LBL-29997
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Fluid Phase Equilibria

Binary Liquid-Liquid Equilibria from a Double-Lattice Model

Y. Hu, H. Liu, D.S. Soane, and
J.M. Prausnitz

November 1990

LOAN COPY
Circulates
for 2 weeks
Bldg. 50 Library.
LBL-29997
Copy 2

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

BINARY LIQUID-LIQUID EQUILIBRIA FROM A DOUBLE-LATTICE MODEL

Ying Hu and Honglai Liu

Thermodynamics Research Laboratory
East China Institute of Chemical Technology, Shanghai, China
and

David S. Soane and John M. Prausnitz

Department of Chemical Engineering
University of California
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

ABSTRACT

Freed's lattice field theory is used to establish a double-lattice model for the Helmholtz energy of mixing for strongly nonideal binary liquid mixtures. The coefficients of Freed's expansion terms are adjusted such that the calculated coexistence curve for the simple Ising lattice is in excellent agreement with that calculated from the Padé-approximant coefficients for spontaneous magnetization proposed by Scesney. For a variety of binary systems, two parameters (ε/k and r_2) are obtained from experimental critical consolute points; here ε/k is the interchange energy and r_2 is the number of lattice sites required by molecule 2, with r_1=1. Calculated coexistence curves are generally in good agreement with experiment for fluid mixtures without specific (oriented) interactions, much better than those calculated using Flory-Huggins theory, especially near critical consolution points. Introducing a secondary lattice to account for highly oriented interactions (hydrogen bonding), requires an additional energy parameter $\delta\varepsilon/k$ and an empirical parameter c_{10}. With these parameters, coexistence curves are fitted well for systems having a miscibility loop with both lower and upper critical solution temperatures.

INTRODUCTION

It has been known for a long time that phase transitions of fluids and their mixtures are similar to transitions due to ferromagnetism, to order-disorder transition in alloys, to localized adsorption or absorption; these phenomena can all be described using a simple lattice model, well-known as the Ising model (Hill, 1956). For pure fluids, a lattice-gas model

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional finding was provided by E.I. du Pont de Nemours & Company, Montedipe s.r.l., shell (Amsterdam), Norsolor Corp., and the donors of the Petroleum Research Fund administered by the American Chemical Society. Ying Hu and Honglai Liu are grateful to the Chinese National Science Foundation and Chinese National Council of Education for financial support.

can be constructed by filling the sites of a lattice with either molecules or vacancies. For binary mixtures, the sites are filled by either the molecules of component 1 or component 2. The model can also be extended to take into account different sizes of the components. In this case, it is usually called the Flory-Huggins model. Different components can have different numbers of segments. We assume that one molecular segment occupies one lattice site. When each component has only one segment, the Flory-Huggins model degrades to the Ising model.

Despite its simple physical picture, however, the thermodynamic properties of the Ising model can be obtained analytically only for one and two dimensions. For a three-dimensional lattice, no analytical solution is available in closed form. The same situation prevails for the Flory-Huggins model. Flory (1941, 1942) and Huggins (1941, 1942) did not solve their model exactly; instead, a mean-field approximation was introduced. In this approximation, the constraint of single occupancy of sites is replaced by site-occupancy probability arguments. A mean-field Helmholtz energy of mixing ΔA was obtained, composed of a combinatorial entropy and a simple energy of mixing:

$$\Delta A/N_r kT = (\Phi_1/r_1)\ln\Phi_1+(\Phi_2/r_2)\ln\Phi_2+g_{12}\Phi_1\Phi_2 \tag{1}$$

where N_r is the total number of lattice sites, r_1, r_2, Φ_1 and Φ_2 are the number of lattice sites and volume fractions of component 1 and 2 respectively; g_{12} is an interaction parameter obtained from nearest-neighbor interaction energies.

Flory-Huggins theory has been widely used for describing the phase behavior of fluid mixtures, including polymer solutions. However, it is known (Fisher, 1967; Heller, 1967; Senger and Senger, 1978) that near critical consolute points, a mean-field approximation cannot correctly describe the shape of the coexistence curve. Predicted coexistence curves are not sufficiently flat near the consolute temperature.

Some refinements have been made. For example, Orofino and Flory (1957), and Koningsveld and Kleintjens (1971) replaced the segment fractions with more accurate site-occupancy probabilities, which correctly take into account the local correlations due to chain connectivity. However, to obtain a fit of experimental data, it was neccessary to express g_{12} as a function of temperature and composition (Kleintjens and Koningsveld, 1980). Recently, de Pablo and Prausnitz (1989,1990), extended the complicated method of Fox (1983) for transforming the coordinates of a classical excess-Gibbs energy function for binary liquid mixtures to non-classical coordinates and obtained excellent agreement with experiment.

Although most binary mixtures possess an upper critical-solution temperature (UCST) which can be described by the Flory-Huggins theory at least qualitatively, some possess a lower critical-solution temperature (LCST) or a closed loop with both UCST and LCST. The Flory-Huggins theory cannot describe such systems. The occurence of LCST may follow from a highly directional, short-range interaction, such as hydrogen bonding, which may be responsible for the mutual solubility of two components at low temperatures, as first suggested by Hirschfelder, Stevenson and Erying (1937). Later, on the basis of that suggestion, Barker and Fock (1953) proposed a lattice model, in which each molecule possesses several contact points with a different interaction energy associated with each contact point. Barker and Fock used a quasichemical method (a version of a mean-field approximation) to develop the model and to obtain qualitatively correct results. However, quantitative agreement was unsatisfactory because of the deficiency of the mean-field approximation. Further

work based on quasichemical theory was reported by Prange et al (1988).

Rigorous analysis of the lattice model has been attempted by theoretical physicists who used series expansions to overcome mathematical complexities. Some useful numerical results have been obtained for the Ising model; for example, coefficients for low and for high-temperature expansions have been reported for the partition function (Sykes, Essan and Gaunt,1965) and Padé-approximant coefficients for spontaneous magnetization have been reported by Scesney (1970). The latter can be transferred to give accurate coexistence curves. On the basis of these results, Wheeler (1975) and Anderson and Wheeler (1978) proposed a decorated-lattice model for binary liquid solutions which can be mapped on a spin-1/2 Ising model. With the use of Scesney's Padé-approximant coefficients for spontaneous magnetization, Anderson and Wheeler could simulate coexistence curves including UCST and LCST in quantitative agreement with those for real systems. Although the language of Ising statistics is unfamiliar to chemical engineers, and because the procedure is too complicated for practical purposes, the achievements obtained by theoretical physicists encourage us to believe that the Ising model could be used as a reliable basis for describing liquid-liquid equilibria.

The deficiency of Flory-Huggins theory probably does not lie in the model itself, but in the mean-field approximation. Recently, Freed and coworkers (1985; Bawendi, Freed and Mohanty 1987; Bawendi and Freed 1988) developed a lattice field theory which formally provides an exact mathematical solution of the Flory-Huggins model. In their theory, the Flory-Huggins parameter g_{12} in Eq.(1) is expressed as a series expansion in the inverse of the coordination number and in the nearest-neighbor interaction energies in units of kT. Some interesting terms appear, especially a term proportional to T^{-2}, which is not obtained through the usual probability arguments, even in the most refined version. It is this term which may play an important role in describing phase behavior near critical points.

The purpose of this work is to develop a molecular-thermodynamic framework based on a double lattice model to describe the phase behavior of strongly nonideal binary fluid mixtures. The publications of Freed and coworkers serve as a starting point because they do not use a mean-field approximation . In this work, we first establish models for describing liquid-liquid equilibria for fluid mixtures containing molecules of ordinary size. Later, we plan to report models for polymer solutions.

MODEL DEVELOPMENT

Our aim is to establish a useful expressions for the Helmholtz energy of mixing for binary liquid mixtures, especially for liquid-liquid equilibria. We start with nonpolar (or weakly polar) mixtures of components of equal size and then proceed to similar mixtures of components with different sizes. Finally, we take into account oriented interactions, as found in mixtures containing strongly polar or hydrogen-bonding components.

1. Mixtures of Equal-Sized Molecules: Ising Lattice

The canonical partition function Q is related to energy E and temperature T by

$$Q = \sum_{\alpha} \exp(-E_{\alpha}/kT) \tag{2}$$

where k is Boltzmann constant and the summation is over all possible configurations of the system, subject to the canonical restrictions (constant T,V,N_i) where V is the total volume

and N_i is the number of molecules of species i, E_α is the potential energy of the system at configuration α. For a binary mixture where only nearest-neighbor interactions contribute to the potetial energy,

$$E_\alpha = -(N_{11}\varepsilon_{11}+N_{22}\varepsilon_{22}+N_{12}\varepsilon_{12})_\alpha \tag{3}$$

here N_{11},N_{22} and N_{12} are numbers of 1-1, 2-2 and 1-2 pairs related by the conservation equations

$$2N_{11}+N_{12} = zN_1$$

$$2N_{22}+N_{12} = zN_2 \tag{4}$$

where z is the coordination number, N_1,N_2 are numbers of molecules of component 1 and component 2, respectively. Here ε_{11},ε_{22} and ε_{12} are positive energy parameters for corresponding nearest-neighbor interactions. For the mixtures of interest, Eq.(2) can also be expressed as

$$Q = \sum_{N_{12}} g(N_1,N_2,N_{12})(\exp(\varepsilon_{11}/kT))^{N_{11}}(\exp(\varepsilon_{22}/kT))^{N_{22}}(\exp(\varepsilon_{12}/kT))^{N_{12}} \tag{5}$$

where $g(N_1,N_2,N_{12})$ is the combinatorial factor which depends on the number of 1-2 pairs [not to confused with g_{12} in Eq.(1)]. The summation is over all possible numbers of 1-2 pairs. The Helmholtz energy of mixing can then be calculated by

$$\Delta A/kT = -N_r\ln Q+N_{r1}\ln Q_1+N_{r2}\ln Q_2 \tag{6}$$

where Q_1 and Q_2 are partition functions for pure components, N_r , N_{r1} and N_{r2} are the numbers of lattice sites for the mixture, and for the pure components, respectively.

To obtain an analytical expression for the Helmholtz energy of mixing from Eq.(5), we use results of Freed's theory recently developed for the simplest Flory-Huggins lattice where r_1=1,r_2=1. Following Freed, we expand to second order in mole fraction; we then obtain an approximate solution for the Ising model:

$$\Delta A/N_rkT = x_1\ln x_1+x_2\ln x_2+z\tilde{\varepsilon}x_1x_2/2-z\tilde{\varepsilon}^2x_1^2x_2^2/4 \tag{7}$$

where $\tilde{\varepsilon}$ is a reduced interaction parameter defined by

$$\tilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12})/kT \tag{8}$$

To test Eq.(7), we calculate the coexistence curve using traditional phase-equilibrium thermodynamics ; we compare the results with those calculated from the Pade-approximant coefficients for spontaneous magnetization reported by Scesney. In these calculations, $\tilde{\varepsilon}_c$ for the critical temperature is evaluated by solving the equation

$$\left(\frac{\partial^2\Delta A}{\partial x_1^2}\right)_{x_1=0.5} = 0 \tag{9}$$

Figure 1 shows the comparison. The deviations of the calculated compositions of the coexistence curve with respect to the accurate results of Scesney are plotted on the abscissa against the difference $\tilde{\varepsilon}_c-\tilde{\varepsilon}$ on the ordinate, which is a measure of the temperature difference from the critical point. Figure 1 also shows results from Flory-Huggins theory given by Eq.(1) and r_1=r_2=1 . The results of Freed's theory [Eq.(7)] are much better than

those from Flory-Huggins theory. The RMSx (standard deviation of the compositions of the conjugated phases for the coexistence curve) obtained for the range from $\tilde{\varepsilon}_c$ to $\tilde{\varepsilon}$=1.2 are 0.0193 and 0.1288 for these two theories, respectively.

However, agreement between phase boundaries calculated by Freed's theory and those from Scesney is not complete probably because Eq.(7) does not include higher terms. There are several ways to revise Eq.(7) to improve the coexistence curves. Two of them are investigated here. One way is to introduce an empirical coefficient c_2 in the $\tilde{\varepsilon}^2$ term. Figure 2(a) shows the RMSx as a function of different c_2 values. As shown in this figure and Figure 1, the best choice is c_2=1.074. The other way is to add to the expansion an additional high-order term, $c_{10}z\tilde{\varepsilon}^{10}x_1^{10}x_2^{10}$; here we arbitrary take a high order (10). As shown in Figure 2(b) and Figure 1, the best choice is c_{10}=380.0 . The results of these two revisions are well-matched. If c_2=1.074,c_{10}=0, RMSx=0.0015; if c_2=1,c_{10}=380.0, RMSx=0.0066. Any linear interpolation between these two limits gives nearly equally good results as shown in Figure 2(c). Therefore, we can write a general expression for the Helmholtz energy of mixing for the Ising model:

$$\Delta A/N_rkT = x_1\ln x_1+x_2\ln x_2+z\tilde{\varepsilon}x_1x_2/2-c_2z\tilde{\varepsilon}^2x_1^2x_2^2/4-c_{10}z\tilde{\varepsilon}^{10}x_1^{10}x_2^{10} \tag{10}$$

where c_2 and c_{10} are related by

$$c_{10} = 5515.1-5135.1c_2 \tag{11}$$

The coefficients of Eq.(11) are obtained from the two limits mentioned above.

The calculated coexistence curve using Eq.(10) is nearly perfect when compared to Scesney's accurate results. In the examples given below, we often use c_2 =1.074 and c_{10}=0. However, as shown later, it is better for some cases to retain the high-order term while restricting constants c_2 and c_{10} according to Eq.(11).

2. Mixtures of Molecules with Different Sizes: Flory-Huggins Lattice

In this work, the Flory-Huggins lattice is the primary lattice for fluid mixtures. We use Eqs(2),(3) and (5) with the tacit assumption that N_{11},N_{22} and N_{12} are numbers of segment-segment pairs; and ε_{11},ε_{22} and ε_{12} are segment-segment interaction energies. Mathematical solutions for the partition function and the corresponding Helmholtz energy of mixing are provided by Freed et al's theory. In their theory, there are three contributions for the Helmholtz energy of mixing for a Flory-Huggins lattice: mean-field contribution plus two corrections for deviations from mean-field behavior, one energetic and one entropic. After rearrangement, the general form for the Helmholtz energy of mixing can be expressed as

$$\boxed{\Delta A/N_rkT = (\Phi_1/r_1)\ln\Phi_1+(\Phi_2/r_2)\ln\Phi_2+\sum_m\sum_n a_{mn}\Phi_1^m\Phi_2^n} \tag{12}$$

where coefficients a_{mn} are functions of z,r_1,r_2 and $\tilde{\varepsilon}$. We now consider three models for applying Eq.(12) to real mixtures.

Model I: We use Freed's mean-field results where the energy-correction term and the entropy-correction term are neglected; we adopt z=6 for a simple cubic lattice. We then have

$$a_{11} = 3\tilde{\varepsilon} \quad , \quad a_{22} = -3c_2\tilde{\varepsilon}^2/2 \tag{13}$$

and all other coefficients vanish. Eq.(12) can be written as

$$\Delta A/N_r kT = (\Phi_1/r_1)\ln\Phi_1+(\Phi_2/r_2)\ln\Phi_2+z\tilde{\varepsilon}\Phi_1\Phi_2/2-c_2z\tilde{\varepsilon}^2\Phi_1^2\Phi_2^2/4 \tag{14}$$

The last term does not appear in the classical Flory-Huggins theory.

Model II: We use Eq.(12) but neglect the entropic correction only. For a cubic lattice,

$$a_{11} = 2\tilde{\varepsilon}$$

$$a_{21} = \tilde{\varepsilon}/r_2 \quad , \quad a_{12} = \tilde{\varepsilon}/r_1$$

$$a_{22} = -3c_2\tilde{\varepsilon}^2/2 \tag{15}$$

All other coefficients vanish.

Model III: We again use Eq.(12) and keep all contributions in Freed's theory obtained when expanding the Helmholtz energy of mixing to the order of $\tilde{\varepsilon}^2$ and z^{-2}. For a cubic lattice,

$$a_{11} = (4/9)(1/r_1-1/r_2)^2+2\tilde{\varepsilon}$$

$$a_{21} = -(1/2-11/54r_2-11/27r_1+1/9r_1r_2)(1/r_1-1/r_2)^2+\tilde{\varepsilon}/r_2$$

$$a_{12} = -(1/2-11/54r_1-11/27r_2+1/9r_1r_2)(1/r_1-1/r_2)^2+\tilde{\varepsilon}/r_1$$

$$a_{31} = (1/3-2/9r_2-4/9r_1+1/18r_2^2+1/6r_1^2+1/9r_1r_2)(1/r_1-1/r_2)^2$$

$$a_{13} = (1/3-2/9r_1-4/9r_2+1/18r_1^2+1/6r_2^2+1/9r_1r_2)(1/r_1-1/r_2)^2$$

$$a_{22} = (2/3-2/3r_1-2/3r_2+1/6r_1^2+1/6r_2^2+1/3r_1r_2)(1/r_1-1/r_2)^2-3c_2\tilde{\varepsilon}^2/2 \tag{16}$$

where c_2=1 in Freed's work. However, we use c_2=1.074. All coefficients not mentioned in Eq.(16) are zero.

Before comparing results from these three models with experiment, we briefly describe a fourth model with a secondary lattice for mixtures of oriented molecules.

3. Mixtures with Highly Oriented Interactions Between Molecules

We now consider mixtures where the interactions between molecules i and j include a highly oriented, short-range interaction (e.g. hydrogen bonding) which occurs only for particular orientations of the molecules. The fraction of a segment's surface which permits oriented interactions is designated by η. In general, η is different for molecules of different components; for simplicity, here we suggest that η is a constant. [Later we show that the numerical value of η is insensitive to the calculated results.] Figure 3 presents a picture of interaction for N_{ij} $i-j$ pairs in the language of a lattice model . This lattice representation is similar to an Ising model of general spin; at present, it is not possible to obtain an analytic expression for the Helmholtz energy of this model. As a reasonable approximation for fluid mixtures with oriented interactions, we imagine a modified simple Ising model which we call a secondary lattice. In this secondary lattice, the total number of lattice sites is N_l which is related to the number of $i-j$ pairs N_{ij} by the conservation equation

$$N_l z/2 = N_{ij} \tag{17}$$

The number of sites available for oriented interaction in this lattice is $N_l\eta$, while the remaining $N_l(1-\eta)$sites cannot participate in oriented interactions.

To fix ideas, we consider an interaction $i-j$ where i may be equal to j or not. The total number of $i-j$ interactions is N_{ij} as determined by the primary lattice; some of these interactions are oriented. In the limit of complete randomness, the number of oriented $i-j$ interactions is $N_{ij}\eta^2$, the number of non-oriented $i-j$ interactions is $N_{ij}[2\eta(1-\eta)+(1-\eta)^2]=N_{ij}(1-\eta^2)$,

$$N_{ij} = \underset{\mathrm{I}}{N_{ij}[\eta^2}+\underset{\mathrm{II}}{(1-\eta)^2}+\underset{\mathrm{III}}{2\eta(1-\eta)]}$$

It is therefore helpful to visualize three types of interactions. The first type (I) occurs when both i and j interact according to their oriented surfaces. The second type (II) occurs when both i and j interact according to their non-oriented surfaces. The third type (III) occurs when i and j interact such that i (or j) exhibits its oriented surface for interaction while j (or i) exhibits its non-oriented surface for interaction. Only the first type contributes to the oriented interactions.

The actual (non-random) number of oriented $i-j$ interactions differs appreciably from $N_{ij}\eta^2$ because of the competition between the energetic effect and the entropic effect. However, it is not necessary to calculate this actual number of oriented interactions when we have the correct expression for the Helmholtz energy of mixing. The secondary lattice is an Ising lattice. The reduced interaction parameter of this secondary lattice is $\delta\tilde{\varepsilon}=\delta\varepsilon/kT$, where $\delta\varepsilon$ is the additional (positive) energy responsible for the oriented interaction for each $i-j$ pair . The oriented interactions contribute to the Helmholtz energy of mixing. This contribution (ΔA^h) is obtained from Eq.(10) for the Ising lattice with two changes; first, x is replaced by η, and second, we add the additional energy of the reference state,

$$\Delta A^h = N_l kT[\eta\ln\eta+(1-\eta)\ln(1-\eta)+z\delta\tilde{\varepsilon}\eta(1-\eta)/2-c_2z(\delta\tilde{\varepsilon})^2\eta^2(1-\eta)^2/4-c_{10}z(\delta\tilde{\varepsilon})^{10}\eta^{10}(1-\eta)^{10}-z\eta\delta\tilde{\varepsilon}/2]$$

$$= N_l kT[\eta\ln\eta+(1-\eta)\ln(1-\eta)-z\delta\tilde{\varepsilon}\eta^2/2-c_2z(\delta\tilde{\varepsilon})^2\eta^2(1-\eta)^2/4-c_{10}z(\delta\tilde{\varepsilon})^{10}\eta^{10}(1-\eta)^{10}] \tag{18}$$

The first two terms on the right hand side account for the Flory-Huggins entropy that arises from mixing $N_l\eta$ sites with $N_l(1-\eta)$ sites. The term $-z\eta\delta\tilde{\varepsilon}/2$ accounts for the energy of the reference state where all the sites in the lattice are responsible for oriented interactions. The contribution of the other reference state (where all the sites in the lattice can not participate in oriented interactions) is zero. Constants c_2 and c_{10} satisfy Eq.(11).

For one $i-j$ pair, the additional Helmholtz energy is,

$$\Delta A_{ij}^h/N_{ij} = 2\Delta A_{ij}^h/zN_l$$

$$= (2kT/z)[\eta\ln\eta+(1-\eta)\ln(1-\eta)-z\delta\tilde{\varepsilon}\eta^2/2-c_2z(\delta\tilde{\varepsilon})^2\eta^2(1-\eta)^2/4-c_{10}z(\delta\tilde{\varepsilon})^{10}\eta^{10}(1-\eta)^{10}] \tag{19}$$

Calculated results are insensitive to η because it is coupled with the additional energy $\delta\varepsilon$. The contribution of one $i-j$ pair of oriented interactions to the partition function is $\exp(\Delta A_{ij}^h/N_{ij}kT)$. Therefore, if oriented interactions occur in 1-2 pairs, Eq.(5) becomes

$$Q = \sum_{N_{12}} g(N_1,N_2,N_{12})(\exp\frac{\varepsilon_{11}}{kT})^{N_{11}}(\exp\frac{\varepsilon_{22}}{kT})^{N_{22}}(\exp\frac{\varepsilon_{12}-\Delta A_{12}^{h}/N_{12}}{kT})^{N_{12}} \tag{20}$$

If oriented interactions occur in 1-1 pairs, the corresponding equation is

$$Q = \sum_{N_{12}} g(N_1,N_2,N_{12})(\exp\frac{\varepsilon_{11}-\Delta A_{11}^{h}/N_{11}}{kT})^{N_{11}}(\exp\frac{\varepsilon_{22}}{kT})^{N_{22}}(\exp\frac{\varepsilon_{12}}{kT})^{N_{12}} \tag{21}$$

If oriented interactions occur in 2-2 pairs, we obtain an equation similar to Eq.(21) by interchanging subscripts 1 and 2.

The secondary-lattice conrtibution is a perturbation to a fixed reference system which is given by the primary lattice, Eq.(12). Eqs.(20) and (21) give the total partition function which includes both reference and perturbation contributions. The general equation for the Helmholtz energy of mixing, Eq.(12), follows from Eq.(5). Eq.(21) and Eq.(22) also follow from Eq.(5). To account for oriented interactions in Models I, II and III, we use Eq.(5) but we must replace ε_{12} by $\varepsilon_{12}-\Delta A_{12}^{h}/N_{12}$, or we must replace ε_{11} or ε_{22} by $\varepsilon_{11}-\Delta A_{11}^{h}/N_{11}$ or $\varepsilon_{22}-\Delta A_{22}^{h}/N_{22}$. Following the definition of $\tilde{\varepsilon}$ in Eq.(8), we replace $\tilde{\varepsilon}$ by $\tilde{\varepsilon}+2\Delta A_{12}^{h}/N_{12}kT$ in Eqs.(12-16) if oriented interactions occur in 1-2 pairs. If oriented interactions occurs in 1-1 or 2-2 pairs, $\tilde{\varepsilon}$ is replaced by $\tilde{\varepsilon}-\Delta A_{11}^{h}/N_{11}kT$ or $\tilde{\varepsilon}-\Delta A_{22}^{h}/N_{22}kT$ in those equations. We call this double-lattice theory Model IV; it has three different versions: Model IV(I) when using Eq.(13); Model IV(II) when using Eq.(15); Model IV(III) when using Eq.(16).

LIQUID-LIQUID EQUILIBRIA CALCULATIONS

For liquid-liquid equilibrium calculations, we require the coordinates of the critical point. We find these coordinates using

$$\frac{\partial^2(\Delta A/N_r kT)}{\partial\Phi_2^2} = 0$$

which leads to

$$\frac{\partial^2(\Delta A/N_r kT)}{\partial\Phi_2^2} = \frac{1}{r_1\Phi_1}+\frac{1}{r_2\Phi_2}+\sum_m\sum_n a_{mn}[[m(m-1)\Phi_1^{m-2}\Phi_2^n-2mn\Phi_1^{m-1}\Phi_2^{n-1}+n(n-1)\Phi_1^m\Phi_2^{n-2}] \tag{22}$$

and

$$\frac{\partial^3(\Delta A/N_r kT)}{\partial\Phi_2^3} = 0$$

which leads to

$$\frac{\partial^3(\Delta A/N_r kT)}{\partial\Phi_2^3} = \frac{1}{r_1\Phi_1^2}-\frac{1}{r_2\Phi_2^2}+\sum_m\sum_n a_{mn}[[-m(m-1)(m-2)\Phi_1^{m-3}\Phi_2^n$$

$$+3mn(m-1)\Phi_1^{m-2}\Phi_2^{n-1}-3mn(n-1)\Phi_1^{m-1}\Phi_2^{n-2}+n(n-1)(n-2)\Phi_1^m\Phi_2^{n-3} \tag{23}$$

Using the experimental upper (or lower) critical coordinates, Equations (22) and (23) are solved to yield the energy and size parameters ε/k and r_2. (r_1=1.) If there are two critical points (upper and lower) we use a different procedure, as discussed later.

For calculating the binary coexistence curve, we need chemical potentials for components 1 and 2. They are found from

$$\mu_1-\mu_1^o = \frac{\partial \Delta A}{\partial N_1}$$

$$\mu_1-\mu_1^o = kT[\ln\Phi_1+\Phi_2(1-\frac{r_1}{r_2})+r_1\sum_m\sum_n a_{mn}(m\Phi_1^{m-1}\Phi_2^{n+1}+(1-n)\Phi_1^m\Phi_2^n)] \tag{24}$$

$$\mu_2-\mu_2^o = \frac{\partial \Delta A}{\partial N_2}$$

$$\mu_2-\mu_2^o = kT[\ln\Phi_2+\Phi_1(1-\frac{r_2}{r_1})+r_2\sum_m\sum_n a_{mn}(n\Phi_1^{m+1}\Phi_2^{n-1}+(1-m)\Phi_1^m\Phi_2^n)] \tag{25}$$

Superscript "o" refers to the standard state (pure close-packed liquid at system temperature T).

1. Results from Model I, II, III and Flory-Huggins Theory

To make a fair comparison, we apply Eqs.(22) and (23) to the same experimental critical coordinates to obtain two parameters ε/k and r_2 (r_1=1) ; we then calculate the coexistence curves using these parameters. Figures 4,5 and 6 show results for the binary systems: pentanol/phenol; 2,2′-dichloro-diethylether/2,2,4-trimethylpentane; and water/nitrile-3-methoxypropanoic acid . Models I, II and III indicate remarkable improvements when compared with Flory-Huggins theory. The calculated coexistence curves are more flat near the critical points and are closer to experiment. They are generally wider than those obtained from Flory-Huggins theory. Table 1 shows results for a variety of systems including some strong polar and hydrogen-bonding systems. For altogether 28 systems, the average RMSx are 0.0443,0.0452 and 0.0508 for Models I, II and III, respectively, while that for Flory-Huggins theory is 0.1017. The more complicated Model III does not behave better than the other two simpler models. In some cases, the simplest model I is good enough to describe the coexistence curves. However, for systems containing water, Model II is better.

2. Results for Model IV

For hydrogen-bonding systems or for systems whose components differ appreciably in molecular size, Models I, II and III always yield a more narrow coexistence curve. For these cases, we have to use Model IV to obtain a satisfactory fit.

For most of these systems, we set c_2=1.074 and c_{10}=0. The results are not sensitive to η. It can be arbitrarily set to some reasonable value such as 0.3 or 0.5. The only additional adjustable parameter is $\delta\varepsilon/k$, the extra energy contributed by the oriented interactions which is obtained from data for one tie line. Figures 7 and 8 show the results for binaries methyl-cyclohexane/perfluorotributylamine and furfural/docosane. Using Model IV, the coexistence curves can be reproduced much better than those obtained using Models I, II, III. Table 2 shows RMSx for some binaries using Model IV .

For systems having closed miscibility loops with both UCST and LCST, c_{10} cannot be set to zero; c_{10} or c_2 must be adjusted to obtain a good fit with the restraint shown by Eq.(11). In these cases, altogether 4 parameters are needed. Besides ε/k and r_2 obtained

from one critical point, we have to use another two, viz., $\delta\varepsilon/k$ for special interactions and c_{10}. They can be obtained by fitting another set of experimental (upper or lower) critical coordinates and one tie line giving the equilibrium compositions for a pair of conjugated phases. If the critical compositions for upper and lower critical points differ appreciably, then r_2 obtained from LCST will differ from that obtained from UCST. In this case, we use a linear relation to calculate r_2 at temperatures between UCST and LCST. Figures 9 and 10 show results for binaries water/nicotine and water/2-butoxyethanol. Additional examples are given in Table 2.

DISCUSSIONS AND CONCLUSIONS

The successful description of coexistence curves by Models I, II and III, especially near the critical consolute points, has led us to the conclusion that, in modified form, the Ising lattice as well as the Flory-Huggins lattice can provide good representations of liquid-liquid equilibria for fluid mixtures. The deficiency of Flory-Huggins theory does not lie in the lattice model but in the approximations used to obtain an expression for the Helmholtz energy of mixing. Once the Helmholtz energy of mixing is expressed correctly, as tested by the accurate results of spontaneous magnetisation of the Ising model, the liquid-liquid phase behavior of mixtures can be reproduced well. This result was first recognized by Widom (1967) and Wheeler (1975). They used directly Scesney's Padé-approximant coefficients for spontaneous magnetization. However, the method they used is too complicated for engineering calculations. Low-temperature and high-temperature expansions for partition functions may appear to provide an attractive choice, because the Helmholtz energy of mixing is easily obtained . However, the expansions converge very slowly; without the Padé technique, reliable results cannot be obtained. Freed et al give us new impetus because their results are comparatively simpler although still too complicated for engineering calculations. The present work suggests that, after minor empirical revision , Freed's results are useful for describing the phase behavior of strongly nonideal binary fluid mixtures.

In our calculations, arbitrarily setting r_1=1 is not an optimum choice. Reasonable values of r for various substances need further investigation. In databooks, such as those compiled by Sorensen et al (1979), we find recommended values of r for various substances obtained from other models. These r values are probably not suitable for the present work. In most cases, they cannot fit the observed critical points, probably because the Flory-Huggins model is designed for flexible chain molecules. However, for most small molecules, a flexible chain gives only a very rough approximation.

For mixtures with oriented interactions, double-lattice Model IV is particularly successful. For those having a closed miscibility loop, we have to adopt c_{10} or c_2 as an additional adjustable parameter, while the other one is fixed according to Eq.(11). Incorprating c_2 and c_{10} makes the model more flexible. Adopting c_2 or c_{10} alone can yield good results for the coexistence curve for an Ising model. However, it is still uncertain what kind of expression is more suitable for the Helmholtz energy of mixing remote from the phase splitting boundary. This is why we should adjust c_2 or c_{10} empirically.

The models presented in this paper are for fluids of high density near close packing. They can serve as a basis for constructing models for fluid mixtures that are subject to density change; for such mixtures, it will be necessary to add free-volume corrections

(Prausnitz et al, 1986). However, extension to polymer solutions is straightforward in principle. Further work along these lines will be presented in future papers.

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76F0098. Additional funding was provided by E. I. du Pont de Nemours & Company, Montedipe s. r. l., Shell (Amsterdam), Norsolor Corp., and the Donors of the Petroleum Research Fund administered by the American Chemical Society. Ying Hu and Honglai Liu are grateful to the Chinese National Science Foundation and Chinese National Council of Education for financial support.

LIST OF SYMBOLS

latin

a coefficent
A Helmholtz function
c constant
E energy of system
g combinatorial factor in Eqs(5,20,21)
g_{12} binary interaction parameter in Eq.(1)
k Boltzmann constant
N_i number of molecules of component i
N_r number of sites
N_l number of sites
N_{ij} number of nearest (nonbonded) neighbors of segment i and j
Q canonical partition function
r_i number of lattice sites occupied by molecule i
$RMSx$ standard deviation of compositions
T temperature
V volume
x mole fraction
z coordination number

greek

ε interaction energy
$\tilde{\varepsilon}$ reduced interaction energy
η fraction of surface available for specific interaction
Φ volume fraction

REFERENCES

Anderson, G. R. and Wheeler, J. C., 1978, Theory of lower critical solution points in aqueous mixtures, J. Chem. Phys., 69: 3403-3413.

Barker, J. A. and Fock, W., 1953, Theory of upper and lower critical solution temperatures, Disc. Fara. Soc., 15: 188-195.

Bawendi, M. G. and Freed, K. F., 1988, Systematic corrections to Flory-Huggins theory: Polymer-solvent-void systems and binary blend-void systems, J. Chem. Phys., 88: 2741-2756.

Bawendi, M. G., Freed, K. F., Mohanty, U., 1987, A lattice field theory for polymer systems with nearest-neighbor interaction energies, J. Chem. Phys., 87: 5534-5540.

de Pablo, J. J. and Prausnitz, J. M., 1989, Liquid-liquid equilibria for binary and ternary systems including the critical region. Transformation to non-classical coordinates, Fluid Phase Equilibria, 50: 101-131.

de Pablo, J. J. and Prausnitz, J. M., 1990, Thermodynamics of LLE including the critical region. Transformation to non-classical coordinates using revised scaling, Fluid Phase Equilibria, 59:1-14.

Fisher, M. E., Rept. Prog. Phys., 1967, The theory of equilibrium critical phenomena, 30: 615-730.

Flory, P. J., 1941, 1942, Thermodynamics of high ppolymer solutions, J. Chem. Phys., 9: 660-661, 10: 51-61.

Fox, J., 1983, Method for construction of nonclassical equation of state, Fluid Phase Equilibria, 14: 45-53.

Freed, K. F., 1985, New lattice model for interacting, avoiding polymers with controlled length distribution, J. Phys. A: Math. Gen., 18: 871-887.

Heller, P., 1967, Experimental investigation of critical phenomena, Rept. Prog. Phys., 30: 731-826.

Hirschfelder, J., Stevenson, D., Erying, H., 1937, A theory of liquid structure, J. Chem. Phys., 5: 896-912.

Huggins, M. L., 1941, 1942, Solutions of long chain compounds, J. Chem. Phys., 9: 440; Some properties of long chain compounds, J. Phys. Chem., 46: 151-158.

Kleintjens, L. A. and Koningsveld, R., 1980, Liquid-liquid phase separation in multicomponent polymer systems. X. Concentration dependence of the pair-interaction parameter in the system cyclohexane-polystyrene, Colloid & Polymer Sci., 258: 711-718.

Koningsveld, R. and Kleintjens, L. A., 1971, Liquid-liquid phase separation in multicomponent polymer systems. XIX. Mean-field lattice-gas treatment of the system n-alkane/linear polyethylene, Macromolecules, 4: 637-641.

Orifino, T. A. and Flory, P. J., 1957, Relationship of the second virial coefficient to polymer chain dimensions and interaction parameters, J. Chem. Phys., 26: 1067-1076.

Prange, M. M., Hooper, H. H., Prausnitz, J. M., 1989, Thermodynamics of Aqueous Systems Containing Hydrophilic Polymers or Gels, A.I.Ch.E.J., 35:803-813.

Prausnitz, J. M., Lichtenthaler, R. N., Azevedo, E. G., 1986, "Molecular Thermodynamics of Fluid-Phase Equilibria", p.569, Prentice Hall.

Scesney, P. E., 1970, Mobile-electron Ising ferromagnet, Phys. Rev., B1: 2274-2288.

Sengers, T. V. and Sengers, J. M. H. L., 1978, Critical phenomena in classical fluids, in "Progress in Liquid Physics", chap. 4, ed. C. A. Croxton, Wiley.

Sorensen, J. M. and Arlt, W., 1979, Liquid-Liquid Equilibrium Data Collection, Vol. V., DECHEMA.

Sykes, M. F., Essan, J. W., Gaunt, J. S., 1965, Derivation of low-temperature expansions for the Ising model of a ferromagnet and an antiferromagnet, J. Math. Phys., 6: 283-298.

Wheeler, J. C., 1975, "Exactly soluble" two-component lattice solution with upper and lower critical solution temperatures, J. Chem. Phys., 62: 433-439.

Widom, B., 1967, Plait points in two- and three-component liquid mixtures, J. Chem. Phys., 46: 3324-3333.

FIGURE CAPTIONS

Figure 1. Comparison of coexistence curves calculated from various models with those from Scesney's accurate results.

Figure 2. Effect of inserting empirical coefficient.
(a) c_2, (b) c_{10}, (c) c_2 and c_{10} with Eq.(3).

Figure 3. A lattice representation of special interactions between molecules of components i and j.

Figure 4. Coexistence curves for pentane(1)/phenol(2) binary.
FH: r_1=1, r_2=1.240, ε/k=198.04K
I: r_1=1, r_2=1.089, ε/k=269.45K
II: r_1=1, r_2=1.535, ε/k=244.18K
III: r_1=1, r_2=1.458, ε/k=240.97K

Figure 5. Coexistence curves for 22'-dichlorodiethylether(1)/2,2,4-trimethylpentane(2) binary.
FH: r_1=1, r_2=1.035, ε/k=190.91K
I: r_1=1, r_2=1.008, ε/k=251.91K
II: r_1=1, r_2=1.194, ε/k=236.14K
III: r_1=1, r_2=1.173, ε/k=236.14K

Figure 6. Coexistence curves for water(1)/nitrile-3-methoxypropanoic acid(2) binary.
FH: r_1=1, r_2=2.197, ε/k=145.54K
I: r_1=1, r_2=1.812, ε/k=182.65K
II: r_1=1, r_2=2.872, ε/k=192.76K
III: r_1=1, r_2=2.520, ε/k=174.27K

Figure 7. Coexistence curves for methylcyclohexane(1)/perfluoro-tributylamine(2) binary.
FH: r_1=1, r_2=2.629, ε/k=161.82K
III: r_1=1, r_2=2.971, ε/k=191.96K
IV: r_1=1, r_2=2.971, ε/k=−203.35K, $\delta\varepsilon_{22}/k$=2239.23K, η=0.3

Figure 8. Coexistence curves for furfural(1)/docosane(2) binary.
FH: r_1=1, r_2=2.687, ε/k=180.09K
II: r_1=1, r_2=3.496, ε/k=246.63K
IV: r_1=1, r_2=3.496, ε/k=−97.81K, $\delta\varepsilon_{11}/k$=2137.49K, η=0.3

Figure 9. Coexistence curves for water(1)/nicotine(2) binary.
IV(II): r_1=1, r_2=6.991, ε/k=959.09K,
$\delta\varepsilon_{12}/k$=1520.56K, η=0.3, c_{10}=0.0591

Figure 10. Coexistence curves for water(1)/2-butoxyethanol(2) binary.
IV(I): r_1=1, r_2=5.2568, ε/k=457.91K,
$\delta\varepsilon_{12}/k$=590.91K, η=0.3, c_{10}=646.69

Table 1. Results of LLE Calculations *

No.	component 1	component 2	100RMSx			
			FH	I	II	III
1	pentane	phenol	8.19	3.75	1.97	2.53
2	2-propanone	glycerol	6.24	2.53	2.12	2.23
3	methylcyclopentane	furfural	10.32	2.69	2.79	2.97
4	2,2'-dichlorodiethylether	2,2,4-trimethylpentane	11.25	1.85	3.73	3.68
5	2-methyl-2-butene	aniline	9.26	2.80	3.56	3.75
6	bezene	1,3-dihydroxybenzene	8.12	4.73	2.82	3.58
7	furfural	methylcyclohexane	11.76	2.60	4.20	4.12
8	water	dimethoxymethane	4.18	4.00	4.45	3.88
9	water	4-hydroxytoluene	4.45	3.71	5.83	3.21
10	2,2'-dichlorodiethylether	octane	13.07	3.06	4.17	4.19
11	nitromethane	cyclohexane	10.90	3.80	4.27	4.35
12	nitromethane	2-methyl-2-pentent	10.50	3.67	4.75	5.01
13	nitromethane	glycerol	10.54	3.36	4.19	4.14
14	cyclohexane	furfural	11.27	3.95	4.42	4.72
15	hexane	3-aminotoluene	10.61	3.95	4.90	5.26
16	heptane	diethylesteroxalic acid	10.56	4.00	5.05	5.33
17	nitromethane	2-methylpentane	13.20	3.52	5.35	5.30
18	glycerol	3-methyl-1-butanol	9.98	5.27	4.72	5.41
19	glycerol	acetophenone	11.92	4.53	5.96	6.19
20	tetrachloromethane	perfluoroheptane	9.48	5.63	3.95	5.30
21	aniline	2,2,4-trimethylpentane	11.89	3.89	5.62	5.81
22	water	nitril-3-methoxypropanoic acid	8.50	6.05	3.71	5.15
23	furfural	heptane	12.15	3.85	6.59	6.61
24	water	benzoic acid	8.02	7.96	3.91	7.79
25	glycerol	2-hydroxybenzaldehyde	11.94	3.97	6.28	6.29
26	nitroethane	2,2,4-trimethylpentane	13.85	5.07	7.31	7.47
27	water	1-nitrosopiperidine	11.76	10.58	4.45	9.64
28	water	dinitrilepentanedioic acid	10.79	9.26	5.35	8.31

* experimental data from the compilation by Sorensen and Arlt (1979).

Table 2. Results of LLE calculations Using Model IV *

No.	component 1	component 2	100RMSx			
			FH	IV(I)	IV(II)	IV(III)
1	methanol	cyclohexane	11.50	2.74	4.14	4.03
2	phenol	octane	11.18	0.83	3.96	3.47
3	nitromethane	octanoic acid	9.10	3.41	1.50	1.92
4	cyclohexane	anhydride acetic acid	12.16	3.87	2.12	2.23
5	nitromethane	1,2-ethanediol	10.36	5.72	2.32	2.85
6	methylcyclohexane	perfluorotributylamine	13.53	2.67	1.92	1.64
7	pentane	tetrafluorobutanoatepentaerytritol	10.04	5.76	2.63	5.32
8	water	dinitrilehexanedioic acid	13.84	3.91	6.34	4.15
9	furfural	docosane	14.54	3.39	1.13	2.16
10	water	2,4-pentanedione	14.39	5.53	3.93	4.95
11	hexane	perfluorotributylamine	15.32	4.24	5.06	4.24
12	nitromethane	1-pentadecanol	17.93	3.71	4.39	3.43
#1	glycerol	3-aminotoluene	----	3.17	2.57	2.44
#2	water	2-propoxy-1-propanol	----	3.95	3.03	3.59
#3	water	4-methylpiperidine	----	2.61	2.81	2.80
#4	water	1-aza-cycloheptane	----	5.83	4.66	5.55
#5	water	1-propoxy-2-propanol	----	3.43	2.65	2.96
#6	glycerol	2-methoxyphenol	----	3.70	2.14	2.24
#7	water	2-butoxyethanol	----	0.98	0.98	0.96
#8	water	2,6-dimethylpyridine	----	2.67	2.02	2.41
#9	water	nicotine	----	3.46	2.50	3.19

* experimental data from the compilation by Sorensen and Arlt (1979).

systems with both LCST and UCST.

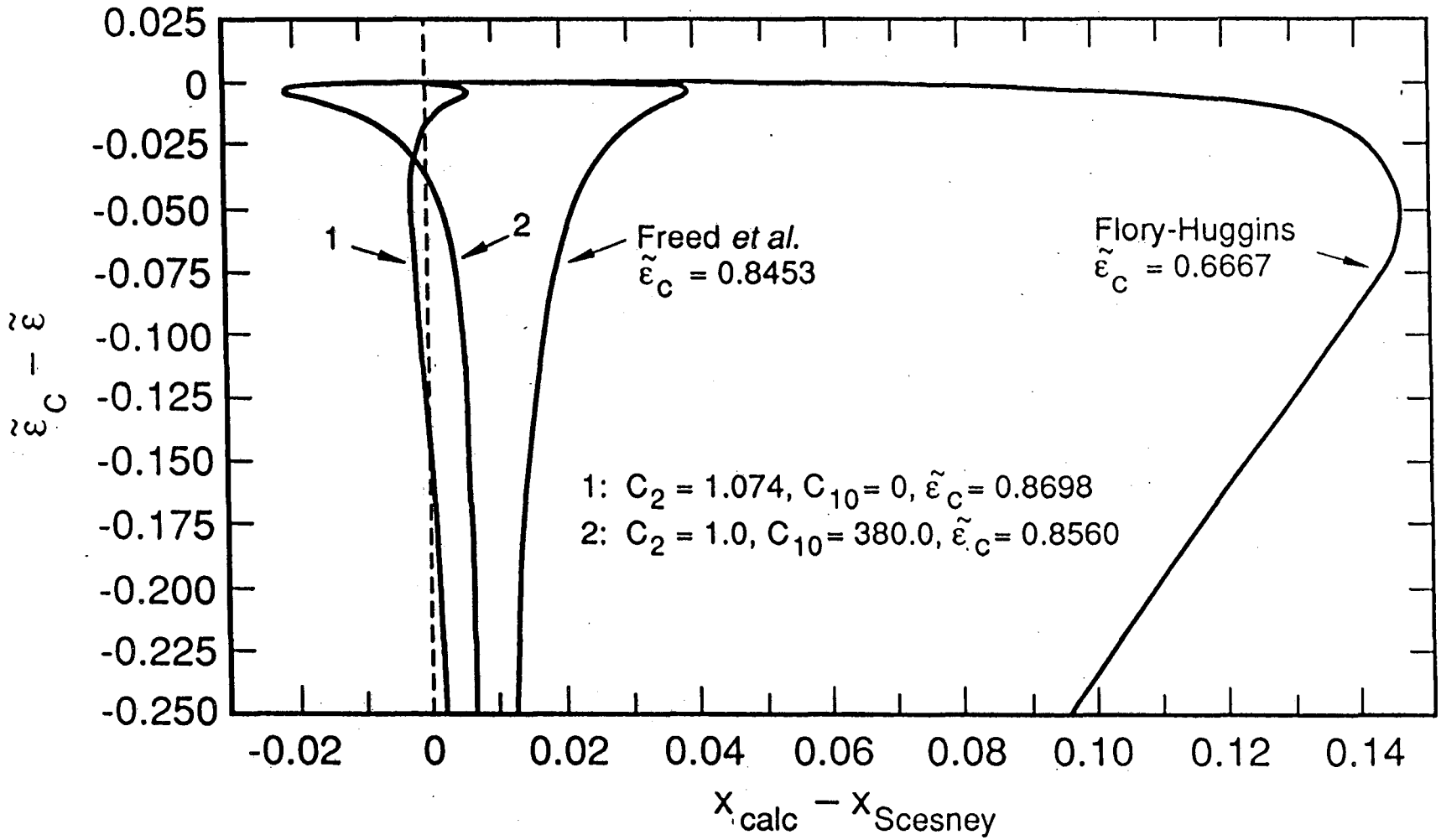
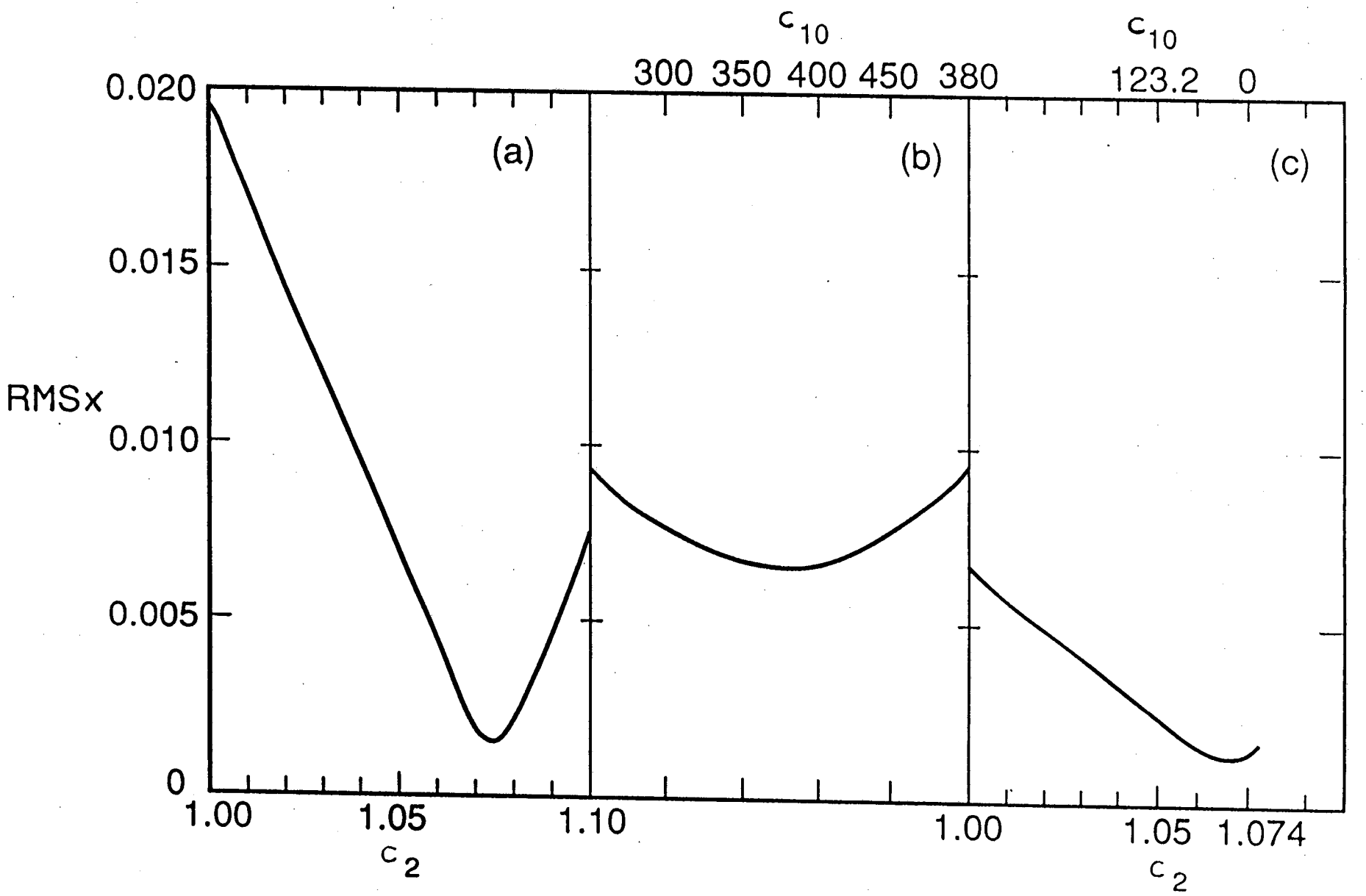

0.025
0
-0.025
-0.050
-0.075
-0.100
-0.125
-0.150
-0.175
-0.200
-0.225
-0.250
-0.02
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
$\tilde{\varepsilon}_c - \tilde{\varepsilon}$
$x_{calc} - x_{Scesney}$
1
2
Freed *et al.*
$\tilde{\varepsilon}_c = 0.8453$
Flory-Huggins
$\tilde{\varepsilon}_c = 0.6667$
1: $C_2 = 1.074$, $C_{10} = 0$, $\tilde{\varepsilon}_c = 0.8698$
2: $C_2 = 1.0$, $C_{10} = 380.0$, $\tilde{\varepsilon}_c = 0.8560$

Figure 1



Prausnitz/Ying-2(73190)

Figure 2

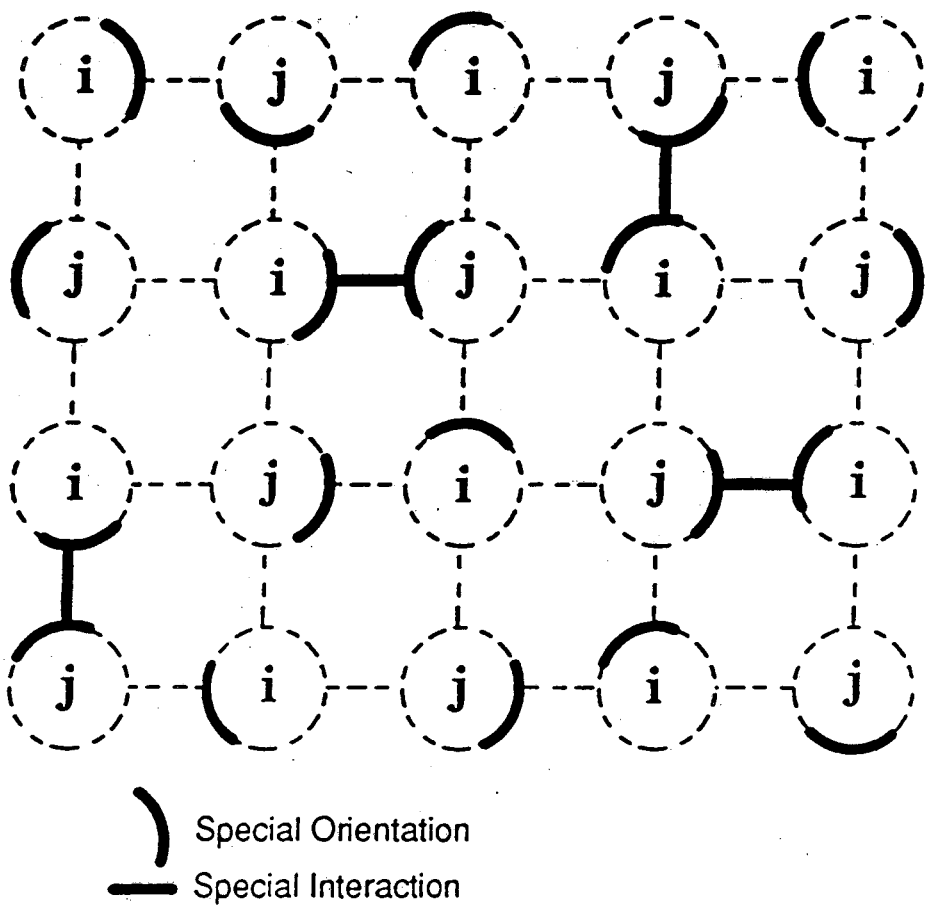

i
j
i
j
i
j
i
j
i
j
i
j
i
j
i
j
i
j
Special Orientation
Special Interaction

Figure 3

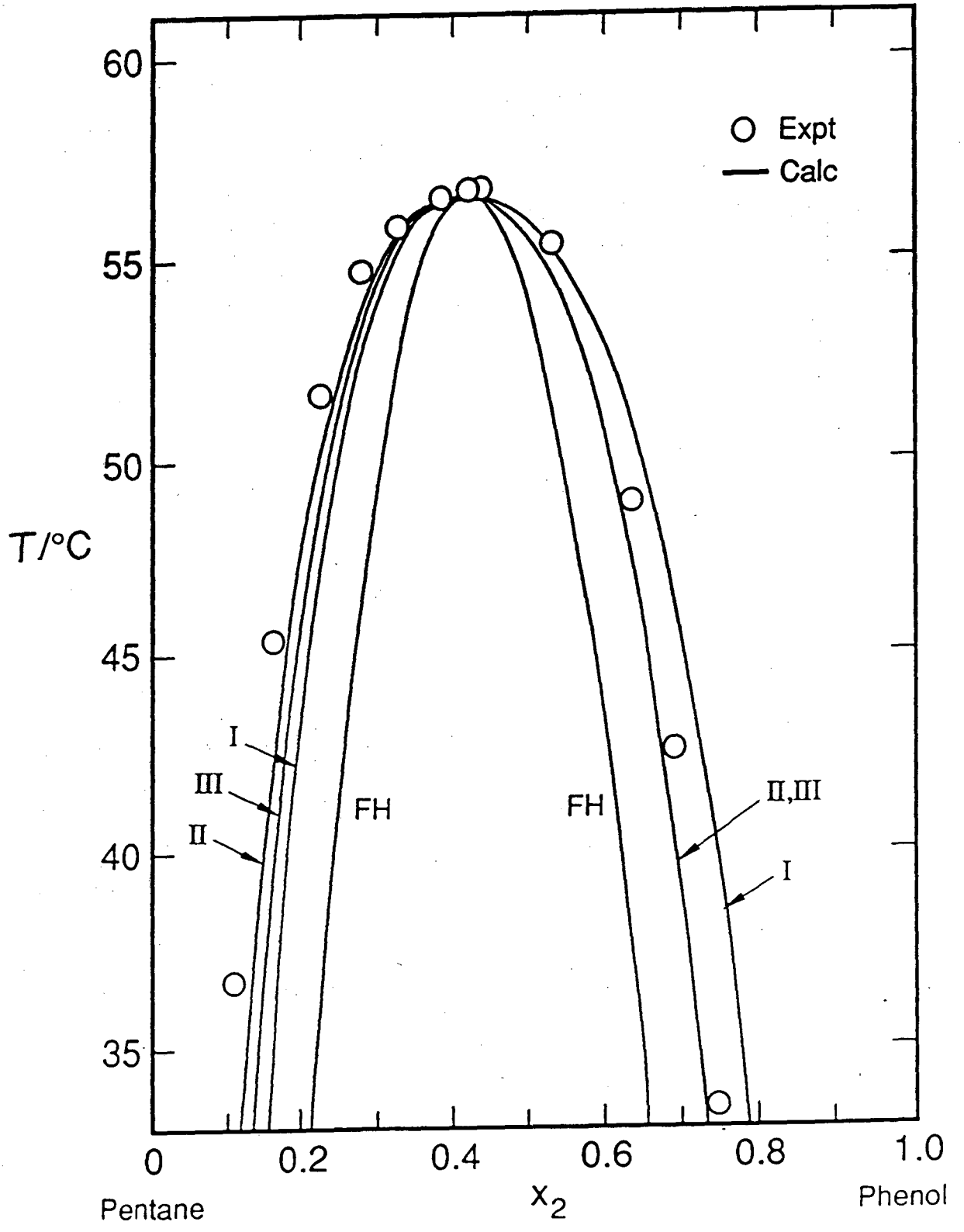

60
55
50
45
40
35
T/°C
Expt
Calc
I
III
II
FH
FH
II,III
I
0
0.2
0.4
0.6
0.8
1.0
Pentane
x_2
Phenol

Figure 4

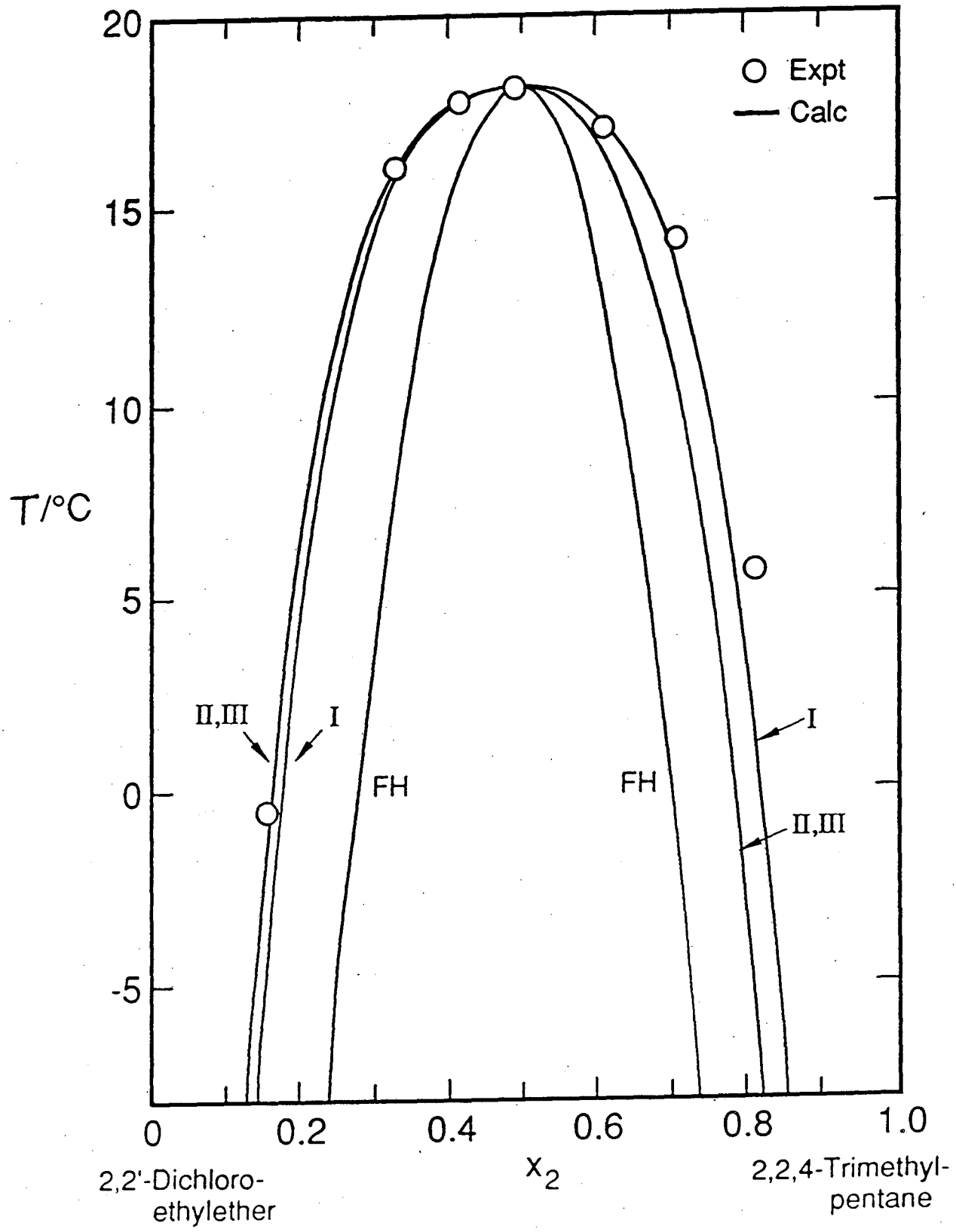

20
15
10
5
0
-5
T/°C
Expt
Calc
II,III
I
FH
FH
I
II,III
0
0.2
0.4
0.6
0.8
1.0
x_2
2,2'-Dichloro-
ethylether
2,2,4-Trimethyl-
pentane

Figure 5

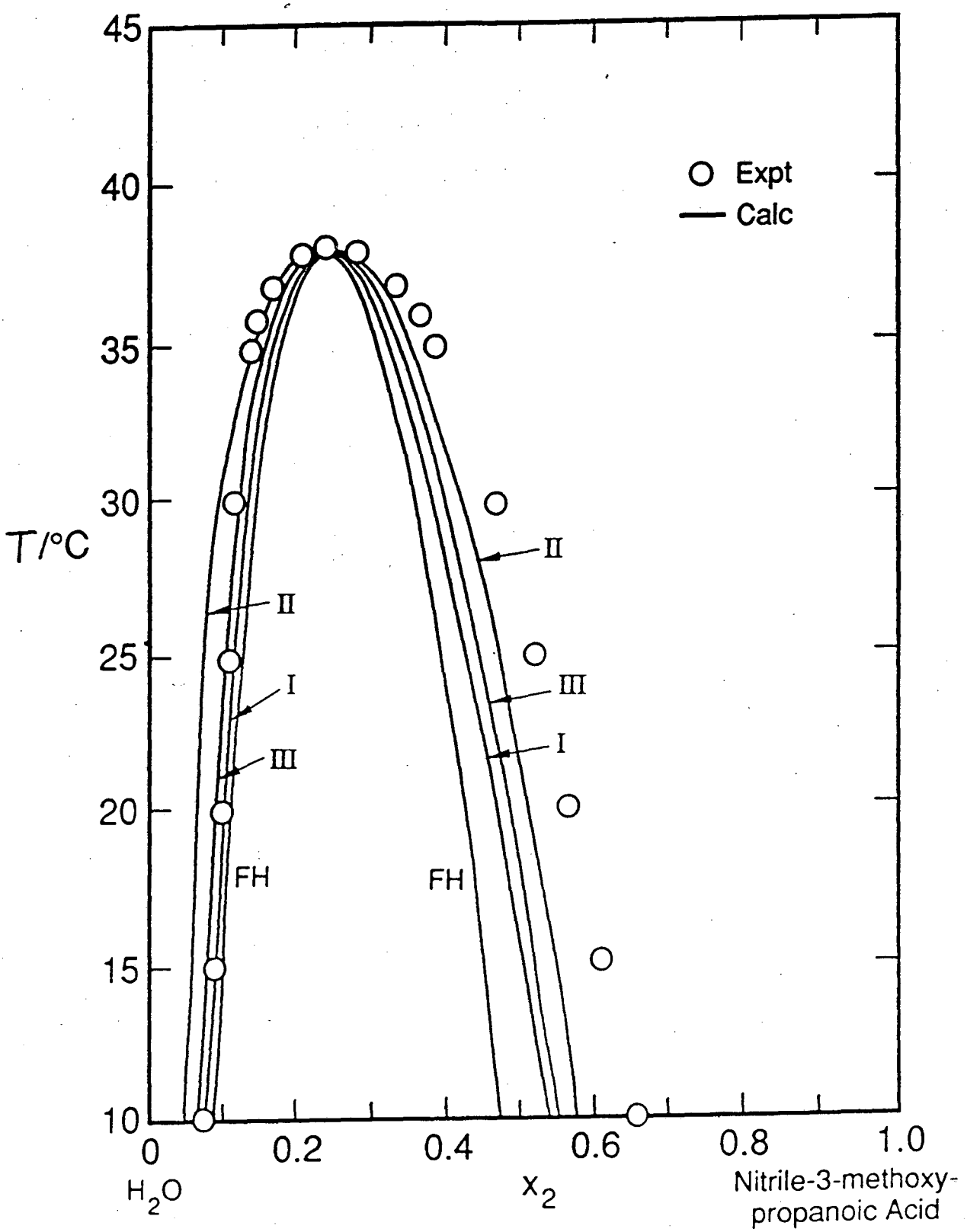

45
40
35
30
25
20
15
10
T/°C
Expt
Calc
II
II
I
III
III
I
FH
FH
0
0.2
0.4
0.6
0.8
1.0
H_2O
x_2
Nitrile-3-methoxy-
propanoic Acid

Figure 6

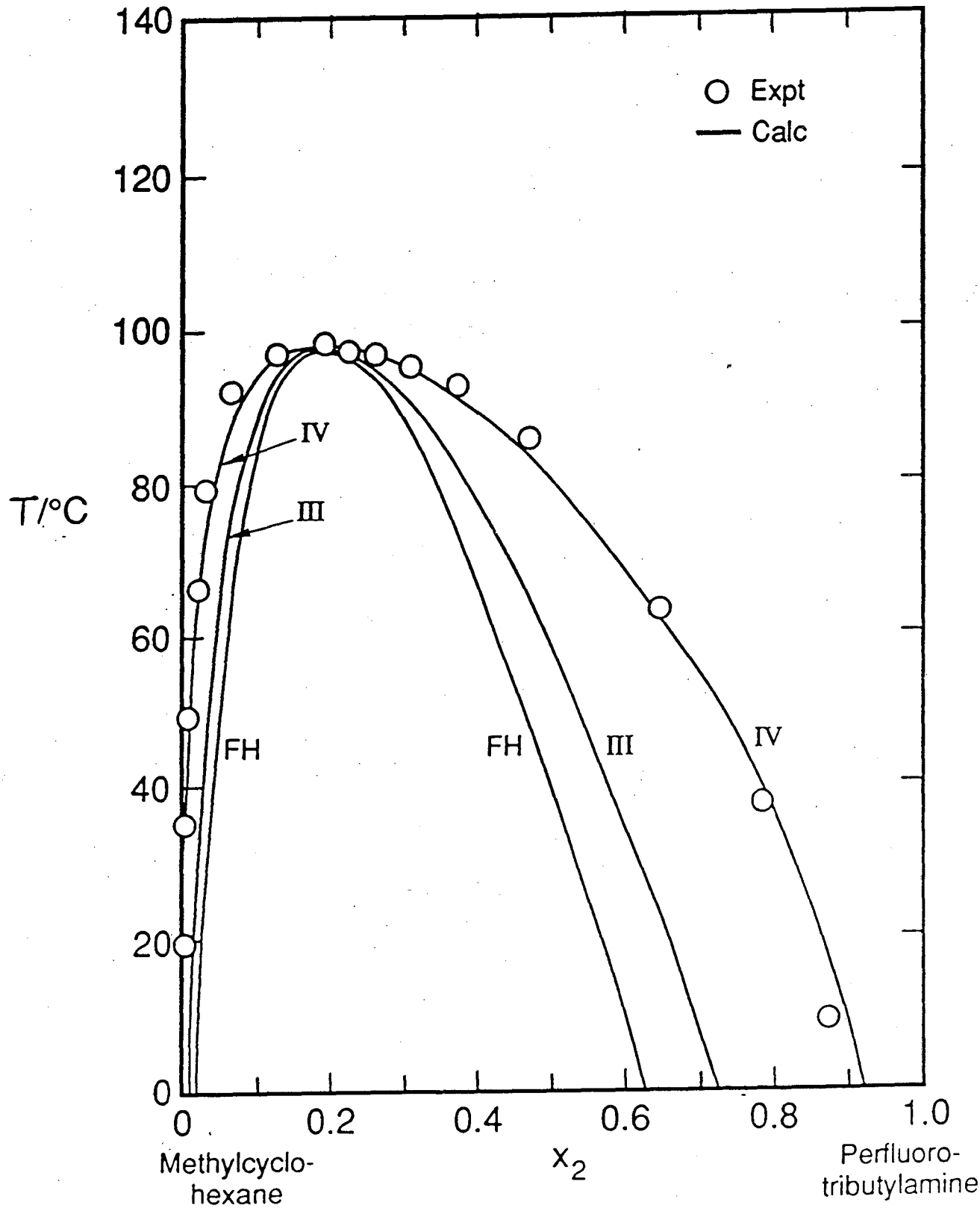

140
120
100
80
60
40
20
0
T/°C
Expt
Calc
IV
III
FH
FH
III
IV
0
0.2
0.4
0.6
0.8
1.0
Methylcyclo-
hexane
x_2
Perfluoro-
tributylamine

Figure 7

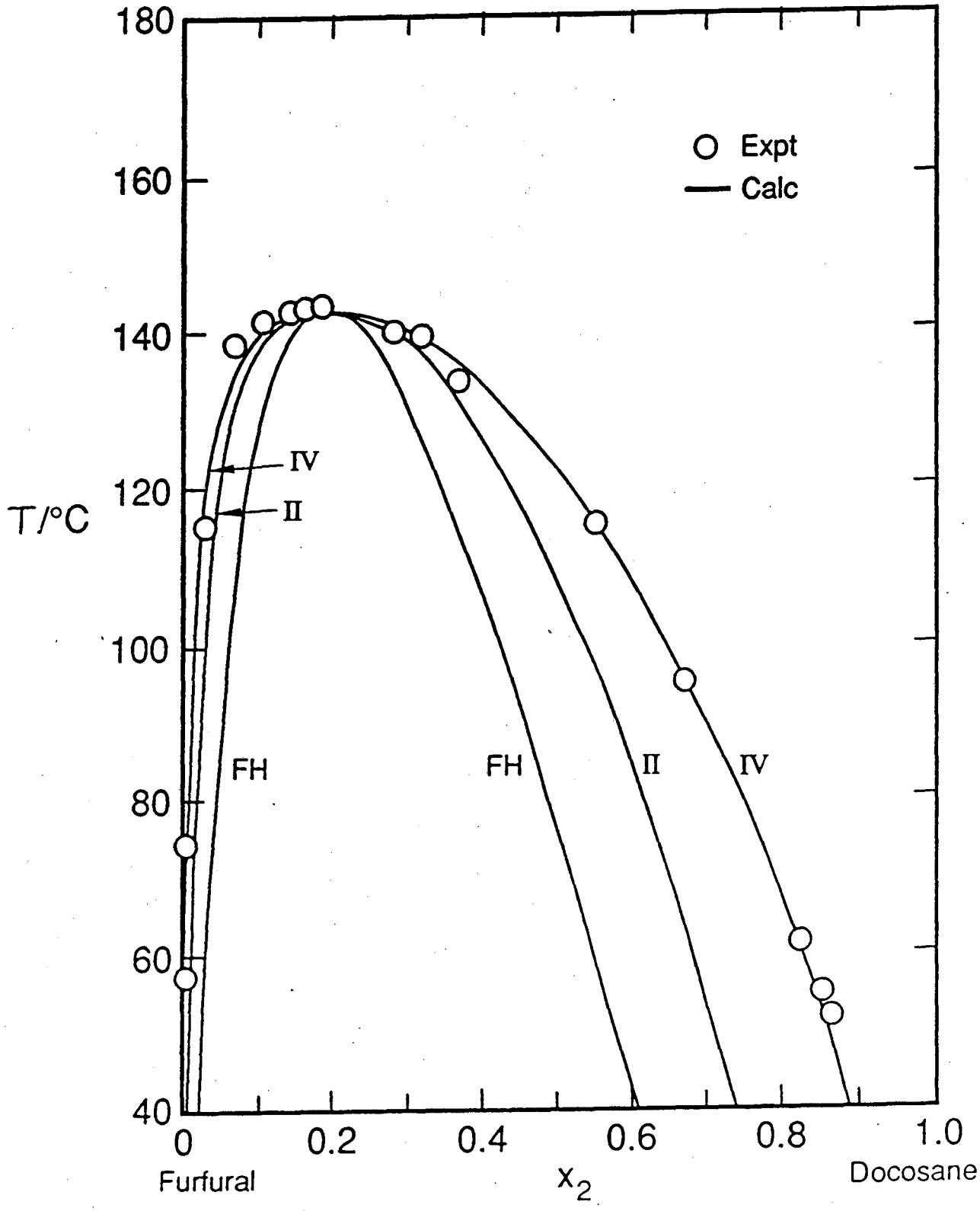

180
160
140
120
100
80
60
40
T/°C
Expt
Calc
IV
II
FH
FH
II
IV
0
0.2
0.4
0.6
0.8
1.0
Furfural
x_2
Docosane

Figure 8

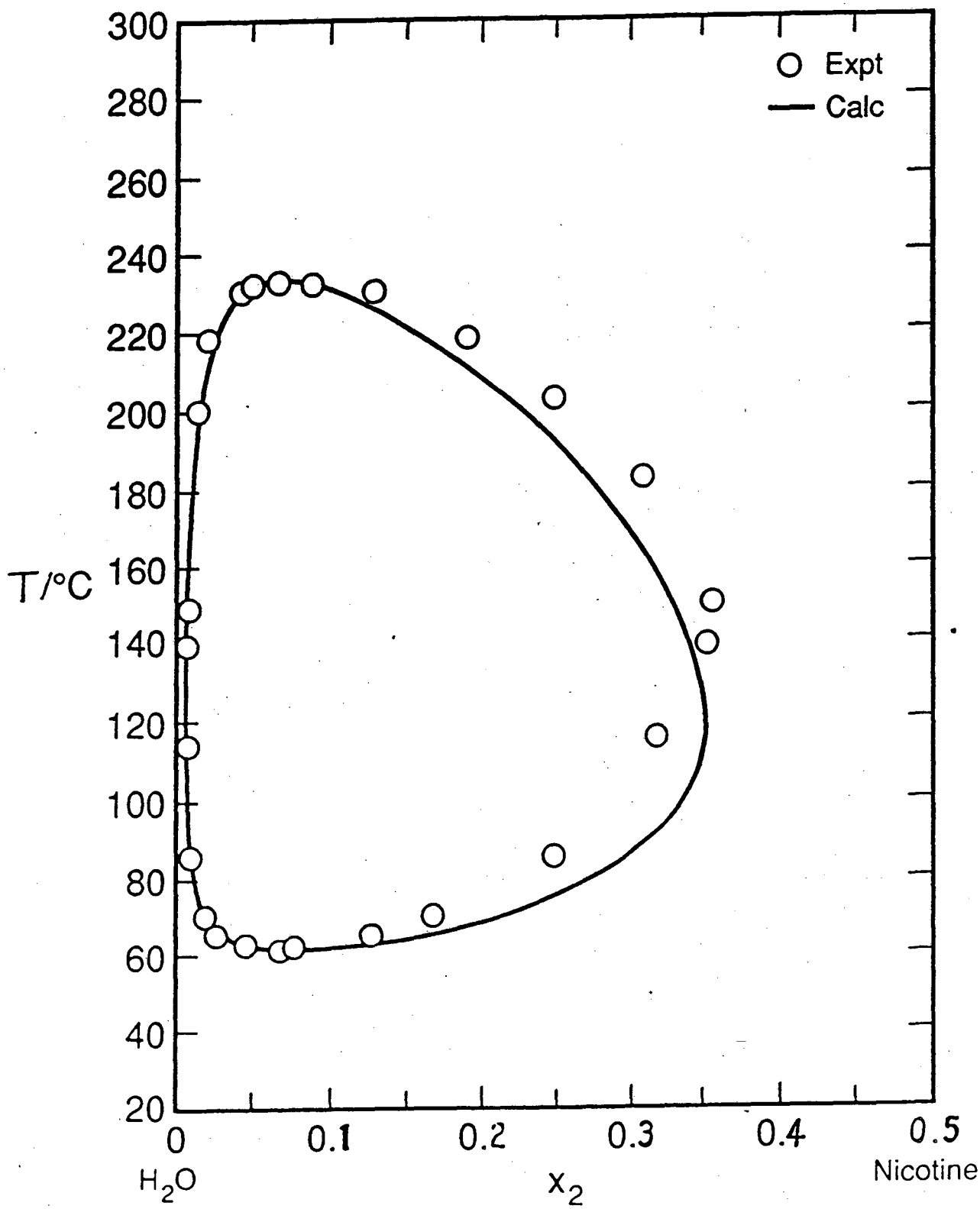

300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
T/°C
Expt
Calc
0
0.1
0.2
0.3
0.4
0.5
H_2O
x_2
Nicotine

Figure 9

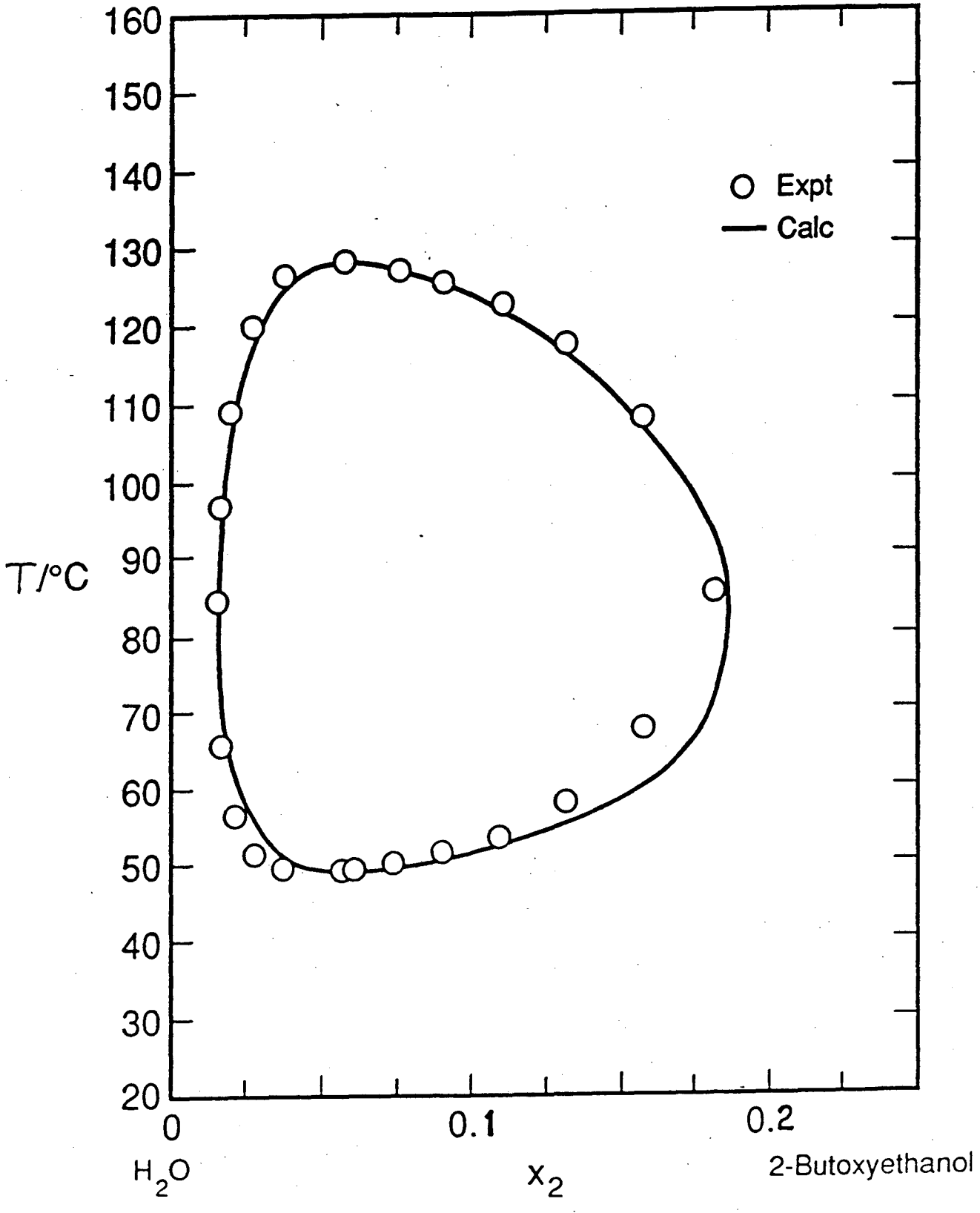

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
T/°C
Expt
Calc
0
0.1
0.2
H_2O
x_2
2-Butoxyethanol

Figure 10

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720