LIQUID–LIQUID–LIQUID EQUILIBRIUM CALCULATIONS

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We developed an algorithm for LLLE calculations based on the method of Lucia et al. (2000). We modified the method of calculating of the initial values. A Matlab program was made to test the algorithm. Calculations were executed for the mixtures of Type III: ethylene glycol – lauryl alcohol – nitromethane and 1-hexanol – nitromethane – water.

KEYWORDS: multiphase equilibrium, flash calculation, three-liquid-phase

INTRODUCTION

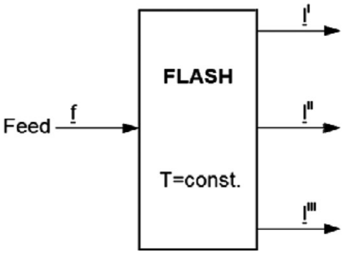
The recovery of the major components from waste solvent streams means an important, actual problem for the industry because of stricter and stricter environmental regulations. The solvent regeneration is performed mainly by distillation and extraction. The waste solvent mixtures often form two and sometimes three equilibrium liquid phases. Polymerisation reactors can also involve three liquid phases. The design, modelling and simulation of these processes demand the accurate description and calculation of the phase equilibria (VLE, LLE, VLLE, LLLE, VLLLE). However the majority of the today's flowsheet simulators (e.g. CHEMCAD, PROSIM) permit only two equilibrium liquid phases. The AspenPlus is an exception.

In the last decade a lot of studies dealt with the numerical solution of the isothermal phase equilibrium problems and the determination of the stability of phases (e.g. Lucia et al., 2000; Guo et al., 2004). The majority of these articles are cited by Wakeham and Stateva (2004) in their comprehensive review. The good estimation of the initial values is always a key issue of the calculations.

The aim of our work is to develop an efficient algorithm and a computer program which is able to compute LLLE. We investigated and modified the algorithm of Lucia et al., developed in collaboration with Aspen Technology Inc.

MODEL OF LLLE FLASHING

For the sake of simplicity when we make the calculations not only the pressure but also the temperature (T) is fixed (isothermal flash). The main problem is that usually the number of phases is not known a priori but it must be determined during the calculation for the mixture of given overall composition.



f_i: moles of component i in the feed (per unit time)
l_i^k: moles of component i in the k-th phase being in equilibrium with all the other phases

In equilibrium: - the chemical potential of each component is the same in each phase,
- the Gibbs free energy of the whole system is minimal.

Figure 1. Three liquid phase flashing

The model equations to be solved:
Material balances:

$$f_i = \sum_{k=1}^{P} l_i^k \quad \text{i} = 1 \ldots \text{C (C: number of components, P: number of phases)} \qquad (1)$$

Equality of activities:

$$\frac{l_i^k}{\sum_{j=1}^{C} l_j^k} \cdot \gamma_i^k = \frac{l_i^{k+1}}{\sum_{j=1}^{C} l_j^{k+1}} \cdot \gamma_i^{k+1} \quad \text{i} = 1 \ldots \text{C},\ \text{k} = 1 \ldots \text{P} - 1 \qquad (2)$$

where γ_i^k is the activity coefficient of component i in the phase k (non-linear function of the composition of phase k).

The number of independent equations:	$C + (P - 1)C = PC$
Fixed parameters:	f_i (i = 1…C), T (and pressure)
Independent variable:	l_i^k (k = 1…P, i = 1…C) (where P is also unknown)

SOLUTION METHOD

Fundamentally two types of method exist for calculating liquid phase equilibriums: the equation solver and the Gibbs free energy minimizer. The first can be succesfully applied for the computation of equilibrium of two liquid phases (e.g. algorithm of Bril et al., 1974) but in the case of three liquid phases difficulties can occur. The algorithms of second type were developed for that very reason. One of these algorithms is the one proposed by Lucia et al. that we studied in detail.

Lucia considered the problem as dimensionless Gibbs free energy (G/RT) minimisation and suggested an overall algorithmic framework for multiphase equilibrium flash calculations based on

- sequential solving of subproblems (LE, LLE, LLLE…) until the global minimum of G/RT is found,

- binary tangent plane analyses to identify all partially miscible pairs and a dominant immiscible pair in the multicomponent mixture,
- generation of initial values for the next subproblem on the basis of the results of binary tangent plane analyses and previously solved subproblems,
- a posteriori testing of phase and solution stability.

The global minimum of the Gibbs free energy surface must be found:

$$G = \sum_{k=1}^{P} \sum_{i=1}^{C} l_i^k G_i^k = \min \tag{3}$$

The final form of the objective function:

$$F = \frac{\Delta G_{mix}}{RT} = \sum_{k=1}^{P} \sum_{i=1}^{C} l_i^k (ln x_i^k + ln \gamma_i^k) = \min \tag{4}$$

where

$$x_i^k = \frac{l_i^k}{\sum\limits_{j=1}^{C} l_j^k} \tag{5}$$

and ΔG_{mix} is the Gibbs free energy of mixing.

By Gautam and Seider (1979) the estimation of the initial values for the minimum search is crucial since poor guesses for phase fractions and compositions can lead to local or constrained minima. Constrained minimum occurs, when too few phases are assumed. Local or constrained minima

- occur, when the correct number of phases is assumed, but composition guesses are poor,
- can occur, when too many phases are assumed.

THE METHOD PROPOSED

We modified several steps of the original method. On the basis of our calculation experience we concluded that:

1. The method of calculating mole fractions of the non-dominant components using relative solubilities
    a. gives smaller mole fractions in both liquid phases than in the feed mixture, and these mole fractions are later further decreased at their normalisation and
    b. the proportion of the two dominant phases is not taken into consideration.
2. The value of the phase fraction increases with the number of components.
3. The selection of the dominant immiscible pair can be ambiguous (e.g. in the case of equal overall mole fractions).

STEP 1. STUDY OF THE MUTUAL MISCIBILITY OF EACH BINARY PAIR

This step corresponds to Step 1 of the original method.

The dimensionless Gibbs free energy of mixing is considered for each binary mixture:

$$\frac{\Delta G_{mix}}{RT} = \Delta g_{mix} = x_1 \cdot ln(\gamma_1 x_1) + x_2 \cdot ln(\gamma_2 x_2) \tag{6}$$

Since $x_1 + x_2 = 1$, Δg_{mix} is a function of only one independent variable. Let $x_1 = x$ then:

$$\Delta g_{mix} = x\, ln(\gamma_1 x) + (1 - x) ln(\gamma_2 (1 - x)) \tag{7}$$

We determine the local minima of the function (7) for all binary mixtures. The function can have just one extremum (minimum) or two (local) minima with a (local) maximum between them. In the latter case the two components are partially miscible. Those mixtures whose function has only one local minimum are stable at any composition. (The second derivative of the function $\Delta g_{mix} - x$ has a nonnegative value in each point.) If there are two local minima we fit a double tangent to the function (Figure 2). The tangency points (T_1, T_2) assign the boundaries (x^{I}, x^{II}) between the stable and unstable liquid phases. If the overall composition of the mixture is found in the opened composition-interval between these two points then the mixture splits into two equilibrium

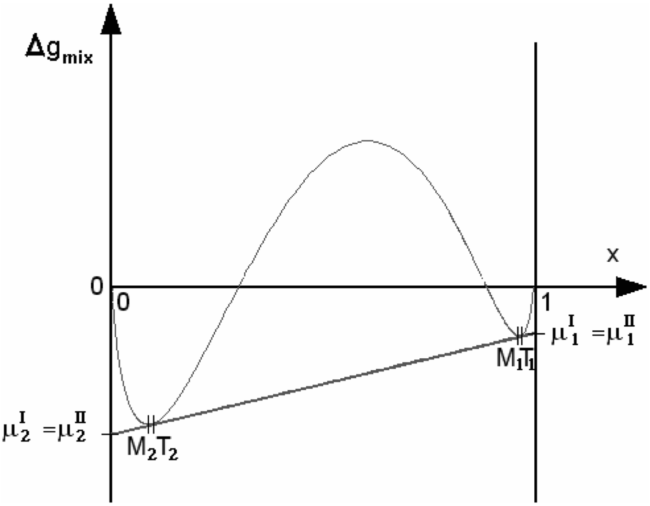


Figure 2. Gibbs free energy of miscibility of a partially miscible pair and the double tangent

liquid phases whose concentrations are the above mentioned boundary-concentrations. (The minimum points (M_1, M_2) and the tangency points (T_1, T_2) do not coincide).

The physical meaning of the double tangent is the following. The values of the tangent of the function $\Delta g_{mix} - x$ drawn at x_0 taken in $x = 0$ and $x = 1$ provide the (dimensionless) chemical potential of the components of the mixture. A two phase mixture is stable if the chemical potential of any component equals in the two phases. This is possible only in the case where the composition of the phases equals the x coordinate of the double tangency points (x^{I}, x^{II}).

STEP 2. SELECTION OF THE DOMINANT IMMISCIBLE PAIR

We select the two dominant (partially miscible) components not only on the basis of the overall mole fractions (z) (as it was made by Lucia et al.) but the mutual solubilities in the binary mixtures are taken into consideration, as well. For a Type III ternary mixture (Figure 3) the lines sl_1, sl_2, sl_3 connect the compositions of the two equilibrium phases of the binary mixtures. We draw straight lines from each pure component vertex through the overall composition point Z of the ternary mixture. Thus we get the points P_i and Q_i (i = 1,2,3). We calculate the ratio $p_i = ZQ_i/P_iQ_i$ for all components and we consider dominant those two components for which we get the two highest values of p_i.

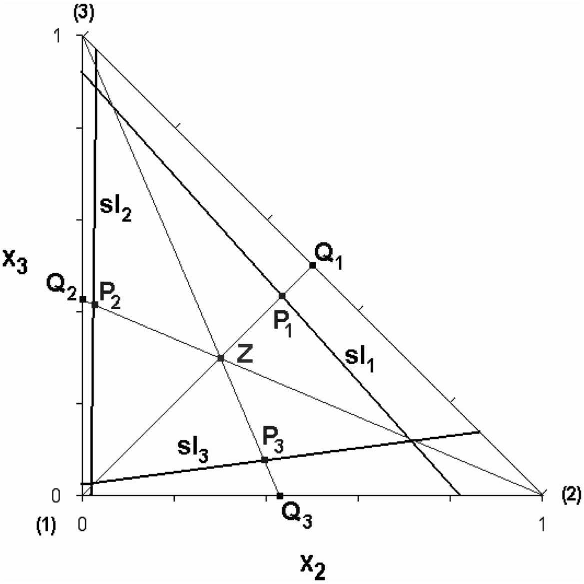


Figure 3. Selection of the dominant pair for a Type III mixture

If there are two p_i values, which are less than 1.0, we select the components belonging to these values as a dominant pair.

STEP 3. ESTIMATION OF COMPOSITION AND RATIO OF TWO LIQUID PHASES ASSUMED

Splitting of the dominant components

A mixture containing only the two dominant components (dom1, dom2) in the same amount as in the feed is considered. Considering their mutual miscibility we calculate the ratio of Phase I to the feed: $\eta = L^I/F$, then molar flows of the dominant components in the two phases.

- Input data:
  - f_{dom1}, f_{dom2}: molar flows of the dominant components in the feed
  - x^I_{dom1}, x^{II}_{dom1}: mole fractions of dom1 in the phases rich (I) and poor (II) in dom1.
- Unknowns: l^I_{dom1}, l^I_{dom2}, l^{II}_{dom1}, l^{II}_{dom2}
- Solution:

$$f_{dom1} = L^I x^I_{dom1} + L^{II} x^{II}_{dom1} \tag{8}$$

where L^I and L^{II} are the molar flows of the equilibrium phases.

Let

$$F = L^I + L^{II} \tag{9}$$

$$F z_{dom1} = \eta F x^I_{dom1} + (1-\eta) F x^{II}_{dom1} \tag{10}$$

where

$$z_{dom1} = \frac{f_{dom1}}{f_{dom1} + f_{dom2}} \tag{11}$$

Equation (10) is divided by F and it is rearranged:

$$\eta = \frac{z_{dom1} - x^{II}_{dom1}}{x^I_{dom1} - x^{II}_{dom1}} \tag{12}$$

The component flows:

$$l^I_{dom1} = \eta F x^I_{dom1} = \eta (f_{dom1} + f_{dom2}) x^I_{dom1} \tag{13}$$

$$l^I_{dom2} = \eta F - l^I_{dom1} \tag{14}$$

$$l^{II}_{dom1} = (1-\eta) F x^{II}_{dom1} \tag{15}$$

$$l^{II}_{dom2} = (1-\eta)F - 1^{II}_{dom1} \tag{16}$$

Splitting of the component(s) totally miscible with both dominant components (Type I)
These components form a ternary mixture of Type I with the dominant components.

- Input data: all data in 3.1 and f_i: molar flow of (splitting) component i in the feed
- Unknowns: l^I_i, l^{II}_i
- Solution: We assume that the equilibrium constant of component i is

$$K_i = \frac{x_i^I}{x^{II}} \tag{17}$$

Hence component i splits by the proportion of the phases, that is, the molar flows of the components of the phases: [l^I_{dom1}, l^I_{dom2}, $\eta\, f_i$] and [l^{II}_{dom1}, l^{II}_{dom2}, $(1-\eta)\, f_i$ and the total molar flows of the phases: $L^I = l^I_{dom1} + l^I_{dom2} + \eta\, f_i$ and $L^{II} = l^{II}_{dom1} + l^{II}_{dom2}(1-\eta)f_i$

The mole fraction vectors:

$$\underline{x}^I = \left[\frac{l^I_{dom1}}{L^I}, \frac{l^I_{dom2}}{L^I}, \frac{\eta f_i}{L^I}\right] \quad \underline{x}^{II} = \left[\frac{l^{II}_{dom1}}{L^{II}}, \frac{l^{II}_{dom2}}{L^{II}}, \frac{(1-\eta)f_i}{L^{II}}\right]$$

The activity of any component is the same in both phases, that is, $\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II}$. Hence K_i can be written in this way:

$$K_i = \frac{\gamma_i^{II}(x^{II})}{\gamma_i^I(x^I)} = \left(\frac{x_i^I}{x_i^{II}}\right)_{new} \tag{18}$$

We calculate the activity coefficients and update K_i then l^I_i and l^{II}_i.

$$x_i^I = \frac{l^I_i}{l^I_{dom1} + l^I_{dom2} + l^I_i} \tag{19}$$

$$x_i^{II} = \frac{f_i - l^I_i}{l^{II}_{dom1} + l^{II}_{dom2} + f_i - l^I_i} \tag{20}$$

$$K_i = \frac{\dfrac{l^I_i}{l^I_{dom1} + l^I_{dom2} + l^I_i}}{\dfrac{f_i - l^I_i}{l^{II}_{dom1} + l^{II}_{dom2} + f_i - l^I_i}} \tag{21}$$

In the quadratic equation (21) only l_i^I is unknown. Always only one of the two solutions corresponds to these conditions: $0 < l_i^I < f_i$. Then component flow l_i^{II} is computed by Equation 2.

Splitting of the components partially miscible with one of the dominant components (Type II) (partial miscibility with dom1, total miscibility with dom2)

- Input data: all data in 3.2 and x_i^{dom1}, x_i^i: mole fraction of component i in the phases of the i-dom1 binary mixture (in the phase rich in dom1 and in the phase rich in i)
- Unknowns: l_i^I, l_i^{II}
- Solution:

Equilibrium constant of the component i in the binary i-dom1 mixture (known):

$$K_i^{dom1} = \frac{x_i^{dom1}}{x_i^i} \tag{22}$$

Equilibrium constant of the component i in the investigated multicomponent mixture (unknown):

$$K_i^I = \frac{x_i^I}{x_i^{II}} \tag{23}$$

We assume that these two equilibium constants are equal:

$$K_i^I = K_i^{dom1} = K_i \tag{24}$$

Molar flows of the components of the phases:$[l_{dom1}^I, l_{dom2}^I, l_i]$ és $[l_{dom1}^{II}, l_{dom2}^{II}, f_i - l_i]$

The component flows l_i^I and l_i^{II} are calculated in the same way as in Step 3.2.

Splitting of the components partially miscible with both dominant components (Type III)

- Input data: all data in 3.2 and x_i^{dom1}, x_i^{dom2}: mole fraction of component i in the phases poor in i of the i-dom1 and the i-dom2 binary mixtures
- Unknowns: l_i^I, l_i^{II}
- Solution:

Let the equilibrium constant of i:

$$K_i = \frac{x_i^I}{x_i^{II}} = \frac{x_i^{dom1}}{x_i^{dom2}} \tag{25}$$

where x_i^I and x_i^{II} are unknown.

The component flows l_i^I and l_i^{II} are calculated in the same way as in Step 3.2.

STEP 4. LIQUID–LIQUID PHASE EQUILIBRIUM CALCULATIONS

We determine the component molar flows belonging to the minimum of the dimensionless Gibbs free energy of mixing of the feed. The above estimated component flows are the initial values of the constrained minimization.
Conditions:

- The component flows are positive: $0 < l_i^k$ where k = I,II and i = 1…C
- The material balances: $l_i^I + l_i^{II} = f_i$ where f_i is the molar flow of i in the feed and i = 1…C
- The activity of any component is the same in both phases: $\gamma_i^I \; x_i^I = \gamma_i^{II} \; x_i^{II}$ where i = 1…C

Objective function:

$$\Delta g_{mix} = \sum_{k=1}^{2} \sum_{i=1}^{C} l_i^k (ln x_i^k + ln \gamma_i^k) \tag{26}$$

If these calculations collapse to a trivial solution ($L^I = 0$ or $L^{II} = 0$ or $\underline{x}^I = \underline{x}^{II}$) then only one liquid phase exists and the calculations are finished. If two phases with different compositions are obtained, further investigations are needed.

STEP 5. ESTIMATION OF THE COMPONENT FLOWS OF THE PHASES BY ASSUMING THREE LIQUID PHASES

We assign the dominant components of both phases on the basis of their composition. (It is not sure at all that the two pairs of dominant components are the same for the two phases.) Then we decompose both phases to two phases by the Step 3. The component flow and mole fraction vectors of the new liquid phases:

$$\underline{l}^I \rightarrow \underline{l}^{I,1}, \underline{l}^{I,2} \quad \text{and} \quad \underline{x}^{I,1}, \underline{x}^{I,2}; \underline{l}^{II} \rightarrow \underline{l}^{II,1}, \underline{l}^{II,2} \quad \text{and} \quad \underline{x}^{II,1} = \underline{x}^{II,2}$$

We select the phases I,j and II,k whose composition is the least different (j = 1,2; k = 1,2), that is, the two phases for which

$$\sum_{i=1}^{C} (x_i^{I,j} - x_i^{II,k}) \tag{27}$$

is minimal. After that we unite these two phases and so we get three liquid phases: $\underline{l}^I, \underline{l}^{II}, \underline{l}^{III}$. These component flows are used as initial values for the LLLE calculation.

STEP 6. LIQUID–LIQUID–LIQUID EQUILIBRIUM CALCULATION

The conditions and the objective function are similar to those of Step 4 but in this case k = I,II,III. If these calculations collapse to a trivial solution (the mole fraction vector of any two phases equals) then only two phases exist.

CALCULATION RESULTS

The algorithm and the program were tested among others for two different mixtures of Type III:

1. ethylene glycol (1) – lauryl alcohol (2) – nitromethane (3) (Type III)
2. 1-hexanol (1) – nitromethane (2) – water (3) (Type III)

> Our method is presented in details for Mixture 1.
> Input data:
> Overall composition of the mixture, mol/s: $f_1 = 40, f_2 = 30, f_3 = 30$.
> The temperature is 25 °C, the activity coefficients are described by the UNIQUAC model.

STEP 1. DETERMINATION OF THE MUTUAL MISCIBILITY OF EACH BINARY PAIR

All the three binary mixtures are partially miscible therefore their $\Delta g_{mix} - x$ functions are similar (See Figure 2). Equilibrium concentrations of the binary mixtures $[x_i^{II}, x_i^{I}]$, where i denotes the component with smaller serial number: (1)–(2): [0.218, 0.994], (1)–(3): [0.094, 0.968], (2)–(3): [0.005, 0.826].

STEP 2. SELECTION OF THE DOMINANT PAIR

Since all binary mixtures are partially miscible all the three could be dominant pair. The calculated p_i-values: [2.4914 53.8438 3.0480]. Hence dom1 = 2, dom2 = 3.

STEP 3. ESTIMATION OF THE COMPONENT FLOWS OF THE TWO LIQUID PHASES ASSUMED

$\underline{l}^{I} = [33.74\ 29.88\ 6.29]$, $\underline{l}^{II} = [6.26\ 0.12\ 23.71]$

STEP 4. LIQUID-LIQUID EQUILIBRIUM CALCULATION

Results: $\Delta g_{mix} = -9.8470$ (mol/s)

$$\underline{l}^{I} = [35.96\ 29.84\ 10.79] \qquad \underline{l}^{II} = [4.04\ 0.16\ 19.21]$$

$$\underline{x}^{I} = [0.4695\ 0.3896\ 0.1409] \quad \underline{x}^{II} = [0.1725\ 0.0066\ 0.8209]$$

Since the compositions of the phases are different further computations are needed.

STEP 5. ESTIMATION OF THE COMPONENT FLOWS OF THE PHASES BY ASSUMING THREE LIQUID PHASES

a. Splitting of Phase I into two new phases:

> The dominant components: (1) and (2).

$$\underline{l}^{I,1} = [8.27\ 29.68\ 9.71] \qquad \underline{l}^{I,2} = [27.69\ 0.17\ 1.08]$$

$$\underline{x}^{I,1} = [0.1736\ 0.6227\ 0.2037] \quad \underline{x}^{I,2} = [0.9567\ 0.0058\ 0.0375]$$

b. Splitting of Phase II into two new phases:
The dominant components: (1) and (3).

$$\underline{l}^{II,1} = [1.99\ 0.141\ 9.14] \qquad \underline{l}^{II,2} = [2.05\ 0.02\ 0.07]$$

$$\underline{x}^{II,1} = [0.0934\ 0.0065\ 0.9001] \quad \underline{x}^{II,2} = [0.9604\ 0.0078\ 0.0318]$$

We determined the pair of phases for which sum of square (27) is the lowest. The compositions of Phases I,2 and II,2 are the least different therefore these phases are united. Initial

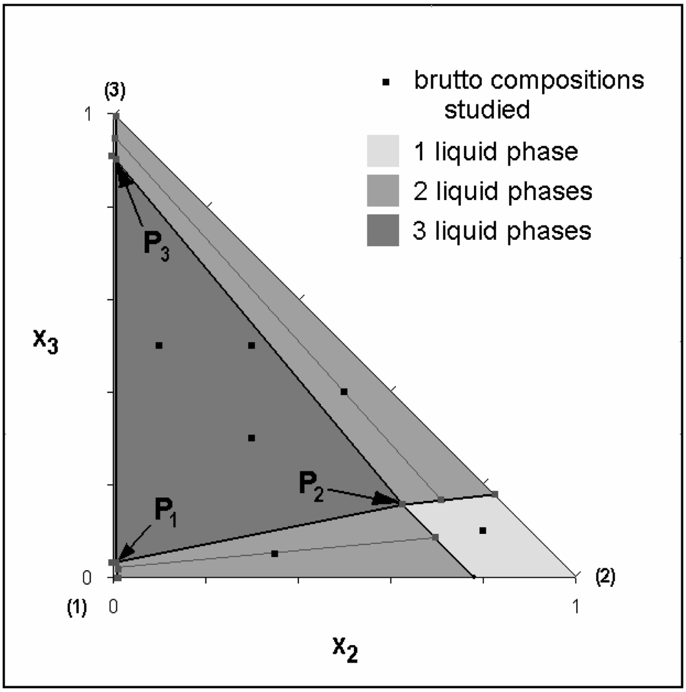


Figure 4. LLLE diagram of the ethylene glycol (1) – lauryl alcohol (2) – nitromethane (3) mixture

values for LLLE calculations:

$$\underline{l}^{I} = \underline{l}^{I,1}; \quad \underline{l}^{II} = \underline{l}^{II,1}; \quad \underline{l}^{III} = \underline{l}^{I,2} + \underline{l}^{II,2} = [29.74 \;\; 0.19 \;\; 1.15]$$

STEP 6. LIQUID–LIQUID–LIQUID EQUILIBRIUM CALCULATION
Results: $\Delta g_{mix} = -14{,}8753$

$$\begin{aligned} &\underline{l}^{I} = [10.206\ 29.679\ 7.459], && \underline{l}^{II} = [2.308\ 0.133\ 21.557], \\ &\underline{l}^{III} = [27.486\ 0.188\ 0.984] && \underline{x}^{I} = [0.9591\ 0.0066\ 0.0343], \\ &\underline{x}^{II} = [0.0962\ 0.0055\ 0.8983], && \underline{x}^{III} = [0.2156\ 0.6269\ 0.1576] \end{aligned}$$

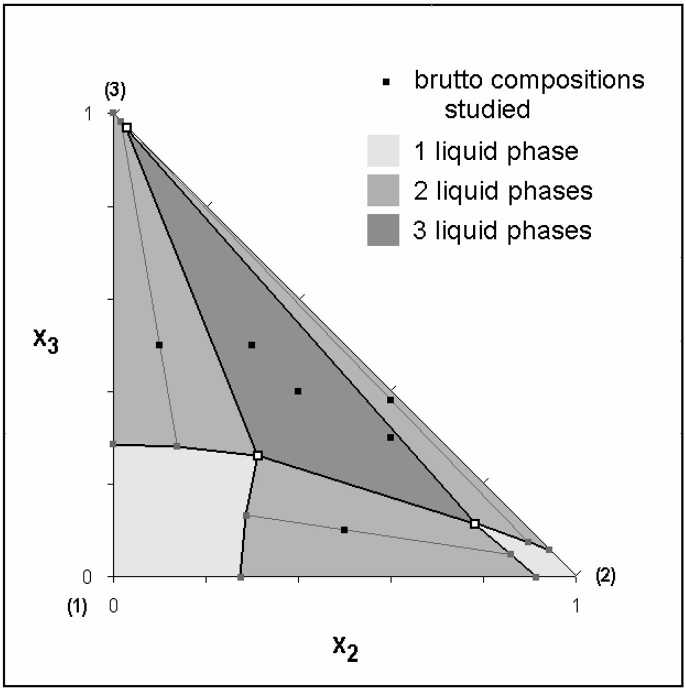


Figure 5. LLLE diagram of the 1-hexanol (1) – nitromethane (2) – water (3) mixture

We executed the flash calculations for several compositions (Figure 4). The triangle determined by the vertices P_1, P_2, P_3 is the area where a mixture of any composition splits into three equilibrium phases of P_1, P_2 and P_3 respectively.

For each composition studied we obtained the same compositions P_1, P_2 and P_3. (Stateva et al. (2000) investigated three different overall compositions in the three-phase area but only for two of them they got three liquid phases of same composition.)

One- and two-phase areas are also denoted in the diagram. The one- and two-phase areas poor in component 2 are very narrow. In the two greater two-phase areas we presented also a tie line.

We present the results obtained for Mixture 2 (studied also by Wasylkiewicz et al. (1996) and Guo et al. (2004)) at 21 °C in Figure 5. (The UNIQUAC parameters are taken from Sörensen and Arlt 1980, Vol. V/3, pp 422 and 423). The three phase region agrees well with those obtained by the above authors (Figure 6). (It practically coincides with that of Wasylkiewicz et al. 1996).

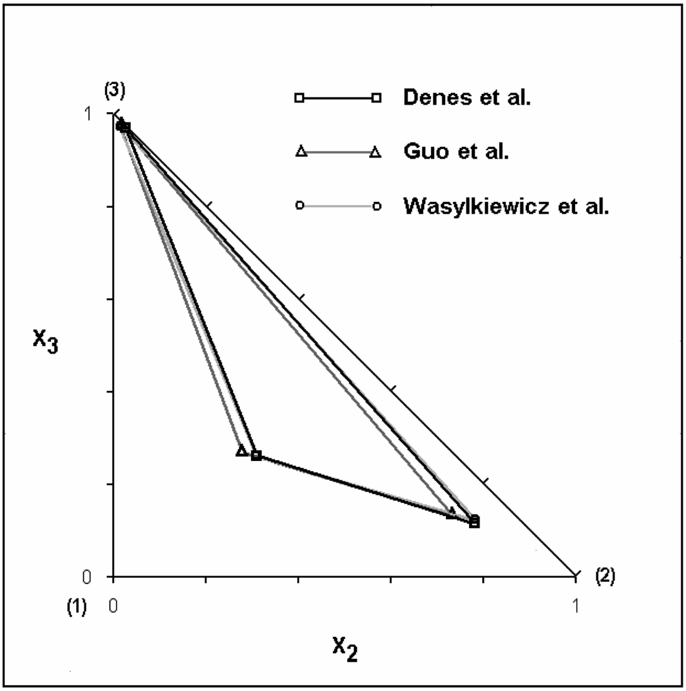


Figure 6. Three liquid phase regions calculated by the different methods for mixture 2

The modified method was succesfully tested for mixtures of Type I (acetone – water – chlorobenzene) and II (ethyl acetate – water – 1-butanol), as well.

CONCLUSIONS

An algorithm and a computer program was developed for the calculation of LLLE modifying the method of Lucia et al. based on the minimization of the dimensionless Gibbs free energy. We changed the original algorithm at several points. We estimated the initial values of the molar flows of the dominant and splitting components in a different way. Instead of the relative solubilities we used the equilibrium ratios (K). We took into consideration the ratio of the phases (η) rich in one and another dominant component. When from the two liquid phases three phases are formed, the pair of dominant components was determined separately for the two phases. We started the calculations from different points of the three-phase area and we got phases with the same mole fraction vectors. We got better initial values with the modified algorithm than with the original one.

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