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Thermodynamics of multiphase liquid equilibria in multicomponent mixtures

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ABSTRACT. A general procedure to calculate multicomponent, multiphase liquid equilibria in terms of excess Gibbs energy models is described. The algorithms presented for the calculation of multiphase equilibria, the thermodynamic stability test based on the tangent plane criterion, as described by Michelsen, and for the estimation of interaction parameters of the NRTL and UNIQUAC models, were tested on the representation of experimental two- and three-liquid phase equilibrium data of ternary and quaternary mixtures. Agreement between calculated and measured equilibrium data was excellent for most systems studied. Also, in order to locate liquid-liquid critical points, *i.e.*, concentrations corresponding to the plait point coordinates, at specified temperature and pressure, an algorithm similar to that of Heidemann and Khalil but in terms of the mixing Gibbs energy was developed. The predictions of the plait points obtained from the NRTL and UNIQUAC models were satisfactory for a wide variety of systems studied.

RESUMEN. Se describe un procedimiento general para calcular los equilibrios líquidos multifásicos de sistemas multicomponentes en términos de modelos de energía libre de Gibbs de exceso. Los algoritmos que se presentan para el cálculo de los equilibrios líquidos multifásicos, la prueba de estabilidad termodinámica basada en el criterio del plano tangente descrito por Michelsen y la estimación de los parámetros de interacción de los modelos NRTL y UNIQUAC, fueron probados en la representación de datos experimentales de mezclas ternarias y cuaternarias con dos y tres fases líquidas en equilibrio. La concordancia entre los datos de equilibrio medidos y los calculados fue excelente para la mayoría de los sistemas estudiados. Además, con el fin de localizar los puntos críticos líquido-líquido, *i.e.*, coordenadas correspondientes a las concentraciones del punto de pliegue, a presión y temperatura específicas, se desarrolló un procedimiento similar al de Heidemann y Khalil, pero en términos de la energía de Gibbs de mezclado. Las predicciones de los puntos de pliegue obtenidos a partir de los modelos NRTL y UNIQUAC fueron satisfactorias para una amplia variedad de sistemas estudiados.

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1. INTRODUCTION

Liquid-liquid equilibria are of great importance in both chemical and petroleum industries and they have been studied with varying degrees of success and many aspects of them need further investigation. In the petroleum industry, the design of chemical flooding processes and the interpretation of process performance requires an understanding of the phase behavior of the chemical systems. Usually, systems which are effective in improving oil recovery are characterized by three-liquid equilibrium phase which appear and disappear as the concentration of one or more components is varied over ranges that are encountered during displacement through porous media. Thus, understanding and modeling this distinct phase behavior pattern known as the simultaneous phase transition from two-phase to three-phase to two-phase, is extremely important not only in chemical flooding processes but also in analyzing the results of coreflooding experiments and computer simulation of multicomponent, multiphase flow through porous media [1]. This phase behavior pattern, which can also been found in systems that do not contain surfactants [2, 3], is considered as one of the major factors governing displacement efficiencies of any chemical flooding process.

In the chemical industry, the solvent extraction technology relies heavily upon limited liquid miscibility and the distribution of a solute between two liquids phases. In azeotropic distillation, the separation of the entrainer from the overhead products after the condenser if often facilitated by the formation of two liquid phases [4]. In the design of the equipment for such processes and simulation of industrial scale chemical processes, it is necessary to know, either from experimental data or calculations, the equilibrium compositions of the components of each phase [5]. In calculating liquid-liquid equilibria, it is essential to have a knowledge of both the chemical potentials of the components in a particular phase and the relative stabilities of various phases at equilibrium. Both of these properties are related to the thermodynamics of the system through excess Gibbs energy functions and should be evaluated together.

At present, there are only few studies concerning the modeling of three-liquid phase equilibria with excess Gibbs free energy models. In particular, Negahban *et al.* [6] presented a reliable procedure for modeling the phase behavior of ternary systems with two- and three-liquid phases and a pseudoternary system with three-liquid-phase progression with increasing salinity. The representation was based in terms of the UNIQUAC [7] equation and the calculated compositions of the different liquid phases in equilibrium corresponding to the experimental data were obtained by using a method similar to that of Renon *et al.* [8], that is, compositions of the two and three-liquid phases were related by the isoactivity criterion. The aim of this work is to describe a general procedure for calculating multiphase liquid equilibria of multicomponent systems. The algorithms presented for the calculation of multiphase liquid equilibrium data, the thermodynamic stability analysis, and the methods to estimate the interaction parameters of the NRTL [9] and UNIQUAC [7] models, have successfully been tested on the representation of experimental two- and three-liquid-phase equilibrium data of ternary and quaternary systems.

2. SOLUTION APPROACH

The problem of the phase equilibria has largely been treated in the literature (see, *e.g.*, Refs. [10–17]). In fact, the specification of the problem imposes to develop efficient procedures of calculation which ensure to find, for any overall composition and for any set of interaction parameters of a given thermodynamic model, the global minimum of the Gibbs energy of the system. It is assumed that the minimization variables are the compositions of all phases in equilibrium where the number is not known *a priori* because it is dependent of the number of phases. Therefore, in order to solve this problem, we have used, on the one hand, the tangent plane criterion, as described by Michelsen [12], to test the stability of either a single phase or an equilibrium between phases which, in case of unstability, it provides good initial estimates of the compositions of the extra phase for the equilibrium calculations and, on the other hand, a method of calculation of phase equilibria with specified number of phases ensuring the descent along the Gibbs energy surface.

A general scheme for the calculation of multiphase equilibria at given temperature and pressure using a single thermodynamic model for all phases in equilibrium is the following: 1) Suppose a homogeneous system. 2) The number of phases being p, carry out a stability test. If the system is stable, end of calculation. 3) In case of unstability or metastability, increase the number of phases by one unit and perform a flash calculation at $p+1$ phases. Let $p = p+1$ and go back to step (2).

2.1. Stability test

It has been recognized (see Refs. [12, 18]) that a severe problem associated with phase equilibrium calculations of a multicomponent system at specified temperature and pressure, is that the number of phases is not known in advance. The conventional approach is to fix arbitrarily this number and to predict the phase equilibrium compositions. However, this may result in a fail of convergence with numerical methods not reliables or may require a substantial amount of calculations only to arrive at a trivial solution in cases where the number of phases is too high. This problem is of particular importance when it is integrated to the calculation of industrial processes such as the simulation of reservoirs in enhanced oil recovery or in azeotropic distillation of multicomponent systems.

The problem of determining whether a homogeneous multicomponent mixture can be divided spontaneously and irreversibly into two or more different phases, was first addressed by Gibbs in 1876 and it has been the object of several publications. The stability criteria, from the thermodynamic point of view, are well known and they has been already discussed in the literature (see Refs. [19, 20]). These criteria, based on the local convexity of the Gibbs free energy are, to date, of limited application for some binary or ternary mixtures. A rigorous extension to multicomponent mixtures was presented by van Dongen *et al.* [21], however, there is still disagreement in the development of practical applications [22], mainly due to the following reasons: firstly, the test is only locally applicable, hence it is a qualitative one; therefore it does not allow to provide the compositions of a new phase if an unstability is detected and, secondly, this approach does not allow, for a given phase, to distinguish the stable zone from the metastable one; the function of the Gibbs free energy being convex for both zones. For overcoming this, several authors (see Refs. [12, 23, 24]) have developed alternative approaches for thermodynamic stability analysis which enables to predict the number and type of phases in equilibrium as well as to obtain the accurate initial estimates for phase equilibrium calculations.

In this work, the stability analysis of a homogeneous system of composition $\boldsymbol{x}^{(\varphi)}$, based on the minimization of the distance separating the Gibbs free energy from the tangent plane at $\boldsymbol{x}^{(\varphi)}$, has been considered. This stability criterion was initially presented as a theorem by Baker *et al.* [18] and it has given place to numerical applications by Michelsen [12] and by Nghiem and Heidemann [25], among others. Baker *et al.* [18] demonstrated that the necessary and sufficient condition for a system to be stable, at a specified temperature and pressure, is that the tangent plane to the Gibbs energy surface at composition $\boldsymbol{x}^{(\varphi)}$, should at no other point intersect the Gibbs energy surface. The resulting corollary would express that at a given composition, a system is unstable if the tangent plane to the Gibbs energy surface at that point intersects the Gibbs energy surface at some other point in the overall composition range. These authors indicate that mathematically the solution of the phase equilibria problem can be obtained by finding a tangent plane to the Gibbs energy surface at two or more points which leads to the least value of the Gibbs energy. Such points of tangency correspond to the compositions of the predicted equilibrium phases being required by the material balance restrictions, so that the global composition of the system lies within the region bounded by theses points. Since the slope of the tangent plane corresponds to the chemical potentials of the components, this tangent plane criterion is equivalent to that requiring equality of chemical potentials, *i.e.*, preservation of the material balance and a state of lowest possible Gibbs energy as the conditions for equilibrium at the specified temperature and pressure.

Following the work of Baker *et al.*, Michelsen [12] suggested a numerically efficient method for solving the stability analysis based on the tangent plane criterion which does not require estimates of the number of phases at equilibrium and that provides compositions of the new phases for unstable systems as a preliminary step in flash calculations. This test has its foundation on the fact that if a decrease in Gibbs energy cannot be achieved when a homogeneous mixture is divided into two phases (formed by removing an infinitesimal amount from the original mixture), then the mixture is stable. In terms of activity coefficients, γ_i, this criterion for stability can be written, for all trial compositions $\boldsymbol{x}$, as

$$F(\boldsymbol{x}) = \sum_{i=1}^{N} x_i [\ln x_i + \ln \gamma_i(\boldsymbol{x}) - h_i] \geq 0, \tag{1}$$

where

$$h_i = \ln x_i^{(\varphi)} + \ln \gamma_i(\boldsymbol{x}^{(\varphi)}), \qquad i = 1, \ldots, N. \tag{2}$$

Therefore, expression (1) requires that the tangent plane at no point lies above the Gibbs energy surface and this is achieved when $F(\boldsymbol{x})$ is positive in all its minima. Consequently, a minimum of $F(\boldsymbol{x})$ should be considered in the interior of the permissible region,

$$\sum_{i=1}^{N} x_i = 1, \qquad \text{for all } \boldsymbol{x} \geq 0. \tag{3}$$

In view of that to test condition (1) for all trial compositions is not physically possible, Michelsen [12] asserts that it is sufficient to test the stability at all stationary points of $F(\boldsymbol{x})$ since this function is non negative at all stationary points, *i.e.*, points where the derivatives of $F(\boldsymbol{x})$ with respect to all independent variables are equal to zero. Hence, the stability can be checked by evaluating only the left-hand side of Eq. (1) at all stationary points; that is, by solving the following equation describing the stationary point:

$$\ln \xi_i + \ln \gamma_i(\boldsymbol{x}) - h_i = 0, \qquad i = 1, \ldots, N, \tag{4}$$

the stability is verified providing that at all stationary points $F(\boldsymbol{x}) \geq 0$, corresponding to $\sum_{i=1}^{N} \xi_i \leq 1$. Conversely, a phase is considered unstable if stationary points where $F(\boldsymbol{x}) < 0$ or $\sum_{i=1}^{N} \xi_i > 1$ can be located. In Eq. (4), the independent variables ξ_i can be interpreted as mole number with corresponding mole fractions, $x_i = \xi_i / \sum_{j=1}^{N} \xi_j$ $(i = 1, \ldots, N)$.

An equivalent stability criterion to that given by Eq. (1) but based on variables ξ_i is formulated as

$$F^*(\boldsymbol{\xi}) = 1 + \sum_{i=1}^{N} \xi_i [\ln \xi_i + \ln \gamma_i(\boldsymbol{x}) - h_i] \geq 0, \tag{5}$$

where no constraints on ξ_i except that $\xi_i > 0$ $(i = 1, \ldots, N)$ are required, so that the stationary points of $F^*(\boldsymbol{\xi})$ correspond to those of $F^*(\boldsymbol{x})$. Moreover, since $F^*(\boldsymbol{\xi})$ is negative in all points where $F(\boldsymbol{x})$ is negative, then a negative value of $F^*(\boldsymbol{\xi})$ indicates an unstability of the system. Hence, solving for Eqs. (4) or (5) and obtaining $\sum_{i=1}^{N} \xi_i$ are all the necessary calculations required to determine the stability of the system of composition $\boldsymbol{x}^{(\varphi)}$ at constant temperature and pressure. The methods proposed by Michelsen [12] for solving the stationary condition, [Eq. (4)], are direct substitution and accelerated direct substitution. Acceleration methods such as the general dominant eigenvalue method [26] or Broyden's method (see Ref. [27]) are recommended while a minimization method applied to the stability function, [Eq. (5)], is also suggested.

In this work, the quasi-Newton BFGS minimization method (see Ref. [28]) has been applied to Eq. (5) to determine the stability of a given system of composition $\boldsymbol{x}^{(\varphi)}$ at specified temperature and pressure. Since the function $F^*(\boldsymbol{\xi})$ allows usually multiple points, which can be minima, maxima, or saddle points, then the adoption of such a method for solving $F^*(\boldsymbol{\xi})$, under the constraints $\xi_i > 0$, will prove to be effective in so far as it leads to the search of local minima of $F^*(\boldsymbol{\xi})$; the sign of $F^*(\boldsymbol{\xi})$ in these minima enables to conclude with regard to the stability of the system.

The iterative procedure used by the quasi-Newton BFGS method can be written as

$$\mathbf{s}^{(k)} = -\mathbf{H}^{(k)} \mathbf{q}^{(k)}, \tag{6}$$

$$\boldsymbol{\alpha}^{(k+1)} = \boldsymbol{\alpha}^{(k)} + \lambda \mathbf{s}^{(k)}, \tag{7}$$

where $\mathbf{q}$ is the gradient of $F^*(\boldsymbol{\xi})$ considered as a function of the iteration variables, $\alpha_i = 2\sqrt{\xi_i}$, and is given by

$$\mathbf{q} = \left(\frac{\partial F^*}{\partial \alpha_i}\right) = \sqrt{\xi_i}(\ln \xi_i + \ln \gamma_i(\boldsymbol{x}) - h_i), \quad i = 1, \ldots, N; \tag{8}$$

while the Hessian matrix is

$$\mathbf{A} = \left(\frac{\partial^2 F^*}{\partial \alpha_i \partial \alpha_j}\right) = B_{ij} + \delta_{ij}(\ln \xi_i + \ln \gamma_i(\boldsymbol{x}) - h_i), \quad i, j = 1, \ldots, N, \tag{9}$$

where

$$\mathbf{B} = (B_{ij}) = \delta_{ij} + \sqrt{\xi_i \xi_j}\left(\frac{\partial \ln \gamma_i(\boldsymbol{x})}{\partial \xi_j}\right), \quad i, j = 1, \ldots, N. \tag{10}$$

In a stationary point, the gradient is null and the Hessian matrix $\mathbf{A}$ equals to matrix $\mathbf{B}$, which is very close to the identity matrix $\mathbf{I}$. Also, it can be seen that the trivial solution $\boldsymbol{\xi} = \boldsymbol{x}^{(\varphi)}$ corresponding to a stationary point, is a local minimum of $F^*(\boldsymbol{\xi})$ if and only if $\mathbf{B}$ is positive definite in that point.

Thus, the approximant $\mathbf{H}$ to the inverse Hessian of $F^*(\boldsymbol{\xi})$, $\mathbf{A}^{-1}$, can be initialized by any symmetric positive definite matrix such as the identity matrix $\mathbf{I}$, and it is corrected or updated by the double-rank BFGS formula

$$\mathbf{H}^{(k+1)} = \mathbf{H}^{(k)} + \left(1 + \frac{\boldsymbol{\gamma}^{(k)T}\mathbf{H}^{(k)}\boldsymbol{\gamma}^{(k)}}{\boldsymbol{\delta}^{(k)T}\boldsymbol{\gamma}^{(k)}}\right)\frac{\boldsymbol{\delta}^{(k)}\boldsymbol{\delta}^{(k)T}}{\boldsymbol{\delta}^{(k)T}\boldsymbol{\gamma}^{(k)}} - \left(\frac{\boldsymbol{\delta}^{(k)}\boldsymbol{\gamma}^{(k)}\mathbf{H}^{(k)} + \mathbf{H}^{(k)}\boldsymbol{\gamma}^{(k)}\boldsymbol{\delta}^{(k)}}{\boldsymbol{\delta}^{(k)T}\boldsymbol{\gamma}^{(k)}}\right), \tag{11}$$

with

$$\boldsymbol{\delta}^{(k)} = \boldsymbol{\alpha}^{(k+1)} - \boldsymbol{\alpha}^{(k)}, \tag{12}$$

$$\boldsymbol{\gamma}^{(k)} = \mathbf{q}^{(k+1)} - \mathbf{q}^{(k)}, \tag{13}$$

during the subsequent iterations. In addition, this method requires a line search algorithm to compute the step length λ. This is done carefully by using a rigorous method such as the proposed by Fletcher [28]. The purpose of the line search being to ensure a satisfactory decrease of the function $F^*(\boldsymbol{\xi})$, then the following two requirements have been set to achieve this aim:

$$F^*(\boldsymbol{\xi})^{(k)} - F^*(\boldsymbol{\xi})^{(k+1)} \geq -\rho\lambda \mathbf{q}^{(k)T}\mathbf{s}^{(k)}, \tag{14}$$

$$\left|\mathbf{q}^{(k+1)T}\mathbf{s}^{(k)}\right| \leq -\sigma \mathbf{q}^{(k)T}\mathbf{s}^{(k)}, \tag{15}$$

starting with an inexact line ($\sigma = 0.9$) and finishing with a fairly line search ($\sigma = 0.1$); the parameter ρ being fixed equal to 0.01.

Restricted, quadratic interpolations or cubic extrapolations and interpolations, depending on the test of Eqs. (14) and (15), are used to reach an acceptable value of λ.

Fletcher [28] has shown that this line-search algorithm takes into account the effect of round-off errors and turns into an exact line search when the parameter σ tends to zero.

In so far as the approximant **H** remains positive definite, the property of descent on $F^*(\boldsymbol{\xi})$ is effective and the convergence is always toward a local minimum, however, it does not guarantee the convergence to a negative one immediately after having found any kind of minimum; the only arbitrary part in this method being the initialization of variables ξ_i. This method has a superlinear rate of convergence at the end of calculations and the converged approximant to the inverse of the Hessian matrix is very close to the real one.

When the stability of a system is studied in relation to multiphase liquid equilibria, several minima of the function $F^*(\boldsymbol{\xi})$ may coexist so that different initializations should be used to reach them. Here, the search is initialized from almost pure phases (N different initializations) and from an equimolar mixture (see Ref. [29]). The initializations corresponding to pure trial phases have the advantage that liquid immiscibility in highly non-ideal systems is promptly detected and component activity coefficients are evaluated cheaply. Nonetheless, it is certain that for a large number of cases, one of these initial guesses involves an approach toward the trivial solution, *i.e.*, $\boldsymbol{\xi} = \boldsymbol{x}^{(\varphi)}$. These calculations can be avoid if after each iteration, the convergence variable

$$r = \frac{2F^*(\boldsymbol{\xi})}{\displaystyle\sum_{i=1}^{N} \left(\frac{\xi_i - x_i^{(\varphi)}}{\alpha_i}\right) \frac{\partial F^*(\boldsymbol{\xi})}{\partial \alpha_i}} \tag{16}$$

is evaluated. Thus, the value of r will approach the unity as $\boldsymbol{\xi}$ approaches the trivial solution, so the search is abandoned when

$$|r - 1| < 0.2 \quad \text{and} \quad F^*(\boldsymbol{\xi}) < 10^{-3}, \tag{17}$$

while the criterion of convergence used for a non-trivial solution was

$$\|\mathbf{q}\|_2^2 = \sum_{i=1}^{N} \left(\frac{\partial F^*(\boldsymbol{\xi})}{\partial \alpha_i}\right)^2 < 10^{-7}. \tag{18}$$

When the stability of a single-phase system is tested, all different initializations are explored until finding two negative minima (if they exist) of the function $F^*(\boldsymbol{\xi})$. Therefore, two minima at least exist if the system is locally unstable; the compositions corresponding to these minima are used to initialize the two-phase equilibrium calculation. On the contrary, if $F^*(\boldsymbol{\xi})$ admits only a minimum, then the system is metastable and the composition which corresponds this minimum together with the overall composition, are used to initialize the equilibrium calculation. A system with several phases in equilibrium is always metastable (the equilibrium having been already calculated). Hence, we search only an unstability and the phase equilibrium calculation is initialized from the new composition and from the compositions of the initial phases in equilibrium.

2.2. Phase equilibrium calculations

The problems that are commonly found when we search to solve a set of equations describing the equilibrium between multiple phases, are translated by a multitude of solutions without physical significance because of the lack of convergence with certain numerical methods or due to the absence of a good initialization.

The number of p phases in equilibrium being *a priori* unknown, then two different approaches have been developed for solving this problem. The first one consists of assuming a maximum number of phases which can be deduced from the phase rule, then to remove that one which does not appear during phase equilibrium calculations. This approach is not economical in terms of the number of calculations that it is necessary to carry out, and may fail to find a solution or may lead to erroneous solutions. The second approach allows to solve the problem a p phases only when an unstability is detected with the solution at $p-1$ phases. This approach, more freculently used, only is effective if it is accompanied of a rigorous stability test for multiphase systems and of an appropriate numerical method of calculation.

Arguably, one of the most useful methods to calculate phase equilibria reported in the literature is based on the minimization of the total Gibbs free energy. This method offers scope for solving a phase equilibrium at p phases immediately after a stability at $p-1$ is carried out. Basically, the formulation of the problem can be stated as the search for the global minimum of the molar Gibbs free energy of the system, G, at specified temperature T and pressure P,

$$\min_{n_i^{(\varphi)}} G = \sum_{\varphi=1}^{p} \sum_{i=1}^{N} n_i^{(\varphi)} \mu_i^{(\varphi)} \tag{19}$$

under the material balance constraints

$$\sum_{\varphi=1}^{p} n_i^{(\varphi)} = z_i, \qquad i = 1, \ldots, N, \tag{20}$$

and the inequality constraints

$$n_i^{(\varphi)} \geq 0, \qquad i = 1, \ldots, N; \ \varphi = 1, \ldots, p, \tag{21}$$

where z_i is the mole fraction of component i in the system, and $n_i^{(\varphi)}$ is the mole number of component i in phase p per mole of the feed. If the chemical potentials $\mu_i^{(\varphi)}$ ($i = 1, \ldots, N$; $\varphi = 1, \ldots, p$) are expressed in terms of activity coefficients and assuming the composition $n_i^{(p)}$ of the phase p as dependent of the variables $n_i^{(\varphi)}$ ($i = 1, \ldots, N$; $\varphi = 1, \ldots, p-1$), then the problem reduces to the following constrained minimization:

$$\min_{n_i^{(\varphi)}} \Delta g = \left(\frac{G - G^0}{RT} \right) = \sum_{\varphi=1}^{p} \sum_{i=1}^{N} n_i^{(\varphi)} \ln \left(x_i^{(\varphi)} \gamma_i^{(\varphi)} \right), \tag{22}$$

with the inequality constraints given by Eq. (21) and

$$\sum_{\varphi=1}^{p-1} n_i^{(\varphi)} \leq z_i, \qquad i = 1, \ldots, N, \tag{23}$$

where $G^0 = \sum_{i=1}^{N} z_i \mu_i^0$ is the molar Gibbs free energy of the system at the reference state, μ_i^0 is the standard chemical potential of component i, and $n_i^{(p)}$, $x_i^{(p)}$, and $\gamma_i^{(p)}$ $(T, P, \boldsymbol{x}^{(p)})$ are considered as functions of $n_i^{(\varphi)}$ $(i = 1, \ldots, N;\ \varphi = 1, \ldots, p-1)$; the inequalities (21) and (23) defining a convex domain of the variables $n_i^{(\varphi)}$ in $\Re^{N(p-1)}$.

The gradient $\mathbf{g}$ and the Hessian matrix $\mathbf{G}$ of Δg can then be evaluated from

$$\mathbf{g} = \left(\frac{\partial \Delta g}{\partial n_i^{(\varphi)}}\right) = \ln\left(\frac{x_i^{(\varphi)}\gamma_i^{(\varphi)}}{x_i^{(p)}\gamma_i^{(p)}}\right), \quad i = 1, \ldots, N;\ \varphi = 1, \ldots, p-1; \tag{24}$$

$$\mathbf{G} = \left(\frac{\partial^2 \Delta g}{\partial n_i^{(\varphi)} \partial n_j^{(\varphi)}}\right) = \left[\delta_{\varphi\phi}\left(\frac{\delta_{ij}}{n_i^{(\varphi)}} - \frac{1}{N^{(\varphi)}} + \frac{\partial \ln \gamma_i^{(\varphi)}}{\partial n_i^{(\varphi)}}\right) + \frac{\delta_{ij}}{n_i^{(p)}} - \frac{1}{N^{(p)}} + \frac{\partial \ln \gamma_i^{(p)}}{\partial n_i^{(p)}}\right],$$
$$i, j = 1, \ldots, N;\ \varphi, \phi = 1, \ldots, p-1. \tag{25}$$

If the equilibrium ratios of each component i between phase φ and the reference phase r (which is generated from a stability analysis),

$$K_i^{(\varphi)} = \frac{x_i^{(\varphi)}}{x_i^{(r)}}, \quad i = 1, \ldots, N;\ \varphi = 1, \ldots, p-1, \tag{26}$$

are introduced, we can then express the Hessian matrix $\mathbf{G}$ as the summation of two symmetrical matrices $\mathbf{A}$ and $\mathbf{Q}$ of order $N(p-1)$, defined as

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{(1)} & \mathbf{0} & \cdots & \cdots & \mathbf{0} \\ \mathbf{0} & \mathbf{A}^{(2)} & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \vdots & & & \ddots & \mathbf{0} \\ \mathbf{0} & \cdots & \cdots & \mathbf{0} & \mathbf{A}^{(p-1)} \end{pmatrix}, \tag{27}$$

$$\mathbf{Q} = \begin{pmatrix} \mathbf{Q}^{(1)} & \mathbf{R} & \cdots & \cdots & \mathbf{R} \\ \mathbf{R} & \mathbf{Q}^{(2)} & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \vdots & & & \ddots & \mathbf{R} \\ \mathbf{R} & \cdots & \cdots & \mathbf{R} & \mathbf{Q}^{(p-1)} \end{pmatrix}, \tag{28}$$

where $\mathbf{A}^{(\varphi)}$, $\mathbf{Q}^{(\varphi)}$, and $\mathbf{R}$ are all symmetrical matrices of order N such that for $\varphi = 1, \ldots, p-1$ we have

$$\mathbf{A}^{(\varphi)} = \left(\frac{\partial \ln K_i^{(\varphi)}}{\partial n_i^{(\varphi)}}\right) = \left[\delta_{ij}\left(\frac{1}{n_i^{(\varphi)}} + \frac{1}{n_i^{(p)}}\right) - \frac{1}{N^{(\varphi)}} - \frac{1}{N^{(p)}}\right], \quad i, j = 1, \ldots, N; \tag{29}$$

$$\mathbf{Q}^{(\varphi)} = \left(\frac{\partial \ln \gamma_i^{(\varphi)}}{\partial n_i^{(\varphi)}}\right) + \left(\frac{\partial \ln \gamma_i^{(p)}}{\partial n_i^{(p)}}\right), \quad i,j = 1,\ldots,N; \tag{30}$$

$$\mathbf{R} = \left[\frac{\delta_{ij}}{n_i^{(p)}} - \frac{1}{N^{(p)}} + \left(\frac{\partial \ln \gamma_i^{(p)}}{\partial n_i^{(p)}}\right)\right], \quad i,j = 1,\ldots,N. \tag{31}$$

Ammar [30] has shown that matrices $\mathbf{A}^{(\varphi)}$ ($\varphi = 1,\ldots,p-1$) are all positive definite inside the same domain of coexistence involving the p phases. Hence, the Hessian matrix $\mathbf{A}$ and its inverse $\mathbf{A}^{-1}$ can easily be evaluated from matrices $\mathbf{A}^{(\varphi)}$ and $\mathbf{A}^{(\varphi)-1}$ which are known analytically.

In this work, the following scheme based on the minimization of the total Gibbs free energy and using $\ln \mathbf{K}^{(\varphi)}$ ($\varphi = 1,\ldots,p-1$) as variables at specified temperature and pressure, has been adopted to solve the multiphase liquid equilibria for multicomponent systems, which is an extension to that presented by Ammar and Renon [17] to solve the single-stage isothermal flash problem:

1. Initialize the equilibrium ratios $\ln \mathbf{K}^{(\varphi)}$ ($\varphi = 1,\ldots,p-1$) from a stability test.
2. Solve the set of non-linear equations by Newton-Raphson iteration

$$\sum_{i=1}^{N} \frac{z_i\left(K_i^{(\varphi)} - 1\right)}{H_i} = 0, \quad \varphi = 1,\ldots,p-1, \tag{32}$$

with

$$H_i = 1 + \sum_{\varphi=1}^{p-1} N^{(\varphi)}\left(K_i^{(\varphi)} - 1\right), \quad i = 1,\ldots,N, \tag{33}$$

to compute the phase fractions $N^{(\varphi)}$,

$$N^{(\varphi)} = \sum_{i=1}^{N} n_i^{(\varphi)}, \quad \varphi = 1,\ldots,p-1. \tag{34}$$

3. Calculate the mole fractions $\boldsymbol{x}^{(\varphi)}$ of the different phases from,

$$x_i^{(p)} = \frac{z_i}{H_i}, \quad i = 1,\ldots,N, \tag{35}$$

$$x_i^{(\varphi)} = K_i^{(\varphi)} x_i^{(p)}, \quad i = 1,\ldots,N;\ \varphi = 1,\ldots,p-1. \tag{36}$$

4. Calculate $\Delta g^{(k)}$, $\mathbf{g}^{(k)}$, and elaborate the test of convergence

$$\|\mathbf{g}^{(k)}\|_2^2 = \sum_{\varphi=1}^{p-1}\sum_{i=1}^{N} \ln^2\left(\frac{x_i^{(\varphi)}\gamma_i^{(\varphi)}}{x_i^{(p)}\gamma_i^{(p)}}\right) < 10^{-10}. \tag{37}$$

5. Define new values of $\ln \mathbf{K}^{(\varphi)}$ ($\varphi = 1,\ldots,p-1$) and go back to step 2.

The whole process is then repeated until convergence is obtained. It has been well identified [17] that Eq. (22) can efficiently be solved from an unconstrained minimization algorithm by keeping the variables $n_i^{(\varphi)}$ $(i = 1, \ldots, N;\ \varphi = 1, \ldots, p-1)$ inside the convex constraints domain given by Eqs. (21) and (23) during the search for the solution. However, mainly for multiphase systems, some algorithms can lead to a violation of these constraints at the earliest iterations when the initialization is far from the solution even if the latter was obtained from a stability test. That is, the projection of the variables $n_i^{(\varphi)}$ $(i = 1, \ldots, N;\ \varphi = 1, \ldots, p-1)$ on the constraints domain can not be numerically justified with some algorithms and results in a singularity of matrix $\mathbf{A}$ and in an erratic behavior of the subsequent calculations.

In order to overcome these difficulties, we have adopted a hybrid approach to minimize the total Gibbs free energy of the system, starting with the steepest-descent method in conjunction with a robust initialization supplied from the stability test to ensure a certain progress from initializations, and ending with the quasi-Newton BFGS method, which has superlinear rate of convergence and ensures the property of strict descent of the Gibbs energy surface; the converged solutions from both methods representing local minima of the Gibbs free energy.

The iterative scheme presented above is common for these two methods and only the form to update the values of $\ln \mathbf{K}^{(\varphi)}$ in step (5) of the scheme will differ from one method to another.

Steepest-descent method

This method is a gradient-type method and it is an extension of the successive substitution algorithm incorporating a line search to estimate the step length λ, and it can be expressed by

$$\mathbf{s}^{(k)} = -\mathbf{A}^{(k)-1}\mathbf{g}^{(k)}, \tag{38}$$

$$\mathbf{p}^{(k)} = \mathbf{A}\mathbf{s}^{(k)} = -\mathbf{g}^{(k)}, \tag{39}$$

$$\ln \mathbf{K}^{(k+1)} = \ln \mathbf{K}^{(k)} + \lambda \mathbf{p}^{(k)}. \tag{40}$$

Quasi-Newton BFGS method

This method has a superlinear rate of convergence at the end calculations and although is slower to reach the solution than with the Newton method (with quadratic convergence rate), it has the advantage of generating a matrix very close to the inverse Hessian matrix $\mathbf{G}^{-1}$ so that this method has the same feature as the Newton method under the circumstances where the initiation procedure is performed near converged points. The BFGS step can be written as

$$\mathbf{s}^{(k)} = -\mathbf{H}^{(k)}\mathbf{g}^{(k)}, \tag{41}$$

$$\mathbf{p}^{(k)} = \mathbf{A}\mathbf{s}^{(k)}, \tag{42}$$

$$\ln \mathbf{K}^{(k+1)} = \ln \mathbf{K}^{(k)} + \lambda \mathbf{p}^{(k)}, \tag{43}$$

where the approximant $\mathbf{H}$ to the inverse of the Hessian matrix is set equal to $\mathbf{A}^{-1}$ at the end of the steepest-descent method and it is updated by the BFGS formula,

$$\boldsymbol{\delta}^{(k)} = \ln \mathbf{K}^{(k+1)} - \ln \mathbf{K}^{(k)}, \tag{44}$$

$$\boldsymbol{\gamma}^{(k)} = \mathbf{g}^{(k+1)} - \mathbf{g}^{(k)}, \tag{45}$$

and Eq. (11), during the subsequent iterations. All matrices $\mathbf{H}$ are positive definite since $\mathbf{A}^{-1}$ is positive definite; hence, the descent property is ensured and convergence is always to local minima.

The common feature of these methods is that both require a partial line search algorithm to compute the step length λ. This is done by imposing the following two requirements upon λ:

$$\Delta g^{(k)} - \Delta g^{(k+1)} \geq -\rho\lambda \mathbf{g}^{(k)T}\mathbf{s}^{(k)}, \tag{46}$$

$$\left|\mathbf{g}^{(k+1)T}\mathbf{s}^{(k)}\right| \leq -\sigma \mathbf{g}^{(k)T}\mathbf{s}^{(k)}, \tag{47}$$

in order to ensure a satisfactory decrease of Δg, and restricted, quadratic interpolations or cubic extrapolations and interpolations are used to find λ.

Finally, it is worth noting that one of most important steps of our algorithm is the switch from the steepest-descent method to the quasi-Newton BFGS one, since it should lead to a decrease in execution time during the calculations; otherwise the switch is not necessary. Therefore, based on extensive testing of phase equilibrium calculations, we suggest that the passage to the quasi-Newton BFGS method takes place after at least five iterations and when the gradient norm is lower than $10^{-3}RT$. Nonetheless, in certain situations corresponding to an ill conditioning of the Hessian matrix, it may be necessary to get back temporally (2–3 iterations) to the steepest-descent method.

3. DATA REGRESSION

In order to use the NRTL or UNIQUAC thermodynamic models (see Appendices A and B) or any other excess Gibbs energy model for liquid-liquid calculations, it is essential to obtain the required adjustable model parameters from regression of experimental data which, in turn, can be used for interpolation of the data or extrapolations in regions beyond where measurements have been made. Therefore, with a given set of model parameters, it is possible to calculate the number of phases in equilibrium and their compositions from the global composition of the system. However, if the minimization of Δg is started from any set of parameters, the phase equilibrium calculation could, for instance, lead to a homogeneous system in which the distance to the experimental system will be independent of the parameter values inside a certain domain, so that it is necessary to initialize these parameters with reasonable values. Toward that end, the following procedures are given to estimate the model parameters from liquid-liquid equilibrium data.

1. Minimization of the sum of squared differences between activity logarithms of each component in each phase,

$$F_a = \sum_{j=1}^{N_{\text{eq}}} \sum_{i=1}^{N} w_{ij} \left\{ \left[\ln(x_{ij}\gamma_{ij})^{\text{I}} - \ln(x_{ij}\gamma_{ij})^{\text{II}} \right]^2 + \left[\ln(x_{ij}\gamma_{ij})^{\text{I}} - \ln(x_{ij}\gamma_{ij})^{\text{III}} \right]^2 \right\}$$

$$+ Q \sum_{m=1}^{N_{\text{par}}} p_m^2, \tag{48}$$

   where w_{ij} is the weighting factor associated to the component i of tie line (or tie triangle) j, x_{ij}^{I} is the experimental mole fraction of component i of tie line (or tie triangle) j in phase I, and γ_{ij}^{I} is the corresponding activity coefficient which is calculated from an excess Gibbs energy model depending on x_{ij}^{I} and the model parameters p_m $(m = 1, \dots, N_{\text{par}})$. Equation (48) has been written for three equilibrium phases but for systems with two equilibrium phases, it reduces to contents of the first bracketed term.

2. Minimization of the sum of squared differences between the calculated and experimental mole fractions,

$$F_x = \sum_{k=1}^{N_{\text{eq}}} \sum_{j=1}^{N_{\text{ph}}} \sum_{i=1}^{N} w_{ijk} \left(x_{ijk} - \hat{x}_{ijk} \right)^2 + Q \sum_{m=1}^{N_{\text{par}}} p_m^2, \tag{49}$$

   where w_{ijk}, x_{ijk}, and $\hat{x}_{ijk}$, represent, respectively, the weighting factor, the experimental mole fraction, and the calculated mole fraction of component i in phase j corresponding to the tie line (or tie triangle) k.

The second term of the right-hand side of Eqs. (48) and (49), *i.e.*, the "penalty" term, is added to the objective functions F_a and F_x to ensure that we can get relatively small parameters without increasing the minimum of these functions, so that the risk of multiple solutions is avoided. This term has also the advantage that the minimum of F_a and F_x becomes sharper promoting thus the convergence, and it is activated only if one or more of the model parameters are greater than a specified value. In this work, we have chosen the value of constant Q in such a way that the quantity $Q(500)^2$ represents approximatively one per cent of the value of the objective function (F_a or F_x). This approach has been systematically used to estimate the NRTL and UNIQUAC parameters. In addition, we have also replaced the experimental uncertainties (which in general are not available) by weighting factors which can be used to force the thermodynamic model to represent with more accuracy certain concentrations. Here, unless otherwise stated, all these factors were fixed equal to unity.

Although the activity objective function F_a has been frequently used in the literature, it suffers from the disadvantage that it only contains the differences between computed activities. Hence, minimization of this function does not necessarily lead to small differences between experimental and calculated mole fractions which is desired in practice. Notwithstanding, to obtain an initial guess of the model parameters, it is often advantageous to use function F_a since it can be evaluated explicitly. Parameters obtained in this fashion provide a sufficiently good initial estimate to enable fairly easy convergence in subsequent iterations based on F_x.

Conversely, minimization of objective function F_x is more complicated and time consuming (see Refs. [8, 31, 32]). It involves the computation of mole fractions $\hat{x}_{ijk}$ for a given current set of model parameters and minimization of Eq. (49) with respect to the model parameters from which will arise a new set of parameters. Computation is then continued until the value of F_x is smaller than a prescribed tolerance.

In Eq. (49), the experimental and calculated phases corresponding to each point of overall composition are coupled by order of decreasing proximity. However, it is possible that during minimization of F_x there exists a mismatch in the number of calculated and experimental phases, *e.g.*, when there are two experimental phases but three calculated ones. In this case, the calculated phase which is the farthest from experimental phases will not be taken into account in the objective function. In fact, it is expected that this last phase will only appear in a very small amount as soon as the other calculated phases are close to the experimental ones since both the experimental and calculated systems correspond to the same overall composition. In this regard, based on the representation of a wide variety of binary, ternary and quaternary systems, this approach always matched correctly the number of calculated and experimental phases for all systems studied.

In this work, the estimation of the NRTL and UNIQUAC parameters was carried out in a two-step procedure which involves the minimization of functions F_a and F_x by using either the Simplex [33] or the Marquardt [34] optimization methods.

4. CALCULATION OF LIQUID-LIQUID CRITICAL POINTS

It has been established (see Ref. [35]) that critical points in liquid systems (*i.e.*, plait points) play an important role in chemical and petroleum industries. Thus, having indicated in previous sections how we can get liquid-phase equilibrium compositions from overall compositions using an excess Gibbs energy model, in this section we have addressed our attention to the calculation of liquid-liquid critical points of multicomponent mixtures using a procedure similar to that suggested by Novák *et al.* [36] which is, in turn, a modification to that presented by Heidemann and Khalil [37].

In general, application of this procedure requires to find a vector $\Delta\boldsymbol{x}$ that satisfy the relation

$$\mathbf{D}\cdot\Delta\boldsymbol{x} = \mathbf{0}, \qquad \Delta\boldsymbol{x}^T\Delta\boldsymbol{x} = 1, \tag{50}$$

where $\mathbf{D}$ is the matrix of second derivatives of the mixing Gibbs energy with respect to the corresponding mole fractions,

$$\mathbf{D} = \left(\frac{\partial^2 \Delta g_m}{\partial x_i \partial x_j}\right)_{T,P}, \qquad i, j = 1, \ldots, N-1, \tag{51}$$

and

$$\Delta g_m = \sum_{i=1}^{N} x_i \ln(x_i \gamma_i) \tag{52}$$

is the mixing Gibbs free energy for an N-component system at constant temperature and pressure, and $\Delta\boldsymbol{x} = \Delta x_1, \Delta x_2, \ldots, \Delta x_{N-1}$ is a non-zero vector of changes in the mole fraction. On the spinodal surface, the determinant of matrix $\mathbf{D}$ should be zero, *i.e.*, $\det(\mathbf{D}) = 0$, which can be evaluated by Gaussian elimination with scaled column pivoting to reduce matrix $\mathbf{D}$ to an upper triangular form which, in turn, is used to find $\Delta\boldsymbol{x}$; then $\det(\mathbf{D})$ is evaluated as the product of the diagonal elements. It is assumed that the last component of vector $\Delta\boldsymbol{x}$ is not zero, and in this way $\Delta x_{N-1} = 1$ can be selected, then use back- substitution to find $\Delta x_1, \Delta x_2, \ldots, \Delta x_{N-2}$.

When vector $\Delta\boldsymbol{x}$ is inserted in Eq. (50), then the following cubic form term should vanish:

$$C = \sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\sum_{k=1}^{N-1}\left(\frac{\partial^3 \Delta g_m}{\partial x_i \partial x_j \partial x_k}\right)_{T,P} \Delta x_i \Delta x_j \Delta x_k. \tag{53}$$

The elements in the quadratic and cubic forms of the critical criteria can easily be obtained from the relations

$$\left(\frac{\partial^2 \Delta g_m}{\partial x_i \partial x_j}\right)_{T,P} = \frac{\delta_{ij}}{x_i} + \frac{1}{x_N} + Q_{ij}^N - Q_{iN}^N - Q_{jN}^N + Q_{NN}^N, \quad i,j = 1,\ldots,N-1; \tag{54}$$

$$\begin{aligned}\left(\frac{\partial^3 \Delta g_m}{\partial x_i \partial x_j \partial x_k}\right)_{T,P} &= -\frac{\delta_{ijk}}{x_i^2} + \frac{1}{x_N^2} + Q_{ijk}^N - Q_{ijN}^N - Q_{ikN}^N - Q_{jkN}^N + Q_{iNN}^N \\ &\quad + Q_{jNN}^N + Q_{kNN}^N - Q_{NNN}^N, \quad i,j,k = 1,\ldots,N-1; \end{aligned} \tag{55}$$

where Q_{ij}^N and Q_{ijk}^N are the second and third derivatives of the excess Gibbs energy with respect to the composition. Nevertheless, for more complicated thermodynamic models where the evaluation of the third order composition derivatives of the excess Gibbs energy is too cumbersome, Michelsen [38] presented a modification to evaluate numerically the cubic form C. That is, all third order partial composition derivatives can completely be avoided if C is rewritten as

$$C = \sum_{i=1}^{N-1}\sum_{j=1}^{N-1} D_{ij}^* \Delta x_i \Delta x_j = \Delta\boldsymbol{x}^T \mathbf{D}^* \Delta\boldsymbol{x}, \tag{56}$$

with

$$\mathbf{D}^* = \left[\frac{\partial \mathbf{D}(\boldsymbol{x} + s\Delta\boldsymbol{x}, T, P)}{\partial s}\right]_{s=0}, \tag{57}$$

where $\mathbf{D}^*$ is a partial composition derivative of $\mathbf{D}$ in the $\Delta\boldsymbol{x}$-direction. Thus, since only a single derivative is required, then numerical differentiation, based on forward or central finite-differences, can efficiently be used.

The implementation of the excess Gibbs energy approach for computing plait points using this procedure at constant temperature and pressure, requires to iterate on mole fractions x_1 and x_2 in a nested way. That is, based on an initial guess of x_1, *e.g.*, for ternary systems, by using the x_1 and x_2 (solute) values corresponding to the closest tie line approaching the plait point or from an equimolar mixture, the composition x_2 is determined in an inner loop until $\det(\mathbf{D}) = \mathbf{0}$ is satisfied; then the convergence criterion of the cubic form C is checked. If C evaluated at the stability limit is zero (or smaller than a prescribed tolerance), the calculation ends; otherwise a new estimated for x_1 is generated in an outer loop and the iteration upon x_2 is carried out again. Once x_1 and x_2 have been obtained, the remaining compositions can then be calculated from the mole fraction constraint equation.

5. NUMERICAL EXAMPLES

The methods described above for the calculation of multiphase liquid equilibria and the estimation of the parameters of a given model from liquid-phase equilibria data exhibiting at most three coexisting phases, are used to represent the phase behavior of the systems presented below. Here, both the NRTL [9] and UNIQUAC [7] equations have been used as the thermodynamic models for all phases in equilibrium.

5.1. Ternary systems

Two ternary systems exhibiting simultaneously two- and three-liquid phase equilibria have been considered to demonstrate the performance of the computational procedure presented in this work: 1-hexanol-nitromethane-water at 21°C and 1-nonanol-nitromethane-water at 23°C. These systems were also represented by Negahban *et al.* [6] using the UNIQUAC equation.

The liquid-phase equilibrium data of the 1-hexanol-nitromethane-water system, reported by Sazonov *et al.* [39], include fourteen two-phase tie-lines and one three-phase tie-triangle while the equilibrium data of the 1-nonanol-nitromethane-water system, reported by Sazonov and Chernysheva [40], include ten two-phase tie-lines and one three-phase tie-triangle. The phase diagrams of these systems show that all component pairs are partially miscible.

In this work we have used both the NRTL and UNIQUAC equations to estimate their interaction parameters which best represent the experimental equilibrium data of these systems, and they are given in Table I. Also reported in this table are the pure-component molecular-structural parameters that were taken from the collection of Sørensen and Arlt [41].

Figures 1 and 2 show the calculated and experimental tie lines for the systems 1-hexanol-nitromethane-water at 21°C and 1-nonanol-nitromethane-water at 23°C, respectively. In both figures, the shaded area depicts the experimental three-liquid-phase region while the adjacent dashed lines show the calculated three-phase boundary domain.

The comparison between calculated and experimental concentrations is carried out from the value of the root-mean-square deviation defined by

$$\sigma_x = \sqrt{\frac{\min(F_x)}{(2N_{\text{bin}} + 3N_{\text{tri}})N - N_{\text{par}}}}, \tag{58}$$

TABLE I. Estimated binary interaction parameters of the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) equations for the systems 1-hexanol-nitromethane-water at 21°C and 1-nonanol-nitromethane-water at 23°C.

	UNIQUAC Molecular-Structural Parameters			UNIQUAC Parameters, K		Root-Mean-Square Dev.	NRTL Parameters, K			Root-Mean-Square Dev.
System	r	q	i,j	a_{ij}	a_{ji}	$\%\sigma_x$	α_{ij}	a_{ij}	a_{ji}	$\%\sigma_x$
1-Hexanol (1)	4.8031	4.1320	1,2	317.97	55.061	0.83	0.2022	134.01	734.57	2.21
Nitromethane (2)	2.0086	1.8680	1,3	37.872	443.51		0.1866	−108.29	1397.87	
Water (3)	0.9200	1.4000	2,3	481.09	165.57		0.3461	681.14	658.64	
1-Nonanol (1)	6.8263	5.7520	1,2	395.12	33.874	0.46	0.1612	33.608	1081.4	0.46
Nitromethane (2)	2.0086	1.8680	1,3	135.42	340.22		0.1674	−180.50	1740.4	
Water (3)	0.9200	1.4000	2,3	416.08	207.64		0.3481	666.83	852.29	

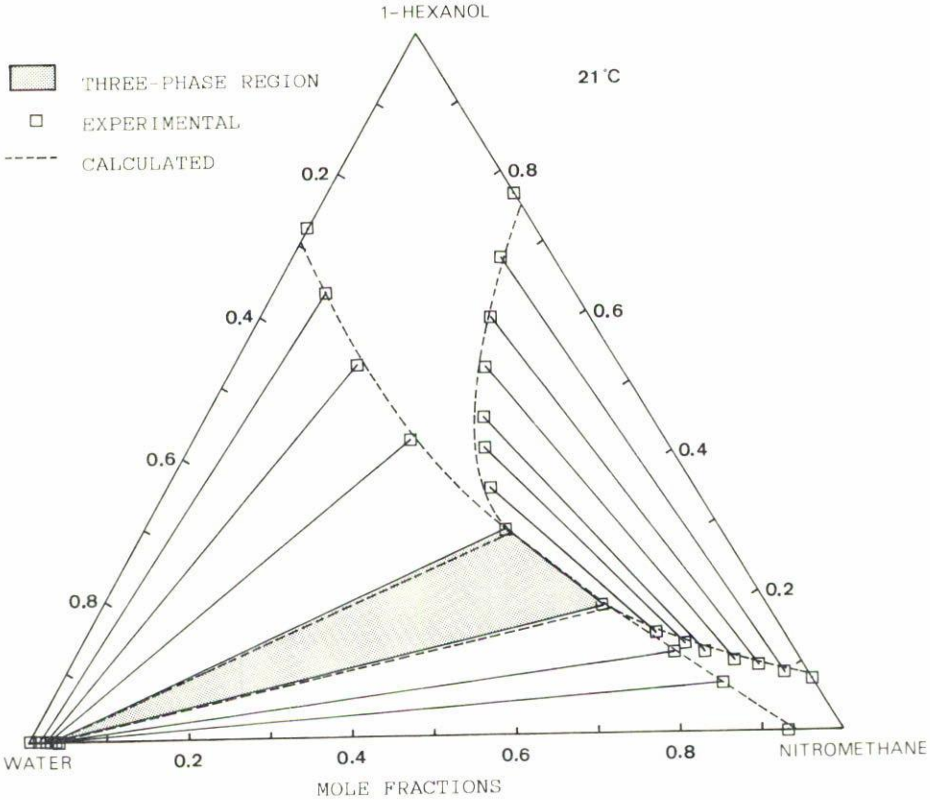

FIGURE 1. Experimental data and calculated phase envelope with the UNIQUAC (Abrams and Prausnitz, 1975) equation for the system 1-hexanol-nitromethane-water at 21°C.

where F_x is the objective function which represents the differences between calculated and experimental mole fractions, and N, N_{bin}, N_{tri}, and N_{par} are, respectively, the number of components, tie lines, tie triangles, and model parameters. The root-mean-square deviation values obtained for the NRTL and UNIQUAC equations are also given in Table I. In general, the results show that the calculated phase behavior describes the experimental data of these systems quite well.

On the other hand, in order to show the evolution of the phase behavior of the 1-nonanol-nitromethane-water system with increasing temperature, the equilibrium data of this system were modeled with the UNIQUAC equation in the temperature range of 20 to 45.1°C. The equilibrium data, reported by Sazonov and Chernysheva [40], contain seven two-phase tie-lines and one three-phase tie-triangle at 20°C, ten two-phase tie-lines and one three-phase tie-triangle at 23°C, and fourteen two-phase tie-lines at 45.1°C. This system display a three-phase evolution pattern with decreasing temperature, *i.e.*, at high temperature, all mixtures split into two equilibrium phases while a three-phase region appears in so far as the temperature decreases.

For each temperature, the phase equilibrium data of this system were regressed with the UNIQUAC equation. Figure 3 shows the estimated UNIQUAC parameters expressed

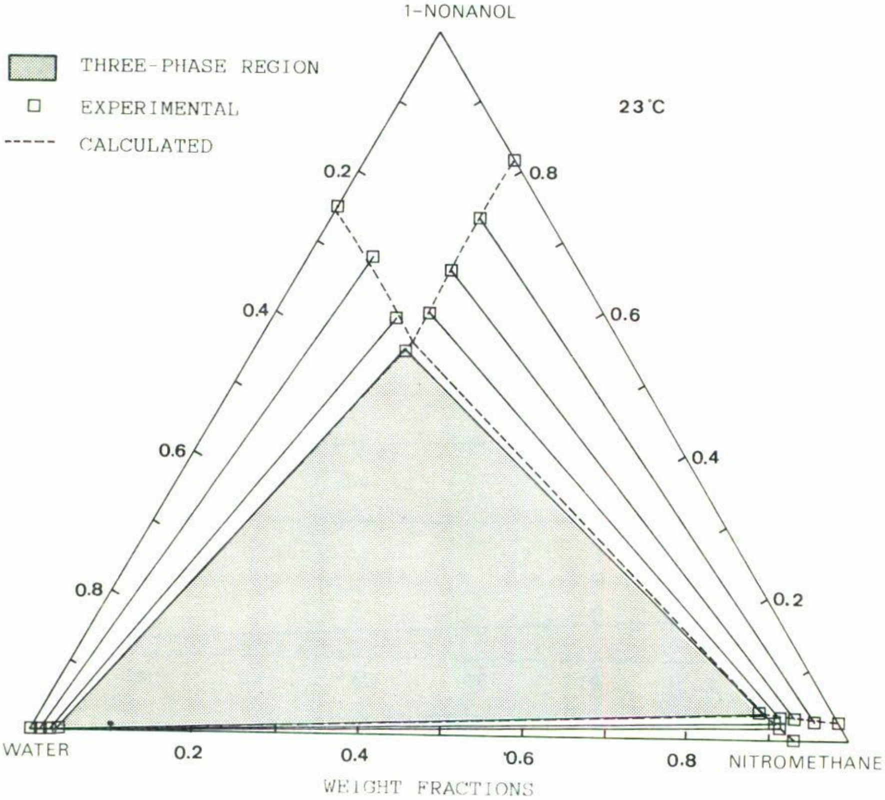

FIGURE 2. Experimental data and calculated phase envelope with the UNIQUAC (Abrams and Prausnitz, 1975) equation for the system 1-nonanol-nitromethane-water at 23°C.

as a function of temperature. An examination of this figure indicates that the estimated parameters either decrease or increase linearly as temperature increases. Consequently, the parameters can adequately be expressed as a linear function of temperature by,

$$a_{ij} = a_{ij}^{0} + a_{ij}^{1}\,(T - 273.15) \tag{59}$$

where T is the temperature in Kelvin. Table II summarizes the results of phase behavior for this system. After applying Eq. (59) at different temperatures, it can be seen that the predicted three-phase region extends beyond the temperature range that was investigated experimentally. Of course, to examine the capability of the model extrapolation, it is necessary to carry out measurements with similar overall compositions as those used in the predicted three-phase regions.

5.2. Quaternary system

Relatively few data exist for systems comprised of four liquid components and, to date, only a few researchers have attempted to calculate quaternary liquid-liquid equilibria [42, 43]. Liquid-liquid equilibrium calculations of quaternary liquid systems having

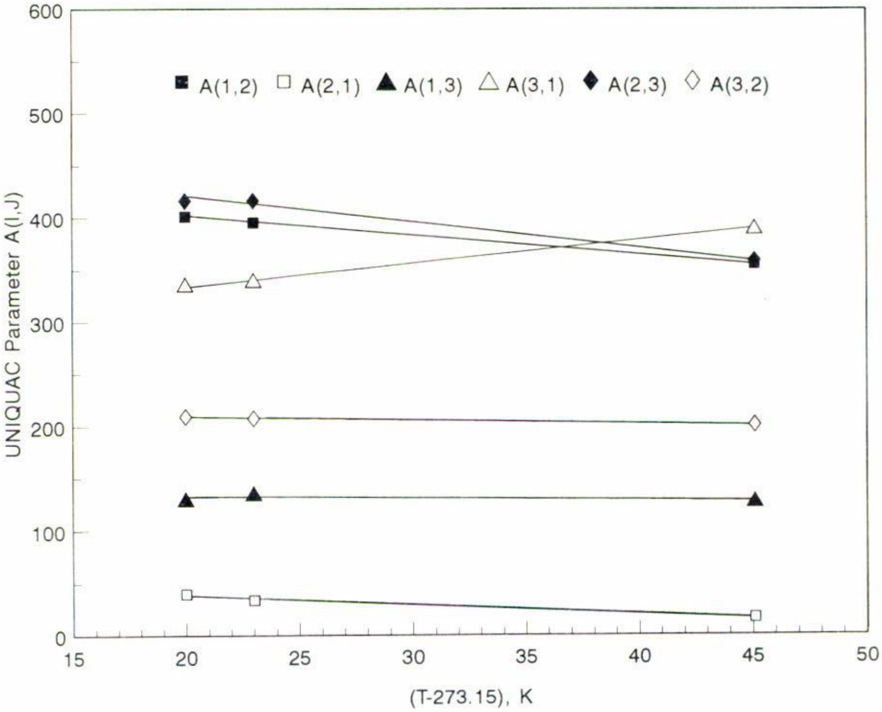

FIGURE 3. Estimated UNIQUAC parameters expressed as a function of temperature for the system 1-nonanol-nitromethane-water. Phase equilibrium data from Sazonov and Chernysheva [40].

up to three immiscible liquid pairs have been investigated (see Ref. [41]) but systems with three-liquid phases, which have potential application in tertiary oil recovery, have not been simulated. In this section, the liquid-phase equilibrium data for the system benzene-n-heptane-sulfolane-water at 25°C, reported by Hartwig *et al.* [44], have been studied. These data include eleven two-phase tie-lines and one three-phase tie-triangle. For this system, the component pairs benzene-water, n-heptane-sulfolane, and n-heptane-water are partially miscible. Previously, to the best of our knowledge, no attempt has been made to represent the phase behavior of this system.

Thus, the equilibrium data of this systems were used to correlate the interaction parameters of both the NRTL and UNIQUAC equations. The estimated parameters for these equations are given in Table III. This table also gives the pure-component molecular-structural parameters of benzene, n-heptane and water, reported by Sørensen and Arlt [41], and those of sulfolane which were estimated during data regression. The root-mean-square deviation values obtained for the NRTL and UNIQUAC equations are, respectively, of 0.94 and 1.00% which is very good.

Deviations between experimental and calculated compositions (expressed in weight fractions) obtained from the UNIQUAC equation are given in Table IV. On the whole, the results show that there exists an excellent agreement between measured and calculated concentrations of the coexisting phases.

TABLE II. Coefficients to estimate the interaction parameters of the UNIQUAC (Abrams and Prausnitz, 1975) equation for the system 1-nonanol-nitromethane-water at 20, 23, and 45.1°C.

	UNIQUAC Molecular-Structural Parameters			UNIQUAC Parameters, K					Root-Mean-Square Dev.
Component	r	q	i,j	a_{ij}^0	a_{ji}^0	a_{ij}^1	a_{ji}^1	$T(°C)$	$\%\sigma_x$
1-Nonanol (1)	6.8263	5.7520	1,2	400.97	39.639			20	0.47(0.48)[a]
Nitromethane (2)	2.0086	1.8680	1,3	130.08	336.11				
Water (3)	0.9200	1.4000	2,3	415.81	209.26				
			1,2	395.12	33.874			23	0.46 (0.50)
			1,3	135.42	340.22				
			2,3	416.08	207.64				
			1,2	354.99	16.250			45.1	0.61 (0.61)
			1,3	127.46	389.82				
			2,3	357.98	200.45				
			1,2	439.18	55.875	−1.8683	−0.8794	20–45.1	
			1,3	137.11	289.01	−0.2088	2.2348		
			2,3	470.76	216.14	−2.4970	−0.3486		

[a] Number in parentheses is the Root-Mean-Square Deviation obtained from Eq. (59).

TABLE III. Estimated binary interaction parameters of the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) equations for the system benzene-n-heptane-sulfolane-water at 25°C.

	UNIQUAC Molecular-Structural Parameters			UNIQUAC Parameters, K		Root-Mean-Square Dev.	NRTL Parameters, K			Root-Mean-Square Dev.
Component	r	q	i, j	a_{ij}	a_{ji}	$\%\sigma_x$	α_{ij}	a_{ij}	a_{ji}	$\%\sigma_x$
Benzene (1)	3.1878	2.4000	1,2	137.93	−190.50	1.00	0.20	473.64	−537.02	0.94
n-Heptane (2)	5.1742	4.3960	1,3	−5.2939	7.7393		0.20	410.86	−318.77	
Sulfolane (3)	4.2704[a]	3.5474[a]	1,4	658.98	116.28		0.20	1804.8	2658.6	
Water (4)	0.9200	1.4000	2,3	742.79	45.887		0.20	1469.1	956.72	
			2,4	963.80	744.47		0.20	899.90	1110.3	
			3,4	373.72	−164.90		0.20	8.5326	303.98	

[a] Estimated from data regression.

Table IV. Experimental and calculated phase equilibrium compositions (expressed in weight fraction units) for the system benzene (1)-*n*-heptane (2)-sulfolane (3)-water (4) at 25°C. Activity coefficients from the UNIQUAC (Abrams and Prausnitz, 1975) equation.

Overall composition weight fraction				Lower Phase Experimental/Calculated/Error				Middle Phase Experimental/Calculated/Error				Upper Phase Experimental/Calculated/Error			
z_1	z_2	z_3	z_4	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.426	0.074	0.474	0.026	0.373	0.035	0.560	0.032					0.604	0.253	0.141	0.002
				0.378	0.028	0.562	0.032					0.610	0.251	0.136	0.003
				−0.005	0.007	−0.002	0.000					−0.006	0.002	0.005	−0.001
0.378	0.122	0.474	0.026	0.289	0.023	0.652	0.036					0.558	0.363	0.077	0.002
				0.301	0.021	0.642	0.036					0.561	0.363	0.074	0.002
				−0.012	0.002	0.010	0.000					−0.003	0.000	0.003	0.000
0.304	0.196	0.474	0.026	0.201	0.013	0.745	0.041					0.444	0.521	0.034	0.000
				0.212	0.015	0.733	0.041					0.462	0.506	0.031	0.001
				−0.011	−0.002	0.012	0.000					−0.018	0.015	0.003	−0.001
0.229	0.271	0.474	0.026	0.143	0.010	0.803	0.044					0.339	0.655	0.006	0.000
				0.142	0.011	0.803	0.044					0.351	0.636	0.012	0.001
				0.001	−0.001	0.000	0.000					−0.012	0.019	−0.006	−0.001
0.149	0.351	0.474	0.026	0.082	0.007	0.864	0.047					0.213	0.778	0.009	0.000
				0.083	0.009	0.861	0.047					0.230	0.766	0.004	0.000
				−0.001	−0.002	0.003	0.000					−0.017	0.012	0.005	0.000
0.075	0.425	0.474	0.026	0.028	0.004	0.918	0.050					0.108	0.888	0.004	0.000
				0.038	0.008	0.905	0.049					0.116	0.883	0.001	0.000
				−0.010	−0.004	0.013	0.001					−0.008	0.005	0.003	0.000

TABLE IV. (Continued).

Overall composition weight fraction				Lower Phase Experimental/Calculated/Error				Middle Phase Experimental/Calculated/Error				Upper Phase Experimental/Calculated/Error			
z_1	z_2	z_3	z_4	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.378	0.122	0.449	0.051	0.227	0.011	0.689	0.081					0.602	0.298	0.098	0.000
				0.238	0.008	0.672	0.082					0.598	0.301	0.098	0.003
				−0.011	0.003	0.017	−0.001					0.004	−0.003	0.000	−0.003
0.304	0.196	0.449	0.051	0.157	0.014	0.744	0.085					0.492	0.471	0.036	0.000
				0.170	0.007	0.737	0.086					0.496	0.466	0.036	0.001
				−0.013	0.007	0.007	−0.001					−0.004	0.005	0.000	−0.001
0.229	0.271	0.449	0.051	0.110	0.006	0.795	0.089					0.358	0.625	0.017	0.000
				0.113	0.006	0.790	0.090					0.377	0.609	0.013	0.001
				−0.003	0.000	0.005	−0.001					−0.019	0.016	0.004	−0.001
0.149	0.351	0.449	0.051	0.065	0.004	0.837	0.094				0.226	0.767	0.007	0.000	
				0.065	0.006	0.834	0.095					0.246	0.750	0.004	0.001
				0.000	−0.002	0.003	−0.001					−0.020	0.017	0.003	−0.001
0.075	0.425	0.449	0.051	0.025	0.004	0.874	0.097					0.111	0.886	0.003	0.000
				0.030	0.005	0.867	0.098					0.124	0.875	0.001	0.000
				−0.005	−0.001	0.007	−0.001					−0.013	0.011	0.002	0.000
0.426	0.074	0.449	0.051	0.000	0.000	0.659	0.341	0.387	0.037	0.544	0.032	0.625	0.193	0.180	0.002
				0.068	0.000	0.594	0.338	0.393	0.027	0.546	0.034	0.618	0.212	0.166	0.004
				−0.068	0.000	0.065	0.003	−0.006	0.010	−0.002	−0.002	0.007	−0.019	0.014	−0.002

5.3. Liquid-liquid critical points of ternary systems

In order to test the ability of the NRTL and UNIQUAC equations for predicting plait points of multicomponent systems together with the computational procedure developed in this work, we have calculated the liquid-liquid critical points of thirty-two ternary systems at 25°C by locating the stable point along the stability limit which satisfies the cubic form $C = 0$ in Eq. (53). In general, the computational procedure converged to the liquid-liquid critical points in a few iterations without any difficulty. Table V presents the calculated plait point compositions (expressed in mole fractions) for the thirty-one systems of type 1 (see Ref. [45]) that were taken from the collection of Sørensen and Arlt [41], and one system, investigated by Negahban *et al.* [46], exhibiting a type 3 phase behavior in which there are one three-phase tie triangle and three two-phase envelopes.

6. CONCLUSIONS

A rigorous and computationally efficient thermodynamic algorithm for calculating multiphase liquid equilibria of multicomponent mixtures from known overall composition of the system, at specified temperature, has been presented. In order to find the stable solution, this calculation procedure uses both the tangent plane criterion for stability test and a robust approach for calculating the multiphase liquid equilibria based on the minimization of the total Gibbs free energy by using the steepest-descent method at the early iterations and finishing it with the quasi-Newton BFGS one.

This procedure coupled to a correlation data method, has allowed to verify that classical thermodynamic models such as the NRTL or UNIQUAC equations can represent correctly the phase behavior of ternary and quaternary systems exhibiting two- and three-liquid phase in equilibrium. In particular, an excellent representation of the liquid equilibrium compositions was obtained with both equations for the systems 1-hexanol-nitromethane-water, 1-nonanol-nitromethane-water, and benzene-n-heptane-sulfolane-water at, respectively, 21, 23 and 25°C. Hence, we believe that our algorithm in conjunction with a more suitable thermodynamic model (see, *e.g.*, Refs. [47–51]), will be able to represent the phase behavior of complex systems such as micellar (water-amphiphile) or microemulsion (water-oil-amphiphile) solutions, which are of central importance in a broad variety of industrial and biological processes including enhanced oil recovery, detergency, emulsion, polymerization, and catalysis.

Finally, a procedure to calculate liquid-liquid critical points at specified temperature and pressure was developed. This algorithm, similar to that presented by Heidemann and Khalil [37] but in terms of the mixing Gibbs energy, was successfully used for calculating the plait point compositions of thirty-two ternary systems by using the NRTL and UNIQUAC equations as the thermodynamic models. On the whole, for all systems so far studied, this procedure converged in a few iterations without any difficulty.

TABLE V. Estimated plait point compositions (expressed in mole fractions) for ternary systems at 25°C with the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) equations[a].

	UNIQUAC Molecular-Structural Parameters			UNIQUAC Parameters, K		Critical Composition	NRTL[b] Parameters, K		Critical Composition
System	r	q	i,j	a_{ij}	a_{ji}		a_{ij}	a_{ji}	
Glycerol (1)	3.5857	3.0600	1,2	−9.5920	−274.21	0.207	−181.37	−468.95	0.225
Ethanol (2)	2.1055	1.9720	1,3	300.09	329.12	0.522	1039.6	1425.6	0.508
Tetrachloromethane (3)	3.3900	2.9100	2,3	74.791	−165.69	0.271	545.76	−497.24	0.268
Tetrachloromethane (1)	3.3900	2.9100	1,2	336.80	−85.423	0.050	703.29	−183.39	0.038
2-Propanol (2)	2.7791	2.5080	1,3	656.78	248.47	0.309	885.90	983.89	0.246
Water (3)	0.9200	1.4000	2,3	76.985	68.463	0.641	−244.79	964.61	0.716
Trichloromethane (1)	2.8700	2.4100	1,2	−146.59	54.545	0.192	−525.92	57.819	0.189
Acetic acid (2)	2.2024	2.0720	1,3	659.85	379.05	0.442	769.74	1518.5	0.421
Water (3)	0.9200	1.4000	2,3	−121.08	−108.23	0.366	−364.94	−98.812	0.390
Trichloromethane (1)	2.8700	2.4100	1,2	417.94	−228.61	0.071	1804.1	−880.74	0.055
Propanoic acid (2)	2.8768	2.6120	1,3	1243.3	257.67	0.316	1943.3	2207.7	0.234
Water (3)	0.9200	1.4000	2,3	176.22	−20.420	0.613	476.94	73.994	0.712
Trichloromethane (1)	2.8700	2.4100	1,2	276.43	−42.811	0.022	955.11	−362.40	0.018
2-Propanol (2)	2.7791	2.5080	1,3	629.70	284.71	0.249	868.79	1297.7	0.210
Water (3)	0.9200	1.4000	2,3	−0.1489	169.40	0.729	−354.02	1132.2	0.772
Furfural (1)	3.1680	2.4840	1,2	−333.21	−480.97	0.232	745.20	−517.04	0.176
Formic acid (2)	1.5280	1.5320	1,3	110.78	190.59	0.116	22.522	1209.4	0.112
Water (3)	0.9200	1.4000	2,3	−627.56	136.29	0.652	−10.682	−492.26	0.712

Table V. (Continued).

System	UNIQUAC Molecular-Structural Parameters		UNIQUAC Parameters, K			Critical Composition	NRTL[b] Parameters, K		Critical Composition
	r	q	i,j	a_{ij}	a_{ji}		a_{ij}	a_{ji}	
Water (1)	0.9200	1.4000	1,2	−177.22	−187.79	0.150	1020.1	−814.90	0.170
Methanol (2)	1.4311	1.4320	1,3	429.01	638.14	0.461	1790.4	944.01	0.471
1,2-Dichloroethane (3)	2.9308	2.5280	2,3	−66.033	307.47	0.389	512.05	−18.927	0.360
Methanol (1)	1.4311	1.4320	1,2	−16.965	−64.745	0.417	169.39	−580.60	0.420
Acetic acid, Methyl ester (2)	2.8042	2.5760	1,3	12.535	625.79	0.044	385.68	467.08	0.088
Cyclohexane (3)	4.0464	3.2400	2,3	−4.7990	−10.666	0.539	−234.39	−218.92	0.492
1-Nitropropane (1)	3.3573	2.9480	1,2	757.36	−183.64	0.107	836.34	−159.44	0.102
Methanol (2)	1.4311	1.4320	1,3	499.46	296.51	0.419	598.47	2472.6	0.396
Water (3)	0.9200	1.4000	2,3	−43.494	182.09	0.473	761.22	−69.326	0.502
Cyclohexane (1)	4.0464	3.2400	1,2	−59.532	−130.17	0.466	−447.04	−336.27	0.473
Tetrahydrofuran (2)	2.9415	2.7200	1,3	618.50	13.935	0.047	445.78	396.55	0.059
Methanol (3)	1.4311	1.4320	2,3	−159.85	8.7418	0.487	−748.38	427.75	0.469
1-Butanol (1)	3.4543	3.0520	1,2	320.76	−199.90	0.133	703.82	−178.09	0.106
Methanol (2)	1.4311	1.4320	1,3	−68.151	396.99	0.116	−344.40	1756.8	0.108
Water (3)	0.9200	1.4000	2,3	−81.520	−319.75	0.751	45.740	−147.43	0.785
Phenol (1)	3.5517	2.6800	1,2	−270.21	−80.219	0.120	−42.444	−33.676	0.078
Methanol (2)	1.4311	1.4320	1,3	−257.86	566.90	0.073	−567.84	1884.0	0.078
Water (3)	0.9200	1.4000	2,3	−235.52	129.16	0.808	55.212	44.631	0.844
Methanol (1)	1.4311	1.3200	1,2	−8.3649	−72.360	0.429	322.69	−921.90	0.419
Benzoic acid (2)	4.3230	3.3440	1,3	12.256	678.14	0.068	373.25	539.45	0.069
Cyclohexane (3)	4.0464	3.2400	2,3	−46.742	−7.8853	0.503	−619.13	−362.75	0.512

TABLE V. (Continued).

	UNIQUAC Molecular-Structural Parameters		UNIQUAC Parameters, K			Critical Composition	NRTL[b] Parameters, K		Critical Composition
System	r	q	i,j	a_{ij}	a_{ji}		a_{ij}	a_{ji}	
Cyclohexane (1)	4.0464	3.2400	1,2	−11.799	−24.202	0.375	−647.20	−376.15	0.391
Naphthalene (2)	4.9808	3.4400	1,3	753.28	−8.1030	0.073	659.47	300.44	0.071
Methanol (3)	1.4311	1.4320	2,3	36.338	110.15	0.552	−681.65	725.01	0.538
Methanol (1)	1.4311	1.4320	1,2	103.66	−179.61	0.520	873.57	−1245.0	0.470
Diphenylamine (2)	6.5760	4.6360	1,3	14.019	704.77	0.034	379.39	578.07	0.044
Cyclohexane (3)	4.0464	3.2400	2,3	−108.50	−75.541	0.446	−987.32	−856.11	0.486
Water (1)	0.9200	1.4000	1,2	−1.4582	−112.24	0.285	319.11	−280.94	0.280
2-Propanol (2)	2.7791	2.5080	1,3	335.30	702.78	0.406	1877.8	708.87	0.402
Tetrachloroethene (3)	3.8879	3.4000	2,3	−85.104	205.12	0.309	−100.12	328.53	0.318
n-Heptane (1)	5.1742	4.3960	1,2	−77.340	119.27	0.279	−82.539	−170.79	0.279
Benzene (2)	3.1878	2.4000	1,3	632.92	29.945	0.282	557.12	689.63	0.278
Acetonitrile (3)	1.8701	1.7240	2,3	18.087	72.756	0.439	−239.57	215.35	0.443
Water (1)	0.9200	1.4000	1,2	−16.853	−58.866	0.319	503.62	−531.48	0.364
Acetic acid (2)	2.2024	2.0720	1,3	642.80	702.87	0.389	1878.8	1023.2	0.387
1,2-Dichloroethane (3)	2.9308	2.5280	2,3	−166.46	399.33	0.292	−62.672	80.132	0.248
1,2-Ethanediol (1)	2.4088	2.2480	1,2	87.971	−391.53	0.482	324.88	−838.73	0.470
Acetic acid (2)	2.2024	2.0720	1,3	72.350	295.47	0.069	462.97	431.49	0.073
Acetic acid, Ethyl ester (3)	3.4786	3.1160	2,3	−303.67	−123.43	0.449	−464.49	−396.64	0.453
1-Butanol (1)	3.4543	3.0520	1,2	155.34	−211.40	0.123	192.64	−412.70	0.102
Acetic acid (2)	2.2024	2.0720	1,3	−30.037	311.03	0.090	−330.50	1601.7	0.085
Water (3)	0.9200	1.4000	2,3	−30.340	−170.32	0.787	−114.89	−182.85	0.813

TABLE V. (Continued).

System	UNIQUAC Molecular-Structural Parameters		UNIQUAC Parameters, K			Critical Composition	NRTL[b] Parameters, K		Critical Composition
	r	q	i,j	a_{ij}	a_{ji}		a_{ij}	a_{ji}	
Diethyl ether (1)	3.3949	3.0160	1,2	−212.01	26.114	0.175	955.63	−679.82	0.145
Acetic acid (2)	2.2024	2.0720	1,3	493.70	127.55	0.199	374.70	1168.1	0.189
Water (3)	0.9200	1.4000	2,3	−254.66	129.86	0.626	65.933	−58.806	0.666
Furfural (1)	3.1680	2.4840	1,2	342.99	−361.92	0.217	514.63	−757.65	0.144
Acetic acid (2)	2.2024	2.0720	1,3	149.81	110.29	0.111	28.810	1248.6	0.102
Water (3)	0.9200	1.4000	2,3	−127.49	−419.83	0.673	−250.83	−502.50	0.754
1-Butanol, 3-Methyl (1)	4.1279	3.5880	1,2	384.62	−318.92	0.103	610.35	−601.10	0.084
Acetic acid (2)	2.2024	2.0720	1,3	182.33	249.91	0.177	27.313	1807.9	0.160
Water (3)	0.9200	1.4000	2,3	17.453	−317.31	0.719	−66.424	−69.290	0.756
Water (1)	0.9200	1.4000	1,2	−266.09	−129.95	0.212	−88.738	−325.86	0.224
Acetic acid (2)	2.2024	2.0720	1,3	596.58	703.31	0.496	1804.8	924.96	0.503
Benzene (3)	3.1878	2.4000	2,3	−69.726	0.0824	0.291	188.14	−154.94	0.273
Acetaldehyde, Diacetate (1)	5.1542	4.5320	1,2	−129.46	109.27	0.117	357.15	−377.74	0.096
Acetic acid (2)	2.2024	2.0720	1,3	351.69	36.746	0.186	−75.473	1586.2	0.179
Water (3)	0.9200	1.4000	2,3	−125.10	125.00	0.697	−2.1213	190.88	0.725
2-Pentanone, 4-Methyl (1)	4.5959	3.9520	1,2	−225.65	−13.128	0.118	696.81	−565.15	0.091
Acetic acid (2)	2.2024	2.0720	1,3	437.77	107.98	0.212	228.70	1827.0	0.204
Water (3)	0.9200	1.4000	2,3	−278.01	128.06	0.670	−11.779	44.146	0.705
Acetic acid, Isobutyl ester (1)	4.8266	4.1920	1,2	−114.20	3.1591	0.116	356.30	−319.24	0.093
Acetic acid (2)	2.2024	2.0720	1,3	494.86	124.58	0.285	350.10	2408.7	0.266
Water (3)	0.9200	1.4000	2,3	−227.48	118.70	0.599	−204.91	318.66	0.641

TABLE V. (Continued).

	UNIQUAC Molecular-Structural Parameters		UNIQUAC Parameters, K			Critical Composition	NRTL[b] Parameters, K		Critical Composition
System	r	q	i,j	a_{ij}	a_{ji}		a_{ij}	a_{ji}	
Water (1)	0.9200	1.4000	1,2	−132.62	198.68	0.180	631.71	−212.84	0.146
Acetic acid (2)	2.2024	2.0720	1,3	−101.73	1033.9	0.395	950.38	811.06	0.392
Aniline, N,N-Dimethyl (3)	5.1094	3.9200	2,3	−30.321	225.39	0.425	50.658	409.82	0.462
1-Butanol (1)	3.4543	3.0520	1,2	190.76	−243.34	0.114	270.88	−450.93	0.097
Ethanol (2)	2.1055	1.9720	1,3	−23.464	308.83	0.093	−311.68	1579.4	0.088
Water (3)	0.9200	1.4000	2,3	−16.989	−199.44	0.793	−35.903	−180.00	0.815
Water (1)	0.9200	1.4000	1,2	266.93	−266.09	0.226	376.33	−441.74	0.264
Ethanol (2)	2.1055	1.9720	1,3	249.80	807.82	0.394	2797.7	986.99	0.397
Benzene (3)	3.1878	2.4000	2,3	−73.352	256.10	0.380	87.744	118.04	0.339
Water (1)	0.9200	1.4000	1,2	−62.614	8.0261	0.097	347.43	−222.42	0.081
Ethanol (2)	2.1055	1.9720	1,3	210.18	692.86	0.446	1488.9	822.47	0.509
2-Chlorotoluene (3)	4.5477	3.4120	2,3	−96.017	381.84	0.457	317.40	204.12	0.410
Water (1)[c]	0.9200	1.4000	1,2	255.88	−35.103	0.256			
2-Butyloxyethanol (2)	4.4697	5.7979	1,3	205.89	4660.3	0.328			
n-Decane (3)[c]	7.1974	6.1060	2,3	684.93	−357.76	0.416			

[a] UNIQUAC and NRTL parameters taken from the collection of Sørensen and Arlt [41]

[b] Nonramdomness parameter, $\alpha_{ij} = \alpha_{ji} = 0.2$ for all calculations

[c] UNIQUAC parameters taken from García-Sánchez *et al.* [29]

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APPENDIX A: THERMODYNAMIC FUNCTIONS FOR THE NRTL EQUATION FOR AN N-COMPONENT SYSTEM

$\tau_{ij} \neq \tau_{ji}$, $\alpha_{ij} = \alpha_{ji}$: Parameters characterizing the interactions between molecules i and j $(\tau_{ii} = \tau_{jj} = 0)$.

$$\tau_{ij} = a_{ij}/T, \qquad i,j = 1,\ldots,N; \tag{60}$$

$$g_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \qquad i,j = 1,\ldots,N; \tag{61}$$

$$S_i = \sum_{j=1}^{N} x_j\, g_{ji}, \qquad i = 1,\ldots,N; \tag{62}$$

$$C_i = \sum_{j=1}^{N} x_j\, \tau_{ji}\, g_{ji}, \qquad i = 1,\ldots,N; \tag{63}$$

$$\ln\gamma_i = \frac{C_i}{S_i} + \sum_{k=1}^{N} \frac{x_k\, g_{ik}}{S_k}\left(\tau_{ik} - \frac{C_k}{S_k}\right), \qquad i = 1,\ldots,N; \tag{64}$$

$$Q_{ij}^{N} = \frac{g_{ij}}{S_j}\left(\tau_{ij} - \frac{C_j}{S_j}\right) + \frac{g_{ji}}{S_i}\left(\tau_{ji} - \frac{C_i}{S_i}\right) + \sum_{k=1}^{N} \frac{x_k\, g_{ik}\, g_{jk}}{S_k^2}\left(\frac{2C_k}{S_k} - \tau_{ik} - \tau_{jk}\right), \qquad i,j = 1,\ldots,N; \tag{65}$$

$$Q_{ijk}^{N} = \frac{g_{ji}\, g_{ki}}{S_i^2}\left(\frac{2C_i}{S_i} - \tau_{ji} - \tau_{ki}\right) + \frac{g_{ij}\, g_{kj}}{S_j^2}\left(\frac{2C_j}{S_j} - \tau_{ij} - \tau_{kj}\right) + \frac{g_{ik}\, g_{jk}}{S_k^2}\left(\frac{2C_k}{S_k} - \tau_{ik} - \tau_{jk}\right)$$
$$+ 2\sum_{l=1}^{N} \frac{x_l\, g_{il}\, g_{jl}\, g_{kl}}{S_l^3}\left(\tau_{il} + \tau_{jl} + \tau_{kl} - \frac{3C_l}{S_l}\right), \qquad i,j,k = 1,\ldots,N. \tag{66}$$

APPENDIX B: THERMODYNAMIC FUNCTIONS FOR THE UNIQUAC EQUATION FOR AN N-COMPONENT SYSTEM

r_i, q_i: Parameters characterizing the volume and surface area of component i; $\tau_{ij} \neq \tau_{ji}$: parameters characterizing the interactions between molecules i and j ($\tau_{ii} = \tau_{jj} = 1$); $z = 10$: coordination number.

$$\tau_{ij} = \exp(-a_{ij}/T), \qquad i, j = 1, \ldots, N; \tag{67}$$

$$r = \sum_{i=1}^{N} x_i r_i, \tag{68}$$

$$q = \sum_{i=1}^{N} x_i q_i, \tag{69}$$

$$\phi_i = x_i r_i / r, \qquad i = 1, \ldots, N; \tag{70}$$

$$\theta_i = x_i q_i / q, \qquad i = 1, \ldots, N; \tag{71}$$

$$S_i = \sum_{j=1}^{N} \theta_j \tau_{ji}, \qquad i = 1, \ldots, N; \tag{72}$$

$$\ln \gamma_i = 1 - \frac{\phi_i}{x_i} + \ln\left(\frac{\phi_i}{x_i}\right) + \left(\frac{z}{2}\right) q_i \left[\frac{\phi_i}{\theta_i} - \ln\left(\frac{\phi_i}{\theta_i}\right) - 1\right] + q_i \left(1 - \ln S_j - \sum_{j=1}^{N} \frac{\theta_j \tau_{ij}}{S_j}\right), \quad i = 1, \ldots, N; \tag{73}$$

$$Q_{ij}^{N} = (x_i x_j)^{-1} \left[-\phi_i x_j - \phi_j x_i + \phi_i \phi_j - \left(\frac{z}{2}\right) q (\phi_i - \theta_i)(\phi_j - \theta_j)\right] + \frac{q_i q_j}{q} \left(1 - \frac{\tau_{ji}}{S_i} - \frac{\tau_{ij}}{S_j} + \sum_{k=1}^{N} \frac{\theta_k \, \tau_{ik} \, \tau_{jk}}{S_k^2}\right), \qquad i, j = 1, \ldots N; \tag{74}$$

$$Q_{ijk}^{N} = (x_i \, x_j \, x_k)^{-1} \Big\{ \phi_i \phi_j x_k + \phi_i \phi_k x_j + \phi_j \phi_k x_i - 2 \phi_i \phi_j \phi_k + \left(\frac{z}{2}\right) q \Big[(\phi_i - \theta_i)(\phi_k - \theta_k)\theta_j + (\phi_j - \theta_j)(\phi_i \phi_k - \theta_i \theta_k) \Big] \Big\} - \frac{q_i q_j q_k}{q^2} \left(1 - \frac{\tau_{ji} \tau_{ki}}{S_i^2} - \frac{\tau_{ij} \tau_{kj}}{S_j^2} - \frac{\tau_{ik} \tau_{jk}}{S_k^2} + 2 \sum_{l=1}^{N} \frac{\theta_l \tau_{il} \tau_{jl} \tau_{kl}}{S_l^3}\right), \quad i, j, k = 1, \ldots, N. \tag{75}$$

REFERENCES

1. R.N. Healy, R.L. Reed and D.G. Stenmark, *Soc. Pet. Eng. J.* **16** (1976) 147.
2. B.M. Knickerbocker, C.V. Pesheck, L.E. Scriven and H.T. Davis, *J. Phys. Chem.* **83** (1979) 1984.
3. B.M. Knickerbocker, C.V. Pesheck, H.T. Davis and L.E. Scriven, *J. Phys. Chem.* **86** (1982) 393.
4. B.P. Cairns and I.A. Furzer, *Ind. Eng. Chem. Res.* **29** (1990) 1364.
5. W.D. Seider, D.D. Brengel and S. Widagdo, *AIChE J.* **37** (1991) 1.
6. S. Negahban, G.P. Willhite and S.M. Walas, *SPE Res. Eng.* **3** (1988) 1017.
7. D.S. Abrams and J.M. Prausnitz, *AIChE J.* **21** (1975) 116.
8. H. Renon, L. Asselineau, G. Cohen and C. Raimbault, *Calcul sur Ordinateur des Equilibres Liquide-Vapeur et Liquide-Liquide*, Editions Technip, Paris (1971).
9. H. Renon and J.M. Prausnitz, *AIChE J.* **14** (1968) 135.
10. J.F. Boston and H.I. Britt, *Comput. Chem. Eng.* **2** (1978) 109.
11. L. Asselineau, G. Bogdanic and J. Vidal, *Fluid Phase Equilibria* **3** (1979) 273.
12. M.L. Michelsen, *Fluid Phase Equilibria* **9** (1982) 1.
13. M.L. Michelsen, *Fluid Phase Equilibria* **9** (1982) 21.
14. R.K. Mehra, R.A. Heidemann and K. Aziz, *Can. J. Chem. Eng.* **61** (1983) 590.
15. L.X. Nghiem and Y.K. Li, *Fluid Phase Equilibria* **17** (1984) 77.
16. M.O. Ohanomah and D.W. Thompson, *Comput. Chem. Eng.* **8** (1984) 147.
17. M.N. Ammar and H. Renon, *AIChE J.* **33** (1987) 926.
18. L.E. Baker, A.C. Pierce and K.D. Luks, *Soc. Pet. Eng. J.* **22** (1982) 731.
19. I. Prigogine and R. Defay, *Chemical Thermodynamics*, Longmans, London (1967).
20. M. Modell and R.C. Reid, *Thermodynamics and its Applications*, Prentice-Hall, Englewood Cliffs, New-Jersey (1974).
21. D.B. van Dongen, M.F. Doherty and J.R. Halght, *Ind. Eng. Chem. Fundam.* **22** (1983) 472.
22. M.L. Michelsen, *Ind. Eng. Chem. Fundam.* **23** (1984) 373.
23. R. Gautam and W.D. Seider, *AIChE J.* **25** (1979) 999.
24. V.B. Shah, Doctoral Dissertation, University of Toledo, Toledo, Ohio (1980).
25. L.X. Nghiem and R.A. Heidemann, *Proc. 2nd. European Symposium on Enhanced Oil Recovery*, Paris (1982).
26. A.M. Crowe and M. Nishio, *AIChE J.* **21** (1975) 528.
27. J.E. Dennis and J.J. Moré, *SIAM Rev.* **19** (1977) 46.
28. R. Fletcher, *Practical Methods of Optimization.* Vol. 1. *Unconstrained Optimization.* Wiley-Interscience, New York (1980).
29. F. García-Sánchez, J. Schwartzentruber, M.N. Ammar and H. Renon, *Fluid Phase Equilibria* **121** (1996) 207.
30. M.N. Ammar, Doctoral Dissertation, Ecole des Mines de Paris, Paris (1986).
31. G. Varhegyi and C.H. Eon, *Ind. Eng. Chem. Fundam.* **16** (1977) 182.
32. J.M. Sørensen, T. Magnussen, P. Rasmussen and A. Fredenslund, *Fluid Phase Equilibria* **3** (1979) 47.
33. J.A. Nelder and R. Mead, *The Computer J.* **7** (1965) 308.
34. D.W. Marquardt, *SIAM J. Appl. Math.* **31** (1963) 431.
35. J.J. de Pablo and J.M. Prausnitz, *AIChE J.* **34** (1988) 1595.
36. J.P. Novák, J. Matous and J. Pick, *Liquid-Liquid Equilibria*, Elsevier Science Publ., Amsterdam (1987).

37. R.A. Heidemann and A.M. Khalil, *AIChE J.* **26** (1980) 769.
38. M.L. Michelsen, *Fluid Phase Equilibria* **4** (1980) 1.
39. V.P. Sazonov, N.P. Markuzin and V.V. Filippov, *Zh. Prikl. Khim. (Leningrad)* **50** (1977) 1524.
40. V.P. Sazonov and M.F. Chernysheva, *Zh. Prikl. Khim. (Leningrad)* **51** (1978) 1764.
41. J.M. Sørensen and W. Arlt, *Liquid-Liquid Equilibrium Data Collection.* Vol. 5, Parts 2 and 3, DECHEMA Chemistry Data Series, Frankfurt/Main, West Germany (1980).
42. S. Negahban, Doctoral Dissertation, University of Kansas, Lawrence, Kansas (1986).
43. F. Ruiz and V. Gomis, *Ind. Eng. Chem. Process Des. Dev.* **25** (1986) 216.
44. G.M. Hartwig, G.C. Hood and R.L. Maycock, *J. Phys. Chem.* **59** (1955) 52.
45. J.M. Sørensen, T. Magnussen, P. Rasmussen and A. Fredenslund, *Fluid Phase Equilibria* **2** (1979) 297.
46. S. Negahban, G.P. Willhite, S.M. Walas and M.J. Michnick, *Fluid Phase Equilibria* **32** (1986) 49.
47. D. Blankschtein, G.M. Thurston and G.B. Benedek, *Phys. Rev. Lett.* **54** (1985) 955.
48. D. Blankschtein, G.M. Thurston and G.B. Benedek, *J. Chem. Phys.* **85** (1986) 7268.
49. S. Puvvada and D. Blankschtein, *J. Chem. Phys.* **92** (1990) 3710.
50. R. Nagarajan and E. Ruckenstein, *Langmuir* **7** (1991) 2934.
51. S. Puvvada and D. Blankschtein, *J. Phys. Chem.* **96** (1992) 5567.