A Simultaneous Method for Two- and Three-Liquid–Phase Stability Determination

Minqiang Guo and Shuqing Wang
Institute of Advanced Process Control, National Laboratory of Industrial Control Technology, Zhejiang University, Hangzhou 310027, China

Jens-Uwe Repke and Günter Wozny
Institute of Process and Plant Technology, Technical University Berlin, KWT 9, Berlin 10623, Germany

DOI 10.1002/aic.10256

The methods for multiphase stability determination are generally based on Gibbs free energy minimization. However, a novel and efficient method is proposed in this work for one-, two-, and particularly three-liquid-phase stability identification in ternary mixtures. The method is designated the extended general line-length (EGL) method, which is based on our previous GL method. Both the EGL and GL methods are equation-solving approaches. The EGL method is easy to understand and can be performed fast. Only parameters of the thermodynamic models, such as UNIQUAC and NRTL, are required for the stability determination. The thermodynamic model applied does not influence the rapidness and validity of the EGL method. Graphical techniques and simultaneous computation are adopted in this method. Its applicability and efficiency are exemplified by three typical examples. For each example, three different phase configurations, consisting of one-, two-, and up to a three-liquid phase, are tested. The results show that the EGL method can be used for the determination of multiphase stability in all liquid-phase configurations of ternary systems. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 2571–2582, 2004

Keywords: ternary mixture, three-liquid phase, stability, graphical techniques, optimization

Introduction

A main concern in the simulation and design of separation processes, such as distillation and extraction, is the phase distribution at equilibrium. At a given pressure *P* and temperature *T*, the first task is to decide whether the liquid phase is stable or unstable and how many liquid phases can coexist at equilibrium with a given liquid mixture of specified overall composition. In particular, process simulations need to be able to reliably and efficiently predict phase distributions and then calculate compositions within these phases. Whereas robust algorithms are widely available for simple vapor–liquid equilibrium, complications arise when a two- or a three-liquid–phase configuration appears. For liquid–liquid equilibrium a novel and robust method, that is, GL method, for determining the phase stability has been developed by Guo et al. (2003a,b,c). This method was found to give a satisfactory description of two-liquid–phase stability. Usually, liquid–liquid–liquid equilibrium (LLLE) or liquid–liquid equilibrium (LLE) can appear and disappear when the concentration of one or more components is varied during separation processes. For ternary systems in which every pair of components is partially miscible, the three-liquid–phase region (tie triangle) is normally enveloped by one- and two-liquid–phase regions (tie

---

Correspondence concerning this article should be addressed to G. Wozny at guenter.wozny@tu-berlin.de.

lines) in the phase diagram at a defined pressure and temperature. Thus, determining this distinct phase behavior pattern, known as the simultaneous phase transition from three-liquid phase to two-liquid phase or from two-liquid phase to one-liquid phase, is extremely important to reach the correct conclusions for simulation and design.

Normally, methods for multiphase stability determination can be classified into two broad groups: Gibbs free energy minimization methods and equation-solving methods. The first group of methods require the solution of an optimization problem to find the global Gibbs free energy minimum depending on material balance constraints, given an initial estimate of the phase splitting. The necessary and sufficient condition for any mixture is the Gibbs tangent-plane criterion. Practical numerical implementation of the Gibbs tangent-plane stability test for two-liquid–phase equilibrium has been developed (Baker et al., 1982; Michelsen, 1982a,b) and was also discussed and reviewed by Cairns and Furzer (1990). Smith et al. (1993) and Jiang et al. (1995, 1996) presented a more general criterion in theory for global multiphase, multireaction, chemical, and phase equilibrium. Kingsley and Lucia (1986, 1988) discussed two- and three-phase flash and distillation processes. Trangenstein (1987) developed a minimization algorithm for the solution of the Gibbs free energy minimization problem involving at most two phases. Nagarajan et al. (1991a,b) reformulated Michelsen's method of phase stability analysis by using the component molar densities as the primary variables in place of the mole numbers or mole fractions, so that the Helmholtz free energy is the proper thermodynamic function describing equilibrium.

Eubank et al. (1992) formulated a new method, which was described as "area method" because it minimized the Gibbs energy by integrating, rather than differentiating, the Gibbs energy curve to provide a maximum area rather than its derivative, the tangent line. Sun and Seider (1995) used a Newton homotopy-continuation method in an attempt to find all the stationary points, which is easier to initialize than the approach of Michelsen (1982a,b). McDonald and Floudas (1995a,b,c, 1997) reformulated the phase stability problem, and solved it by powerful global optimization techniques, generally involving the deterministic branch and bound using convex underestimating functions. Hua et al. (1996, 1998a,b, 1999) proposed the use of the interval Newton method for stability analysis. Zhu et al. (1999a,b, 2000) introduced a simulated annealing algorithm and a new branch and bound algorithm to search the global optimal solutions for the multipeak phenomena that generally exist in phase-stability problems based on the Gibbs free energy minimization. Lucia et al. (2000) used binary tangent plane analyses instead of finding all stationary points in the tangent-plane distance function to solve a sequence of subproblems until the global minimum dimensionless Gibbs free energy was found. In their work, 26 multicomponent mixtures including some four-phase (VLLLE) emulsion polymerization problems were tested. Rangaiah (2001) evaluated and compared two stochastic algorithms, genetic algorithms and simulated annealing, for phase-equilibrium and stability problems. Recently, Nichita et al. (2002a,b) used the tunneling method for multiphase equilibria calculations by direct minimization of the Gibbs free energy.

Even though the problem of determining whether a given liquid mixture will spontaneously and irreversibly split into two or more distinct phases was solved theoretically more than 100 years ago by Gibbs (1873, 1876), there are only a few studies concerning the determination of three-liquid–phase (LLLE) stability where three liquid phases could coexist. To the best of our knowledge, very few studies (Sridhar et al., 1999; Stateva et al., 2000; Wasylkiewicz et al., 1996) have discussed such a case. There were almost no reports for this case where equation-solving methods were used as opposed to the Gibbs free energy minimization methods. However, several repeated LL flash calculations were required for the determination of stability by most of the above methods through applying the Gibbs tangent-plane criterion in three-liquid–phase equilibrium calculations. The procedures by Stateva et al. (2000) and Sridhar et al. (1999) were conceptually similar, that is, liquid–liquid phase equilibrium solution was first obtained, and then both of bulk phase solutions were tested for stability. If any bulk phase solution was found unstable, three-liquid–phase calculation was performed. Wasylkiewicz et al. (1996) addressed the problem of three-liquid–phase equilibrium in more detail. For the algorithm described by Wasylkiewicz et al. (1996), all stationary points of the tangent-plane distance function were first determined, and then LLE calculations were performed until the actual phase number was identified. If too few phases are supposed, convergence to constrained minima can occur and the nonsmooth problems or spurious solutions to the phase equilibrium equations could appear. If too many phases are assumed, numerical problems, such as Jacobian singularities in Newton-based methods, convergence to trivial solutions, or local extrema may arise.

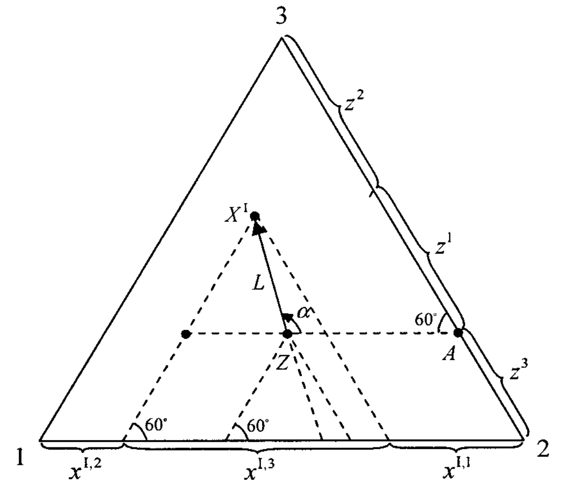

Figure 1. Representation of principle for calculating the composition X^{I}.

In this work, a novel efficient method that can describe all of liquid-phase patterns for ternary systems (that is, one-liquid–phase, two-liquid–phase, and three-liquid–phase equilibrium) is formulated. Only parameters of thermodynamic models are required and the phase quantities are not needed. The EGL method is very simple in principle, and the computer routine can be programmed easily to satisfy the systems studied.

Proposed Method

In Figure 1, an equilateral-triangle phase equilibrium diagram for a ternary system is considered. Point Z is the overall

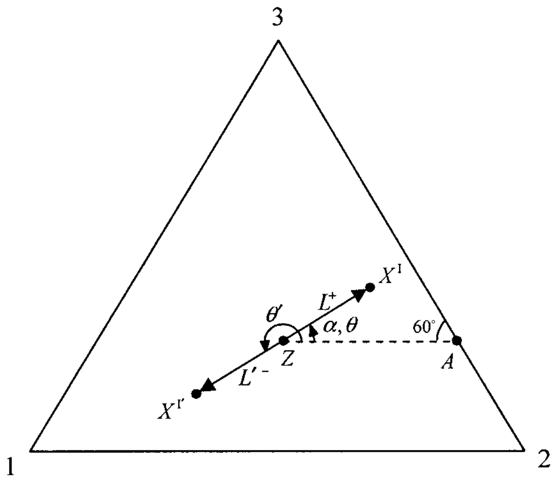

Figure 2. *L* is positive with $\alpha = \theta$; *L′* is negative with $\alpha = \theta' - 180°$.

feed composition of a given liquid mixture whose stability is unknown. Point X^{I} is another liquid composition. $\overrightarrow{ZX^{\mathrm{I}}}$ is defined as a vector with the length L. Therefore, point X^{I} is not an independent variable and can be calculated based on point Z. The angle α is defined as the included angle between the horizontal line from point Z rightward and $\overrightarrow{ZX^{\mathrm{I}}}$.

According to sine theorem, the mole fractions $x^{\mathrm{I},3}$ and $x^{\mathrm{I},2}$ can be written in terms of L, α, and Z (Eqs. 1a–1b). The mole fraction $x^{\mathrm{I},1}$ is deduced because the mole fraction summation X^{I} is treated to be equal to unity in this algorithm (Eq. 1c).

$$x^{\mathrm{I},3} = z^3 + \frac{L\sin(\pi - \alpha)}{\sin(\pi/3)} \tag{1a}$$

$$x^{\mathrm{I},2} = z^2 - \frac{L\sin(\alpha - (\pi/3))}{\sin(\pi/3)} \tag{1b}$$

$$x^{\mathrm{I},1} = 1 - x^{\mathrm{I},2} - x^{\mathrm{I},3} \tag{1c}$$

If the angle α and the sign of vector $\overrightarrow{ZX^{\mathrm{I}}}$ are defined, Eqs. 1a–1c can satisfy all cases in different directions from Z to point X^{I} in the phase diagram. For a clear and systematic explanation, an included angle θ is first defined to be measured counterclockwise from the positive x-axis $\overrightarrow{ZA}$ to $\overrightarrow{ZX}$ (such as $\angle AZX^{\mathrm{I}}$ and $\angle AZX^{\mathrm{I}'}$) (Figure 2). When θ is not greater than π, α is defined equal to θ and L is defined as positive. Otherwise, when θ is greater than π, α is defined as θ minus π and L is defined as negative. Thus α is located only in the range of $[0, \pi]$ and the sign of vector $\overrightarrow{ZX^{\mathrm{I}}}$ is consistent with the BL and GL methods (Guo et al. 2003a,b,c).

There is a remarkable characteristic that can distinguish a homogeneous region from a heterogeneous region. Given a feed composition Z, L, and α, a characteristic function is defined by Eq. 2a. X^{II} in Eq. 2a is directly calculated by phase-equilibrium relations at a given pressure and temperature (Eq. 2b). X^{I} in Eq. 2b is obtained from Eqs. 1a–1c. Because X^{II} is calculated irrespective of whether the corresponding phase exists or not, the mole fraction summation of X^{II} is allowed to differ from unity, whereas the mole fraction summation of X^{I} is always equal to unity. This may be contradictory to the conventional concept that the mole fraction summation should be equal to unity. However, it is true for existent phases that mole fraction summation is unity. Mole fraction summation of a nonexistent phase is either less than unity or greater than unity. Consider two different compositions $X^{\mathrm{I}'}$ and $X^{\mathrm{I}''}$ in Figure 3. The length between $X^{\mathrm{I}'}$ and $X^{\mathrm{I}''}$ is supposed to be $|X^{\mathrm{I}'}X^{\mathrm{I}''}|$. $X^{\mathrm{I}'}$ is located in the heterogeneous region, whereas $X^{\mathrm{I}''}$ is located in the homogeneous region. When the composition is varied from $X^{\mathrm{I}'}$ to $X^{\mathrm{I}''}$, this is equivalent to changing L from 0 to $|X^{\mathrm{I}'}X^{\mathrm{I}''}|$ with the feed composition $Z = X^{\mathrm{I}'}$ in Eq. 2a. After Eq. 2a is calculated, the function f is found to decrease monotonically. Values of the function f in the heterogeneous region are positive, whereas values of the function f in the homogeneous region are negative. It is only when the composition X^{I} is located at the binodal curve that the value of the function f is equal to zero. That means the mole fraction summation of X^{II} is equal to unity and the liquid phase with composition X^{II} really exists

$$f(Z, L, \alpha) = \sum_{i=1}^{3} x^{\mathrm{II},i} - 1 \tag{2a}$$

where

$$\gamma^{\mathrm{I},i}(T, P, X^{\mathrm{I}})x^{\mathrm{I},i} = \gamma^{\mathrm{II},i}(T, P, X^{\mathrm{II}})x^{\mathrm{II},i} \tag{2b}$$

Equation 2b constitutes three unknown variables with the same equations. The characteristic function f provides useful information on phase existence and its formation. The composition X^{I} shifts from the heterogeneous region to the homogeneous region when f decreases monotonically from a positive value to a negative value. Therefore, the feed composition Z is located in the heterogeneous region. The feed composition is near the phase boundary when the characteristic function decreases/increases to zero with small L.

In the past, Whitson and Michelson (1989) developed the

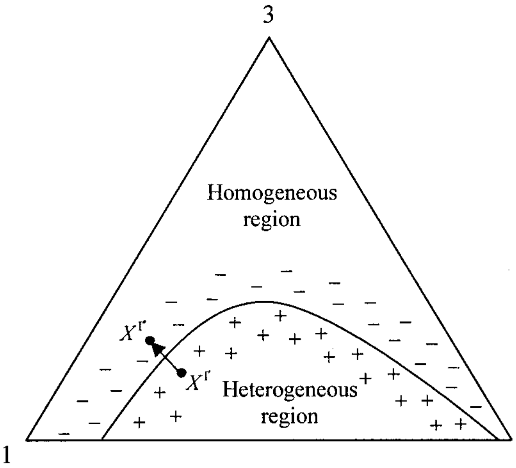

Figure 3. Opposite signs of *f* between homogeneous region and heterogeneous region.

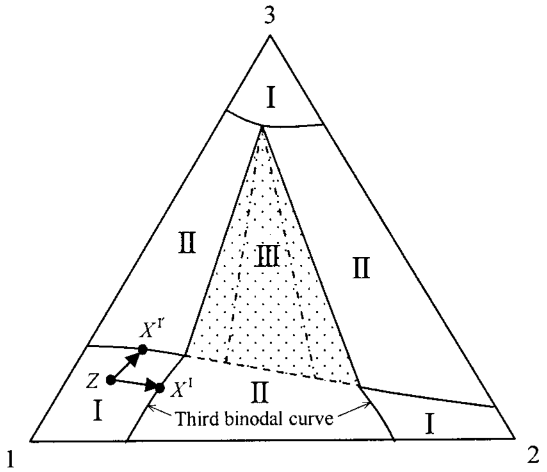

Figure 4. Typical three-liquid–phase diagram.

I: one-liquid–phase region; II: two-liquid–phase region; III: three-liquid–phase region (shaded region); dashed line: pseudo-binodal curve; dashed–dotted line: pseudo-tie lines; Z is located in region I.

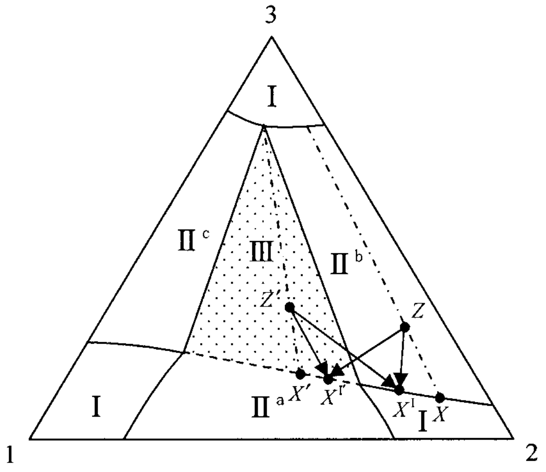

Figure 6. Typical three-liquid–phase diagram.

I: one-liquid–phase region; II: two-liquid–phase region; III: three-liquid–phase region; Z is located in region II^b; Z' is located in region III.

negative flash for vapor–liquid equilibrium by allowing a variable to take values beyond the physical limits. Gupta et al. (1991) provided a stability criterion by introducing stability variables to formulate a unified set of equations. In the EGL method, instead of the usual requirement of unity the mole fraction summation is relaxed to overcome computational difficulties. The procedure of the EGL method is different from those of Whitson and Michelson (1989) and Gupta et al. (1991).

Analysis of EGL method

The novel method is based on the GL method, although further development is needed for this complex application. A typical three-liquid–phase diagram is considered in Figure 4. There are three one-liquid–phase regions (I), three two-liquid–phase regions (II), and one three-liquid phase region (III). Below a certain temperature, a three-liquid–phase region can appear. The critical temperature can be determined in advance corresponding to a given ternary system (Wasylkiewicz et al., 1996). Normally, with decreasing temperature, two separate binodal curves will meet first at their respective plait points forming a band, then with further decreasing temperature the third binodal curve meets with its plait point on one side of the band whose border just before contact is concave at that point. One of the tie lines splits to form a tie triangle (Figure 4, III) whose corners indicate the compositions of three liquid phases (Francis, 1956). Thus, the tie triangle can be regarded as the overlap between a third binodal curve and a band.

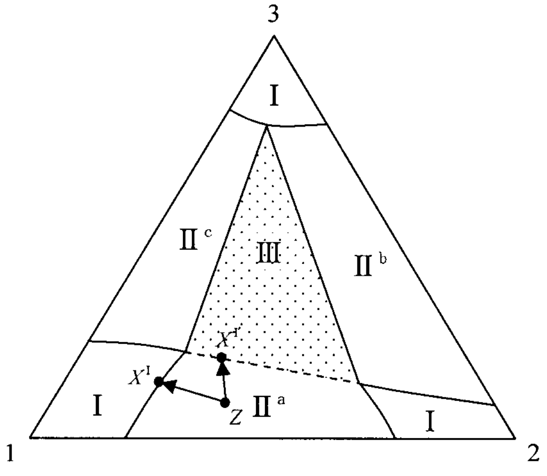

Figure 5. Typical three-liquid–phase diagram.

I: one-liquid–phase region; II: two-liquid–phase region; III: three-liquid–phase region; Z is located in region II^a.

For determining phase stability including LLLE, two different computations given by Eqs. 3a–3b are performed simultaneously. As discussed above, they show the deviation from the equilibria in terms of L and α. Note that, even though the expressions of Eqs. 3a–3b are almost the same, the different results between them can be obtained easily in the program by setting distinct initial values of X^{II} and X^{III}

$$\Phi_1(Z, L, \alpha) = \sum_{i=1}^{3} x^{\mathrm{II},i} - 1 \tag{3a}$$

$$\Phi_2(Z, L, \alpha) = \sum_{i=1}^{3} x^{\mathrm{III},i} - 1 \tag{3b}$$

Table 1. Phase Configurations with the Characteristic Signs of Φ_1 and Φ_2

$\Phi_1(\cdot)$	$\Phi_2(\cdot)$	Further Procedure: GL Method*	Phase Configuration
−	−	(not needed)	One-liquid phase
+	−	(not needed)	Two-liquid phase
−/+	+	−	Two-liquid phase
		+	Three-liquid phase

*A phase characteristic sign is given by the optimization results of the GL method, which can be either negative ("−") or positive ("+"); "−", homogeneous region; "+", heterogeneous region.

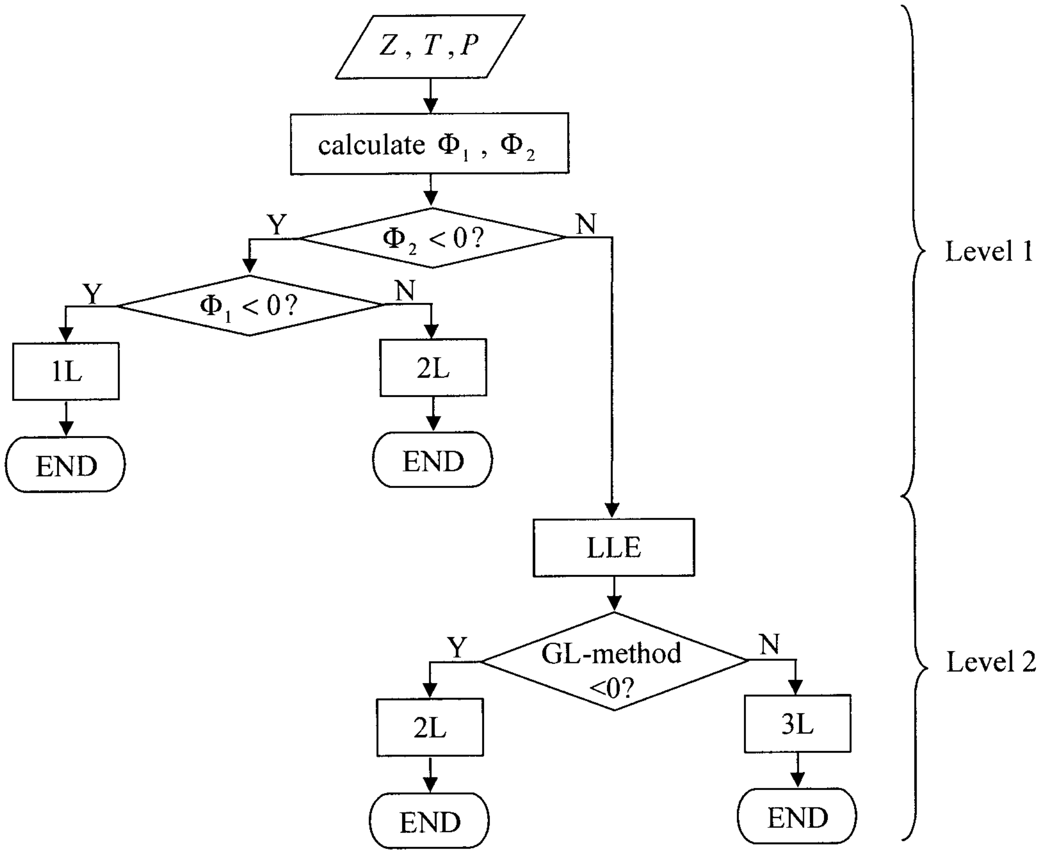

Figure 7. Algorithm for the EGL method.

1L: one-liquid–phase equilibrium; 2L: two-liquid–phase equilibrium; 3L: three-liquid–phase equilibrium.

where

$$\gamma^{\mathrm{I},i}(T, P, X^{\mathrm{I}})x^{\mathrm{I},i} = \gamma^{\mathrm{II},i}(T, P, X^{\mathrm{II}})x^{\mathrm{II},i} \tag{3c}$$

$$\gamma^{\mathrm{I},i}(T, P, X^{\mathrm{I}})x^{\mathrm{I},i} = \gamma^{\mathrm{III},i}(T, P, X^{\mathrm{III}})x^{\mathrm{III},i} \tag{3d}$$

Case 1. The feed composition Z is located in one-liquid–phase region I (Figure 4). For Eqs. 4a–4b, initial values of X^{II} and X^{III} are set to be close to vertex 2 and vertex 3, respectively (that is, X^{II} is rich in component 2 and X^{III} is rich in component 3). Based on the above analysis, Φ_1 will vary from a negative value to zero, whereas Φ_2 will keep a negative value with the increasing length L along $\overrightarrow{ZX^{\mathrm{I}}}$, which is oriented by angle α. On the other hand, when the length L increases along $\overrightarrow{ZX^{\mathrm{I'}}}$, oriented by another angle α, Φ_1 will keep a negative value, whereas Φ_2 will vary from a negative value to zero. If the length L reaches the binodal curve, Φ_1 is zero. If the length L reaches the boundary of the band, Φ_2 will be equal to zero. Both Φ_1 and Φ_2 are negative before the length L reaches the binodal curve or the boundary of the band. Φ_1 and Φ_2 will be positive if the length L increases further in either direction of $\overrightarrow{ZX^{\mathrm{I}}}$ or $\overrightarrow{ZX^{\mathrm{I'}}}$.

Case 2. When the feed composition Z is located in the two-liquid–phase region II^{a} (Figure 5), Φ_1 will be positive, whereas Φ_2 will be negative before the length L reaches the binodal curve or the boundary of the band in the directions of $\overrightarrow{ZX^{\mathrm{I}}}$ and $\overrightarrow{ZX^{\mathrm{I'}}}$.

Case 3. When the feed composition Z is located in the two-liquid–phase region II^{b} (or II^{c}, Figure 6), Φ_2 will be positive before the length L reaches the boundary of the band.

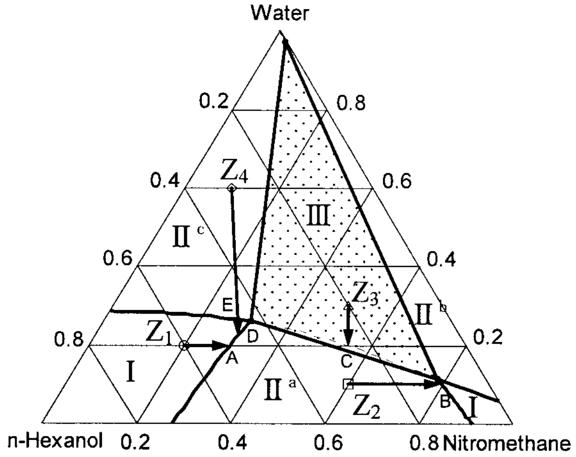

Figure 8. Three-liquid–phase diagram for example 1.

Dotted line: pseudo-binodal curve predicted by the UNIQUAC model.

Table 2. Initial Scheme for Example 1: *n*-Hexanol + Nitromethane + Water System at T = 294.15 K and Atmospheric Pressure

Case	Feeds*	X^{I},* X^{II}, X^{III}	α	L
1	(0.6, 0.2, 0.2)	(0.98, 0.01, 0.01), (0.01, 0.98, 0.01), (0.01, 0.01, 0.98)	0	0.06
2	(0.3, 0.6, 0.1)	(0.01, 0.98, 0.01), (0.98, 0.01, 0.01), (0.01, 0.01, 0.98)	0	0.20
3	(0.2, 0.5, 0.3)	(0.98, 0.01, 0.01), (0.01, 0.98, 0.01), (0.01, 0.01, 0.98)	1.57(π/2)	−0.09
4	(0.3, 0.1, 0.6)	(0.98, 0.01, 0.01), (0.01, 0.98, 0.01), (0.01, 0.01, 0.98)	1.65	−0.29

*For each composition, the three values refer to mole fractions of *n*-hexanol, nitromethane, and water, respectively.

However, Φ_1 is not strictly determined: Φ_1 will always be negative in the direction of $\overrightarrow{ZX^{I}}$, whereas Φ_1 will vary from a negative value to a positive value in the direction of $\overrightarrow{ZX^{I'}}$.

Case 4. When the feed composition Z' is located in the three-liquid–phase region III (Figure 6), Φ_2 will also be positive before the length L reaches the boundary of the band. Similar to case 3, Φ_1 is undetermined.

For cases 3 and 4, the directions of $\overrightarrow{ZX^{I}}/\overrightarrow{Z'X^{I}}$ and $\overrightarrow{ZX^{I'}}/\overrightarrow{Z'X^{I'}}$ depend on the angle α only. Given that α is an independent variable, the information of Φ_1 and Φ_2 cannot be used to determine the phase stability. This can be attributed to the fact that the regions II^b, II^c, and III are all located in the band. They share the common boundary of the band. Therefore, a further procedure should be performed for cases 3 and 4.

Note that Φ_2 is positive for both cases 3 and 4, and the feed composition should be located in the band (II^b, III, II^c). Two liquid-phase compositions can be obtained if an LLE calculation is performed (Figure 6). When Z is located in the two-liquid–phase region II^b or II^c, both liquid-phase compositions can be demonstrated to be located out of the region II^a by use of the GL method (Guo et al., 2003b). However, one of the liquid-phase compositions will be located in the region II^a when Z' is located in the three-liquid phase (region III). In practice, only one of the liquid-phase compositions is chosen to carry out further procedures according to the initial scheme, such as X and X'. Table 1 lists all of possible phase configurations with the corresponding characteristic signs of a ternary system.

The generalized procedure of the EGL method for phase stability determination is summarized as follows:

(1) Specify Z, T, and P.

(2) Calculate Φ_1 and Φ_2 and simultaneously. If Φ_2 is negative before it reaches zero, END. Otherwise, go to step 3.

(3) Run an LLE calculation on Z and choose one typical solution among the two liquid-phase compositions according to the initial values; test its stability by the GL method; END.

The algorithm flowchart of the EGL method is shown in Figure 7.

Differing from the GL method, the optimization problem for the first level is formulated as follows

$$\text{min:}\quad \min\left(\left|\sum_{i=1}^{3} x^{II,i} - 1\right|, \left|\sum_{i=1}^{3} x^{III,i} - 1\right|\right) \tag{4a}$$

$$\text{s.t.}\quad L_{Lower} \le L \le L_{Upper} \tag{4b}$$

$$0^\circ \le \alpha \le 180^\circ \tag{4c}$$

$$0 \le x^{I,i}(i), x^{II,i}(i), x^{III,i}(i) \le 1 \qquad \text{for } i = 1, 2, 3 \tag{4d}$$

Here, $x^{II,i}(i)$ and $x^{III,i}(i)$ are calculated by Eqs. 3c and 3d, respectively. Both L and α are optimized. The objective function (Eq. 4a) can also be written as Eq. 5. A computer program incorporating gPROMS© is developed for this method. Both optimization problems using Eq. 4a and Eq. 5 can be solved successfully. [Refer to Guo et al. (2003b) for definitions of phase characteristic sign in optimization problem.]

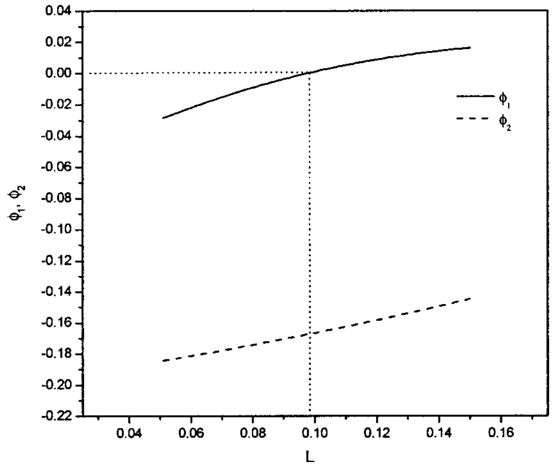

Figure 9. Φ_1 and Φ_2 with increasing L for feed 1.

$\Phi_1 = 0$ with $L = 0.0970$ and $\alpha = 0$.

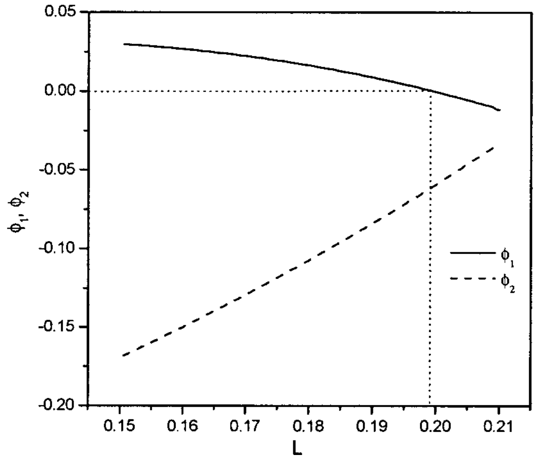

Figure 10. Φ_1 and Φ_2 with increasing L for feed 2.

$\Phi_1 = 0$ with $L = 0.1998$ and $\alpha = 0$.

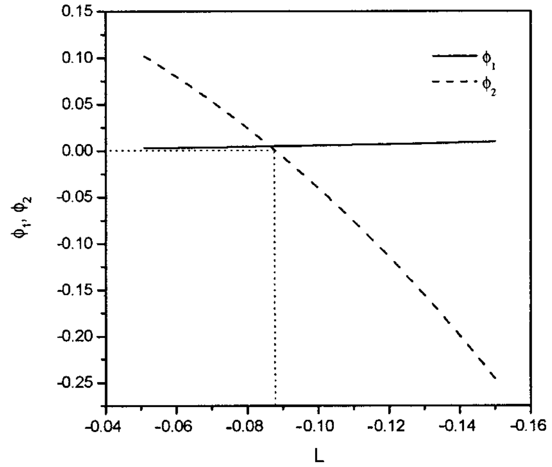

Figure 11. Φ_1 and Φ_2 with increasing *L* for feed 3.

$\Phi_2 = 0$ with $L = -0.0880$ and $\alpha = 1.57$ ($\pi/2$).

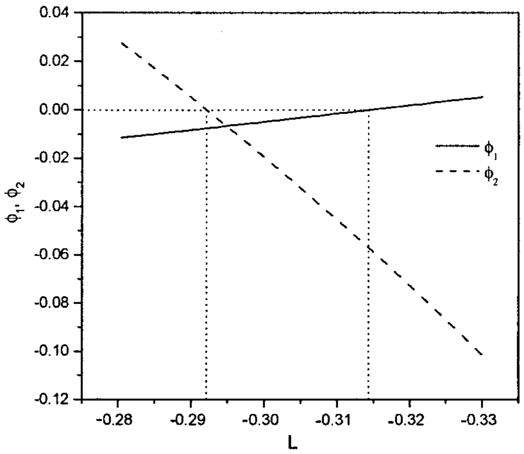

Figure 12. Φ_1 and Φ_2 with increasing *L* for feed 4.

$\Phi_1 = 0$ with $L = -0.3145$ and $\alpha = 1.65$; $\Phi_2 = 0$ with $L = -0.2925$ and $\alpha = 1.65$.

$$\text{min:}\quad \min\left[\left(\sum_{i=1}^{3} x^{\text{II},i} - 1\right)^2, \left(\sum_{i=1}^{3} x^{\text{III},i} - 1\right)^2\right] \qquad (5)$$

Application of EGL Method

The application of the EGL method will be illustrated by three examples. The first example discusses the phase stability for system *n*-hexanol + nitromethane + water obtained from the literature (McDonald and Floudas, 1997; Sorensen and Arlt, 1979–1987; Walas, 1985; Wasylkiewicz et al., 1996; Zhu and Xu, 1999b). The second one is a ternary system of methylcyclohexane + aniline + water. The third one presents the solution of the LLLE problem for *n*-nonanol + nitromethane + water. The last two examples are taken from Sorensen and Arlt (1979–1987). All three pairs of components in the above systems are partially miscible, and there is a potential for three liquid phases. In this work, computational runs are performed on a Pentium III/1.0G/Windows2000 computer.

Example 1: n-hexanol + nitromethane + water

Based on bifurcation temperature analysis (Wasylkiewicz et al., 1996), this system is tested at a temperature of 294.15 K and atmospheric pressure. Wasylkiewicz et al. (1996) studied this system using the UNIQUAC model. In this study, the UNIQUAC binary interaction parameters are from Sorensen and Arlt (1979–1987). Four feed compositions are considered for different positions in the phase diagram (Figure 8, Table 2). Cases 2 and 3 are obtained from McDonald and Floudas (1997).

Feed 1. The EGL method stops on the first level and finds that both Φ_1 and Φ_2 are negative before any of them reaches zero (Figure 9). The stability analysis indicates that Z_1 is located in the homogeneous region. X^{I} approaches the binodal curve until $L = 0.0970$ (point A, Figure 8). X^{I} will fall at the second binodal curve (boundary of the band) if L increases further, given that Φ_2 increases monotonously.

Feed 2. It is found that Φ_1 is positive and Φ_2 is negative before any of them reaches zero (Figure 10). Thus, the phase

Table 3. Optimization Results for Example 1: *n*-Hexanol + Nitromethane + Water System at *T* = 294.15 K and Atmospheric Pressure

Case	X^{I} *	X^{II} *	X^{III} *	α	L	Φ_1**	Φ_2**	IT[†]	CPU (s)	Phase Configuration
1	0.502518	0.097217	0.001591	0.00000	0.097482	0_-	−0.16758	3	0.07	1L
	0.297482	0.823180	0.030860							
	0.200000	0.079603	0.799971							
2	0.100400	0.457344	0.001315	0.00001	0.199598	0_+	−0.06020	2	0.01	2L
	0.799597	0.305602	0.028222							
	0.100003	0.237054	0.910261							
3	0.244537	0.104327	0.001218	1.65654	−0.090969	0.00442	0_+	4	0.04	2L/3L[††]
	0.560119	0.785762	0.027342							
	0.195344	0.114330	0.971440							
4	0.453228	0.125240	0.001203	1.61965	−0.290301	−0.01184	0_+	3	0.01	2L/3L[††]
	0.281583	0.732735	0.016510							
	0.265189	0.130181	0.972287							

*For each composition, the three values refer to mole fractions of *n*-hexanol, nitromethane, and water, respectively.

**0_- denotes Φ_1 is negative before it reaches zero; 0_+ denotes Φ_1 or Φ_2 is positive before it reaches zero.

[†] Number of iterations.

[††] After the second level is performed, the phase configuration can be determined. The results are 3L and 2L corresponding to cases 3 and 4, respectively.

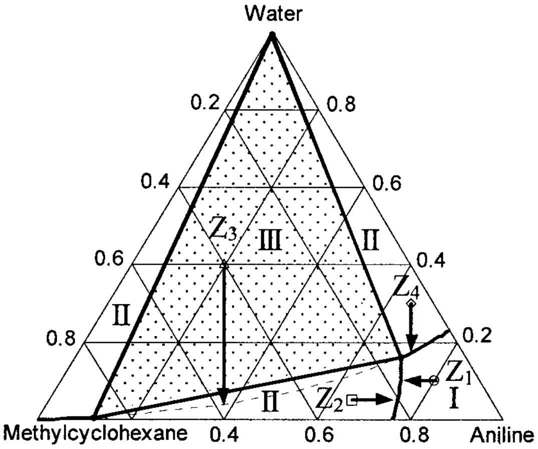

Figure 13. Three-liquid–phase diagram for example 2.

Dotted line: pseudo-binodal curve predicted by UNIQUAC model.

configuration is identified as LLE, which is consistent with the prediction by McDonald and Floudas (1997). Φ_1 decreases monotonously, whereas Φ_2 increases monotonously with the increase L. The curves in Figure 10 mean that X^{I} is moving out of a two-liquid–phase region and is approaching another two-/three-liquid–phase region. To some extent, the slopes of the curves reflect qualitatively the positional relationship between the binodal curve and L.

Feeds 3 and 4. Contrary to feeds 1 and 2, Φ_2 is positive on the first level for feeds 3 and 4 (Figures 11 and 12). Therefore, the second level is required. It is true that feeds 3 and 4 are located in the heterogeneous region according to Φ_2. To determine whether these feeds fall on the three-liquid–phase region, LLE calculations are first performed on feeds 3 and 4. The converged solutions are obtained easily because some information about the phase is known. Two specified solutions are chosen for further calculations based on the initial scheme. Other converged solutions that are rich in water are discarded.

When α is initialized to 2.5 for both feeds 3 and 4 and L is initialized to 0.2 and -0.15 for feeds 3 and 4, the second level runs successfully with the iteration numbers of 3 and 4 for feeds 3 and 4, respectively. The phase characteristic sign is found to be positive for feed 3, whereas for feed 4 it is negative. Therefore, the results show feed 3 is located in the three-liquid–phase region, which is consistent with the prediction by McDonald and Floudas (1997), and the configuration is a two-liquid–phase equilibrium for feed 4. Additionally, feed 4 is interesting because by turns Φ_1 and Φ_2 cross over the axis $y = 0$ with a special angle α (Figure 12).

Results of the optimization problem (Eqs. 4a–4d) are the same as the above analysis for the first level. The initial scheme is given in Table 2 and the results are shown in Table 3.

Example 2: methylcyclohexane + aniline + water

This system is tested at a temperature of 313.15 K and atmospheric pressure. The phase diagram with a large three-phase region is shown in Figure 13. The UNIQUAC model is used for describing the phase behavior. The UNIQUAC binary interaction parameters are from Sorensen and Arlt (1979–1987). Four feed compositions are chosen for different positions in the phase diagram. Applying the initial scheme given in Table 4, the optimization problems are performed with limited iterations and the results are shown in Table 5. The

Table 4. Initial Scheme for Example 2: Methylcyclohexane + Aniline + Water System at $T = 313.15$ K and Atmospheric Pressure

Case	Feeds*	X^{I} *, X^{II}, X^{III}	α	L
1	(0.10, 0.80, 0.10)	(0.001, 0.998, 0.001), (0.998, 0.001, 0.001), (0.001, 0.001, 0.998)	3.14(π)	0.04
2	(0.30, 0.65, 0.05)	(0.001, 0.998, 0.001), (0.998, 0.001, 0.001), (0.001, 0.001, 0.998)	0	0.04
3	(0.40, 0.20, 0.40)	(0.998, 0.001, 0.001), (0.001, 0.998, 0.001), (0.001, 0.001, 0.998)	1.57(π/2)	−0.3
4	(0.05, 0.65, 0.30)	(0.001, 0.998, 0.001), (0.998, 0.001, 0.001), (0.001, 0.001, 0.998)	1.57(π/2)	−0.12

*For each composition, the three values refer to mole fractions of methylcyclohexane, aniline, and water, respectively.

Table 5. Optimization Results for Example 2: Methylcyclohexane + Aniline + Water System at $T = 313.15$ K and Atmospheric Pressure

Case	X^{I} *	X^{II} *	X^{III} *	α	L	Φ_1**	Φ_2**	IT[†]	CPU (s)	Phase Configuration
1	0.167053	0.864458	0.000006	3.05437	0.708879	0_-	−0.228537	3	0.02	1L
	0.725816	0.129763	0.007416							
	0.107131	0.005779	0.764041							
2	0.199972	0.851156	0.000014	0.02189	0.988029	0_+	−0.552689	6	0.02	2L
	0.747531	0.145153	0.012255							
	0.052497	0.003691	0.435042							
3	0.576914	0.136314	0.000005	1.57911	−0.310912	0.052508	0_+	3	0.02	2L/3L[††]
	0.382085	0.754196	0.007080							
	0.041001	0.161998	0.992915							
4	0.131165	0.852651	0.000005	1.45654	−0.118043	−0.016612	0_+	4	0.03	2L/3L[††]
	0.704250	0.123343	0.006522							
	0.164585	0.007394	0.993473							

* For each composition, the three values refer to mole fractions of methylcyclohexane, aniline, and water, respectively.

**0_- denotes Φ_1 is negative before it reaches zero; 0_+ denotes Φ_1 or Φ_2 is positive before it reaches zero.

[†] Number of iterations.

[††] After the second level is performed, the phase configuration can be determined. The results are 3L and 2L corresponding to cases 3 and 4, respectively.

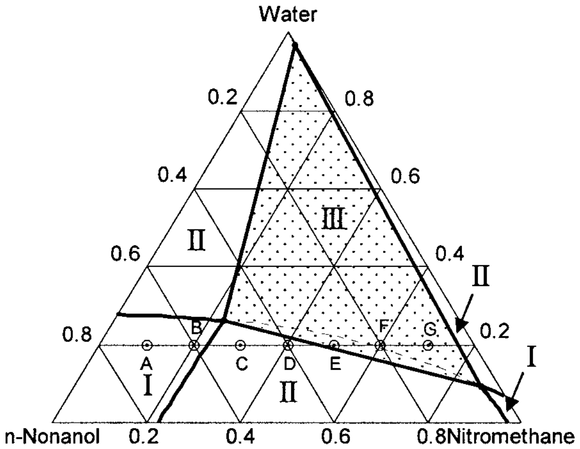

Figure 14. Three-liquid–phase diagram for example 3.

Dotted line: pseudo-binodal curve predicted by UNIQUAC model.

correct phase identifications of the system are realized on the first level.

When α is initialized to 0 and 0.5 and L is initialized to 0.4 and -0.1 for feeds 3 and 4, the second level runs successfully with the iteration numbers of 4 for both feeds 3 and 4. The phase determination agrees well with the phase diagram.

Example 3: n-nonanol + nitromethane + water

For this system, seven feeds are considered at a temperature of 313.15 K and atmospheric pressure (Figure 14, points A–G). For all feeds, the mole fraction of water is the same, and the mole fraction of nitromethane is varied from 0.1 to 0.7 at intervals of 0.1. A three-phase region is found by UNIQUAC binary interaction parameters reported by Sorensen and Arlt (1979–1987). In all tests except one (Figure 14, point E), the EGL method identifies the configurations correctly and without any numerical difficulties in one-, two-, and three-liquid–phase regions. The optimization results of the first level are listed in Table 6. However, the EGL method shows that point E is located in the two-liquid–phase region. As a matter of fact, point E lies in the tie triangle. In Figure 14, the position of point E is peculiar because it is located between one side of the tie triangle and the corresponding pseudo-binodal curve, which is predicted by the UNIQUAC model and is only valid mathematically. Such a case exists only in three-liquid phase systems.

Similar to example 3, there are also some uncertainties in examples 1 and 2 (Figures 8 and 13). These uncertainties in examples 1 and 2 are less than those in example 3. Thus, example 3 is chosen for error analysis. Five points that are located in the pseudo-binodal curve with the same intervals are chosen (Figure 15, points A–E). LLE and LLLE calculations are performed for all five points, and the results are presented in Table 7. The analysis shows that the average error for phase splitting is not more than 5% and the maximum error is not more than 9%. The errors caused by binary interaction parameters of thermodynamic model are of sufficient magnitude that they can be accepted.

In fact, it is difficult to establish reliable multicomponent liquid–liquid equilibria by using only binary interaction parameters of thermodynamic models. For reliable results it is usually necessary to use at least some multicomponent liquid–liquid

Table 6. Optimization Results for Example 3: *n*-Nonanol + Nitromethane + Water System at *T* = 313.15 K and Atmospheric Pressure

Case	X^{I} *	X^{II} *	X^{III} *	α**	$L^{\dagger}$	Φ_1 ††	Φ_2 ††	IT‡	CPU (s)	Phase Configuration
A	0.570945 0.229055 0.200000	0.033917 0.902150 0.063933	0.006938 0.220791 0.538393	0.00000	0.129055	0_-	−0.233878	12	0.08	1L
B	0.542831 0.230592 0.226577	0.035085 0.888798 0.076117	0.011813 0.268342 0.541694	0.48307	0.049551	0_-	−0.178151	13	0.07	1L
C	0.589967 0.228221 0.181812	0.033193 0.910531 0.056276	0.004338 0.184855 0.533007	0.19236	−0.082392	0_+	−0.277800	12	0.06	2L
D	0.570933 0.229068 0.199999	0.033909 0.902167 0.063924	0.006937 0.220788 0.538402	0.00000	−0.170933	0_+	−0.233873	12	0.07	2L
E	0.287893 0.488722 0.223385	0.462633 0.287096 0.256484	0.000054 0.035610 0.964336	1.55034	0.020256	0.006213	0_+	6	0.01	(fail)
F	0.210319 0.594109 0.195572	0.546839 0.230206 0.260505	0.000046 0.033662 0.966292	0.44189	−0.008966	0.037550	0_+	8	0.02	2L/3L‡‡
G	0.134039 0.708668 0.157293	0.643564 0.195642 0.260583	0.000052 0.032141 0.967807	1.24038	−0.039101	0.099789	0_+	13	0.03	2L/3L‡‡

* For each composition, the three values refer to mole fractions of *n*-nonanol, nitromethane, and water, respectively.

**For cases A–D, the initial value is 0.0; for cases E–G, the initial value is 1.57($\pi/2$).

† For cases A and B, the initial value is 0.1; for cases C and D, the initial value is −0.1; for case E, the initial value is 0.02; for cases F and G, the initial value is −0.03.

††0_- denotes Φ_1 is negative before it reaches zero; 0_+ denotes Φ_1 or Φ_2 is positive before it reaches zero.

‡ Number of iterations.

‡‡After the second level is performed, the phase configuration can be determined. The results are 3L for cases F and G.

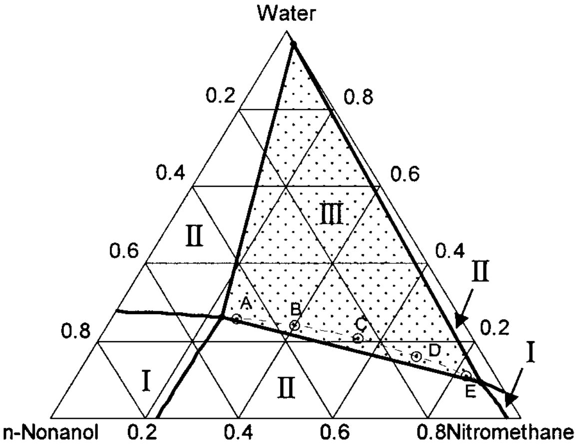

Figure 15. Three-liquid–phase diagram for example 3.

Points A–E for error analysis; dotted line: pseudo-binodal curve predicted by UNIQUAC model.

equilibrium data (Reid et al., 1987). Because such errors are directly related to parameters of thermodynamic model, they can be reduced by improving the parameters. The errors may be reduced if the UNIQUAC multicomponent interaction parameters can be adopted instead of the binary interaction parameters in the above examples. Unfortunately, such parameters are not easy to obtain because three-liquid–phase systems are not often published. Only five ternary systems with three-liquid–phase equilibrium are included in the collection of liquid–liquid equilibrium data compiled by Sorensen and Arlt (1979–1987) (Negahban et al., 1986). Thus, there are also some errors between experiment and predicted phase diagram by certain thermodynamic models, especially for three-liquid–phase systems.

Conclusions

A novel method, the EGL method, is developed for liquid-phase stability determination for ternary systems, including one-, two-, and three-liquid–phase configurations. The EGL method allows the composition to take values beyond the physical limits (but mathematically valid) to demonstrate new characteristics about phase configurations. As the name implies, the EGL method is an advanced method of our previous GL method, which has been proved able to determine efficiently the phase stability for two-liquid–phase systems. The EGL method can be understood easily. Only the parameters of the thermodynamic model, such as UNIQUAC and NRTL, are required for phase-stability determination. The thermodynamic model applied to a system does not influence the validity of this method. Simultaneous computation is adopted in this method and the convergence is not strongly dependent on the initialization, especially for the initial scheme of mole fractions. In general iteration numbers for convergence are limited. The results obtained from three examples show that the EGL method can be applied to determine the stability of ternary systems. Even though the stability identification for the three-liquid phase could have some errors arising from parameters of the thermodynamic model, such cases normally occur in the vicinity of the side of the tie triangle and, besides, such errors are not very significant. Potential applications of the EGL method include multiphase distillation, liquid–liquid extraction, and distillation with chemical reaction.

Acknowledgments

The first author thanks the international network OptiNet for providing a DAAD (Deutscher Akademischer Austausch Dienst) scholarship to pursue further research in Germany.

Table 7. Error Analysis for Example 3: *n*-Nonanol + Nitromethane + Water System at T = 313.15 K and Atmospheric Pressure

Z*	X_1**	X_2**	$\psi_{LL\text{-}1}$†	$\psi_{LL\text{-}2}$†	$\psi_{LLL\text{-}1}$††	$\psi_{LLL\text{-}2}$††	$\Delta\psi_1$‡	$\Delta\psi_2$‡	Percent$_1$ (%)‡‡	Percent$_2$ (%)‡‡
0.47465	0.49833	0.03728	0.9486	0.0514	0.9372	0.0545	0.0114	−0.0031	1.216	−0.057
0.26624	0.23383	0.86473								
0.25911	0.26784	0.09799								
0.35902	0.47558	0.03860	0.7333	0.2667	0.6919	0.2734	0.0414	−0.0067	5.984	−0.025
0.39995	0.23597	0.85076								
0.24103	0.28846	0.11064								
0.24115	0.45953	0.03963	0.4799	0.5201	0.4404	0.5146	0.0395	0.0055	8.969	0.011
0.55098	0.23769	0.84008								
0.20787	0.30278	0.12029								
0.14201	0.46341	0.03937	0.2420	0.7580	0.2274	0.7396	0.0146	0.0184	6.420	0.025
0.69618	0.23726	0.84273								
0.16181	0.29933	0.11790								
0.06046	0.49060	0.03771	0.0502	0.9498	0.0510	0.9405	−0.0008	0.0093	−1.569	0.010
0.82871	0.23452	0.86013								
0.11083	0.27488	0.10216								
Average									4.204	−0.007

*Overall compositions corresponding to *n*-nonanol, nitromethane, and water, respectively. For each test, the initial mole fractions: X^{I} = [0.98, 0.01, 0.01], X^{II} = [0.01, 0.98, 0.01], X^{III} = [0.001, 0.001, 0.998]. Mole fractions of LLL equilibrium: X_1 = [0.50431, 0.23333, 0.26236], X_2 = [0.03696, 0.86819, 0.09485], X_3 = [0.00005, 0.03246, 0.96749].

**Mole fractions of LL flash calculation corresponding to *n*-nonanol, nitromethane, and water, respectively.

†Phase splitting for two-liquid–phase flash.

††Phase splitting for three-liquid–phase flash.

‡$\Delta\psi_1 = \psi_{LL\text{-}1} - \psi_{LLL\text{-}1}$, $\Delta\psi_2 = \psi_{LL\text{-}2} - \psi_{LLL\text{-}2}$.

‡‡Percent$_1$ = $\Delta\psi_1/\psi_{LLL\text{-}1}$, Percent$_2$ = $\Delta\psi_2/\psi_{LLL\text{-}2}$.

Notation

A = UNIQUAC binary interaction parameter, K
f = characteristic function
L = length, mol/mol
LLE = liquid–liquid equilibrium
LLLE = liquid–liquid–liquid equilibrium
P = specified pressure, Pa
T = specified temperature, K
VLLLE = vapor–liquid–liquid–liquid equilibrium
X = liquid composition, mol/mol
x = mole fraction of liquid phase, mol/mol
Z = feed composition of liquid mixture, mol/mol
z = mole fraction of feed liquid mixture, mol/mol

Greek letters

α = angle, rad
γ = liquid-phase activity coefficient
$\pi = 3.14159\cdots$
θ = included angle, rad
Φ = function for determining the phase stability
ψ = phase splitting

Subscripts and superscripts

$'$ = another composition; another angle
$''$ = another composition
1 = first liquid phase; function 1
2 = second liquid phase; function 2
$+$ = positive sign of L
$-$ = negative sign of L
i = component i
I = liquid phase I
II = liquid phase II
III = liquid phase III

Literature Cited

Baker, L. E., A. C. Pierce, and K. D. Luks, "Gibbs Energy Analysis of Phase Equilibria," *Soc. Petrol. Eng. J.*, **22**, 731 (1982).

Cairns, B. P., and I. A. Furzer, "Multicomponent Three-Phase Azeotropic Distillation. 2. Phase-Stability and Phase-Splitting Algorithms," *Ind. Eng. Chem. Res.*, **29**(7), 1364 (1990).

Eubank, P. T., A. E. Elhassan, M. A. Barrufet, and W. B. Whiting, "Area Method for Prediction of Fluid-Phase Equilibria," *Ind. Eng. Chem. Res.*, **31**(3), 942 (1992).

Francis, A. W., "Ternary Systems with Three Separate Binodal Curves," *J. Phys. Chem.*, **60**(1), 20 (1956).

Gibbs, J. W., "A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces," *Trans. Conn. Acad. Arts Sci.*, **II**, 382 (1873) [Reprinted in *Scientific Papers of J. Willard Gibbs*, Dover, New York, Vol. 1, pp. 33–54 (1961).]

Gibbs, J. W., "On the Equilibrium of Heterogeneous Substances," *Trans. Conn. Acad. Arts Sci.*, **III**, 108 (1876) [Reprinted in *Scientific Papers of J. Willard Gibbs*, Dover, New York, Vol. 1, pp. 55–129, especially the section "Geometrical Illustrations," pp. 115–129 (1961).]

Guo, M. Q., J. U. Repke, G. Wozny, and S. Q. Wang, "A New Robust Method for Determination of Multiphase Stability. 1. Basic Method for Ternary mixture with Two Liquid Phases," *Comput. Chem. Eng.*, in preparation (2003a).

Guo, M. Q., J. U. Repke, G. Wozny, and S. Q. Wang, "A New Robust Method for Determination of Multiphase Stability. 2. General Method for Ternary Mixture with Two Liquid Phases," *Comput. Chem. Eng.*, in preparation (2003b).

Guo, M. Q., J. U. Repke, G. Wozny, and S. Q. Wang, "Rapid Phase Determination for Liquid–Liquid Equilibrium Calculations," ESAT 2003, Proc. of 20th European Symposium on Applied Thermodynamics, Oct. 8–12, 2003, Lahnstein, Germany, pp. 307–310 (2003c).

Gupta, A. K., P. R. Bishnoi, and N. Kalogerakis, "A Method for the Simultaneous Phase Equilibria and Stability Calculations for Multiphase Reacting and Non-Reacting Systems," *Fluid Phase Equilibr.*, **63**(1–2), 65 (1991).

Hua, J. Z., J. F. Brennecke, and M. A. Stadtherr, "Reliable Prediction of Phase Stability Using an Interval Newton Method," *Fluid Phase Equilibr.*, **116**(1–2), 52 (1996).

Hua, J. Z., J. F. Brennecke, and M. A. Stadtherr, "Enhanced Interval Analysis for Phase Stability: Cubic Equation of State Models," *Ind. Eng. Chem. Res.*, **37**(4), 1519 (1998a).

Hua, J. Z., J. F. Brennecke, and M. A. Stadtherr, "Reliable Computation of Phase Stability Using Interval Analysis: Cubic Equation of State Models," *Comput. Chem. Eng.*, **22**(9), 1207 (1998b).

Hua, J. Z., R. W. Maier, S. R. Tessier, J. F. Brennecke, and M. A. Stadtherr, "Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach," *Fluid Phase Equilibr.*, **158**, 607 (1999).

Jiang, Y., G. R. Chapman, and W. R. Smith, "On the Geometry of Chemical Reaction and Phase Equilibria," *Fluid Phase Equilibr.*, **118**(1), 77 (1996).

Jiang, Y., W. R. Smith, and G. R. Chapman, "Global Optimality Conditions and Their Geometric Interpretation for the Chemical and Phase Equilibrium Problem," *SIAM J. Optim.*, **5**(4), 813 (1995).

Kingsley, J. P., and A. Lucia, "Equilibrium Flash Calculations When the Number of Phases Present Is Unknown," *Modeling and Simulation in Engineering*, B. Wahlstrom and K. Leiviska, eds., Elsevier Science Publishers, Amsterdam, pp. 147–152 (1986).

Kingsley, J. P., and A. Lucia, "Simulation and Optimization of Three-Phase Distillation Processes," *Ind. Eng. Chem. Res.*, **27**(10), 1900 (1988).

Lucia, A., L. Padmanabhan, and S. Venkataraman, "Multiphase Equilibrium Flash Calculations," *Comput. Chem. Eng.*, **24**(12), 2557 (2000).

McDonald, C. M., and C. A. Floudas, "Global Optimization for the Phase Stability Problem," *AIChE J.*, **41**(7), 1798 (1995a).

McDonald, C. M., and C. A. Floudas, "Global Optimization for the Phase and Chemical Equilibrium Problem: Application to the NRTL Equation," *Comput. Chem. Eng.*, **19**(11), 1111 (1995b).

McDonald, C. M., and C. A. Floudas, "Global Optimization and Analysis for the Gibbs Free Energy Function Using the UNIFAC, Wilson, and ASOG Equations," *Ind. Eng. Chem. Res.*, **34**(5), 1674 (1995c).

McDonald, C. M., and C. A. Floudas, "GLOPEQ: A New Computational Tool for the Phase and Chemical Equilibrium Problem," *Comput. Chem. Eng.*, **21**(1), 1 (1997).

Michelsen, M. L., "The Isothermal Flash Problem. Part I: Stability," *Fluid Phase Equilibr.*, **9**(1), 1 (1982a).

Michelsen, M. L., "The Isothermal Flash Problem. Part II: Phase-Split Calculation," *Fluid Phase Equilibr.*, **9**(1), 21 (1982b).

Nagarajan, N. R., A. S. Cullick, and A. Griewank, "New Strategy for Phase-Equilibrium and Critical-Point Calculations by Thermodynamic Energy Analysis. 1. Stability Analysis and Flash," *Fluid Phase Equilibr.*, **62**(3), 191 (1991a).

Nagarajan, N. R., A. S. Cullick, and A. Griewank, "New Strategy for Phase-Equilibrium and Critical-Point Calculations by Thermodynamic Energy Analysis. 2. Critical-Point Calculations," *Fluid Phase Equilibr.*, **62**(3), 211 (1991b).

Negahban, S., G. P. Willhite, S. W. Walas, and M. J. Michnick, "Three-Liquid–Phase Equilibria of Ternary and Quaternary Mixtures, Water/*n*-Decane/2-Butyloxyethanol and Water/*n*-Octane/1-Propanol-Sodium Chloride: Experimental Measurements and Their Correlation," *Fluid Phase Equilibr.*, **32**, 49 (1986).

Nichita, D. V., S. Gomez, and E. Lunna, "Multiphase Equilibria Calculation by Direct Minimization of Gibbs Free Energy with a Global Optimization Method," *Comput. Chem. Eng.*, **26**(12), 1703 (2002a).

Nichita, D. V., S. Gomez, and E. Lunna, "Phase Stability Analysis with Cubic Equations of State by Using a Global Optimization Method," *Fluid Phase Equilibr.*, **194**(Special Issue), 411 (2002b).

Rangaiah, G. P., "Evaluation of Genetic Algorithms and Simulated Annealing for Phase Equilibrium and Stability Problems," *Fluid Phase Equilibr.*, **187–188**, 83 (2001).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York (1987).

Smith, J. V., R. W. Missen, and W. R. Smith, "General Optimality Criteria for Multiphase Multireaction Chemical Equilibrium," *AIChE J.*, **39**(4), 707 (1993).

Sorensen, J. M., and W. Arlt, *Liquid–Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, DECHEMA, Frankfurt, Germany, Vol. 5, Parts 2–4 (1979–1987).

Sridhar, L. N., and M. Torres, "The Three-Liquid Phase Nonequilibrium Problem," *Chem. Eng. Commun.*, **172**, 1 (1999).

Stateva, R. P., G. S. Cholakov, A. A. Galushko, and W. A. Wakeham, “A Powerful Algorithm for Liquid–Liquid–Liquid Equilibria Predictions and Calculations,” *Chem. Eng. Sci.*, **55**(11), 2121 (2000).

Sun, A. C., and W. D. Seider, “Homotopy-Continuation Method for Stability Analysis in the Global Minimization of the Gibbs Free Energy,” *Fluid Phase Equilibr.*, **103**, 213 (1995).

Trangenstein, J. A., “Customized Minimization Techniques for Phase Equilibrium Computations in Reservoir Simulation,” *Chem. Eng. Sci.*, **42**(12), 2847 (1987).

Walas, S. M., *Phase Equilibria in Chemical Engineering*, Butterworth, Stoneham, MA, p. 376 (1985).

Wasylkiewicz, S. K., L. N. Sridhar, M. F. Doherty, and M. F. Malone, “Global Stability Analysis and Calculation of Liquid–Liquid Equilibrium in Multicomponent Mixtures,” *Ind. Eng. Chem. Res.*, **35**(4), 1395 (1996).

Whitson, C. H., and M. L. Michelsen, “The Negative Flash,” *Fluid Phase Equilibr.*, **53**(Special Issue), 51 (1989).

Zhu, Y. S., H. Wen, and Z. H. Xu, “Global Stability Analysis and Phase Equilibrium Calculations at High Pressures Using the Enhanced Simulated Annealing Algorithm,” *Chem. Eng. Sci.* **55**(17), 3451 (2000).

Zhu, Y. S., and Z. H. Xu, “A Reliable Prediction of the Global Phase Stability for Liquid–Liquid Equilibrium through the Simulated Annealing Algorithm: Application to NRTL and UNIQUAC Equations,” *Fluid Phase Equilibr.*, **154**, 55 (1999a).

Zhu, Y. S., and Z. H. Xu, “Calculation of Liquid–Liquid Equilibrium Based on the Global Stability Analysis for Ternary Mixtures by Using a Novel Branch and Bound Algorithm: Application to UNIQUAC Equation,” *Ind. Eng. Chem. Res.*, **38**(9), 3549 (1999b).

Manuscript received Aug. 18, 2003, and revision received Feb. 9, 2004.