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J.J. de Pablo and J.M. Prausnitz

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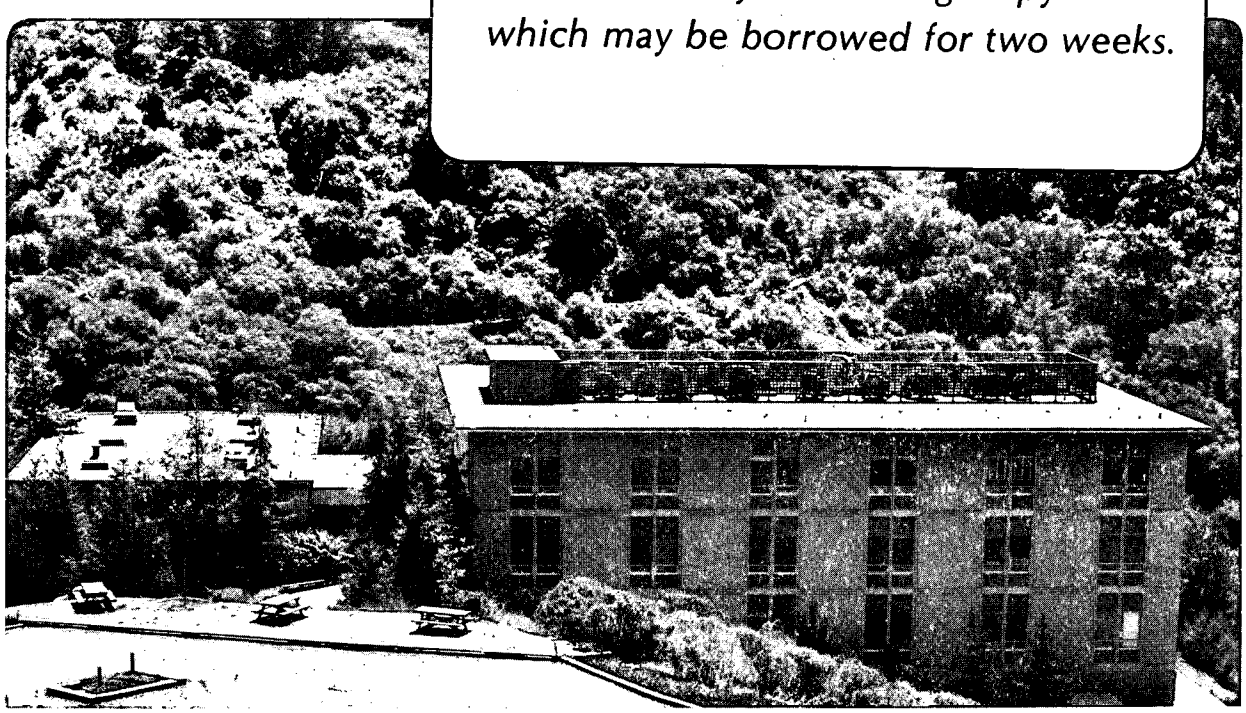

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THERMODYNAMICS OF LIQUID-LIQUID EQUILIBRIA INCLUDING THE CRITICAL REGION: BINARY AND TERNARY MIXTURES

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ABSTRACT

To obtain good representation in the critical region, a semi-theoretical correction is added to a conventional expression (e.g. van Laar or NRTL) for the excess Gibbs energy of a binary or ternary system. This correction is an exponential function of a carefully defined distance from the critical point; it is appreciable in the critical region but not elsewhere. In the correction function, the pre-exponential factor is determined from stability considerations. In the exponential argument, two parameters are determined from theoretical scaling 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 semi-classical method presented here provides an excellent continuous approximation for phase equilibria close to and remote from critical conditions. Further, the method allows simultaneous representation of VLE and LLE including the critical region.

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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 significant change in the molecular-thermodynamic models used to describe liquid-liquid equilibria for nonelectrolytes.

For nonelectrolyte liquid mixtures, conventional models often provide a good representation of experimental data except in the critical region, where there is much need for improvement. The so-called "classical" treatments typically overpredict the two-phase region of partially miscible mixtures. 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 et al., 1978); in our work here we have incorporated into a classical model some of the features observed in the critical region. We propose some modifications to conventional expressions for the excess Gibbs energy; these modifications are guided by the modern theory of critical phenomena but in essence, they remain classical. Our modified expressions are here called semi-classical.

In the first part of this paper we consider the effect of temperature on those binary liquid mixtures which exhibit an upper consolute point. In the second part 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, it is often desirable to have a single model that can represent adequately 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 part of this paper we suggest a procedure toward better simultaneous representation of ternary VLE and LLE.

PART I - 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:

$$g^E = A_{12}x_1x_2 \tag{1}$$

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 Equation (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 Equation (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 et al., 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, 1982). For a binary liquid mixture, the order parameter is the difference in composition between coexisting phases; 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 theory that describes 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), as the consolute point of a binary mixture is approached, the shape of the coexistence curve is given by:

$$|x'_1 - x''_1| = H^{(1)} t^{\beta} + \ldots \tag{2a}$$

$$\frac{x'_1 + x''_1}{2} = x_{1c} + H^{(2)} t^{1-\alpha} + \ldots \tag{2b}$$

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 non zero in the low-temperature phase. The observed critical exponent β is approximately 0.35, regardless of the system; a classical treatment predicts a value of 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, we would recover the familiar "law of rectilinear diameter". Since α is small compared to unity, it is difficult to verify Equation (2b) experimentally. Further, Scott (1978) has shown that if a non-symmetric 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 et al. (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.

Equations (2a) and (2b) 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 et al., 1981, and Scott, 1978).

A simple way for introducing 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 $\bar{x}$ through

$$x_i = \bar{x}_i + \delta x_i \tag{3}$$

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

$$g^E = A_{12}\overline{x_1 x_2} = A_{12}\,(\bar{x}_1\bar{x}_2 + \overline{\delta x_1 \delta x_2}) \tag{4}$$

where the bars denote time averages. We now propose a reasonable but essentially empirical expression for the fluctuation term. We restrict attention to the coexistence curve, i.e. to temperatures below T_c and to compositions at saturation.

The fluctuation term must satisfy two boundary conditions: first, fluctuations are significant in the critical region, and second, they are negligible remote from the critical region. We propose the "semi-classical" expression:

$$g^E = A_{12}\bar{x}_1\bar{x}_2\,(1 + K\exp\,(a(1-T_r)^b)\,) \tag{5}$$

where binary constant A_{12} is obtained from experimental data remote from critical conditions; T_r is the reduced temperature, T/T_c ; 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.

At the critical temperature, Equation (5) reduces to

$$g_c{}^E = A_{12}\bar{x}_1\bar{x}_2\,(1 + K) \qquad at\ T=T_c. \tag{6}$$

As we move away from the critical temperature, the distance $(1-T_r)$ increases; since parameter a is negative and parameter b is positive, we recover the original equation (fluctuations disappear):

$$g^E = A_{12}\bar{x}_1\bar{x}_2 \qquad at\ T<<T_c. \tag{7}$$

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

$$\left(\frac{\partial^2\Delta g}{\partial x^2}\right)_c = 0 \tag{8a}$$

$$\left(\frac{\partial^3\Delta g}{\partial x^3}\right)_c = 0 \tag{8b}$$

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 Equation (5) into Equation (8a) gives

$$K = \frac{2RT_c}{A_{12}} - 1 \tag{9}$$

When K is calculated from Equation (9), 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 which is symmetric in mole fraction. Real systems seldom behave this way. To correct approximately for asymmetry, we use the van Laar equation

$$g^E = A_{12}(x_1 q_1 + x_2 q_2)\phi_1\phi_2 \tag{10}$$

where the effective volume fraction of component i is defined as

$$\phi_i = \frac{q_i x_i}{q_i x_i + q_j x_j} \tag{11}$$

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 data remote from critical conditions. To take into account the effect of the critical region, we write as before

$$g^E = g^E{}_{co}\,(1 + K\exp(a(1-T_r)^b)\,) \tag{12}$$

where $g^E{}_{co}$ is now given by Equation (10) (subscript co denotes "conventional"). Using stability criteria as before, parameter K is now given by

$$K = \frac{RT_c(\frac{q_1}{q_2}x_{1c} + x_{2c})}{2x_{1c}x_{2c}A_{12}\frac{q_1^2}{q_2}} - 1 \tag{13}$$

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

$$x_{1c} = \frac{(\,(\frac{q_1}{q_2})^2 + 1 - \frac{q_1}{q_2}\,)^{1/2} - \frac{q_1}{q_2}}{1 - \frac{q_1}{q_2}} \tag{14}$$

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 Equation (12), parameters a and b are adjusted such that Equations (2a) and (2b) 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 Equation (12), we calculate the coexisting compositions ϕ' and ϕ'' using the known value of K and using first approximations for a and b. Our experience indicates that b is always very 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.

We recognize that, because our semi-classical method (Equation 12) is analytic, at exactly $T=T_c$ critical exponent β is erroneously given by the classical value. 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 Equation (12) and experimental 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 Equation (13). Parameters a and b were found as shown in Figure 3, where the slopes of the lines are β=0.34 and $(1-\alpha)$=0.72. While Equation (12) fails very close to Tc, it provides good results for the practical region of interest in engineering calculations without requiring new adjustable parameters from binary data. 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 Equation (12). In Figures 2 and 4, we used only experimental data remote from the critical point and the coordinates of the critical point. Appendix I gives parameters for these examples.

We now turn 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 fluctuations are significant. This is not surprising, since the van Laar model with temperature-independent parameters cannot represent adequately 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 equation (Prausnitz et al., 1986) which has a moderate built-in temperature dependence. However, this built-in temperature dependence is also insufficient. We obtain considerable improvement when we allow the NRTL parameters to vary linearly with temperature, as Sorensen et al. (1979) have suggested. In Figure 5, the left curve was calculated with the NRTL equation and parameters having a simple linear temperature dependence . However, that moderate temperature 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 (12) 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 is used in Equation (12), the calculated critical composition is slightly affected by our modification. The magnitude of K is now around 0.07, giving only a 7% correction to the conventional equation. The curve shown on the right of Figure 5 was calculated with the modified NRTL equation and parameters linearly dependent on temperature.

PART II - 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 on binary mixtures with an upper consolute point, we proposed a correction to the conventional g^E ; that correction depends on D, a dimensionless "distance" from the critical point:

$$D = (1 - T_r) \quad . \tag{15}$$

For isothermal ternary systems, we propose a distance that can be best 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 et al., 1954, Reid et al., 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 spinodal (Prigogine et al., 1954); it is defined by

$$\frac{\partial \Delta g}{\partial x_2}\frac{\partial \Delta g}{\partial x_3} - \left(\frac{\partial^2 \Delta g}{\partial x_2 \partial x_3}\right)^2 = 0 \quad . \tag{16}$$

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

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

$$\mu'_i = \mu''_i \qquad i = 1,2 \text{ and } 3 \quad . \tag{17}$$

where (') and (") denote the coexisting phases. It can be shown (Prigogine et al., 1954) that at the two points representing coexisting phases in Figure 6, the tangent planes coincide; therefore Equations 17 are equivalent to:

$$\left(\frac{\partial \Delta g}{\partial x_2}\right)' = \left(\frac{\partial \Delta g}{\partial x_2}\right)'' \tag{18a}$$

$$\left(\frac{\partial \Delta g}{\partial x_3}\right)' = \left(\frac{\partial \Delta g}{\partial x_3}\right)'' \tag{18b}$$

$$\Delta g' - x_2'\left(\frac{\partial \Delta g}{\partial x_2}\right)' - x_3'\left(\frac{\partial \Delta g}{\partial x_3}\right)' = \Delta g'' - x_2''\left(\frac{\partial \Delta g}{\partial x_2}\right)'' - x_3''\left(\frac{\partial \Delta g}{\partial x_3}\right)''. \tag{18c}$$

We add Equations (18a) and (18b) to obtain a definition for D. The proposed dimensionless distance for a ternary mixture is :

$$D = \frac{\left(\frac{\partial \Delta g}{\partial x_2} + \frac{\partial \Delta g}{\partial x_3}\right)_{co} - \left(\frac{\partial \Delta g}{\partial x_2} + \frac{\partial \Delta g}{\partial x_3}\right)_{c}}{\left(\frac{\partial \Delta g}{\partial x_2} + \frac{\partial \Delta g}{\partial x_3}\right)_{c}} \tag{19}$$

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

$$g^E = g^E{}_{co}\,(1 + K\exp\,(aD^b)\,) \tag{20}$$

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 Equation (19). 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 Equation (20) 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 et al., 1974) :

$$\xi = \begin{vmatrix} \dfrac{\partial^2\Delta g}{\partial x_2{}^2} & \dfrac{\partial^2\Delta g}{\partial x_2\partial x_3} \\ \dfrac{\partial^2\Delta g}{\partial x_2\partial x_3} & \dfrac{\partial^2\Delta g}{\partial x_3{}^2} \end{vmatrix} = 0 \tag{21a}$$

$$\zeta = \begin{vmatrix} \dfrac{\partial\xi}{\partial x_2} & \dfrac{\partial\xi}{\partial x_3} \\ \dfrac{\partial^2\Delta g}{\partial x_2\partial x_3} & \dfrac{\partial^2\Delta g}{\partial x_2\partial x_3} \end{vmatrix} = 0 \tag{21b}$$

Solution of Equations (21) 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 II), 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, Equations (17) were satisfied; therefore a numerical value is available for the derivatives appearing in Equations (18). These values correspond to the conventional model. It is precisely these values that we use in Equation (19) where, as elsewhere, subscript co stands for "conventional".

In a ternary system, we have three equilibrium equations (17) 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 (2). Consider one mole of mixture splitting into two phases (') and ("). We have three material balances:

$$\begin{aligned} L' + L'' &= 1 \\ x'_2L' + x''_2L'' &= x_2 \\ x'_3L' + x''_3L'' &= x_3 \end{aligned} \tag{22}$$

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 Equation (19) those derivatives with subscript c. These calculations provide a numerical value for the distance function D.

The second step in our procedure is to solve the isothermal flash problem again for the same overall composition, but this time using Equation (20) to obtain the desired set of equilibrium compositions. To use Equation (20), 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

$$l = d^{\beta/(1-\alpha)} \tag{23}$$

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 Equation (23) 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 the classical value is 1/2). Variables l and d are illustrated in Figure 7. Unfortunately , there is a substantial lack of data for ternary mixtures in the vicinity of the plait point. To the best of our knowledge, the exponent in Equation (23) has been measured in only a few mixtures (Zollweg, 1971, van Dael et al., 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 left curve was calculated with the conventional NRTL model and parameters from 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 right curve was calculated with the modified NRTL equation and parameters from LLE data remote from the plait point.

When the "non-randomness" 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 non-randomness parameters are not fixed, then nine parameters must be determined). On the other hand, constant K appearing in Equation (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 to 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 simultaneously we satisfy Equations (21). 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 Equation (20), we require the observed or estimated plait point. An experimental value is seldom available, but often it can be found using empirical methods summarized in Appendix II.

Our experience indicates that in Equation (20), 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. It is not perfectly correct because very close to the plait point, our semi-classical equations give the erroneous classical result.

The example shown in Figure 10 is based on conventional NRTL model parameters obtained from LLE data remote from the plait point.

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 Equation (20)), the coexistence curve is always overpredicted. Figure 11 shows illustrative results.

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 slopes 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.

PART III - 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 et al., 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. As long as the parameters lie inside a certain 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 (1968), 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 12 shows typical results for the ternary system N-heptane/benzene/acetonitrile. In this example, the 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 Equation (20). To use that equation, we proceed as follows. We begin by estimating the position of the plait point (Appendix II). 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 correspondent binary confidence ellipses. The objective functions are the difference between the experimental and calculated equilibrium compositions and the conditions of incipient inmiscibility at the critical point (Equations (21)). 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 12 shows results for the system n-heptane/benzene/acetonitrile; Figures 13 and 14 show the corresponding binary VLE for the two miscible pairs.

Finally, in Table I we show experimental and calculated ternary VLE for the same system. Throughout this work we have restricted our attention to compositions along the coexistence curve. While our VLE results are not conclusive, they seem to indicate that the modification proposed does not affect significantly the prediction of ternary VLE. When the correction factor (last column in Table I) 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 the ones 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.

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

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

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

Ex stands for experimental, Co stands for conventional NRTL model, and M stands for modified NRTL model.The ratio g^E/g^E_{co} represents the correction factor to the conventional model, g^E_{co}.

CONCLUSIONS

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

In this work we have proposed a semi-classical 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 classical in nature (and therefore theoretically incorrect very near the critical point); nevertheless, they provide an accurate description of coexistence curves in the critical region of binary and ternary liquid mixtures.

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

ACKNOWLEDGMENTS

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APPENDIX - I 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 describe briefly two of these. For information concerning other methods, see text by Treybal [19].

Treybal's method [19,20], consists of plotting on log-log coordinates the ratios x_{31}/x_{11} *vs.* x_{32}/x_{22} where, following the author's notation, x_{ij} denotes the mol fraction of component i in the j phase, and 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 A-1 illustrates the method.

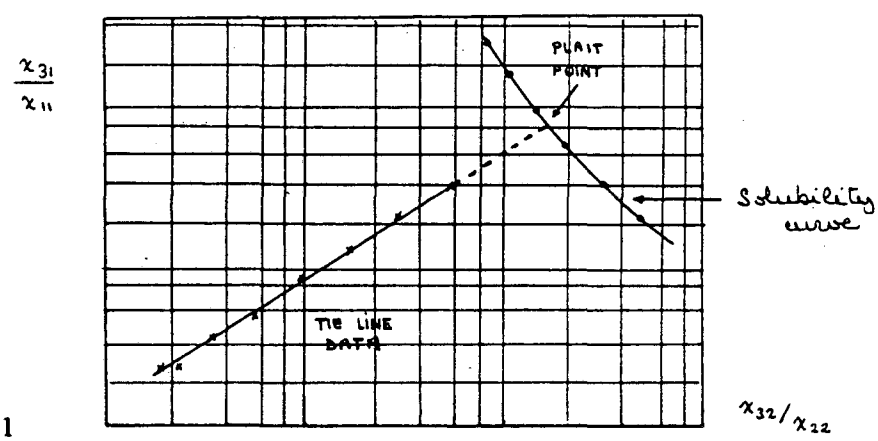


Figure A-1

Fleming et al. [21] propose a method which takes into account non-classical 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 A-2, where the ratio of component 1 to component 3 is held fixed.

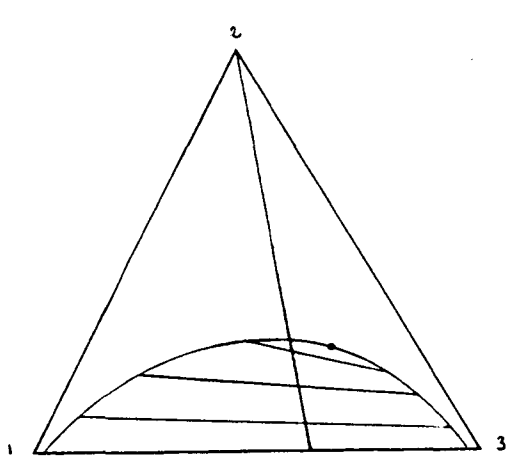


Figure A-2

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

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

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 will be the concentration of a given component at the plait point; from the path's ratio, the other two concentrations are calculated.

APPENDIX - II Parameters used for calculations

In this Appendix we give the parameters for several examples, including the ones shown in this paper. We use the following notation:

(VL) van Laar equation. Parameter $A_{12}q_1$ is denoted by A_{12} and parameter $A_{12}q_2$ is denoted by A_{21}.

(NRTL-LTD) NRTL equation with parameters linearly dependent on temperature. (This equation is only used for binary systems.) The g_{ij} parameters are thus replaced by $g_{ij} = A_{ij}T + O_{ij}$. Parameters A_{ij}, O_{ij}, and α appear in Table A-1. (Since $\alpha_{ij}=\alpha_{ji}$ we omit the subscript.)

(NRTL) NRTL 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 the superscript r is used ($NRTL^r$). When NRTL parameters are determined from LLE data remote and near the critical region we use superscript rc ($NRTL^{rc}$). Finally, for NRTL parameters obtained from binary VLE data and ternary LLE data (remote from the plait point), we use superscript VLE ($NRTL^{VLE}$).

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

Table A-1 Parameters for some binary systems

System	Equation	A_{12}	A_{21}	O_{12}	O_{21}	α	K	a	b	T_c	x_{1c}
1) Nitroethane 2) 3-Methylpentane	*VL*	7973.00	7900.00	–	–	–	0.373	–19.0	0.36	299.60	0.497
1) Perfluoro methyl cyclohexane 2) Toluene	*VL*	9085.00	5096.00	–	–	–	0.167	–12.3	0.38	362.07	0.300
1) Hexane 2) Nitrobenzene	*VL*	5000.00	6036.90	–	–	–	0.118	-8.3	0.35	293.17	0.570
1) Carbon disulfide 2) Acetic anhydride	*NRTL LTD*	–3.60	–3.12	2004.7	865.9	–0.2	0.072	–20.0	0.36	302.95	0.722
1) Aniline 2) Hexane	*NRTL LTD*	4.80	–8.38	–1000.9	3074.8	–0.2	0.075	–16.0	0.36	339.16	0.586

Table A-2 Parameters for some ternary systems

System	Equation	i	j	g_{ij}	g_{ji}	α_{ij}	K	a	b	x_{1c}	x_{2c}
(1) Acetonitrile		1	2	1388.5	–305.9	–0.2					
(2) Benzene	$NRTL^{r}$	1	3	467.3	676.3	–0.2	0.040	–6.0	0.84	0.433	0.202
(3) Cyclohexane		2	3	–168.8	1051.7	–0.2					
(T = 298.15 K)											
(1) 1-Hexene		1	2	87.5	246.2	–0.2					
(2) Benzene	$NRTL^{rc}$	1	3	2233.0	529.5	–0.2	0.0				
(3) Sulpholane		2	3	82.5	457.8	–0.2					
(T = 348.15 K)											
(1) 1-Hexene		1	2	–74.4	–45.8	–0.2					
(2) Benzene	$NRTL^{r}$	1	3	1227.3	468.7	–0.2	0.091	–1.55	0.70	0.295	0.450
(3) Sulpholane		2	3	504.7	–271.2	–0.2					
(T = 348.15 K)											
(1) n-Heptane		1	2	–308.2	536.3	–0.3					
(2) Benzene	$NRTL^{VLE}$	1	3	415.3	780.9	–0.2	0.227	–0.54	0.84	0.317	0.186
(3) Acetonitrile		2	3	257.8	83.3	–0.3					
(T = 318.15 K)											

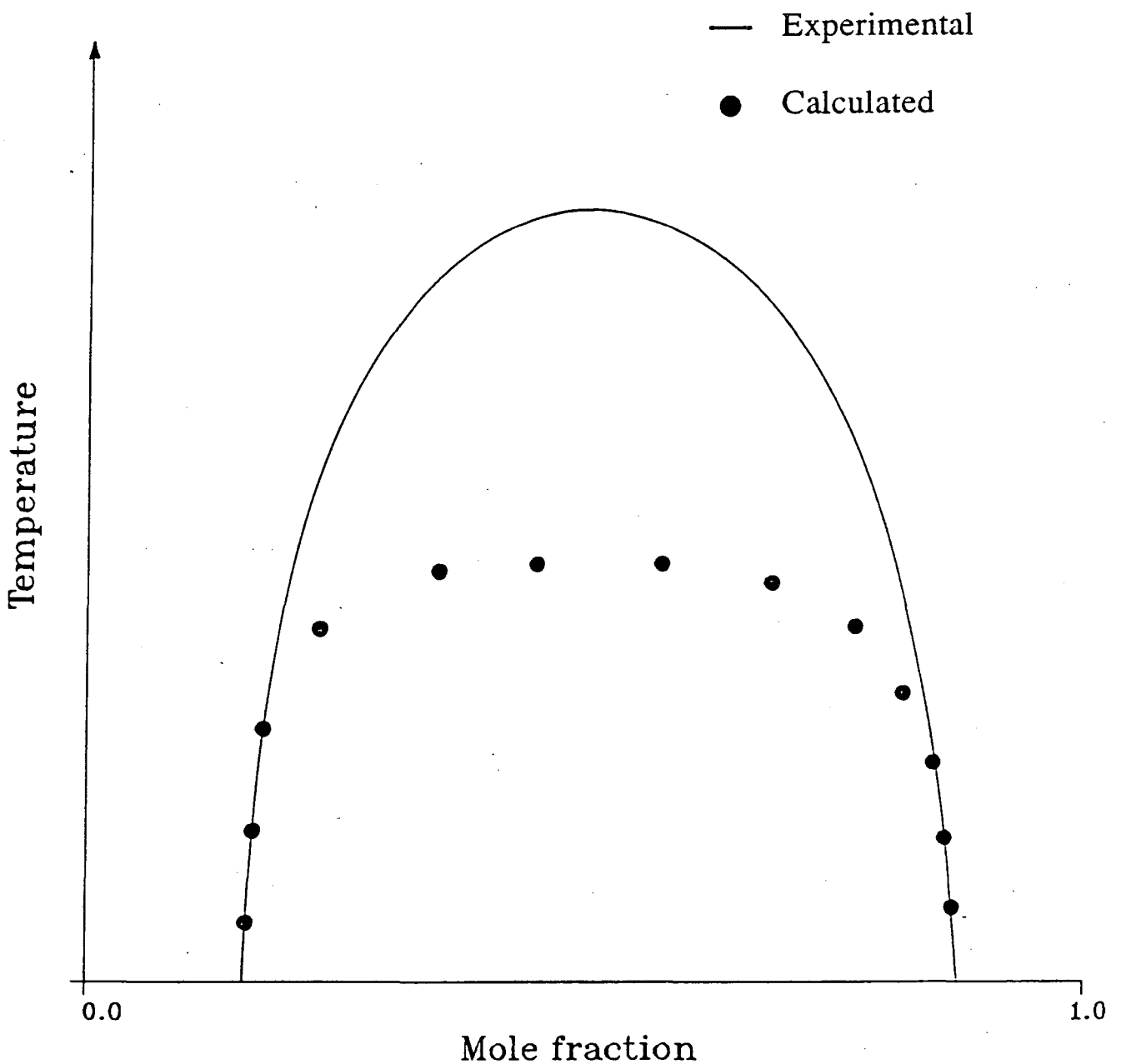


FIGURE 1 - Typical coexistence curve for a binary mixture showing an upper consolute point.

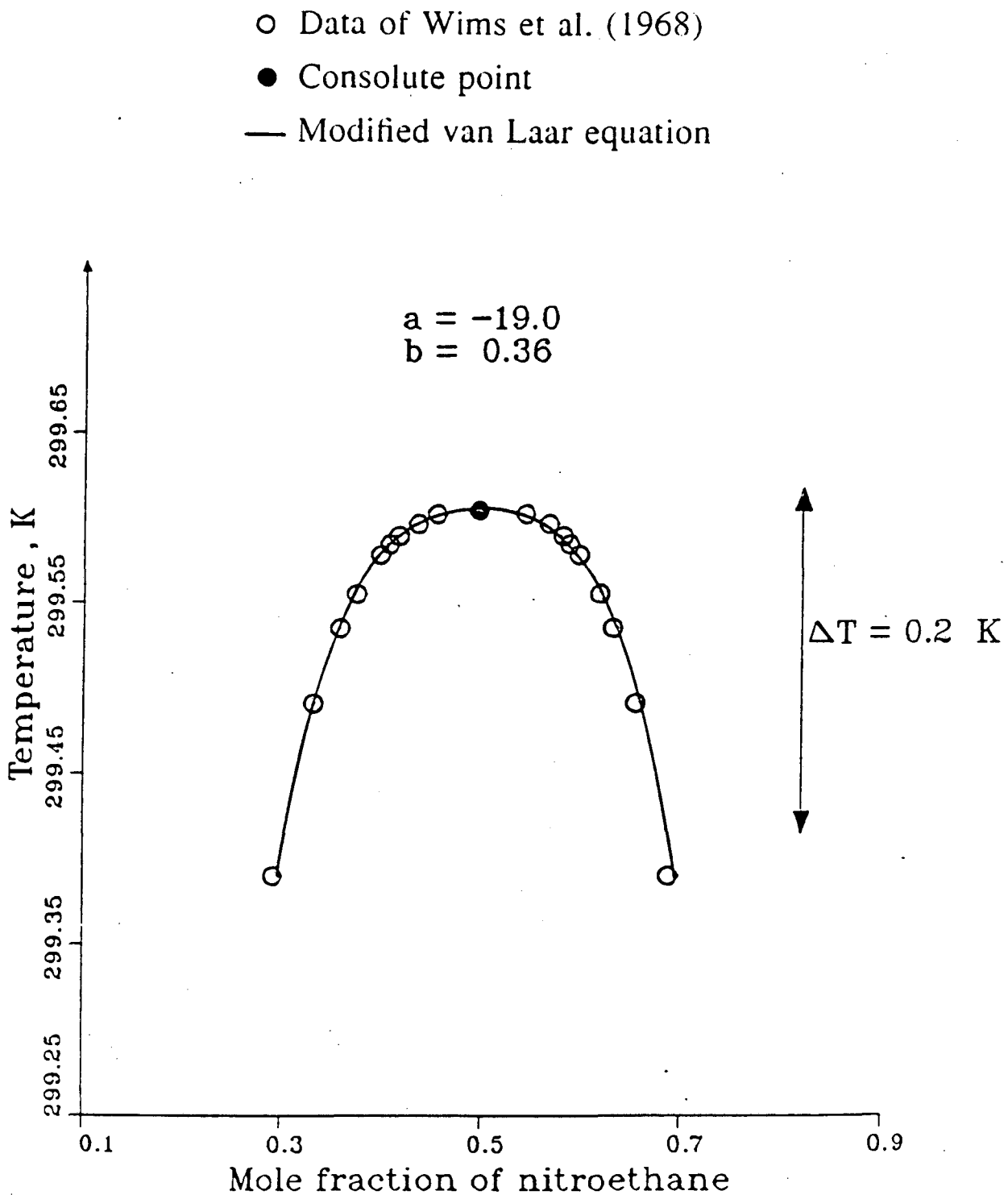


FIGURE 2 – Coexistence curve for the system nitroethane / 3–methylpentane. Note the expanded temperature scale.

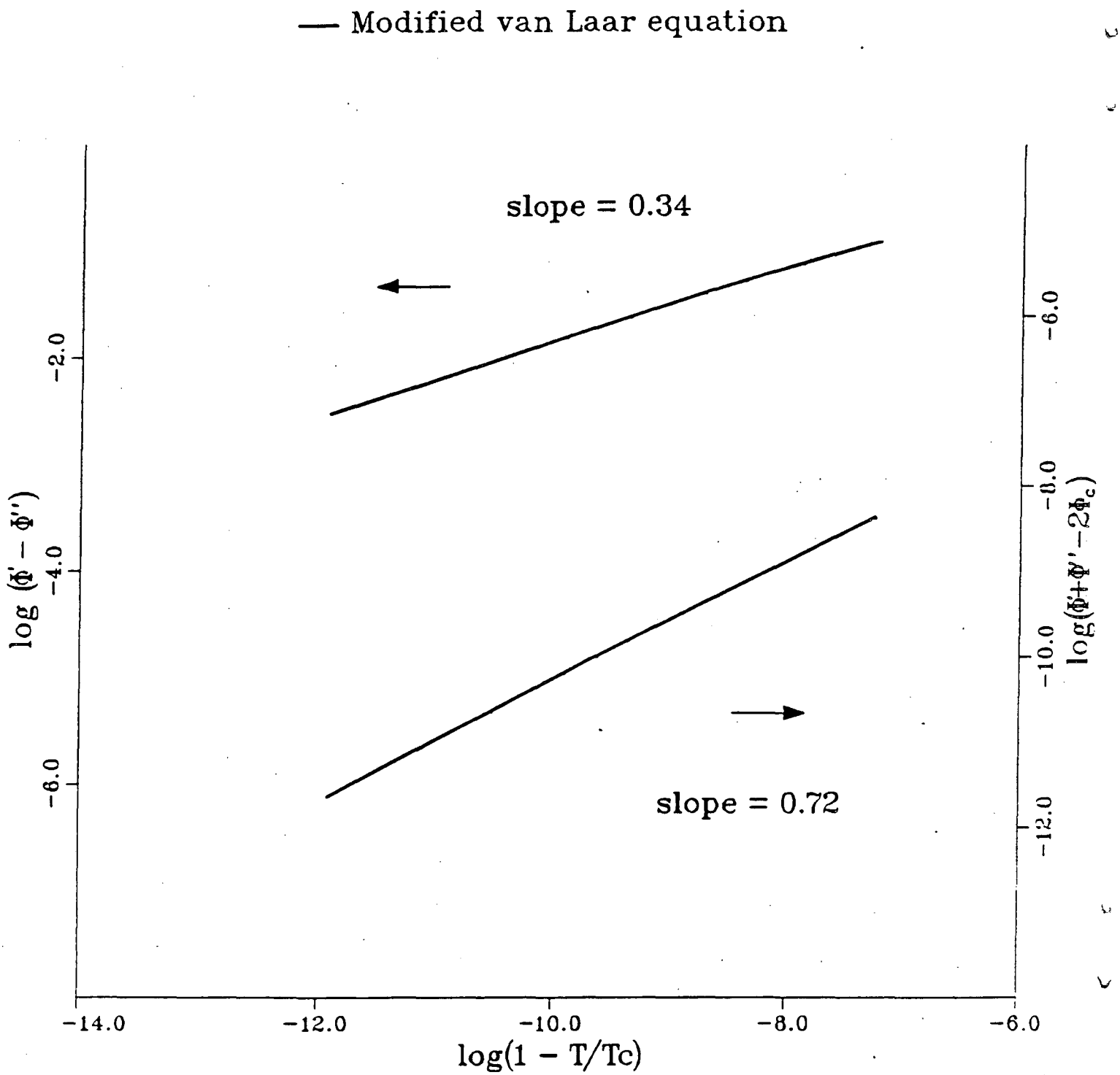


FIGURE 3 – Calculation of parameters a and b for the system nitroethane / 3–methyl pentane.

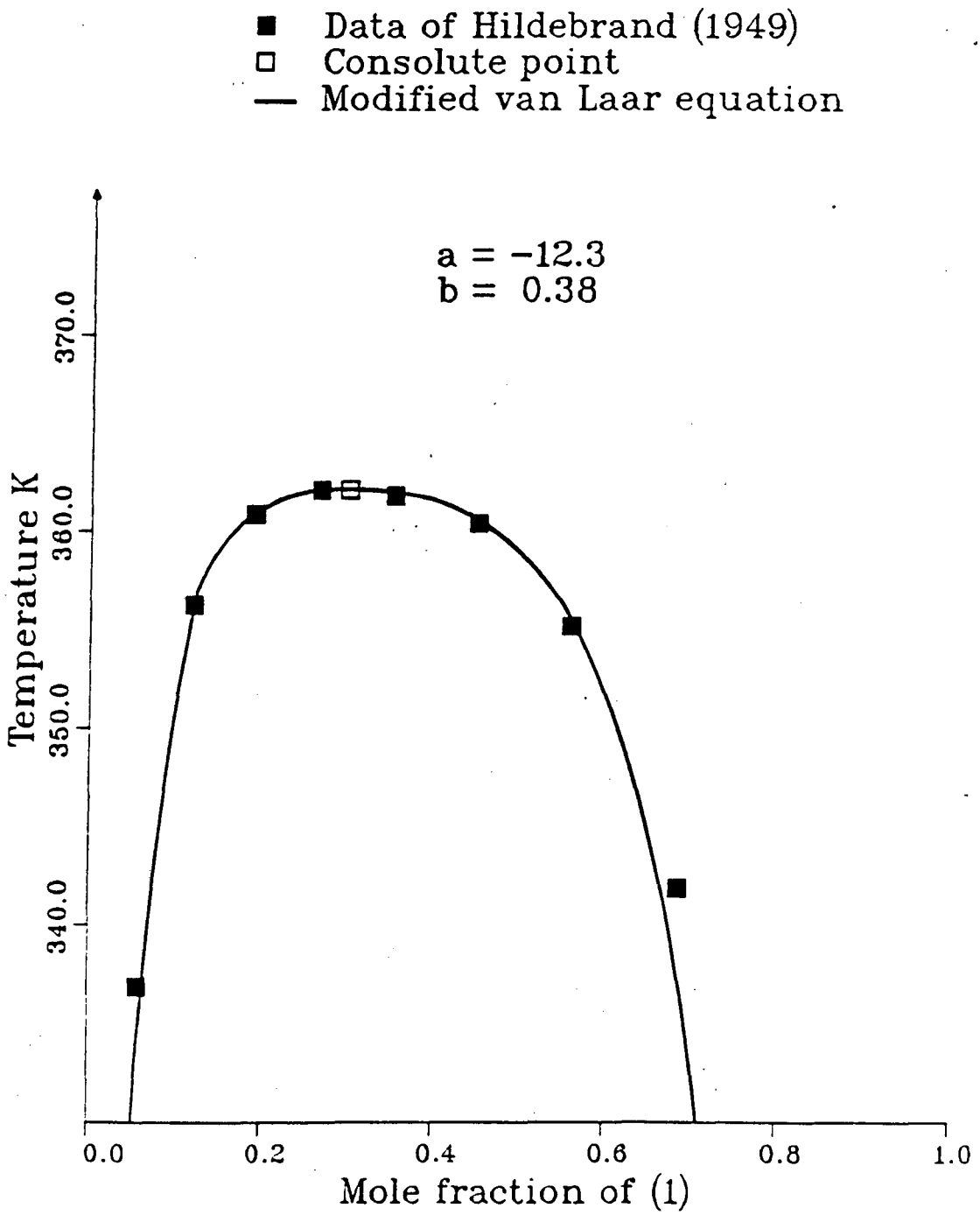


FIGURE 4 – Coexistence curve for the system perfluoro methyl cyclohexane (1) / toluene (2).Parameters a and b are obtained from universal critical exponents.

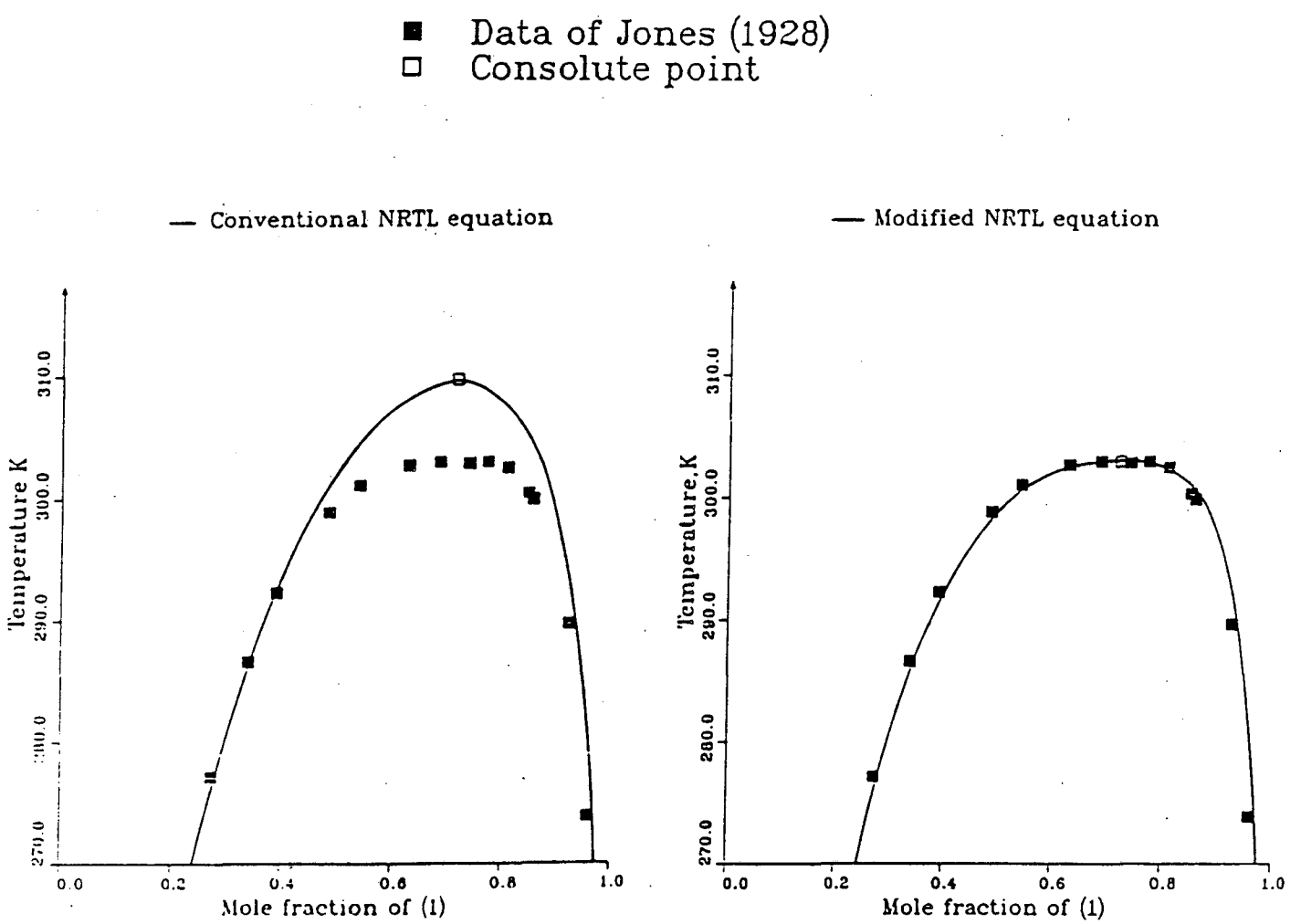


FIGURE 5 - Coexistence curve for the system carbon disulfide (1) / acetic anhydride (2). Calculations shown on the left are based on the conventional NRTL model with binary parameters linearly dependent on temperature. Calculations shown on the right are based on the same NRTL equation with the same binary parameters but with the modification proposed in this work.

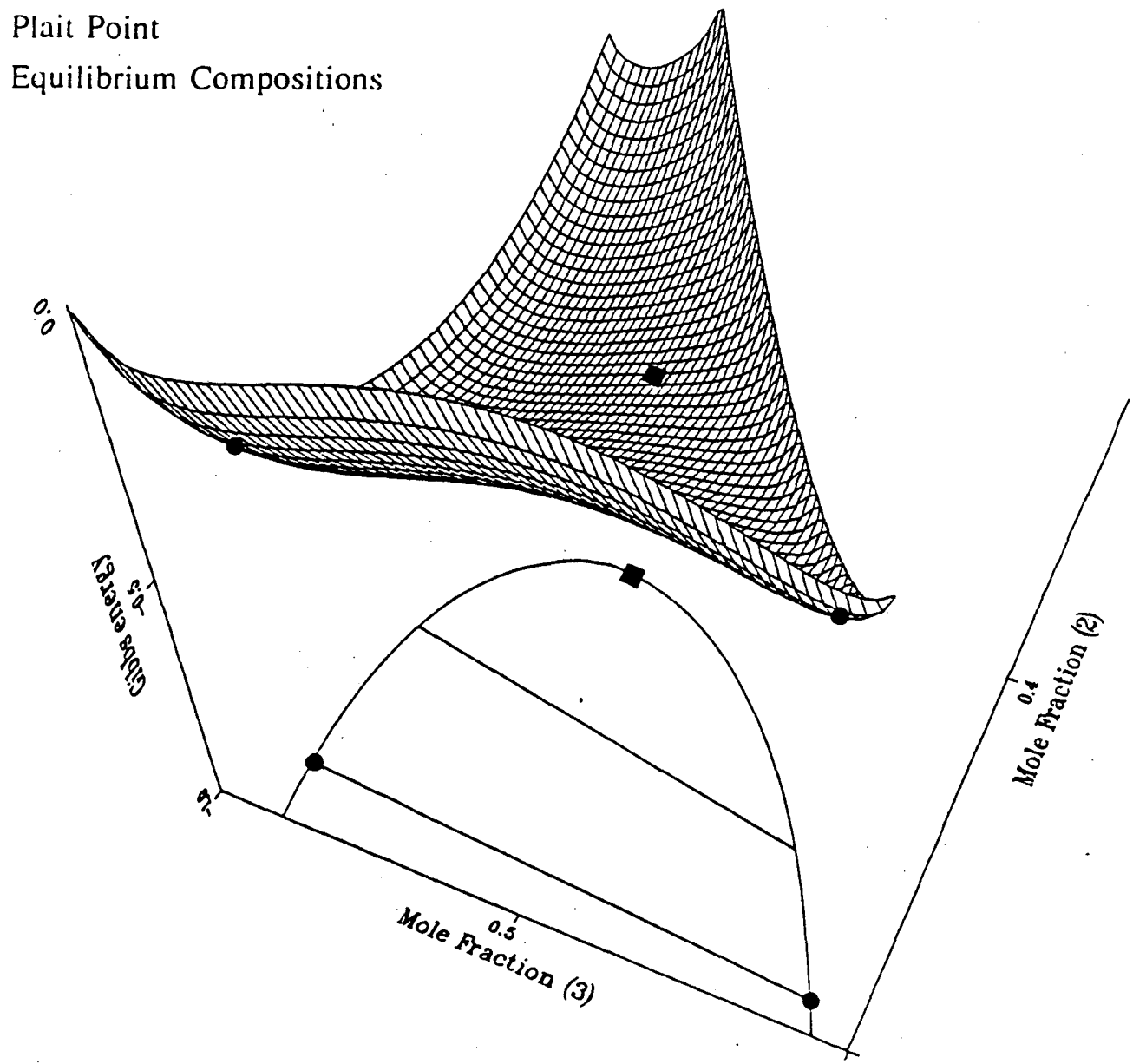


FIGURE 6 - Molar Gibbs energy of mixing surface $\Delta g / RT$, at constant temperature and pressure, showing stable and unstable regions. Coexisting compositions on this surface have a common tangent plane. The projection on the (x_2, x_3) plane is the familiar ternary diagram.

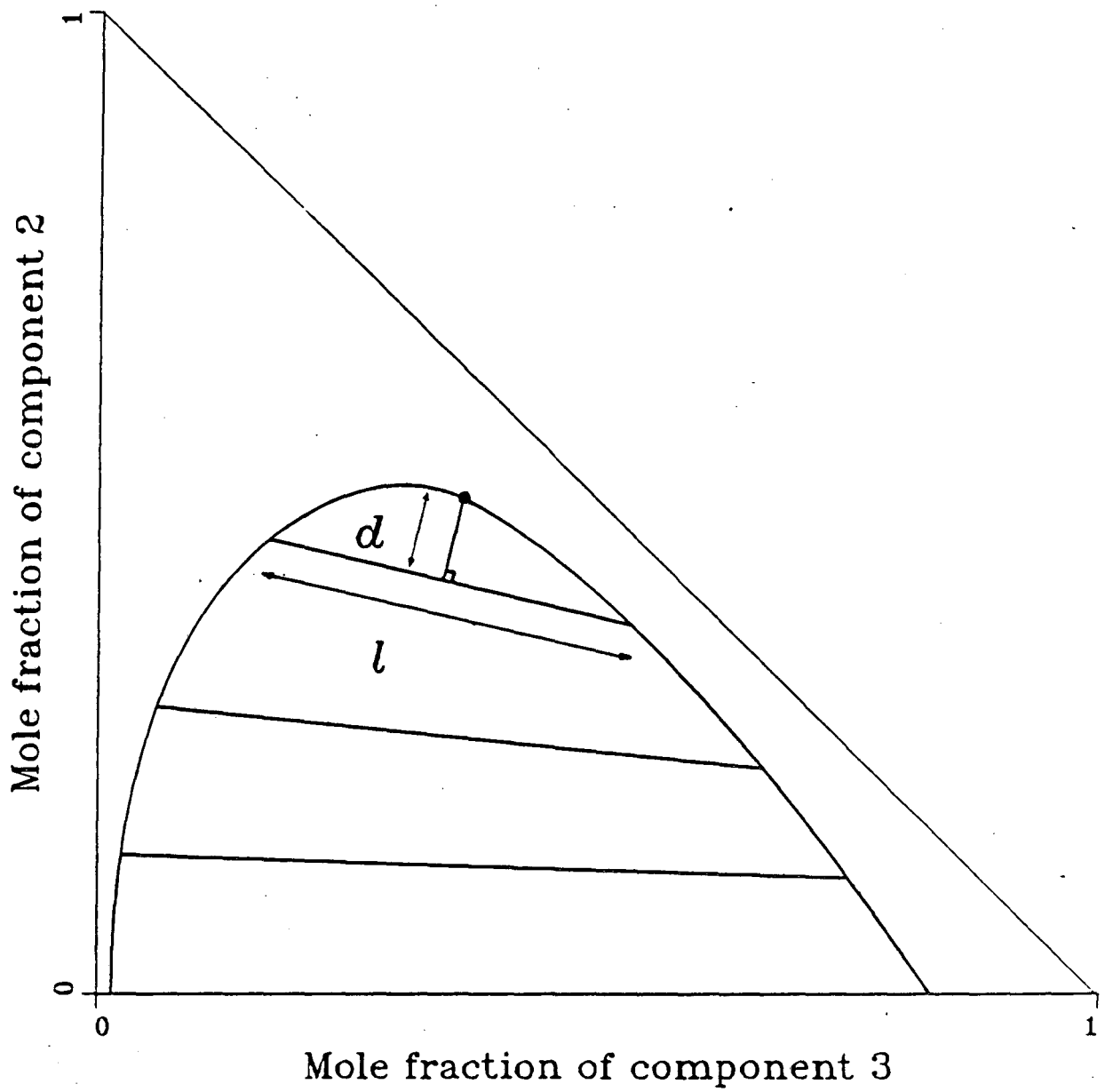


FIGURE 7 - Definition of order parameter l and distance d for a ternary system at constant temperature. The distance from the plait point to the tie line is d. The length of the tie line is l.

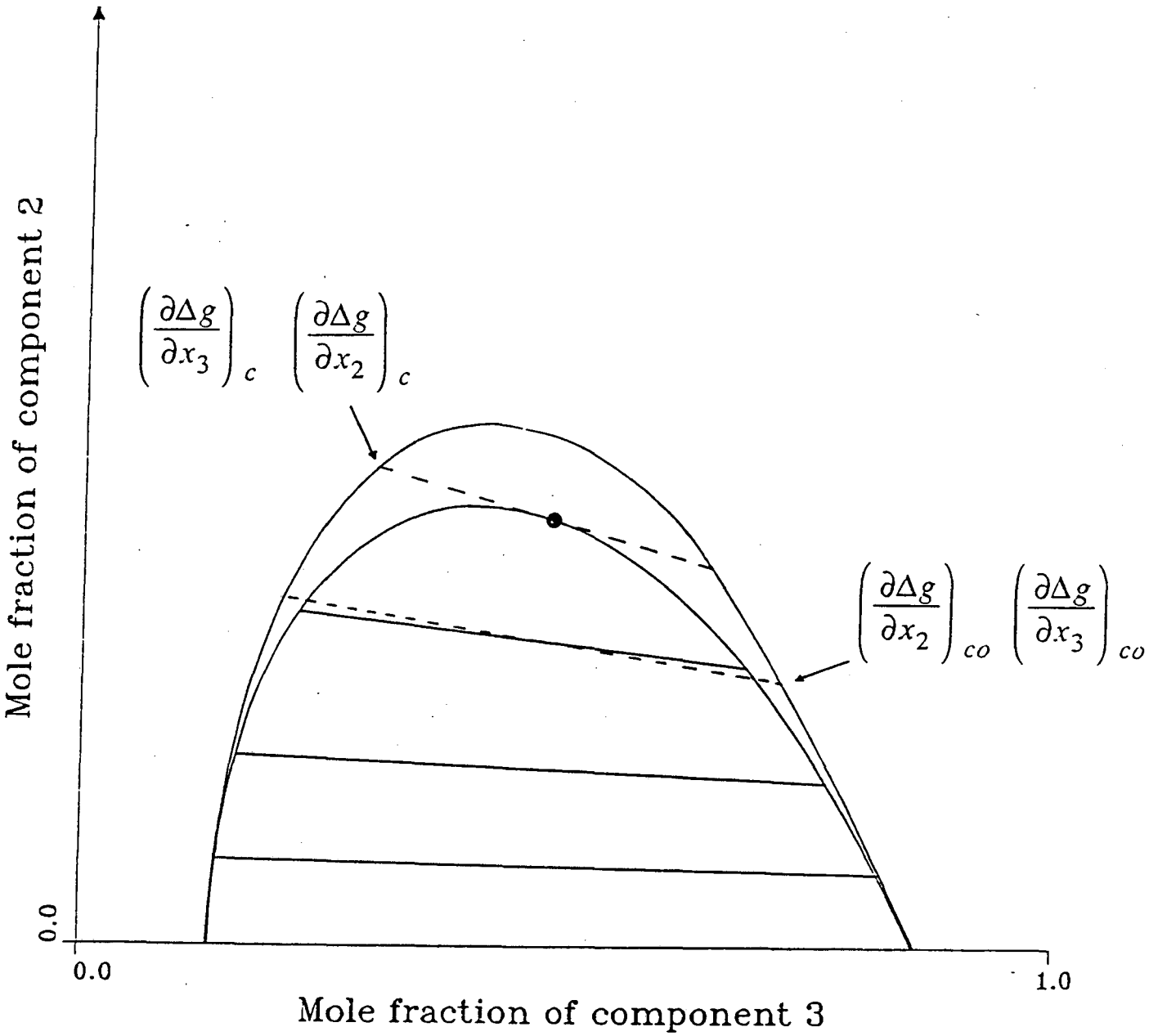


FIGURE 8 - Proposed method for the calculation of ternary LLE. The upper curve represents calculations with the conventional model. The lower curve represents calculations with the modified model. The overall composition used to calculate a tie line is the same for both models. The result obtained with the modified model depends on the first derivatives of the Gibbs energy of mixing Δg, evaluated at the equilibrium compositions predicted by the conventional model.

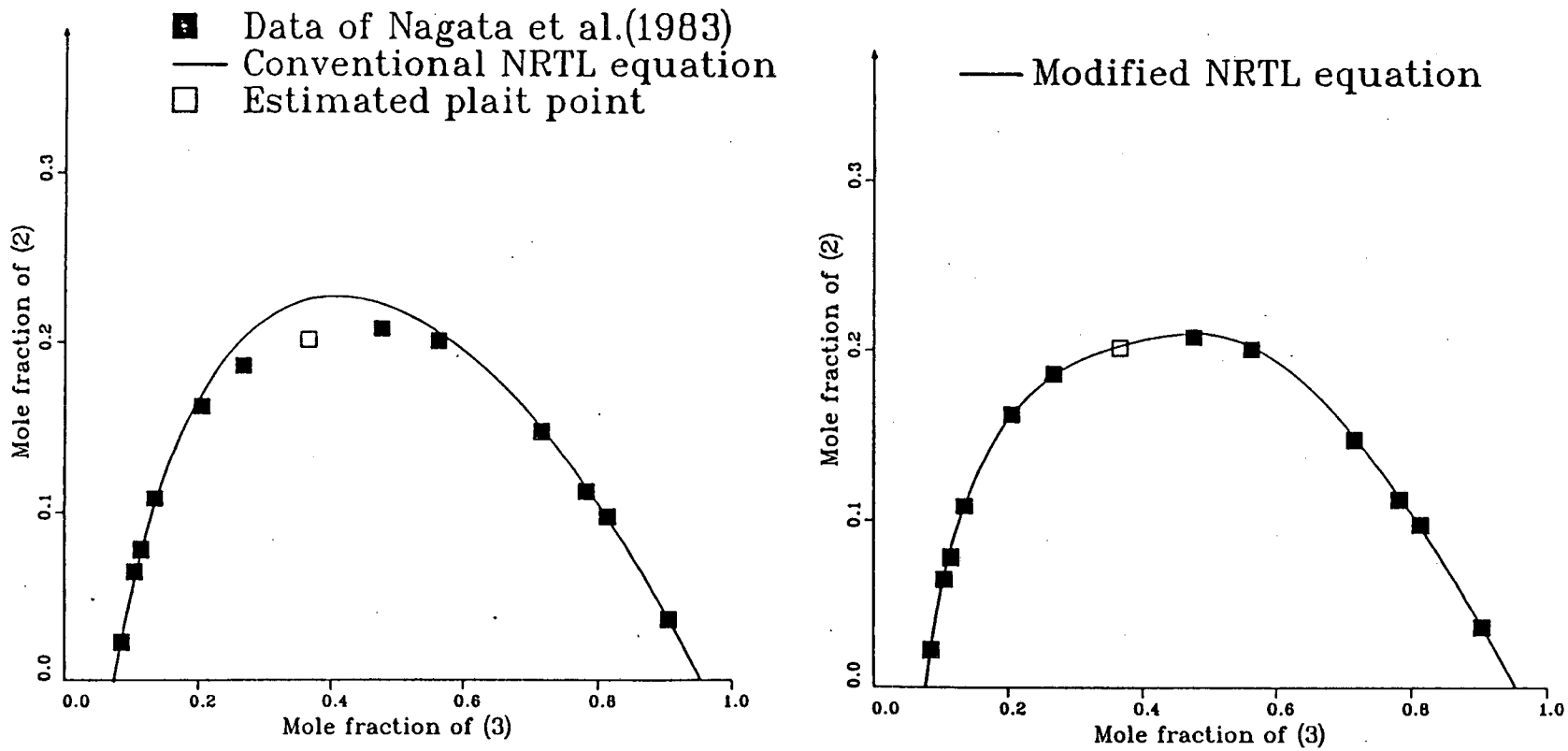


FIGURE 9 - Ternary diagram at 25 C for the system acetonitrile (1) / benzene (2) / cyclohexane (3). The calculations on the left are based on the conventional NRTL equation with parameters from LLE data remote from the plait point. The calculations on the right are based on the same model with the same parameters but with the modification proposed in this work.

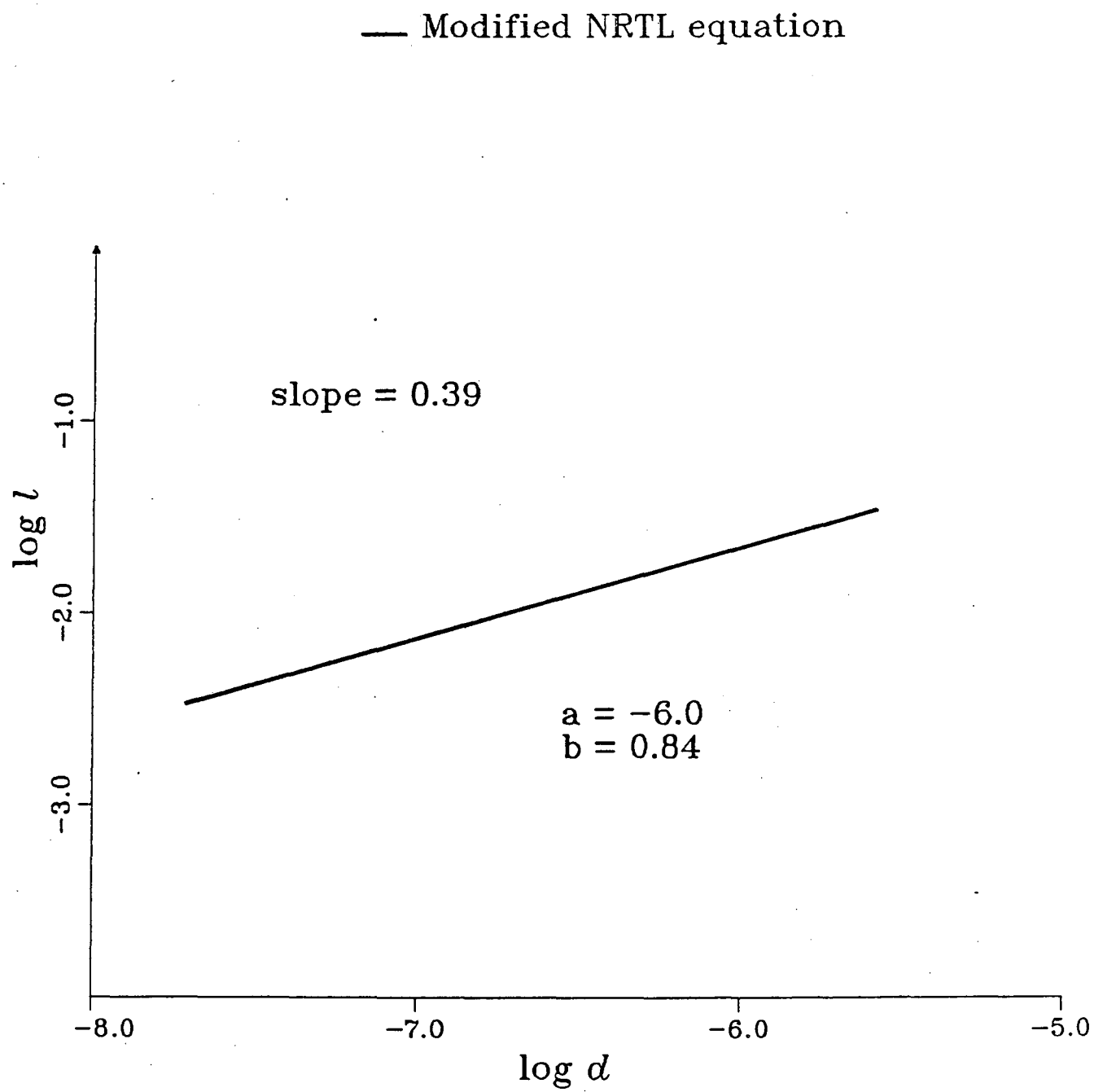
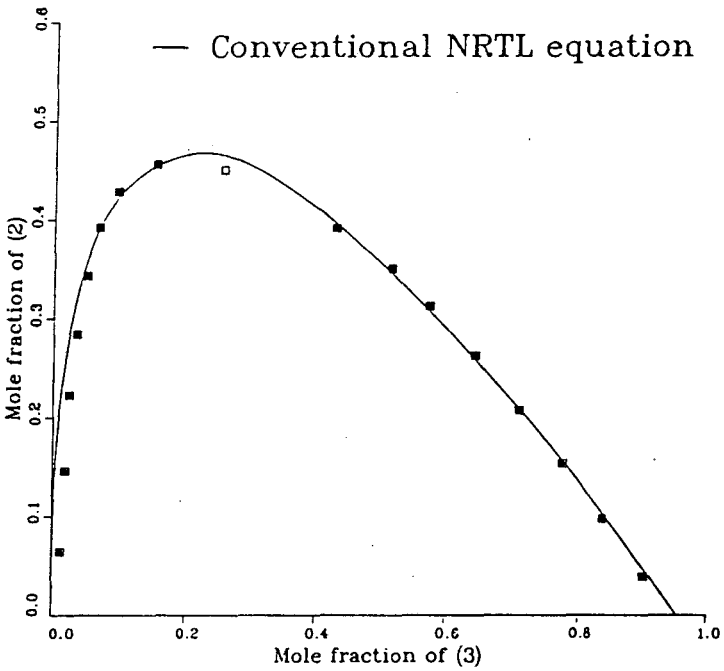
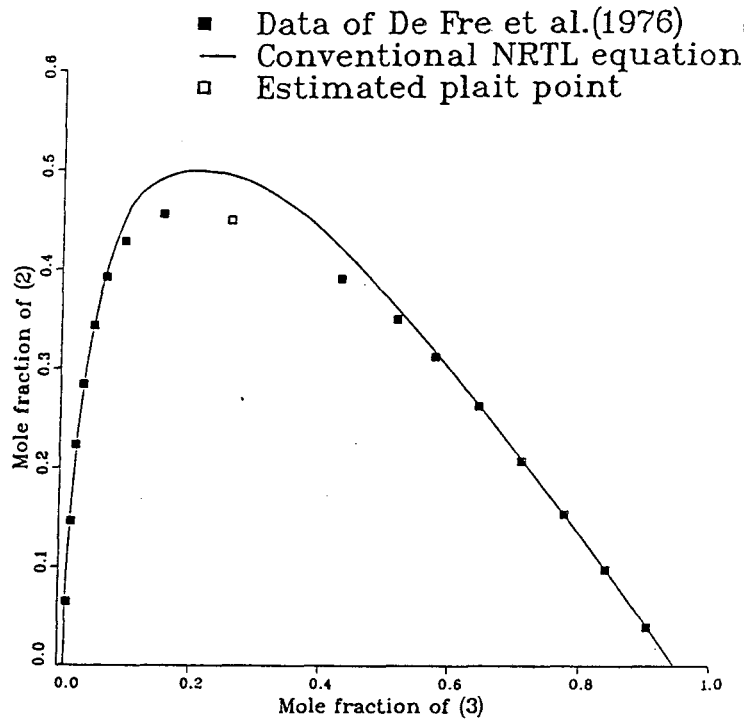


FIGURE 10 – Calculation of parameters a and b for the system acetonitrile / benzene / cyclohexane at 25 C. In this calculation, b is restrained to be close to unity.





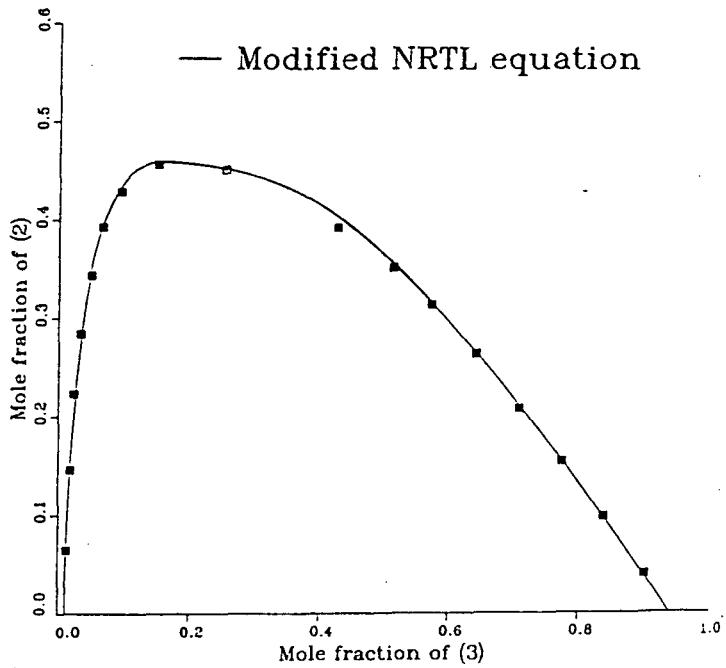


FIGURE 11 – Ternary LLE at 75 C for the system 1–hexene (1) / benzene (2) / sulpholane (3).

I) Conventional NRTL equation with parameters from LLE data remote and near the plait point.
II)Conventional NRTL equation with parameters from LLE data remote from the plait point.
III) Modified NRTL equation with parameters from LLE data remote from the plait point.

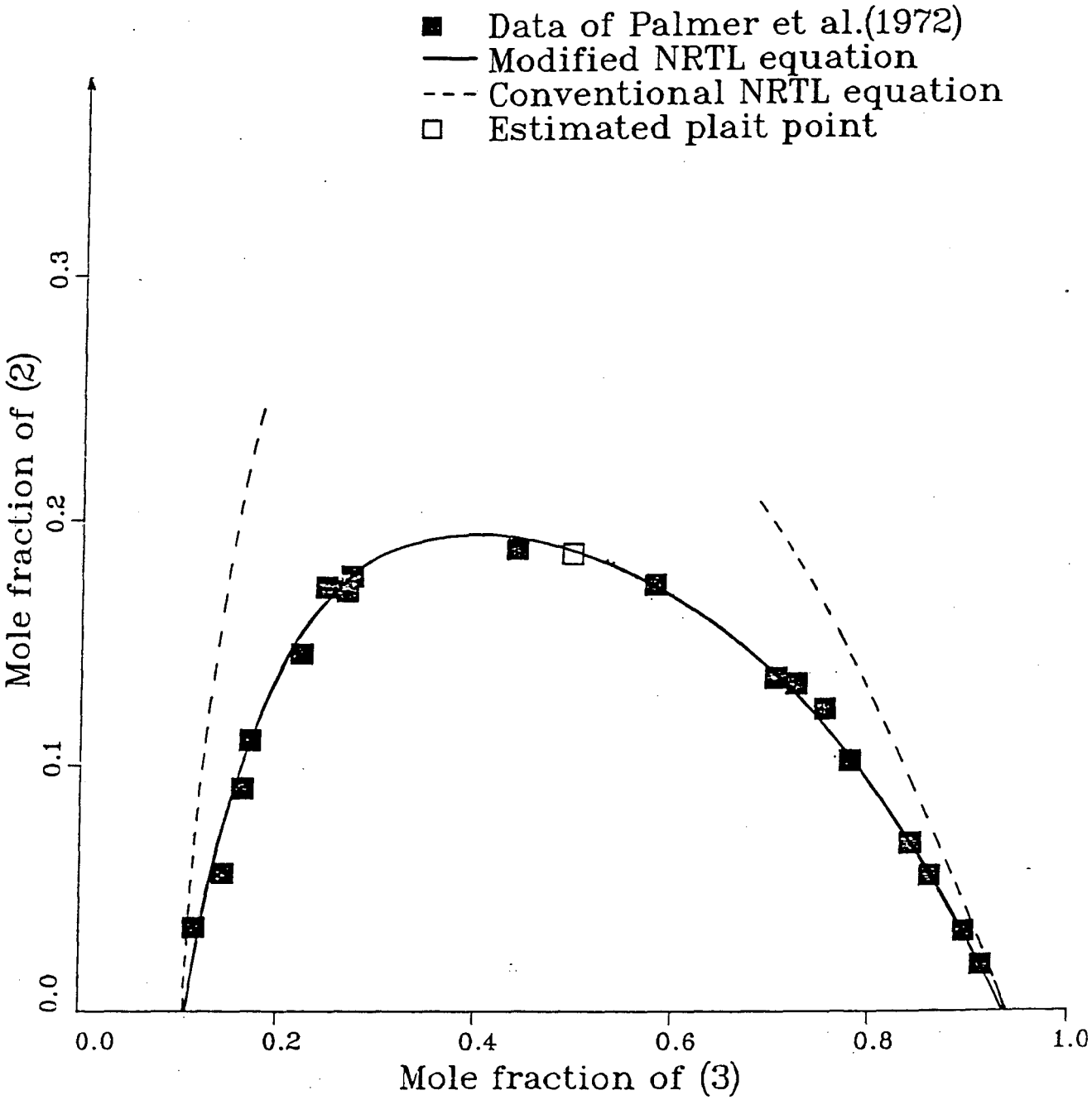


FIGURE 12 - Ternary LLE at 45 C for the system n-heptane (1) / benzene (2) / acetonitrile (3). The NRTL parameters used for this ternary calculation are the same as those used to calculate the VLE shown in Figures 13 and 14.

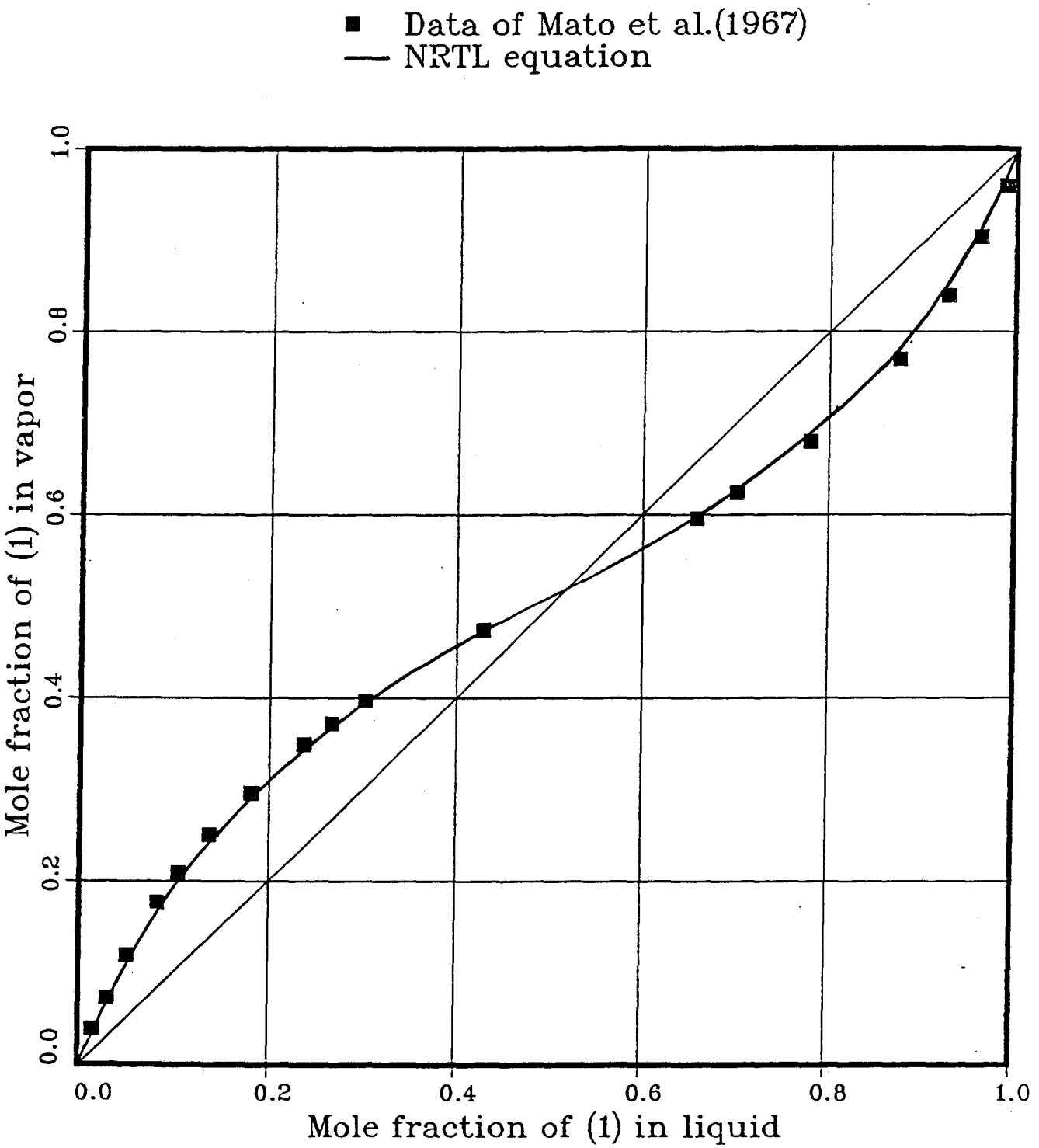


FIGURE 13 – Binary vapor–liquid equilibria for the system benzene (1) / acetonitrile (2) at 760 torr. The NRTL parameters used for this calculation are the same as those used to calculate ternary LLE (see Figure 12).

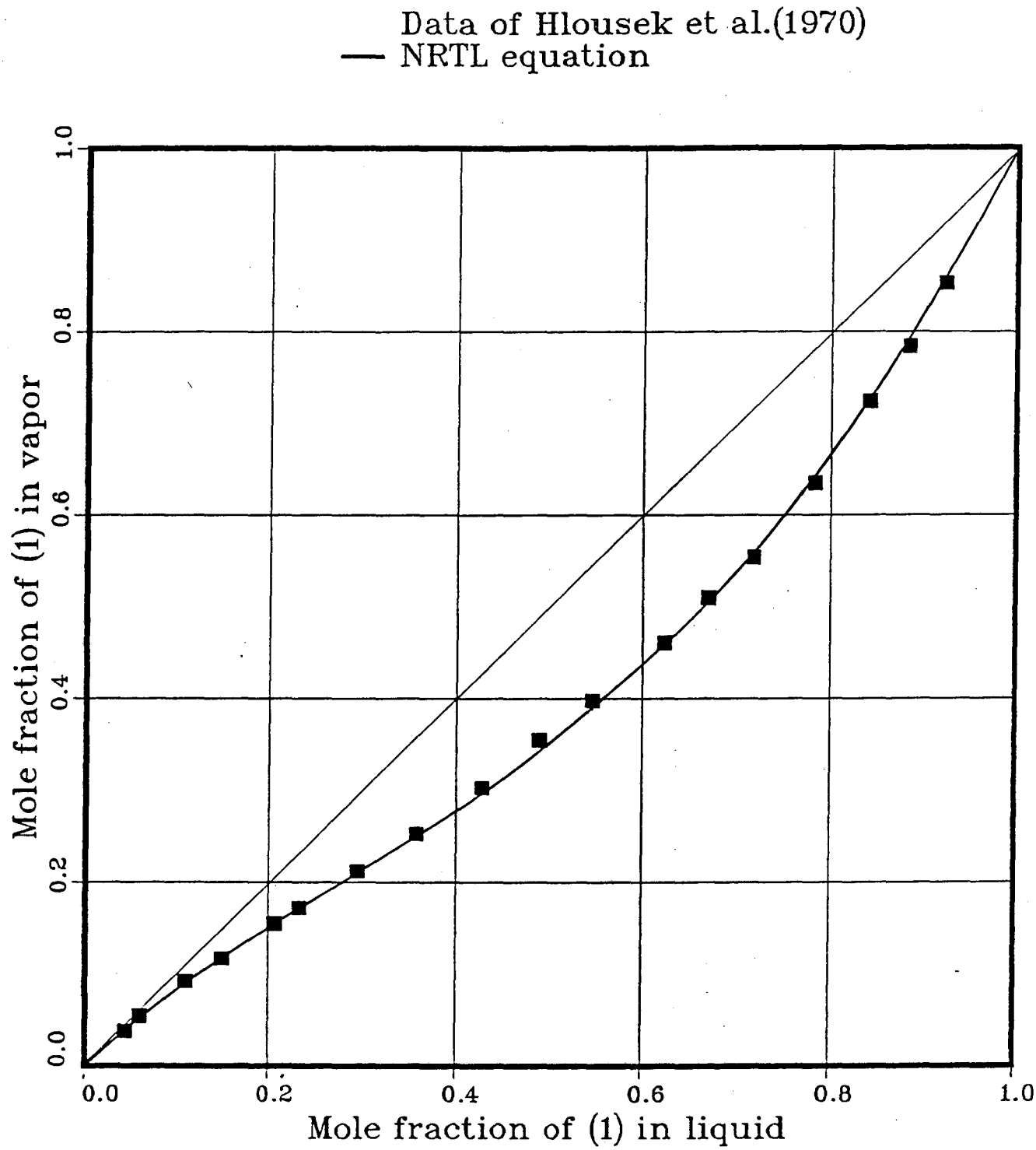


FIGURE 14 – Binary vapor–liquid equilibria for the system heptane (1) / benzene (2) at 760torr. The NRTL parameters used for this calculation are the same as those used to calculate ternary LLE (see Figure 12).

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