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Thermodynamics of Liquid-Liquid Equilibria Including the Critical Region: Transformation to Non-Classical Coordinates Using Revised Scaling

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

October 1988

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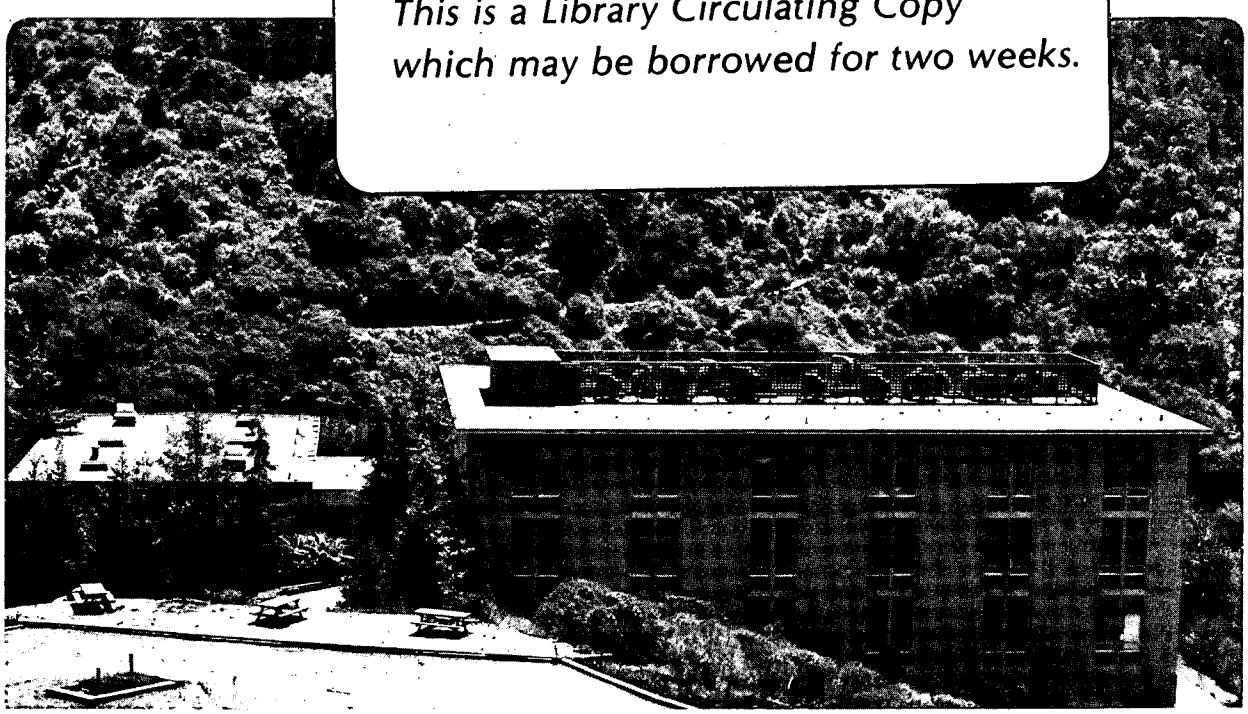

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THERMODYNAMICS OF LIQUID-LIQUID EQUILIBRIA INCLUDING THE CRITICAL REGION. TRANSFORMATION TO NON-CLASSICAL COORDINATES USING REVISED SCALING

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ABSTRACT

Classical or mean-field models for equilibrium properties of fluids and fluid mixtures fail near a critical point. To improve the performance of such models near the critical point of a pure fluid, Fox [1] proposed a method of transforming the coordinates of a classical equation of state to non-classical coordinates. Recently, we have extended the method of Fox to binary liquid mixtures at constant pressure and to ternary liquid mixtures at constant pressure and temperature [2]. However, our previous extension has used simple scaling where transformation to non-classical coordinates is symmetric with respect to the critical point. In this work, our extension is applied to binary and ternary liquid mixtures in a revised-scaling context that allows for the asymmetry found in real systems. Results are shown for binary and ternary liquid mixtures. For a few illustrative examples, good agreement is obtained between experimental and calculated coexistence curves.

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I Introduction

It is well known that mean-field models cannot describe the behavior of pure fluids or fluid mixtures near a critical point. At a critical point, the correlation length diverges and mean-field approximations break down.

Over the last few decades, considerable effort has been directed towards a correct description of equilibrium thermodynamic properties near a critical point. These efforts, however, have been conducted mainly for pure fluids and, while significant progress has been made, the sophistication reached in the description of pure fluids is far ahead of that reached for fluid mixtures [3,10].

Thermodynamic properties near a critical point in pure fluids or in fluid mixtures can be calculated accurately using a scaled equation of state. Unfortunately, scaled formulations suffer from narrow ranges of applicability. These ranges, however, can be increased substantially using revised-scaling or extended-scaling formulations [3].

It is desirable to have a single model capable of representing thermodynamic properties near and remote from critical conditions. Albright et al. [4] and Chen and Sengers [5] have developed a formal theory for the cross-over behavior of pure fluids and fluid mixtures. That work, however, is not as yet suitable for practical applications. For the global representation of pure-fluid or fluid-mixture properties, we need to devise methods for bringing together mean-field formulations, accurate everywhere but the critical region, with scaled formulations, useful only in the critical region.

To describe the non-classical behavior of a pure fluid near its critical point, Fox [1,6] has proposed a mathematical method for transforming a classical equation of state (EOS). Recently, we have extended the method of Fox to binary liquid mixtures at constant pressure and to ternary liquid mixtures at constant pressure and temperature [2]. Until now, however, Fox's ideas have only been used in conjunction with a simple-scaling formulation reminiscent of perfectly-symmetric lattice gas models.

In this work, we extend the method of Fox to the calculation of thermodynamic properties of asymmetric liquid mixtures. In contrast to our earlier work, we use a revised-scaling formulation which allows for the asymmetry found in real systems. We begin by recalling briefly some concepts of simple and revised scaling. We then extend our previous work to liquid mixtures in conjunction with revised scaling. In the last section, we compare calculated and experimental results for a few illustrative binary and ternary liquid-liquid equilibria (LLE).

II Brief Overview of Simple and Revised Scaling

The modern theory of critical phenomena is based on the assumption of generalized homogeneity of the Helmholtz energy [7]. If Φ denotes the Helmholtz energy density (A/V), this assumption implies that

$$\Phi\,(k^{\xi} a_1\,,\, k^{\eta} a_2) \;=\; k\,\Phi\,(a_1\,,\, a_2) \tag{1}$$

for all values of k, where ξ and η are two independent (but fixed) exponents, and where a_1 and a_2 are two independent thermodynamic variables [8] (or some as yet unspecified combination of them).

If a function is homogeneous, it is always possible to derive a scaling law [3], i.e. the dependence of Φ on the two variables a_1 and a_2 can be reduced to a dependence on only one new variable by a change of scale. If, for example, we take $k = a_1^{-1/\xi}$, Equation (1) becomes

$$\frac{\Phi\,(a_1\,,\, a_2)}{a_1^{1/\xi}} \;=\; \Phi\,(1\,,\, \frac{a_2}{a_1^{\eta/\xi}}) \tag{2}$$

Equation (2) says that, after scaling with the factor $a_1^{1/\xi}$, function Φ depends only on the ratio $a_2/a_1^{\eta/\xi}$. Further, along a path of constant $C = a_2/a_1^{\eta/\xi}$, function Φ obeys a simple power law:

$$\Phi(a_1, a_2) = a_1^{1/\xi}\, \Phi(1, C) \quad . \tag{3}$$

The postulate of generalized homogeneity of the Helmholtz energy was originally supported by studies of lattice gas models. The particle-hole symmetry of these models leads to the choice of temperature T and chemical potential μ for the independent field variables a_1 and a_2 [9].

Real fluids, however, don't have the symmetry inherent to lattice gas models. Subsequent studies of decorated lattice models (which lack this symmetry) have suggested that a_1 be a function of both temperature and chemical potential. This sugestion has been further substantiated by results of the renormalization group theory [3,10]. In the revised scaling of decorated lattice models, a_1 is a linear combination of temperature and chemical potential, while a_2 is only a function of chemical potential.

III Method of Transformation to Non-Classical Coordinates

Classical scaling can be expressed by

$$\Phi(a_1, a_2) = k^{-4}\, \Phi(k^3 a_1, k^2 a_2) \tag{4}$$

The essence of Fox's method is to construct a new Helmholtz energy density Φ', with a new scaling form that differs from the classical by the small exponents θ and ϕ:

$$\Phi'(a_1, a_2) = k^{-4}\, \Phi'(k^{3+\phi} a_1, k^{2+\theta} a_2) \tag{5}$$

The desired scaling is obtained [6] when

$$\beta = \frac{1-\phi}{2+\theta} \tag{6a}$$

$$1-\alpha = \frac{2-\theta}{2+\theta} \tag{6b}$$

where α and β are experimental critical exponents. In Fox's original work, a_1 and a_2 are given by

$$a_1 = \Delta\mu = \mu(T) - \mu(\rho_c, T) \quad , \tag{7a}$$

$$a_2 = \Delta T = T - T_c \tag{7b}$$

The scaling fields are chosen to be chemical potential and temperature (rather than pressure and temperature), because on a diagram of $\Delta\mu$ vs. density ρ, isotherms are remarkably antisymmetric with respect to the critical isochore [9]. As in simple scaling, in Equations (7) a_1 is only a function of chemical potential and a_2 is only a function of temperature.

To allow for asymmetry, using the principle of revised scaling discussed above, a_2 becomes a function of both temperature and chemical potential. Instead of Equations (7), we use

$$a_1 = \Delta\bar{\mu} \tag{8a}$$

$$a_2 = \Delta\bar{T} + c\,\Delta\bar{\mu} \tag{8b}$$

where $\Delta\bar{T} = \Delta T/T_c$ and $\Delta\bar{\mu} = \Delta\mu/\mu_c$. Constant c is a system-dependent parameter that allows for the combination of the "physical" fields $\Delta\bar{T}$ and $\Delta\bar{\mu}$ into the scaling field a_2.

To obtain the rescaled Helmholtz energy density of Equation (5), the scaling fields are multiplied by a suitable homogeneous scaling function raised to the ϕ and θ powers, respectively:

$$a_1' = a_1\,[g(\psi)]^{\phi} \tag{9a}$$

$$a_2' = a_2\,[g(\psi)]^{\theta} \tag{9b}$$

Equations (9) provide the transformation of classical coordinates to non-classical coordinates (denoted here with a prime). In Equations (9), g is a damping function defined by

$$g(\psi) = \left[\frac{\psi^{\lambda/4}}{W + \psi^{\lambda/4}}\right]^{1/\lambda} , \tag{10}$$

where ψ is some measure of distance to the critical point, and where λ and W are two system-dependent parameters. This definition, however, is somewhat arbitrary and other forms of g can also be used [11].

For pure fluids, a suitable measure of distance to the critical point is

$$\psi_p = \frac{P - P_c - \rho_c(\mu - \mu_c) - s_c(T - T_c)}{P_c} . \tag{11}$$

Here μ_c and s_c are, respectively, the entropy and the chemical potential at the critical point, relative to the ideal gas at the same temperature and pressure. Geometrically, ψ_p represents the normalized distance from the $P(\mu,T)$ surface to the plane tangent to this surface at the critical point. Thermodynamic stability requires that this surface be everywhere convex and therefore, ψ_p is always positive.

The method of Fox for pure fluids reduces to the following expressions:

$$[\Delta T]' = [\Delta T]\,[g(\psi_p)]^{\theta} \tag{12a}$$

$$[\Delta \mu]' = [\Delta \mu]\,[g(\psi_p)]^{\phi} \tag{12b}$$

$$P' = P + \rho_c(\mu' - \mu) + s_c(T' - T) . \tag{12c}$$

Recently [2], this method has been applied to isobaric binary mixtures, and to isobaric-isothermal ternary mixtures. For the binary case, the constitutive equations become

$$[\Delta T]' = [\Delta T]\,[g(\psi_b)]^{\theta} \tag{13a}$$

$$[\Delta(\Delta_{12})]' = [\Delta(\Delta_{12})]\,[g(\psi_b)]^{\phi} \tag{13b}$$

$$-\mu_2' = -\mu_2 + x_{1c}(\Delta_{12}' - \Delta_{12}) + s_{mc}(T' - T) , \tag{13c}$$

where subscript mc denotes a property of mixing evaluated at the (known) critical coordinates (consolute point, x_{1c} and T_c), and where ψ_b is a normalized binary distance function given by

$$\psi_b = \frac{-\mu_2 + \mu_{2c} - x_{1c}(\Delta_{12} - \Delta_{12c}) - s_{mc}(T - T_c)}{-\mu_{2c}} \quad . \tag{14}$$

In Equation (13b), $\Delta(\Delta_{12}) = \Delta_{12} - \Delta_{12}(x_{1c}, T)$, and Δ_{12} is given by $\mu_1 - \mu_2$. For the ternary case, the constitutive equations are

$$[\Delta(\Delta_{12})]' = [\Delta(\Delta_{12})]\,[g(\psi_t)]^{\theta} \tag{15a}$$

$$[\Delta(\Delta_{32})]' = [\Delta(\Delta_{32})]\,[g(\psi_t)]^{\phi} \tag{15b}$$

$$-\mu_2' = -\mu_2 + x_{1c}(\Delta_{12}' - \Delta_{12}) + x_{3c}(\Delta_{32}' - \Delta_{32}) \quad , \tag{15c}$$

with

$$\Delta(\Delta_{12}) = \Delta_{12} - \Delta_{12c} \tag{16a}$$

$$\Delta(\Delta_{32}) = \Delta_{32} - \Delta_{32}(x_{3c}, \Delta_{12}) \quad , \tag{16b}$$

and where normalized distance ψ_t is given by

$$\psi_t = \frac{-\mu_2 + x_{1c}(\Delta_{12} - \Delta_{12c}) + x_{3c}(\Delta_{32} - \Delta_{32c})}{-\mu_{2c}} \quad . \tag{17}$$

Equations (13) and (15) correspond to simple-scaling. In accordance with the principle of revised scaling discussed above, we now propose for binary systems

$$[\Delta\tilde{T} + c\Delta(\tilde{\Delta}_{12})]' = [\Delta\tilde{T} + c\Delta(\tilde{\Delta}_{12})]\,[g(\psi_b)]^{\theta} \tag{18a}$$

$$[\Delta(\tilde{\Delta}_{12})]' = [\Delta(\tilde{\Delta}_{12})]\,[g(\psi_b)]^{\phi} \tag{18b}$$

$$-\mu_2' = -\mu_2 + x_{1c}(\Delta_{12}' - \Delta_{12}) + s_{mc}(T' - T) \quad . \tag{18c}$$

Similarly, for ternary systems, we propose

$$[\Delta(\tilde{\Delta}_{12}) + c\Delta(\tilde{\Delta}_{32})]' = [\Delta(\tilde{\Delta}_{12}) + c\Delta(\tilde{\Delta}_{32})]\,[g(\psi_t)]^{\theta} \tag{19a}$$

$$[\Delta(\tilde{\Delta}_{32})]' = [\Delta(\tilde{\Delta}_{32})]\,[g(\psi_t)]^{\phi} \tag{19b}$$

$$-\mu_2' = -\mu_2 + x_{1c}(\Delta_{12}' - \Delta_{12}) + x_{3c}(\Delta_{32}' - \Delta_{32}) \quad . \tag{19c}$$

IV Calculation of Thermodynamic Properties of Liquid Mixtures

Thermodynamic properties of liquid mixtures can be calculated from an equation of state or from an excess-Gibbs-energy model; the latter is more useful when all components in the mixture are subcritical. Consistent with our earlier work, we use an excess Gibbs energy model.

To represent the molar excess Gibbs energy of mixing, we arbitrarily use the NRTL Equation [12]. Expressions for the NRTL model are given in the Appendix.

Liquid-liquid equilibria (LLE) are calculated from the iso-activity condition of coexisting phases *I* and *II* :

$$(x_i\gamma_i)^I = (x_i\gamma_i)^{II} \qquad i = 1,\ldots,N \ , \tag{20}$$

where γ_i is the activity coefficient of component i and N is the number of components in the system.

A) Binary liquid mixtures at constant pressure

Equations (18) are used to transform classical coordinates to non-classical coordinates. Classical chemical potentials are calculated using the NRTL model. Equations (18) provide a self-consistent set of equations from which non-classical coordinates are calculated. This set of equations can either be solved with a direct substitution method or with a Newton-Raphson method; however, in view of the numerical difficulties that are generally encountered in calculations near a critical point, the latter technique is preferred.

To calculate derivative properties, we use the Gibbs-Duhem equation. For a binary mixture at constant pressure, the Gibbs-Duhem equation can be written as

$$s dT + d\mu_2 + x_1 d\Delta_{12} = 0 \ . \tag{21}$$

Non-classical composition x_1', for example, can be obtained by numerical differentiation:

$$x_1' = \left(\frac{\partial \mu_2'}{\partial \Delta_{12}'}\right)_{T',P'} = \left(\frac{\Delta \mu_2'}{\Delta(\Delta_{12}')}\right)_{T',P'} \tag{22}$$

Details concerning the numerical algorithms for these calculations are given elsewhere [1,2,11].

In Fox's method, the critical point remains invariant upon transformation of coordinates. Two classical-model parameters (NRTL parameters, in this case) are therefore calculated from the conditions of incipient immiscibility at the known (or estmated) critical point [2,13]. Three adjustable parameters, W, λ and c, are obtained by regression of experimental data. To calculate coexistence curves (i.e. coexisting compositions), all available LLE data are used to determine these parameters.

For symmetric systems, $c = 0$, and the simple-scaling method of Equations (13) is recovered. As the magnitude of c increases, so does the asymmetry in the calculated properties. Figure (1) illustrates the effect of parameter c on the shape of the calculated coexistence curve of a representative binary system.

B) Ternary liquid mixtures at constant pressure and temperature

Equilibrium-property calculations for isobaric binary systems, [using Equations (18)] and equilibrium-property calculations for isothermal-isobaric ternary systems [using Equations (19)] are entirely analogous. For ternary systems, the number of equations that have to be solved is larger, but the procedure to solve them is the same as that for binary systems.

Derivative properties are calculated from the Gibbs-Duhem equation which, for an isothermal-isobaric ternary system, can be written

$$x_1 d\Delta_{12} + d\mu_2 + x_3 d\Delta_{32} = 0 \ . \tag{23}$$

As for binary systems, equilibrium compositions are obtained by numerical differentiation:

$$x_1 = \left(\frac{\partial \mu_2'}{\partial \Delta_{12}'}\right)_{T',P',\Delta_{12}'} = \left(\frac{\Delta \mu_2'}{\Delta[\Delta_{12}']}\right)_{T',P',\Delta_{12}'} . \tag{24}$$

Reference [2] gives examples of coexistence curves calculated using the simple-scaling method [Equations (15)]. Figure (2) shows representative results using the revised-scaling method [Equations (19)]; depending on its sign, parameter c "shifts" the coexistence curve to the left or to the right, allowing good correlation of highly asymmetric systems.

V Results and Discussion

Figure (3) shows the calculated coexistence curve [Equations (18)] for the system nitromethane/1-nonanol. This system is asymmetric because nonanol molecules are about twice as large as nitromethane molecules. Figure (4) shows the calculated ternary diagram [Equations (19)] for the system heptane/tri(9,12-octadienoate)glycerol/furfural at 70.0 C. For both examples, we have selected mixtures that exhibit a high degree of asymmetry; these systems cannot be correlated using the simple-scaling method described previously [2]. Parameters for these examples are given in the Appendix.

The results of the revised-scaling method presented here are in good agreement with experiment, and are significantly better than those obtained using the simple-scaling method. Three parameters (W, λ and c) are necessary, in addition to the experimental (or estimated) critical coordinates. It is important to point out, however, that in principle these three parameters should allow simultaneous correlation of different thermodynamic properties, provided that we use a classical model capable of doing so.

In Figure (3), the dotted curve represents the results of the NRTL model with classical coordinates. Two NRTL parameters are obtained from the coordinates of the (known) consolute point and from stability criteria. Parameters W and c (λ is

fixed at $\lambda = 1$; see below) are obtained from solubility data. The corresponding coexistence curve, in nonclassical coordinates, is given by the solid line.

To illustrate the improvement of the method proposed here over conventional methods for LLE calculation, Figure (4) shows (dotted curve) the results of the NRTL model, with classical coordinates, and with parameters reported in the literature [14]. After recalculating NRTL parameters from the coordinates of the plait point, and applying the transformation of coordinates proposed here, the solid curve is obtained.

If the method proposed here is only used to correlate coexistence curves, then one of the two parameters in Equation (10) is superfluous, i.e. parameter λ can be kept constant and only W and c are adjusted. The examples shown in Figures (3) and (4) were calculated with $\lambda = 1$.

VI Conclusions

Recently, we extended and applied to liquid mixtures [2] a method of transformation to nonclassical coordinates originally presented by Fox [1]. Fox's method and our previous extension, however, were developed in the context of simple scaling, and therefore their use was limited to relatively symmetric systems.

In this work we have applied the method of transformation to nonclassical coordinates in the context of revised scaling. The introduction of an asymmetry parameter allows correlation of asymmetric as well as symmetric systems. We have used the method to calculate coexistence curves for highly asymmetric systems. Agreement between experimental and calculated coexistence curves is very good.

The method presented here requires calculations that are longer and more complicated than those required when using conventional, classical-coordinate methods. With readily available computers, this disadvantage is not important when compared to the improved results obtained through transformation of coordinates as proposed

in this work.

Acknowledgment

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Appendix: Excess Gibbs Energy Model for a Liquid Mixture

Several excess-Gibbs-energy models are available for the calculation of phase equilibria for liquid mixtures. The so-called "local-composition" models are widely used in practice. In this work, we use the NRTL model [12] because it usually

provides a reasonable representation of liquid-liquid equilibria for nonelectrolytes [14].

The NRTL model for g^E, the molar excess Gibbs energy of a liquid mixture with N components, is given by

$$\frac{g^E}{RT} = \sum_{i=1}^{N} x_i \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{N} G_{li} x_l} , \tag{A1}$$

where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$. In the NRTL equation, τ_{ij} and τ_{ji} are two binary interaction parameters for the ij pair. In our work, $\alpha_{ij} = \alpha_{ji} = 0.2$.

Activity coefficients γ are obtained from the thermodynamic relation

$$RT \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T,P,n_j} , \tag{A2}$$

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

Table 1 gives parameters for the examples shown in Figures (3) and (4).

Table 1 - NRTL and other required parameters for fitting binary and ternary LLE for some asymmetric systems.

Components	i	j	τ_{ij}	τ_{ji}	T_c	x_{1c}	x_{2c}	x_{3c}	λ	W	c
(1) Nitromethane [M.W. = 61.0] (2) 1-Nonanol [M.W. = 144.3]	1	2	1002.3	-150.0	327.92	0.736	0.264	-	1	4.20	-0.155
(1) Heptane [M.W. = 100.2] (2) Glycerol tri(9,12-octadienoate) [M.W. = 878.0]	1	2	-962.5	-720.9							
	1	3	279.0	694.8	343.15	0.245	0.025	0.730	1	0.04	4.00
(3) Furfural [M.W. = 96.1]	2	3	-1227.1	1474.0							

where M.W. = molecular weight.

FIGURE CAPTIONS

FIGURE 1

Effect of asymmetry parameter c on the shape of the calculated coexistence curve for a representative isobaric binary system. When c=0, the simple-scaling (symmetric) method is recovered.

FIGURE 2

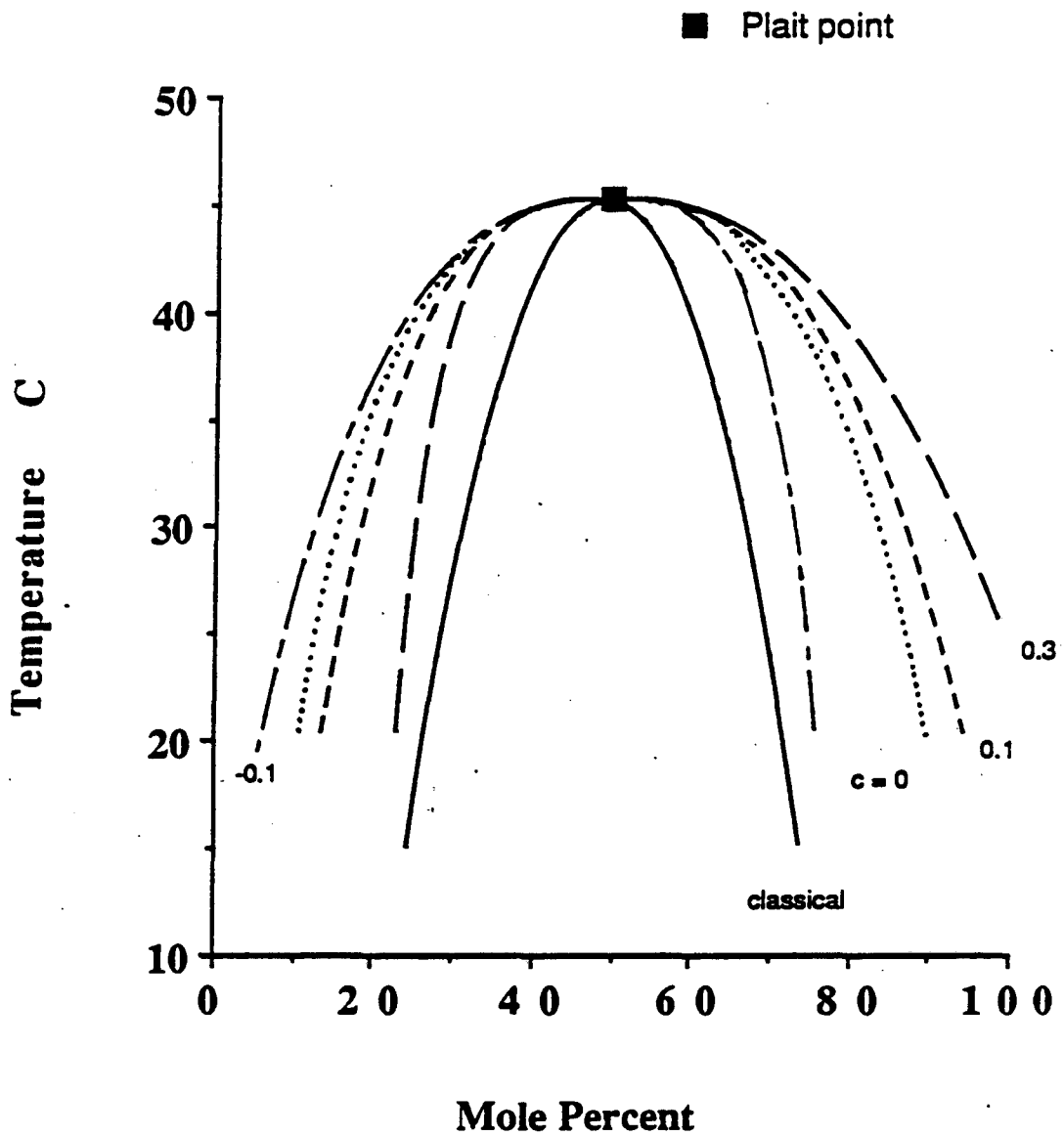
Effect of asymmetry parameter c on the shape of the calculated coexistence curve of a representative ternary system at constant temperature and pressure. When c=0, the simple-scaling version of the method is recovered.

FIGURE 3

Calculated coexistence curve for the system nitromethane/1-nonanol. The dotted curve shows calculations using the NRTL model with two NRTL parameters calculated from the (known) coordinates of the consolute point. The solid curve represents calculations with the same NRTL model but using the transformation of coordinates proposed in this work with c = -0.155.

FIGURE 4

Calculated ternary diagram for the system heptane/glycerol tri(9,12-octadienoate)/furfural at 70 C. The dotted curve shows calculations using the NRTL equation with parameters reported in the literature. The solid line shows calculations with the NRTL equation, but with NRTL parameters determined from the known plait-point coordinates and one tie line, and with transformation of coordinates as proposed in this work.


Plait point
50
40
30
20
10
Temperature C
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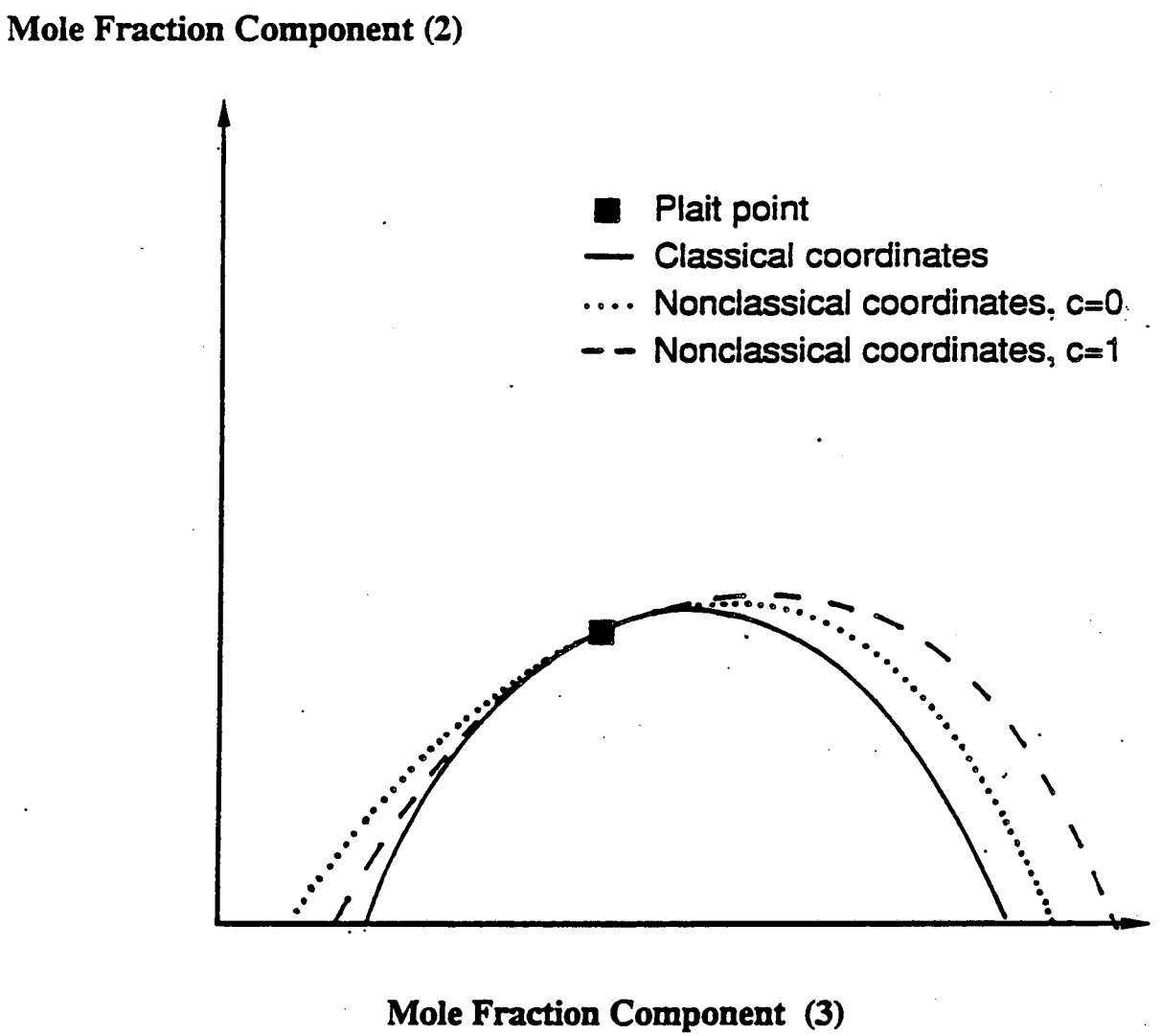
20
40
60
80
100
Mole Percent
-0.1
0.3
0.1
c = 0
classical

FIGURE 1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Plait point
Classical coordinates
Nonclassical coordinates, c=0
Nonclassical coordinates, c=1
Mole Fraction Component (3)

FIGURE 2

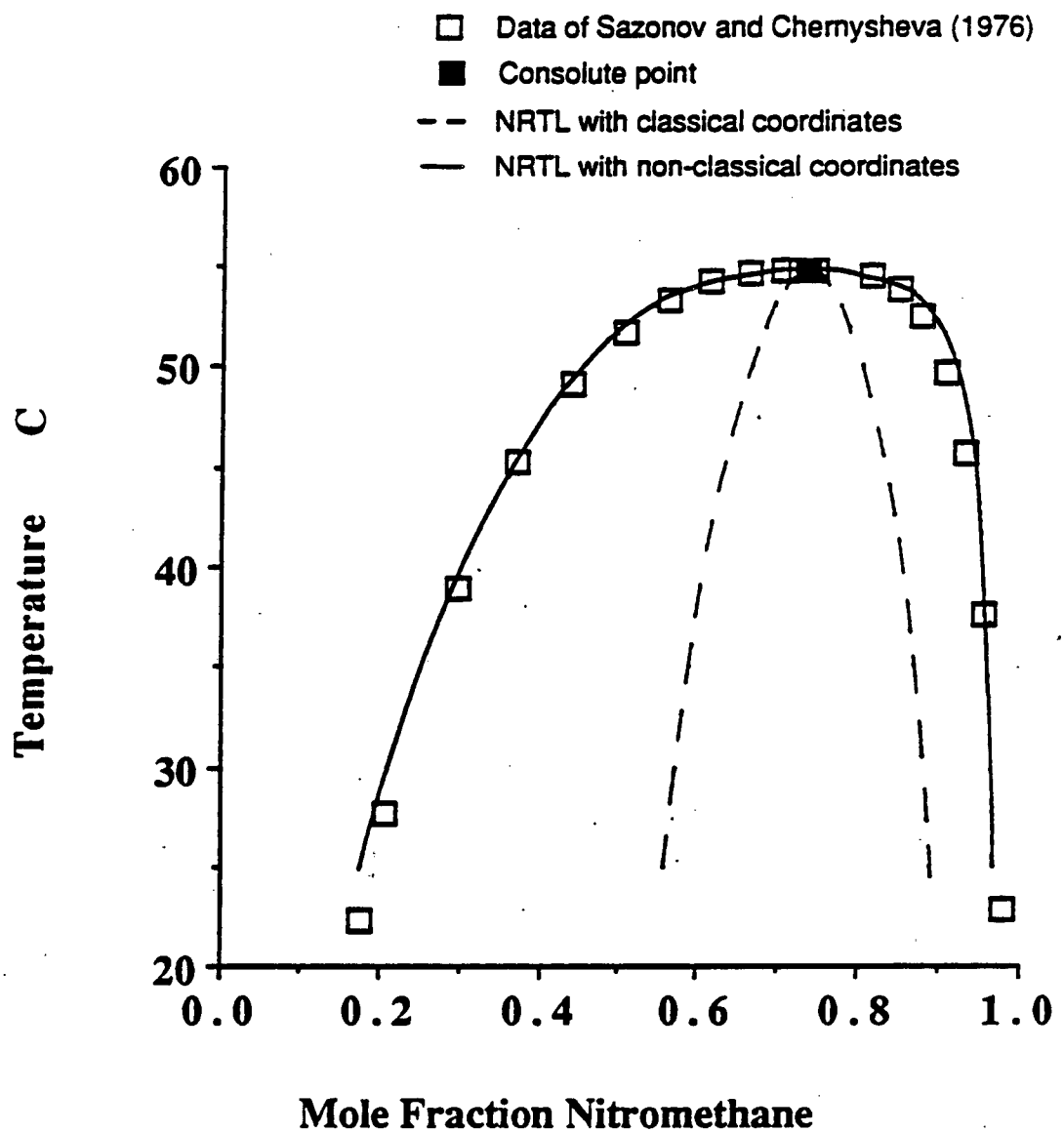
Data of Sazonov and Chernysheva (1976)
Consolute point
NRTL with classical coordinates
NRTL with non-classical coordinates
60
50
40
30
20
Temperature C
0.0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Nitromethane

FIGURE 3

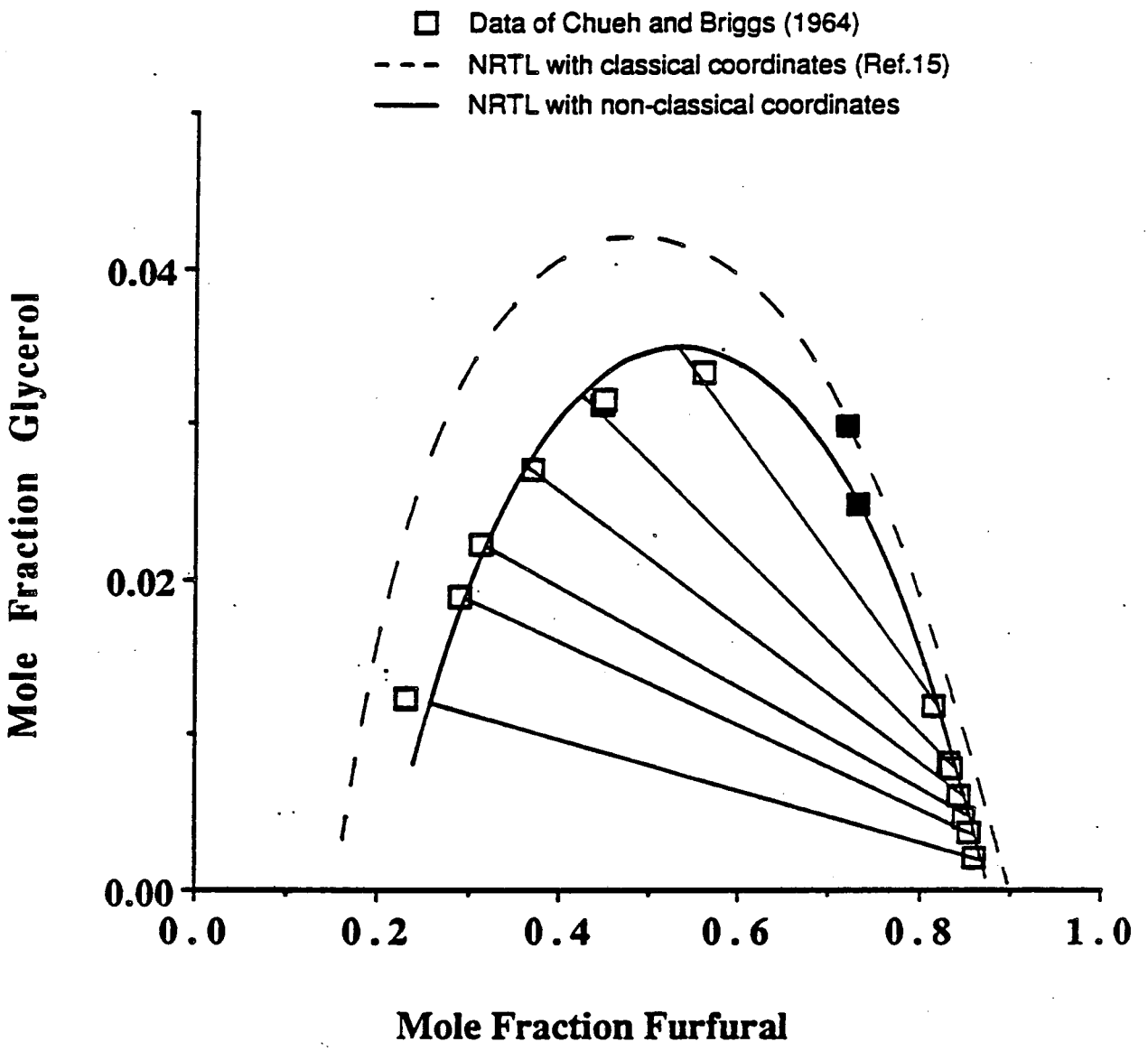
Data of Chueh and Briggs (1964)
NRTL with classical coordinates (Ref.15)
NRTL with non-classical coordinates
Mole Fraction Glycerol
0.04
0.02
0.00
0.0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Furfural

FIGURE 4

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1 CYCLOTRON ROAD
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