | 0.028    | 0.027       | 0.001               |
| 0.312    | 0.028    | 0.027       | 0.001               |
| 0.314    | 0.031    | 0.029       | 0.002               |
| 0.306    | 0.036    | 0.036       | 0.000               |
| 0.295    | 0.042    | 0.042       | 0.000               |
| 0.293    | 0.046    | 0.43        | 0.003               |
| 0.271    | 0.069    | 0.054       | 0.015               |

It is noticed however in the literature that the standard local composition models (NRTL, UNIQUAC) cannot correctly predict a closed binodal curve surrounded by a homogeneous ternary solution.\textsuperscript{12, 13}

Using the NRTL parameters of Reference 12 in association with the arc-length continuation procedure produces exactly the same calculated miscibility curve and the corresponding tie-lines as reported in Reference 12. Figure 10 (fig. 9 in Reference 12) shows that the predicted enclosed heterogeneous region is less extended than the experimental one. Particularly the compositions of the aqueous phase are affected: The calculated solubility of tetra-hydrofuran (THF) in the aqueous phase is larger than it is effectively in reality. Similar results are also obtained in Reference 13 using NRTL as well as UNIQUAC models. Our calculations using UNIQUAC model with parameters deduced from tie-lines compositions by a PSO procedure, with an RMSD equal to 3.401\%, yields a somewhat different closed binodal curve (Figure 11). Now the solubility of Dimethyl-sulfoxide (DMSO) is affected. It is overestimated for larger compositions of DMSO and underestimated for lower compositions.

FIGURE 10  Calculated binodal solubility curve (red line, NRTL) and experimental data (blue dots)\textsuperscript{12} for the system DMSO-THF-water (1 bar, 20$^\circ$C). Dashed blue lines: experimental tie lines
3.8 | *n*-Hexane-methyl cyclopentane-aniline: Temperature effect

As last illustration of the arc-length method, we calculate the binodal curve and the tie lines of the ternary liquid system *n*-hexane-methyl cyclopentane-aniline for three increasing temperatures: 25°C, 34.5°C, and 45°C. The experimental solubility data of the system at these temperatures are reported in Reference 33. At 25°C, the binodal curve is of Type II: both binary systems *n*-hexane-aniline and methyl cyclopentane-aniline exhibit a miscibility gap. Figure 12 shows the reference data for this temperature as well as the calculated binodal curve and tie lines using the NRTL model. The model parameter is deduced from the tie line data using the PSO procedure. The RMSD was equal to 0.976%. As can be noticed, the predicted values reproduce fairly well the experimental data. By increasing the temperature to 34.5°C, methyl cyclopentane becomes just enough soluble in aniline that the plain point of the ternary curve is now located on the corresponding side of the triangle. The binary *n*-hexane-aniline shows still a miscibility gap. This condition represents the transition border of the binodal curve from type II to type I. Figure 13 depicts this behavior in comparison between calculated and experimental data. We notice once more the good agreement between prediction and bibliographical data. Figure 14 and Table 8 reproduce graphically and numerically the calculated and measured methyl cyclopentane distribution between the two coexisting phases. For the higher temperature of 45°C, the miscibility curve is typically of type I. Figure 15 shows a comparison between
FIGURE 13  Calculated solubility curve (red line, NRTL + PSO) and experimental data (blue dots) for the system methyl cyclopentane–aniline–n-hexane (1 bar, 34.5°C). Dashed blue lines: experimental tie lines, red thin lines: calculated tie lines.

FIGURE 14  Distribution diagram of methyl cyclopentane between aniline and n-hexane phases (1 bar, 25°C). Blue: calculated curve, red dots: experimental data.

TABLE 8 – Calculated equilibrium methyl cyclopentane composition in aniline and n-hexane phases in comparison with experimental data.

| $x_1''$ | $x_1'$ | $x_{Le}'$ | |$x_1' - x_{Le}'$|
|---------|--------|----------|----------------|
| 0.000   | 0.000  | 0.000    | 0.000          |
| 0.109   | 0.010  | 0.008    | 0.002          |
| 0.230   | 0.008  | 0.024    | 0.016          |
| 0.300   | 0.035  | 0.037    | 0.002          |
| 0.479   | 0.065  | 0.081    | 0.016          |
| 0.698   | 0.131  | 0.158    | 0.027          |
| 0.796   | 0.191  | 0.200    | 0.008          |
| 0.857   | 0.242  | 0.227    | 0.015          |
**FIGURE 15** Calculated solubility curve (red line, NRTL + PSO) and experimental data (blue dots)\(^3\) for the system methyl cyclopentane–aniline–n-hexane (1 bar, 45°C). Dashed blue lines: experimental tie lines, red thin lines: calculated tie lines.

Calculated binodal curve and tie lines in comparison with the literature values. As can be noticed, the agreement is fairly good.

**4 | CONCLUSION**

In the present paper, we calculated LLE data for eight ternary systems using a novel numerical method based on arc-length continuation technique. Systems treated include:

- three type I systems (water-ethanol-benzene, 5-HMF-1-butanol-water, and methanol-benzene-water),
- three type II mixtures (isobutyl alcohol-cyclohexane-water, methanol-cyclohexane-water and 4-methyl-2-pentanone-2-butanol-water),

and

- a type 0 system (DMSO-THF-water).

In addition, transition from type II to type I behavior was observed when the temperature is increased for the ternary mixture: methyl cyclopentane-aniline-n-hexane. The LLE predictions involved the two ubiquitous activity coefficient models namely NRTL and UNIQUAC. When binary interaction parameters were unavailable in the open literature, we used the PSO technique to estimate such parameters from the experimental tie-lines. When our LLE predictions were benchmarked against their experimental counterparts, excellent agreement was found in all eight case studies. Our new method was implemented using the computer algebra, MATHEMATICA©. Each LLE calculation took only a few seconds to generate literally an infinite number of tie lines.

**PEER REVIEW INFORMATION**

*Engineering Reports* thanks the anonymous reviewers for their contribution to the peer review of this work.

**CONFLICT OF INTEREST**

The authors declare no potential conflict of interest.

**DATA AVAILABILITY STATEMENT**

The computer notebooks are available upon request from the corresponding author.
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