Thermodynamics of Liquid-Liquid Equilibria Including the Critical Region

To obtain good representation in the liquid-liquid critical region, a semitheoretical correction is added to a conventional expression (e.g., van Laar or NRTL) for the excess Gibbs energy of a binary or ternary system along the coexistence curve. This correction is an exponential function of a suitable distance from the critical point; it is significant in the critical region but not elsewhere. In the correction function, the preexponential factor is determined from stability considerations. In the exponential argument, two parameters are determined from theoretical power laws. While the coordinates of the critical point must be known (or estimated), no phase-equilibrium data in the critical region are required to determine parameters. The correction presented here provides an excellent approximation for phase equilibria along the coexistence curve close to and remote from critical conditions. Further, the correction facilitates simultaneous representation of isothermal vapor-liquid and liquid-liquid equilibria including the liquid-liquid critical region.

Juan José de Pablo,
John M. Prausnitz
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
and Chemical Engineering Department
University of California
Berkeley, CA 94720

Introduction

Liquid-liquid extraction has found extensive applications in the pharmaceutical, fine-chemical, and petrochemical industries. While industrial processes have become more sophisticated during the last 20 years, there has been no comparable change in the molecular-thermodynamic models used to describe liquid-liquid equilibria (LLE) for nonelectrolytes.

For nonelectrolyte liquid mixtures, conventional models often provide good representation of experimental data except in the critical region, where there is much need for improvement. Coexistence curves are of particular importance in the design of extraction operations; the so-called "classical" models typically predict a two-phase region of partially miscible mixtures larger than that observed. The unusual behavior of a fluid mixture near a critical point is now well understood, and a thermodynamic treatment of critical points is now available (Sengers and Levelt Sengers, 1978); in our work here we have incorporated into a classical model some of the nonclassical features observed in the critical region. We propose some modifications to conventional expressions for the excess Gibbs energy along the coexistence curve; these modifications are guided by the modern theory of critical phenomena. Our modified expressions are here called semiclassical.

In the first section of this paper we consider the effect of temperature on those binary liquid mixtures which exhibit an upper consolute point. In the second section we consider isothermal ternary liquid mixtures having a plait point.

The extent to which the miscibility gap is overpredicted depends strongly on the kind of data used (VLE or LLE or both) to determine the parameters of a given model. For engineering work (for example, design of azeotropic distillation operations), it is often desirable to have a single model that can adequately represent both vapor-liquid and liquid-liquid equilibria. However, when parameters obtained from VLE data are used to predict LLE, the prediction is almost always very poor in the critical region. In the third section of this paper we suggest a procedure toward better simultaneous representation of isothermal ternary VLE and LLE.

Binary Liquid-Liquid Equilibria

We consider first a simple binary liquid mixture whose molar excess Gibbs energy g^E is given by a two-suffix Margules expansion:

$$g^E = A_{12}x_1x_2 \qquad (1)$$

Coexisting compositions, x_i' and x_i'' of component i in phases (′) and (″), are calculated from the equilibrium conditions

$$x_i'\gamma_i' = x_i''\gamma_i'' \quad i = 1, 2 \qquad (2)$$

The activity coefficient γ_i of component i is given by

$$RT \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_j} \tag{3}$$

where n_T is the total number of moles and n_i is the number of moles of component i.

Equation 1 gives the molar excess Gibbs energy as a quadratic function of mole fraction x. Figure 1 shows a typical temperature-composition diagram obtained from Eq. 1 when (positive, temperature-independent) binary constant A_{12} is determined from experimental data remote from critical conditions. The calculated critical temperature T_c is too large.

Classical models for the excess Gibbs energy not only overpredict the coexistence region; in addition, such models give a coexistence curve which, near T_c, is quadratic in composition, in conflict with experimental data and the modern theory of critical phenomena. Near the upper consolute temperature, the coexistence curve is much flatter than that predicted by Eq. 1.

Classical models are not appropriate near a critical point because they fail to take fluctuations into account. When a critical point is approached, the correlation length rises rapidly, producing large fluctuations of the order parameter (Rowlinson and Swinton, 1982). For a pure fluid, the order parameter is the difference between liquid and vapor densities. The fluctuations take the form of drops of liquid interdispersed with bubbles of gas, and there are drops and bubbles of many sizes (Wilson, 1979). For a binary liquid mixture, the order parameter is the difference in composition between coexisting phases (Scott, 1978); fluctuations are drops of phase (′) traveling through phase (″) and vice versa. Near a critical point, the properties of a liquid mixture are dominated by the long-range correlation rather than by molecular details, and therefore all liquid mixtures exhibit similar behavior very close to critical conditions. A quantitative description of a mixture near its critical point must take into account the effect of fluctuations.

Critical points are properly described in terms of critical exponents. As discussed, for example, by Greer and Moldover (1981), and more recently by Ewing et al. (1988), as the consolute point of a binary liquid mixture is approached, the shape of the coexistence curve is given by:

$$|x_1' - x_1''| = H^{(1)} t^{\beta} + \cdots \tag{4a}$$

$$\frac{x_1' + x_1''}{2} = x_{1c} + H^{(2)} t^{1-\alpha} + \cdots \tag{4b}$$

where $t = (T - T_c)/T_c$ and where $H^{(1)}$ and $H^{(2)}$ are mixture-dependent amplitudes. Here x_{1c} is the mole fraction of component 1 at the critical point.

The difference $|x' - x''|$ is the order parameter. For an upper consolute point, it is so defined that it is zero in the high-temperature phase and nonzero in the low-temperature phase. The observed critical exponent β is approximately 0.34, regardless of the system; a classical treatment predicts a value of $\frac{1}{2}$.

The variable $(x' + x'')/2$ is the diameter of the coexistence curve. Critical exponent α is the same as that of the divergence of the specific heat at constant volume for a pure fluid. The observed value is approximately 0.12. If critical exponent α were zero (the classical value), we would recover the familiar law of rectilinear diameter. Since α is small compared to unity, it is difficult to verify Eq. 4b experimentally. Further, Scott (1978) has shown that if a nonsymmetric composition variable is used, the observed exponent for the diameter tends to 2β, rather than $(1 - \alpha)$. It has often been suggested that volume fractions, rather than mole fractions should be used because coexistence curves for binary mixtures are then more nearly symmetric. Unfortunately, this choice of variables does not necessarily guarantee that the true $(1 - \alpha) = 0.88$ will be observed; for the system 3-methyl pentane/nitroethane, for example, Stein and Allen (1973) obtained $(1 - \alpha) = 0.62$ from the precise measurements of Wims et al. (1969), using volume fractions. In this regard, complete agreement between theory and experiment has not been achieved.

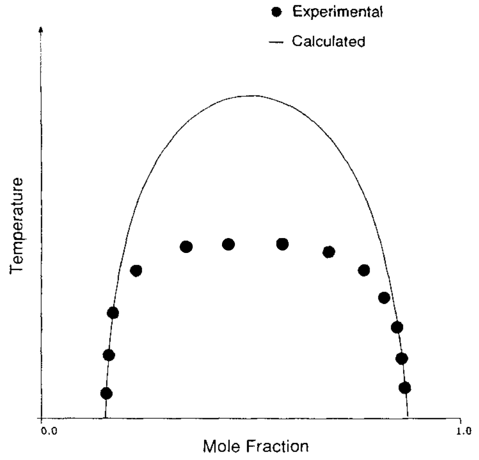

Figure 1. Typical coexistence curve for a binary mixture showing an upper consolute point.

Equations 4a and 4b can only describe the asymptotic behavior of the coexistence curve as the consolute point is approached; they only hold in its immediate vicinity. The region of validity depends on the system and on the choice of composition variable (Greer and Moldover, 1981; Scott, 1978).

The thermodynamic properties of fluids near a critical point are represented successfully by the so-called scaled equations of state (Levelt Sengers et al., 1983). Unfortunately, the range of validity of such equations is severely limited; for mixtures, a large number of parameters is required (Sengers and Levelt-Sengers, 1986).

Recently, a theoretical framework has been developed for the crossover from a critical region to a classical region of a pure fluid (Albright, 1985; M. Ley-Koo, personal communication, 1986). The implementation of this formalism has been carried out with the van der Waals equation of state (Albright, 1985; Albright et al., 1986), but quantitative conclusions are not yet possible due to the lack of experimental data necessary to test the theory. Research concerning the crossover behavior of fluid mixtures is currently in progress (J. V. Sengers, personal communication, 1988), but it still is at an early stage.

LLE can be calculated from a g^E model. While, in theory, other thermodynamic properties, such as entropy or heat capacity, could also be calculated from g^E, in engineering practice a model for g^E is seldom used for calculations other than LLE or VLE (vapor-liquid equilibria). Indeed, if any of the commonly used g^E models, with the corresponding parameters determined from LLE data, were used to calculate heat capacity, the results would be very poor. In this work, we restrict our attention to the coexistence curve, that is, temperatures below T_c and to compositions at saturation. We propose a modification of classical g^E models that allows simultaneous representation of a coexistence curve near and remote from the critical point.

A simple way to introduce fluctuations in a conventional model for the excess Gibbs energy is through composition averages. The instantaneous mole fraction x is related to the time-average mole fraction $\overline{x}$ through

$$x_i = \overline{x}_i + \delta x_i \tag{5}$$

where δx is a fluctuation. To take into account the effect of fluctuations on g^E, we must rewrite Eq. 1:

$$g^E = A_{12}\overline{x_1 x_2} = A_{12}\,(\overline{x}_1\overline{x}_2 + \overline{\delta x_1 \delta x_2}) \tag{6}$$

where the overbars denote time averages. We now propose a reasonable but essentially empirical expression for the fluctuation term.

The fluctuation term must satisfy two boundary conditions: first, fluctuations are significant in the critical region; second, they are negligible remote from the critical region. To calculate their effect on g^E, we introduce a measure of distance to the critical point, designated by D. Because we confine attention to the coexistence curve, the distance is a function only of temperature. We propose the semiclassical expression:

$$g^E = A_{12}\overline{x}_1\overline{x}_2\,[1 - K\exp{(aD^b)}] \tag{7a}$$

$$D = t^2 = \left(\frac{T - T_c}{T_c}\right)^2 \tag{7b}$$

where binary constant A_{12} is obtained from experimental LLE data remote from critical conditions; K, a, and b are parameters which, as shown later, are found from purely thermodynamic considerations. LLE data in the critical region are not used to determine these parameters. However, T_c must be known. Because of symmetry, when Eq. 7a is used, the critical mole fraction is $1/2$.

At the critical temperature, Eq. 7 reduces to

$$g_c^E = A_{12}\overline{x}_1\overline{x}_2(1 - K) \quad \text{at } T = T_c \tag{8}$$

As we move away from the critical temperature along the coexistence curve, distance D increases; since parameter a is negative and parameter b is positive, we recover the original equation (fluctuations disappear):

$$g^E = A_{12}\overline{x}_1\overline{x}_2 \tag{9}$$

In the remainder of this paper we need only average mole fractions; therefore, we omit the overbars for simplicity.

We obtain parameter K from thermodynamic criteria for incipient immiscibility at the critical point. In a binary mixture these criteria are:

$$\left(\frac{\partial^2 \Delta g}{\partial x^2}\right)_c = 0 \tag{10a}$$

$$\left(\frac{\partial^3 \Delta g}{\partial x^3}\right)_c = 0 \tag{10b}$$

where subscript c refers to critical conditions. The molar Gibbs energy of mixing Δg is given by the sum of the excess Gibbs energy of mixing and the ideal Gibbs energy of mixing:

$$\Delta g = g^E + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

Substitution of Eq. 7 into Eqs. 10 gives

$$K = 1 - \frac{2RT_c}{A_{12}} \tag{11}$$

When K is calculated from Eq. 11, the temperature-composition curve goes through the critical point, regardless of parameters a and b. However, the curvature of that curve depends on parameters a and b. We return to these parameters presently, but we first consider a model for g^E somewhat more realistic than the two-suffix Margules equation.

As shown in Figure 1, the two-suffix Margules equation leads to a coexistence diagram that is symmetric in mole fraction. Real systems seldom behave this way. To correct approximately for asymmetry, we use the van Laar equation

$$g^E = A_{12}(x_1 q_1 + x_2 q_2)\phi_1\phi_2 \tag{12}$$

where the effective volume fraction of component i is defined by

$$\phi_i = \frac{q_i x_i}{q_i x_i + q_j x_j} \tag{13}$$

Here q_i is the cross section of component i. Binary parameters $A_{12}q_1$ and $A_{12}q_2$ are found from experimental LLE data remote from critical conditions. To take into account the effect of the critical region, we write as before

$$g^E = g_{co}^E[1 - K\exp{(aD^b)}] \tag{14}$$

where g_{co}^E is now given by Eq. 12; subscript *co* denotes "conventional." Using stability criteria as before, parameter K is now given by

$$K = 1 - \frac{RT_c\left(\dfrac{q_1}{q_2}x_{1c} + x_{2c}\right)^3}{2x_{1c}x_{2c}A_{12}\dfrac{q_1^2}{q_2}} \tag{15}$$

where subscript c refers to the critical state. To find K, we need to know the coordinates of the critical point, T_c and x_c. For a two-suffix Margules equation $q_1 = q_2$ and $x_c = 1/2$. For the more realistic case where $q_1 \neq q_2$, x_{1c} is given by

$$x_{1c} = \frac{\left[\left(\dfrac{q_1}{q_2}\right)^2 + 1 - \dfrac{q_1}{q_2}\right]^{1/2} - \dfrac{q_1}{q_2}}{1 - \dfrac{q_1}{q_2}} \tag{16}$$

Note that x_c is not affected by our correction to the conventional van Laar equation.

Parameters a and b are determined from critical exponents α and β. In Eq. 14 parameters a and b are adjusted such that Eqs.

4a and 4b hold over a reasonable range of temperatures. We say "reasonable" because a critical exponent, as pointed out by Scott (1978), represents the limiting behavior as T approaches T_c. Using Eq. 14, we calculate the coexisting volume fractions ϕ' and ϕ'' using the known value of K and using first approximations for a and b. Our experience indicates that b is always close to 0.36. We then plot $\ln(\phi' - \phi'')$ and $\ln(\phi' + \phi'' - 2\phi_c)$ vs. $\ln(t)$ in the region $10^{-2} > t > 10^{-6}$, and obtain the average slopes [β and $(1 - \alpha)$, respectively] by numerical techniques. The procedure is repeated, using new values of a and b, until the calculated slopes agree with the accepted values. While Eq. 14 is not sensitive to small changes in a, when the magnitude of K is large better results are obtained if parameter a is also adjusted to experimental data remote from the critical point, in addition to the fitting procedure initiated above.

We emphasize that our semiclassical method, Eq. 14 only holds for the coexistence curve; it is clear that Eq. 14 should not be used to calculate thermodynamic properties (i.e., heat capacity) other than coexistence curves. However, by fixing a and b as indicated above, we can obtain excellent agreement with experimental liquid-liquid equilibrium data in the critical region, including very small values of $t(\approx 10^{-6})$.

Figure 2 shows typical results. The calculated coexistence curve was obtained using Eq. 14 and experimental LLE data obtained remote from critical conditions. The data shown in Figure 2 represent some of the most precise measurements available near the consolute point of a binary mixture (Wims et al., 1969). Parameter K was obtained from Eq. 15. Parameters a and b were found as shown in Figure 3, where the slopes of the lines are $\beta = 0.34$ and $(1 - \alpha) = 0.72$. When T_c is known and LLE data are available at conditions remote from critical, parameters K, a, and b are found entirely from theoretical criteria.

Figure 4 shows the calculated coexistence curve for another binary system obtained with Eq. 14. In Figures 2 and 4, we used only experimental LLE data remote from the critical point and the coordinates of the critical point. Appendix 2 gives parameters for these examples.

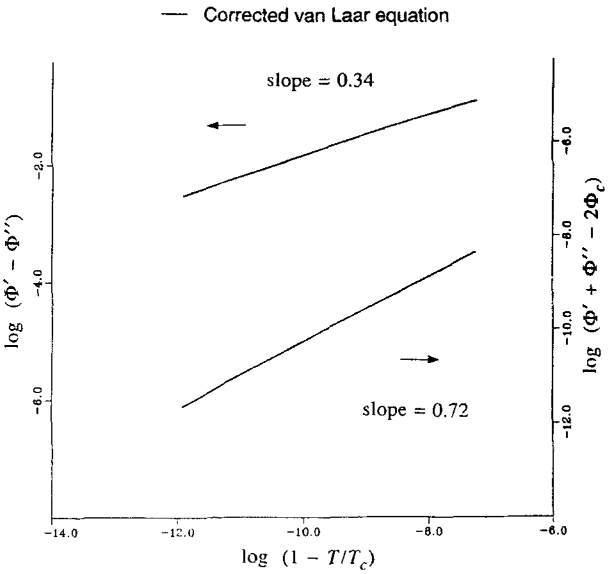

Figure 3. Calculation of parameters *a*, *b* for system nitroethane/3-methylpentane.

We now turn our attention to the magnitude of constant K. When using the van Laar equation, its value is approximately 0.4, providing a correction of 40% to that conventional model at the critical point. The range of temperatures where the correction has a noticeable effect is probably much larger than the region where critical effects are significant. This is not surprising, since the van Laar model with temperature-independent parameters cannot represent precisely the coexistence curve of a binary mixture, even for a temperature range well removed from critical.

To include a reasonable temperature effect on binary g^E_{co} parameters, we consider the NRTL (nonrandom two-liquid) equation (Prausnitz et al., 1986), which has a moderate built-in temperature dependence. However, this built-in temperature dependence is also insufficient for adequate representation of LLE. We obtain considerable improvement when we allow the NRTL parameters to vary linearly with temperature, as suggested in the literature (Sorensen and Arlt, 1979; Sorensen et al., 1979). In Figure 5, the dotted curve was calculated with the NRTL equation and parameters having a simple linear temperature dependence. However, that moderate temperature

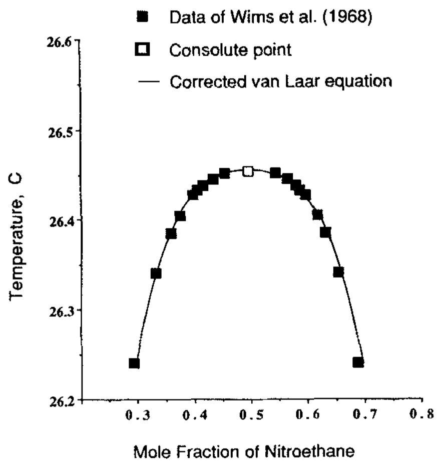

Figure 2. Coexistence curve for system nitroethane/3-methylpentane.

Note expanded temperature scale

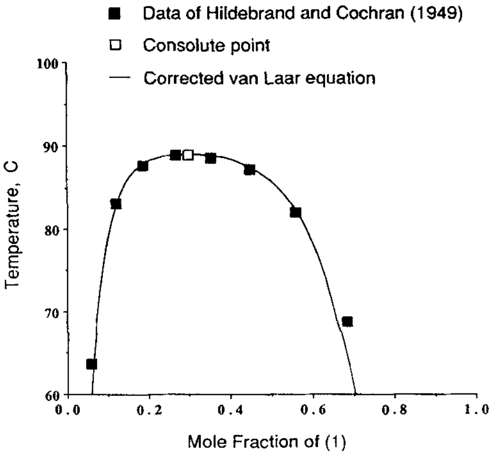

Figure 4. Coexistence curve for system perfluoromethylcyclohexane (1)/toluene (2).

Parameters *a*, *b* obtained from universal critical exponents

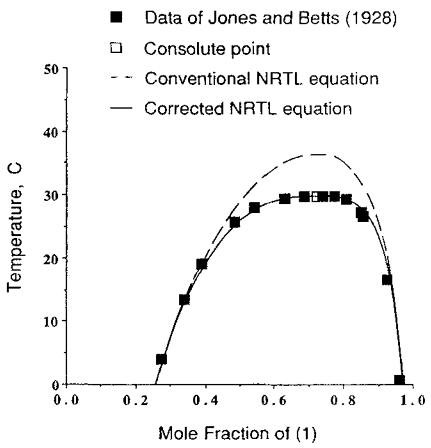

Figure 5. Coexistence curve for system carbon disulfide (1)/acetic anhydride (2).

--- Calculations based on conventional NRTL equation with parameters linearly dependent on temperature

— Calculations based on same NRTL equation with same parameters but with modification proposed in this work

dependence is not useful for the critical region. To describe the coexistence curve in the critical region, we require a strong temperature dependence which decays rapidly as the reduced temperature falls. Equation 14 supplies that desired temperature dependence without requiring LLE data in the critical region. The coordinates of the critical point must be known, but parameters K, a, and b are found from theoretical considerations.

Unlike the van Laar equation, when the NRTL model (with parameters linearly dependent on temperature) is used in Eq. 14, the magnitude of K is around 0.07, giving only a 7% correction to the conventional equation. The solid curve of Figure 5 was calculated with the corrected NRTL equation and parameters linearly dependent on temperature.

Ternary Liquid-Liquid Equilibria

For engineering applications, ternary liquid-liquid equilibria are more interesting than binary equilibria. When isothermal ternary liquid-liquid equilibria are calculated for a plait-point system using conventional models for g^E, the predicted two-phase region is too large. The plait point of a ternary mixture is analogous to the consolute point of a binary mixture.

In our discussion for binary mixtures with an upper consolute point, we proposed a correction to the conventional g^E; along the coexistence curve, that correction depends on D, a dimensionless distance from the critical point, Eq. 7b. Ternary composition diagrams, however, are calculated at fixed temperature and fixed pressure; along the coexistence curve, a difference in temperature is no longer an appropriate measure of distance.

For isothermal ternary systems, we propose a distance that can best be understood using a geometric representation of the Gibbs energy surface $\Delta g(x_2, x_3)$ at constant temperature and pressure. Figure 6 shows this surface for a ternary system that exhibits a plait point. One condition for the stability of the system is the convexity of the energy surface (Prigogine and Defay, 1954; Reid and Modell, 1974). When a fold appears in the surface, convexity is lost and the system splits into two phases. The boundary which separates that part of the surface which is convex-convex from that which is convex-concave is called the spinodal (Prigogine and Defay, 1954); it is defined by

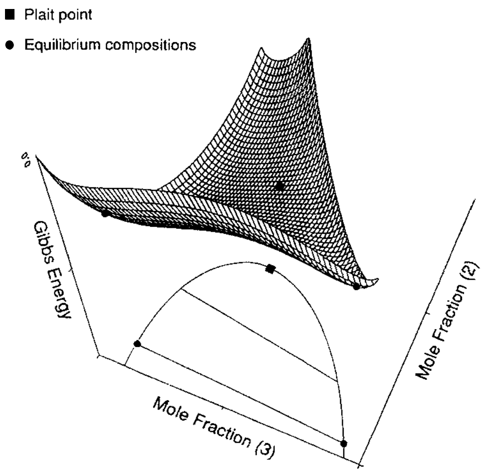

Figure 6. Molar Gibbs energy of mixing surface $\Delta g/RT$, at constant temperature and pressure, showing stable and unstable regions.

Coexisting compositions on this surface have a common tangent plane. Projection on the (x_2, x_3) plane is the familiar ternary diagram

$$\frac{\partial \Delta g}{\partial x_2}\frac{\partial \Delta g}{\partial x_3} - \left(\frac{\partial^2 \Delta g}{\partial x_2 \partial x_3}\right)^2 = 0 \tag{17}$$

The spinodal indicates the appearance of a fold in the Δg surface.

For a ternary two-phase mixture, the conditions of equilibrium are

$$x_i'\gamma_i' = x_i''\gamma_i'' \qquad i = 1, 2, \text{and } 3 \tag{18}$$

It can be shown (Prigogine and Defay, 1954) that at the two points representing coexisting phases in Figure 6, the tangent planes coincide; therefore Eqs. 18 are equivalent to:

$$\left(\frac{\partial \Delta g}{\partial x_2}\right)' = \left(\frac{\partial \Delta g}{\partial x_2}\right)'' \tag{19a}$$

$$\left(\frac{\partial \Delta g}{\partial x_3}\right)' = \left(\frac{\partial \Delta g}{\partial x_3}\right)'' \tag{19b}$$

$$\Delta g' - x_2'\left(\frac{\partial \Delta g}{\partial x_2}\right)' - x_3'\left(\frac{\partial \Delta g}{\partial x_3}\right)' = \Delta g'' - x_2''\left(\frac{\partial \Delta g}{\partial x_2}\right)'' - x_3''\left(\frac{\partial \Delta g}{\partial x_3}\right)'' \tag{19c}$$

We add Eqs. 19a and 19b to obtain a definition for D. The proposed dimensionless distance for a ternary mixture is:

$$D = \frac{\left(\frac{\partial \Delta g}{\partial x_2} + \frac{\partial \Delta g}{\partial x_3}\right)_{co} - \left(\frac{\partial \Delta g}{\partial x_2} + \frac{\partial \Delta g}{\partial x_3}\right)_c}{\left(\frac{\partial \Delta g}{\partial x_2} + \frac{\partial \Delta g}{\partial x_3}\right)_c} \tag{20}$$

where the meaning of subscripts *co* and *c* will become clear as we explain the calculation procedure. Distance D vanishes at the plait point and increases smoothly as we move away from it.

To calculate the ternary LLE diagram, we first choose a conventional model for g^E that is adequate for representing the excess Gibbs energy of a ternary mixture at conditions well removed from critical. In the examples that follow we use the NRTL equation, but other models could also be used. Consistent with our proposal for binary mixtures, we now suggest

$$g^E = g^E_{co}[1 - K \exp(aD^b)] \tag{21}$$

where g^E_{co} is the conventional NRTL model, using parameters obtained from experimental data at conditions remote from critical. Distance D is given by Eq. 20. Parameter K is found from incipient inmiscibility conditions. Parameters a and b are found from adjusting the curvature of the binodal curve (near the plait point) to the appropriate critical exponents, as discussed below.

At the plait point, $D = 0$, and Eq. 21 becomes:

$$g^E_c = g^E_{co}(1 - K)$$

Stability criteria yield a value of K that forces the binodal curve to go through the plait point. For a ternary mixture these criteria are (Reid and Modell, 1974):

$$\xi = \begin{vmatrix} \dfrac{\partial^2 \Delta g}{\partial x_2^2} & \dfrac{\partial^2 \Delta g}{\partial x_2 \partial x_3} \\ \dfrac{\partial^2 \Delta g}{\partial x_2 \partial x_3} & \dfrac{\partial^2 \Delta g}{\partial x_3^2} \end{vmatrix} = 0 \tag{22a}$$

$$\zeta = \begin{vmatrix} \dfrac{\partial \xi}{\partial x_2} & \dfrac{\partial \xi}{\partial x_3} \\ \dfrac{\partial^2 \Delta g}{\partial x_2 \partial x_3} & \dfrac{\partial^2 \Delta g}{\partial x_2 \partial x_3} \end{vmatrix} = 0 \tag{22b}$$

Solution of Eqs. 22 gives the coordinates of the plait point; note that these coordinates depend not only on K, but also on the excess Gibbs energy parameters. The calculated plait-point coordinates are compared with those obtained experimentally or by empirical estimation procedures (see Appendix 1), and the difference between both sets of coordinates is minimized.

The procedure we propose is composed of two steps. The first step is the calculation of the equilibrium compositions, using the conventional NRTL model with its standard parameters (determined from data remote from the plait point). To calculate coexisting equilibrium compositions, Eqs. 18 were satisfied; therefore, a numerical value is available for the derivatives appearing in Eqs. 19. These values correspond to the conventional model. It is precisely these values that we use in Eq. 21 where, as elsewhere, subscript *co* stands for "conventional." The advantage of using conventional values in Eq. 21 stems from the fact that iterative calculations are avoided, and implementation of the procedure to existing routines can be performed easily.

In a two-phase ternary system, we have three equilibrium equations, Eqs. 18, and four unknowns: two mole fractions in each phase. To equate the number of unknowns and equations, a material balance is introduced to perform an isothermal flash calculation (Prausnitz et al., 1986). Consider one mole of mixture splitting into two phases (′) and (″). We have three material balances:

$$\begin{aligned} L' + L'' &= 1 \\ x_2'L' + x_2''L'' &= x_2 \\ x_3'L' + x_3''L'' &= x_3 \end{aligned} \tag{23}$$

where x_2 and x_3 are overall mole fractions, and L' and L'' are, respectively, the number of moles in phases (′) and (″). The number of unknowns and equations is equal to six: four mole fractions, L', and L''. The overall composition is fixed externally each time a new set of equilibrium compositions is calculated; by setting this composition equal to that of the observed plait point, and using the conventional model, we calculate in Eq. 20 those derivatives with subscript c. These calculations provide a numerical value for distance D.

The second step in our procedure is to solve the isothermal flash problem again for the same overall composition, but this time using Eq. 21 to obtain the desired set of equilibrium compositions. To use Eq. 21, we require parameters a and b. We obtain these parameters from critical exponents.

Widom (1966) derives an expression for order parameter l in a ternary mixture. As the plait point of a ternary mixture is approached

$$l \approx d^{\beta/(1-\alpha)} \tag{24}$$

Order parameter l is the length of a tie line and d represents the orthogonal distance from this tie line to the plait point, as shown in Figure 7. The exponent in Eq. 24 is obtained through a renormalization of exponents (β and α are the same as those for binary systems). The observed value of $\beta/(1 - \alpha)$ is approximately 0.38 (Zollweg, 1971). A classical treatment predicts $\beta = 1/2$ and $\alpha = 0$. Classically, therefore, $\beta/(1 - \alpha) = 1/2$.

Disagreement between classical theory and experiment is not as pronounced near a ternary plait point as it is near a binary consolute point (where the observed exponent is about 0.34 and

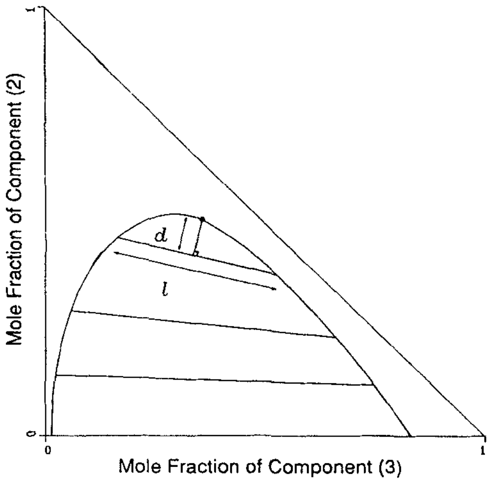

Figure 7. Definition of order parameter *l* and distance *d* for a ternary system at constant temperature and pressure.

d, distance from plait point to tie line; *l*, length of tie line

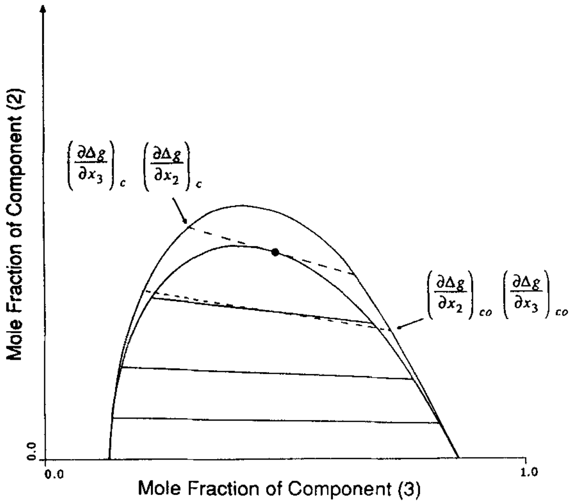

Figure 8. Proposed method for calculation of ternary LLE.

Upper curve, conventional NRTL model; lower curve, corrected model

Overall composition used to calculate a tie line the same for both models

Results obtained with corrected model depends on first derivatives of Gibbs energy of mixing Δg, evaluated at equilibrium compositions predicted by conventional model

the classical value is ½). Unfortunately, there is substantial lack of data for ternary mixtures in the vicinity of the plait point. To the best of our knowledge, the exponent in Eq. 24 has been measured in only a few mixtures (Zollweg, 1971; van Dael and Mijlemans, 1982).

Figure 8 illustrates our proposed method for calculating ternary liquid-liquid equilibria. The "conventional" results as well as the final equilibrium compositions are shown for a hypothetical ternary system showing a plait point.

Figure 9 shows a composition diagram for the system benzene/acetonitrile/cyclohexane. The points represent data by Nagata et al. (1983); the dotted curve was calculated with the conventional NRTL model and parameters from ternary LLE data obtained remote from critical conditions. The two-phase region is overpredicted, but to a somewhat lesser extent than it was in binary mixtures (e.g., Figure 5). The solid curve was calculated with the corrected NRTL equation and parameters from LLE data remote from the plait point.

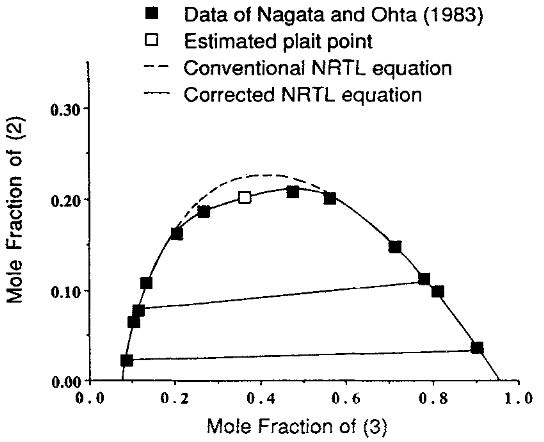

Figure 9. Ternary diagram at 25°C for system acetonitrile (1)/benzene (2)/cyclohexane (3).

--- Conventional NRTL equation with parameters from LLE data remote from plait point

— Same model with same parameters but with correction proposed in this work

When the nonrandomness constants of the conventional NRTL equation are fixed, the six remaining binary parameters for a ternary mixture must be determined from experimental data. (If the nonrandomness parameters are not fixed, nine parameters must be determined.) In either event, constant K appearing in Eq. 21 has to be calculated from the observed or estimated position of the plait point. In general, if NRTL parameters and constant K are determined independently, the coordinates of the plait point are close to, but not equal to those estimated. Rather than perform these data-reduction calculations one after the other, we have found that simultaneous fitting of the NRTL parameters and constant K yields better results. In this calculation we minimize the difference between calculated and experimental equilibrium compositions, and we simultaneously satisfy Eqs. 22. NRTL parameters are not significantly altered by this procedure, but a small change in these parameters can improve the calculated coordinates of the plait point.

To use Eq. 21, we require the coordinates of the plait point. An experimental value is seldom available, but often it can be found using empirical methods summarized in Appendix 1.

Our experience indicates that in Eq. 21, exponent b is always close to unity. A good starting value of b is 0.85. Parameter a is negative. Both parameters are adjusted to obtain the correct curvature of the binodal in the vicinity of the plait point. The procedure we follow to find these parameters is the same as that for binary mixtures. The only difference is that now we adjust a and b until a plot of ln (l) vs. ln (d) gives the desired slope = 0.38. We emphasize once again that determination of K, a, and b does not require LLE data in the critical region, but only an estimate of the plait-point coordinates.

As shown in Figure 10 for the system acetonitrile/benzene/cyclohexane, the curvature near the plait point is essentially correct. The example shown in Figure 10 is based on conventional NRTL model parameters obtained from ternary LLE data remote from the plait point.

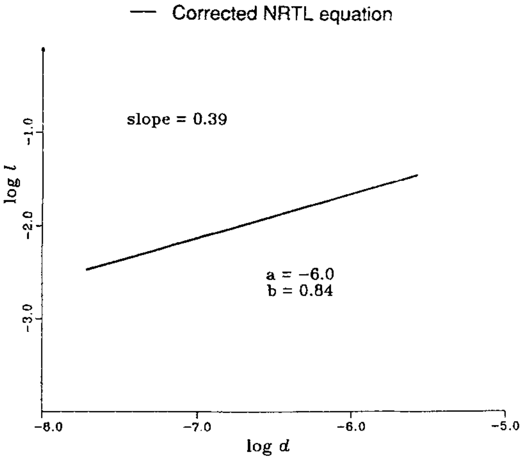

Figure 10. Calculation of parameters a, b for system acetonitrile/benzene/cyclohexane at 25°C.

In this calculation, b is restrained to be close to unity

While the conventional g^E models overpredict the two-phase region, this overprediction is sometimes masked by simultaneously fitting data in the critical region and data remote from the critical region. In some cases the overall representation of the equilibrium compositions is then fairly good but, in general, a moderately good representation of the critical region is obtained only at the expense of unsatisfactory representation of the region remote from critical. In any event, if only data remote from the plait point are used to determine the parameters of the conventional NRTL expression (when K is set equal to zero in Eq. 21), the coexistence curve is always overpredicted.

While it is important to calculate correctly the size of the two-phase region, in a ternary diagram a second, and equally important, requirement is correct calculation of the slope of the tie lines. Extraction processes are usually designed to operate well below the plait point of the mixture. Accurate tie lines for this region can be obtained from a conventional g^E model provided that the fit is based only on data from this region; if critical data are also used in data reduction, these tie lines can be adversely affected.

Simultaneous Representation of Vapor-Liquid and Liquid-Liquid Equilibria

In all previous examples, only LLE experimental data were used to obtain the parameters appearing in the excess Gibbs energy model. A more conventional procedure is to use LLE data only for the partially miscible binary and to use VLE data for the two completely miscible pairs. When that procedure is used to predict ternary LLE, the miscibility gap is overpredicted to an extent larger than that when parameters are obtained from ternary LLE (Fabries et al., 1977; De Fré and Verhoeye, 1976). Poor agreement with experiment follows, in part, from fluctuations in the critical region and from a lack of three-body terms in conventional Gibbs energy models.

Calculated ternary LLE diagrams are very sensitive to the method used to determine the conventional excess Gibbs energy parameters from VLE data. When the regression of experimental binary VLE data uses a method that takes into account the experimental error (e.g., the maximum likelihood method), many sets of parameters are obtained that represent the data equally well (Prausnitz et al., 1980). As long as the parameters lie inside a specified confidence ellipse, any one set is as good as any other for the representation of binary VLE. However, the choice of binary parameters has important consequences on the calculation of liquid-liquid equilibria (Novák et al., 1987).

As discussed by Anderson (1978), when ternary LLE data are available it is advantageous to fit LLE and VLE experimental data simultaneously. However, when using a conventional expression for g^E, simultaneous fitting does not guarantee a correct description of the miscibility curve. Figure 11 shows typical results for the ternary system *n*-heptane/benzene/acetonitrile. In this example, regression of the three sets of experimental data was performed simultaneously (only two LLE tie lines were used); nevertheless, the calculated two-phase region is too large. How large it is depends on the weight assigned to each experimental point but, in any event, a large correction is necessary to obtain a good fit of the entire two-phase region.

Much better results are obtained using Eq. 21. To use that equation, we proceed as follows. We begin by estimating the position of the plait point (Appendix 1). Second, binary VLE experimental data for the miscible pairs and a few tie lines (remote from the plait point) are regressed along with the critical coordinates to obtain conventional NRTL parameters and constant K. To guarantee adequate representation of the binary systems, conventional NRTL parameters are restricted to lie within the corresponding binary confidence ellipses. The objective functions are the difference between the experimental and calculated equilibrium compositions and the conditions of incipient inmiscibility at the plait point (Eqs. 22). Finally, parameters a and b in the correction term can be determined by the method described earlier. However, in this case it is advisable to use all LLE data to determine appropriate values for a and b. Since the correction can sometimes be significant (up to 20%), it not only affects the region in the immediate vicinity of the plait point but may extend well outside that region. One must therefore verify that agreement between experimental data and calculations is also good at conditions removed from critical.

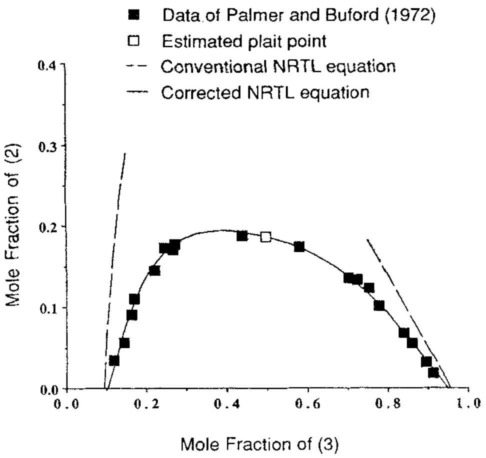

Figure 11. Ternary LLE at 45°C for system *n*-heptane (1)/benzene (2)/acetonitrile (3).

NRTL parameters used are the same as those used to calculate VLE in Figures 12, 13

Figure 11 shows results for the system *n*-heptane/benzene/acetonitrile; Figures 12 and 13 show the corresponding binary VLE for the two miscible pairs.

Finally, in Table 1 we show experimental and calculated isothermal ternary VLE for the same system. Throughout this work we have restricted our attention to compositions along the coexistence curve. A disadvantage of our definition of distance is that it is the same all along a given tie line, calculated with the conventional model, regardless of the position on this tie line. While our ternary VLE results are not conclusive, they indicate that the modification proposed does not significantly affect the prediction of ternary VLE. When the correction factor (last column in Table 1) is close to unity, the results obtained with the modified model are essentially equal to those obtained with the conventional model. When the correction becomes important, the calculated pressures obtained with the conventional model are somewhat closer to the experimental values than those obtained with the modified model. The vapor phase compositions, however, are somewhat closer to the experimental data when calculated with the modified model. Further, in this example the correction to the conventional Gibbs energy model is quite large. The magnitude of the correction (constant K) determines the extent to which calculated ternary VLE are affected by the proposed modification.

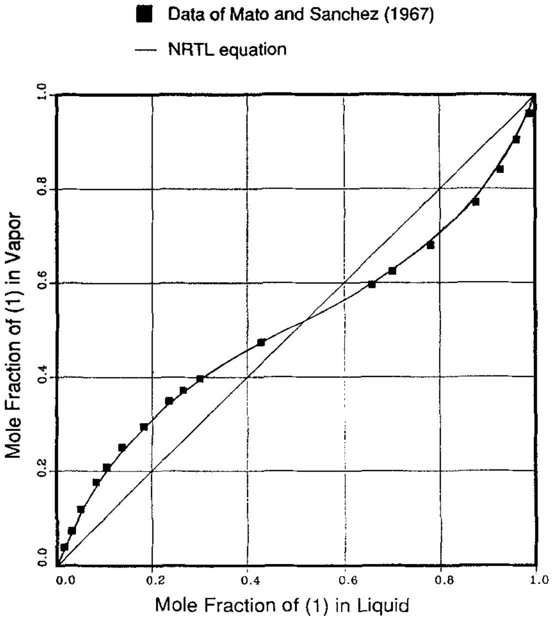

Figure 12. Binary VLE for system benzene (1)/acetonitrile (2) at 760 torr.

NRTL parameters used are the same as for ternary LLE calculation, Figure 11

Our limited experience indicates that while a critical-region correction has a profound effect on isothermal ternary LLE, its effect on ternary VLE at the same temperature is much smaller.

Conclusions

In the last decade much progress has been achieved in understanding critical phenomena. Theoretical equations have been proposed for accurate representation of thermodynamic properties of fluids and fluid mixtures near their critical points. However, these equations are not useful for conditions well removed from critical.

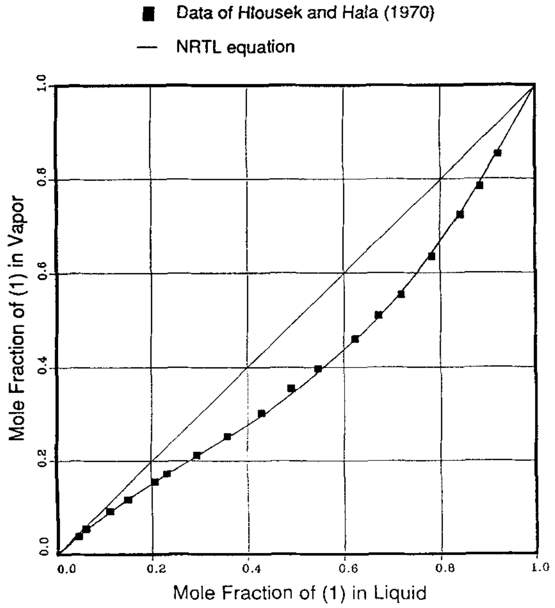

Figure 13. Binary VLE for system heptane (1)/benzene (2) at 760 torr.

NRTL parameters used are the same as for ternary LLE calculation, Figure 11

Table 1. Calculated and Experimental Total Pressures and Vapor Composition for the System *n*-Heptane(1)/Benzene(2)/Acetonitrile(3) at 45° C

Source*	P bar	x_1	x_2	y_1	y_2	$(g^E/g^E\ co)$**
Ex	0.316	0.1055	0.8648	0.0760	0.8370	—
Con	0.302	—	—	0.0677	0.8453	—
Cor	0.301	—	—	0.0675	0.8479	0.974
Ex	0.373	0.0130	0.5137	0.0260	0.5050	—
Con	0.362	—	—	0.0262	0.5213	—
Cor	0.362	—	—	0.0261	0.5214	0.998
Ex	0.371	0.1725	0.6930	0.1280	0.5860	—
Con	0.345	—	—	0.1079	0.5884	—
Cor	0.338	—	—	0.1078	0.6010	0.943
Ex	0.422	0.5162	0.1880	0.2750	0.1450	—
Con	0.436	—	—	0.2453	0.1180	—
Cor	0.409	—	—	0.2551	0.1264	0.926
Ex	0.422	0.3896	0.2314	0.2600	0.1790	—
Con	0.419	—	—	0.2459	0.1563	—
Cor	0.395	—	—	0.2480	0.1665	0.911
Ex	0.423	0.3595	0.2123	0.2640	0.1680	—
Con	0.418	—	—	0.2590	0.1466	—
Cor	0.396	—	—	0.2575	0.1552	0.914

*Ex: experiment; Con: conventional NRTL model; Cor: corrected NRTL model.

**$(g^E/g^E\ co)$ = correction factor to conventional model, $g^E\ co$.

In this work we have proposed a semiclassical modification to conventional excess Gibbs energy models which allows simultaneous representation of coexistence curves at conditions both near and well removed from critical. The modifications we propose are only valid for the liquid-liquid coexistence curve; they are not suitable for a full thermodynamic description of a fluid near a critical point. However they provide a simple and accurate description of coexistence curves in the critical region of binary and ternary liquid mixtures. Further, these modifications can easily be incorporated into existing programs or simulation packages that perform LLE calculations.

Finally, we have presented a procedure for calculating the excess Gibbs energy of an isothermal ternary system that permits simultaneous representation of VLE and LLE data, including the critical region.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. Juan J. de Pablo is grateful to the Mexican Council of Science and Technology (CONACYT) for a fellowship.

Appendix 1: Methods to Estimate the Plait Point of a Ternary Mixture

The coordinates of a ternary system's plait point can be estimated by a variety of methods. Here we briefly describe two of these. For information concerning other methods, see the text by Treybal (1963).

The method of Treybal et al. (1946), consists of plotting on

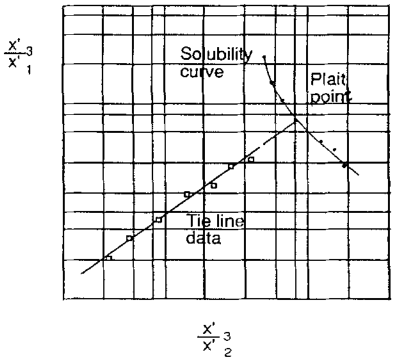

Figure A1. Method of Treybal et al. (1946) for obtaining plait point position.

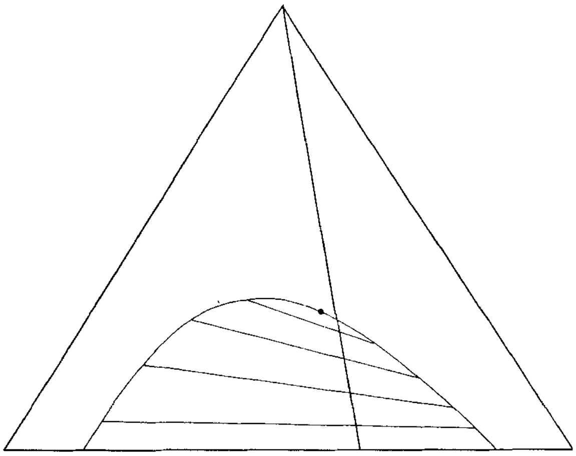

Figure A2. Method of Fleming and Vinatieri (1979) for obtaining plait point position.

log-log coordinates the ratios x'_3/x'_1 *vs.* x''_3/x''_2, where components 1 and 2 represent the partially miscible pair. This plot should give a straight line.

On the same scale, solubility data are plotted in the form x_3/x_1 *vs.* x_3/x_2. A solubility curve is then obtained. The straight line described in the previous paragraph intersects the solubility curve at the plait point; by extrapolating both plots, we can estimate the ratios $(x_3/x_1)_c$ and $(x_3/x_2)_c$ and obtain the position of the plait point. Figure A1 illustrates the method.

Fleming and Vinatieri (1979) propose a method that takes into account nonclassical behavior. Using the appropriate critical exponents, the authors derive a function for the mass fraction of a given phase along a path of constant concentration ratio of two of the components. Such a path is shown in Figure A2, where the ratio of component 1 to component 3 is held fixed.

Since the derivation of this function is long, we give here only its final form. The mass fraction F of one of the coexisting phases is given by

$$F = \frac{1}{2}\left\{1 - \left(\frac{\overline{C^o} - C^o}{C - C^o}\right)^{\beta/(1-\alpha)}[1 + \lambda(C - \overline{C^o})]\right\}$$

This expression contains three adjustable parameters, C^o, $\overline{C^o}$, and λ; C denotes the concentration of one of the components. Function F is calculated along a path of constant concentration ratio of two of the components; fixing this ratio and the concentration C of one component, determines the overall composition. C^o is the concentration at which a phase disappears, and $(C^o - \overline{C^o})$ represents the "closeness" of a certain path to the plait point. Thus the problem is that of finding the path (ratio of compositions) that minimizes the difference $(C^o - \overline{C^o})$. Using this criterion of minimization, tie line data are fitted to find that ratio and the parameters appearing in the equation for F. Following this procedure, C^o is the concentration of a given component at the plait point; from the path's ratio, the other two concentrations are calculated.

Appendix 2: Parameters Used for Calculations

In Tables A1 and A2 we give parameters for several examples, including those used in this paper. We use the following notation:

VL: van Laar equation. Parameter $A_{12}q_1$ is denoted by A_{12} and parameter A_{12q_2} is denoted by A_{21}. These parameters are divided by R and reported in K.

NRTL-LTD: NTRL equation with parameters linearly dependent on temperature. (This equation is used here only for binary systems.) The g_{ij} parameters are thus replaced by $g_{ij} = A_{ij}T + O_{ij}$. Parameters A_{ij}, O_{ij}, and nonran-

Table A1. Parameters for Some Binary Systems

System	Eq.*	A_{12}	A_{21}	O_{12}	O_{21}	α	K	a	b	T_c	x_{1c}
Nitroethane (1), 3-methylpentane (2)	VL	959.0	950.2	—	—	—	0.373	−19.0	0.36	299.60	0.497
Perfluoro methyl cyclohexane (1), toluene (2)	VL	1,092.7	612.9	—	—	—	0.167	−12.3	0.38	362.07	0.300
Hexane (1), nitrobenzene (2)	VL	601.4	726.1	—	—	—	0.118	−8.3	0.35	293.17	0.570
Carbon disulfide (1), acetic anhydride (2)	NRTL-LTD	−3.60	−3.12	2004.7	865.9	−0.2	0.072	−20.0	0.36	302.95	0.722
Aniline (1), hexane (2)	NRTL-LTD	4.80	−8.38	−1000.9	3074.8	−0.2	0.075	−16.0	0.36	339.16	0.586

*See explanation, Appendix 2.

Table A2. Parameters for Some Ternary Systems

System	Eq.*	i	j	g_{ij}	g_{ji}	α_{ij}	K	a	b	x_{1c}	x_{2c}
Acetonitrile (1),		1	2	1,388.5	−305.9	−0.2					
benzene (2),	NRTL^r	1	3	467.3	676.3	−0.2	0.040	−6.0	0.84	0.433	0.202
cyclohexane (3)		2	3	−168.8	1,051.7	−0.2					
$T = 298.15$ K											
1-hexene (1),		1	2	87.5	246.2	−0.2					
benzene (2),	NRTL^{rc}	1	3	2,233.0	529.5	−0.2	0.0	—	—	—	—
sulpholane (3)		2	3	82.5	457.8	−0.2					
$T = 348.15$ K											
1-hexene (1),		1	2	−74.4	−45.8	−0.2					
benzene (2),	NRTL^r	1	3	1,227.3	468.7	−0.2	0.091	−1.55	0.70	0.295	0.450
sulpholane (3)		2	3	504.7	−271.2	−0.2					
$T = 348.15$ K											
n-Heptane (1),		1	2	−308.2	536.3	−0.3					
benzene (2),	NRTL^{VLE}	1	3	415.3	780.9	−0.2	0.227	−0.54	0.84	0.317	0.186
acetonitrile (3)		2	3	257.8	83.3	−0.3					
$T = 318.15$ K											

*See explanation, Appendix 2.

domness parameter α appear in Table A1. (Since $\alpha_{ij} = \alpha_{ji}$ we omit the subscripts.)

NRTL: NTRL equation with conventional NRTL parameters. This model is used for ternary LLE systems (and the corresponding binary and ternary VLE systems). When conventional NRTL parameters are obtained from LLE data remote from the critical region superscript r is used ($NRTL^r$). When NRTL parameters are determined from LLE data remote and near the critical region we use superscript rc ($NTRL^{rc}$). Finally, for NRTL parameters obtained from binary VLE data and ternary LLE data (remote from the plait point), we use superscript VLE ($NRTL^{VLE}$). g_{ij} parameters are divided by R and reported in K.

For the binary systems, we give consolute temperature T_c and critical composition x_{1c}. For the ternary systems, we give plait point coordinates x_{1c}, x_{2c}, x_{3c}. Parameters for binary systems are given in Table A1, and parameters for ternary systems are given in Table A2.

Literature Cited

Albright, P. C., "A Description of the Crossover from the Critical to the Classical Behavior of the Thermodynamic Properties of Fluids," Ph.D. Diss., Univ. Maryland (1985).

Albright, P. C., J. V. Sengers, J. F. Nicoll, and M. Ley-Koo, "A Crossover Description for the Thermodynamic Properties of Fluids in the Critical Region," *Int. Thermophys.*, **7**, 75 (1986).

Anderson, T., "Molecular Thermodynamics of Vapor-Liquid and Liquid-Liquid Equilibria," Ph.D. Diss., Univ. California, Berkeley (1978).

De Fré, R. M., and L. A. Verhoeye, "Phase Equilibria in Systems Composed on an Aliphatic and an Aromatic Hydrocarbon," *J. Appl. Chem. Biotechnol.*, **26**, 469 (1976).

Ewing, M. B., K. A. Johnson, and M. L. McGlashan, "The (Liquid + Liquid) Critical State of (Cyclohexane + Methanol). IV: $(T, x)p$ Coexistence Curve and the Slope of the Critical Line," *J. Chem. Thermody.*, **20**(1), 49 (1988).

Fabries, J. F., J. L. Gustin, and H. Renon, "Experimental Measurements of Phase Equilibria Properties for Systems Containing n-Heptane, Benzene, n-Methylpyrrolidone, and Monoethanolamine. Representation by the NRTL Equation," *J. Chem. Eng. Data*, **22**, 303 (1977).

Fleming, P. D., and J. E. Vinatieri, "Quantitative Interpretation of Phase Volume Behavior of Multicomponent Systems Near Critical Points," *AIChE J.*, **25**, 493 (1979).

Greer, S. C., and M. R. Moldover, "Thermodynamic Anomalies at Critical Points of Fluids," *Ann. Rev. Phys. Chem.*, **32**, 233 (1981).

Hildebrand, J. H., and D. R. F. Cochran, "Liquid-Liquid Solubilities of Perfluoromethylcyclohexane with Benzene, Carbon Tetrachloride, Chlorobenzene, Chloroform and Toluene," *J. Am. Chem. Soc.*, **71**, 22 (1949).

Hloušek, K., and E. Hála, "Liquid-Vapor Equilibrium. XLIII: The System Benzene–n-Heptane at 720, 740 and 760 mm Hg," *Coll. Czech. Chem. Commun.*, **35**, 1030 (1970).

Jones, D. C., and H. F. Betts, "Some Miscibility Relations of Acetic Anhydride," *J. Chem. Soc.*, **131**, 1177 (1928).

Levelt-Sengers, J. M. H., B. Kamgar-Parsi, F. W. Balfour, and J. V. Sengers, "Thermodynamic Properties of Steam in the Critical Region," *J. Phys. Chem. Ref. Data*, **12**, 1 (1983).

Mato, F., and M. Sanchez, "Equilibrio Líquido-Vapor de Mezclas Binarias de Acetonitrilo I," *An. Real. Soc. Espan. de Fis. y Quim.*, Ser. B, **63**, 1 (1967).

Nagata, I., and T. Ohta, "Liquid-Liquid Equilibria for the Systems Acetonitrile-Benzene-Cyclohexane, Acetonitrile-Toluene-Cyclohexane, and Methanol-Ethanol-Cyclohexane," *J. Chem. Eng. Data*, **28**, 256 (1983).

Novák, J. P., J. Matouš, and J. Pick, *Liquid-Liquid Equilibria*, Modern Thermodynamics, 7, Elsevier, Czechoslovakia (1987).

Palmer, D. A., and D. S. Buford, "Thermodynamic Excess Property Measurements for Acetonitrile–Benzene–n-Heptane System at 45°C," *J. Chem. Eng. Data*, **17**(1), 71 (1972).

Prausnitz, J. M., T. F. Anderson, E. A. Grens, C. A. Eckert, R. Hsieh, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1980).

Prausnitz, J. M., R. N. Lichtenthaler, and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2d ed., Prentice-Hall, Englewood Cliffs, NJ (1986).

Prigogine, I., and R. Defay, *Chemical Thermodynamics*, Longmans, London (1954).

Reid, R., and M. Modell, *Thermodynamics and Its Applications*, Prentice-Hall, Englewood Cliffs, NJ (1974).

Rowlinson, J. S., and F. L. Swinton, *Liquids and Liquid Mixtures*, 3d. ed., Butterworth Scientific, London (1982).

Scott, R. L., "Critical Exponents in Binary Fluid Mixtures," *Specialist Periodical Repts., Chemical Thermodynamics*, **2**, The Chemical Society, London (1978).

Sengers, J. V., and J. M. H. Levelt Sengers, "Critical Phenomena in Classical Fluids," *Progress in Liquid Physics*, C. A. Croxton, ed., Wiley, Chichester, UK (1978).

Sengers, J. V., and J. M. H. Levelt Sengers, "Thermodynamic Behavior of Fluids Near the Critical Point," prepr. *Ann. Rev. Phys. Chem.*, **37**, (Mar., 1986).

Sorensen, J. M., and W. Arlt, *Liquid-Liquid Equilibrium Data Collection—Binary Systems*, Chemistry Data Series, V, Pt. 1, DECHEMA, Frankfurt, W. Germany (1979).

Sorensen, J. M., T. Magnussen, P. Rasmussen, and A. Fredenslund, "Liquid-Liquid Equilibrium Data: Their Retrieval, Correlation and Prediction. II: Correlation," *Fluid Ph. Equil.*, **3**, 47 (1979).

Stein, A., and G. F. Allen, "An Analysis of Coexistence Curve Data for Several Binary Liquid Mixtures Near their Critical Points," *J. Phys. Chem. Ref. Data*, **2**(3), 443 (1973).

Treybal, R. E., *Liquid Extraction*, 2d ed., McGraw-Hill, New York (1963).

Treybal, R. E., L. D. Weber, and J. F. Daley, "The System Acetone–Water–1,1,2-Trichloroethane," *Ind. Eng. Chem.*, **38**, 817 (1946).

Van Dael, W., and P. Mijlemans, *Proc. 8th Symp. Thermophys. Properties*, J. V. Sengers, ed., **I**, 405 ASME, New York (1982).

Widom, B., "Plait Points in Two- and Three-Component Mixtures," *J. Chem. Phys.*, **46**, 3324 (1966).

Wilson, K. G., "Problems in Physics with Many Scales of Length," *Sci. Am.*, **241**(2), 158 (1979).

Wims, A. M., D. McIntyre, and F. Hynne, "Coexistence Curve for 3-Methylpentane/Nitroethane Near the Critical Point," *J. Chem. Phys.*, **50**, 616 (1969).

Zollweg, J., "The Shape of the Coexistence Curve Near a Plait Point in a Three-Component System," *J. Chem. Phys.*, **55**, 1430 (1971).

Manuscript received Nov. 9, 1987, and revision received Mar. 31, 1988.