Lawrence Berkeley National Laboratory
Recent Work

Title

Vapor-liquid equilibria for mixtures of chain fluids near-to and far-from the critical region

Permalink

https://escholarship.org/uc/item/9bf8951t

Author

Jiang, J.

Publication Date

2000

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Vapor-Liquid Equilibria for Mixtures of Chain Fluids Near-To and Far-From the Critical Region

J. Jiang and J.M. Prausnitz

Chemical Sciences Division

DISCLAIMER

Vapor-Liquid Equilibria for Mixtures of Chain Fluids Near-to and Far-from the Critical Region

J. Jiang and J. M. Prausnitz

Department of Chemical Engineering

University of California

and

Chemical Sciences Division

Lawrence Berkeley National Laboratory

University of California

Berkeley, CA 94720, U.S.A.

January 2000

Vapor-Liquid Equilibria for Mixtures of Chain Fluids Near-to and Far-from the Critical Region

Jianwen Jiang and John M. Prausnitz

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

A recently-established crossover equation of state for pure chain fluids is extended to mixtures of chain fluids. Far from the critical region, where density fluctuations are small, it reduces to the classical equation of state. Near or at the critical point, the crossover equation of state incorporates contributions from long-wavelength density fluctuations. Using segment-segment parameters for pure components, and one cross parameter k_{12} for every binary pair as obtained from data remote from the critical region, this crossover equation of state gives vapor-liquid equilibria in good agreement with experiment for binary asymmetric mixtures of n-alkanes far-from, near-to and at the critical point.

Correspondence should be addressed to John M. Prausnitz.

Introduction

Critical conditions are sometimes encountered in some industrial operations, especially in production and subsequent processing of petroleum and natural gas. Near the critical region, retrograde condensation is often observed. For quantitative process calculations, we require an equation of state (EOS) for mixtures that is valid near-to and far-from critical conditions. An EOS that meets this requirement is called a crossover EOS. This work presents a crossover EOS for mixture of chain fluids.

To illustrate retrograde condensation, Figure 1 shows the pressure-temperature loci for a mixture at fixed composition. The solid line is the bubble-point curve and the dashed line is the dew-point curve; they join at critical point C (first recognized by Andrews in 1869) where the two phases become identical. Point C shows the limiting condition where the system can exist in two phases. Near the critical point, the density-dependent properties change dramatically with small changes in temperature or pressure. One century ago, Kuenen (1893, 1897) first observed isothermal retrograde condensation shown in line 1; isobaric retrograde vaporization, shown in line 2, was observed by Duhem (1896, 1901). The maximum pressure at point A is called cricondenbar or maxcondenbar, and the maximum temperature at point B is called cricondentherm or maxcondentherm (Sage et al., 1934). These points give the upper bounds where phase separation can take place. Quantitative understanding of these phase-equilibrium phenomena is useful for design of production, storage and transportation of fossil-fuel products.

Although extensive experimental studies have been reported (for a review, see Dohrn and Brunner, 1995), it has been difficult to develop a universal model to describe the thermodynamic properties and phase behavior of fluid mixtures at high pressures over a wide range of conditions including the critical region. Most previous studies are concerned with empirical or phenomenological correlations for vapor-liquid equilibria (VLE) (e.g., Chao and Seader, 1961; Dastur and Thodos, 1963; Stevens and Thodos, 1963; Van Horn and Kobayashi, 1968; Reid et al., 1987); these studies use any one of several popular EOS like RK (Redlich and Kwong, 1949), SRK (Soave, 1972) and PR (Peng and Robinson, 1976). These cubic EOS provide improvement over the original van der Waals EOS (van der Waals, 1873) through modifications of the attraction terms as reviewed by Yelash and Kraska (1999). It has long been recognized, however, that although these analytical EOS can describe fluid properties fairly well far away from the critical point, because they are mean-field-based, they fail to reproduce

the non-analytical, singular properties at the critical point and therefore give poor results in the critical region (Ma, 1976). Mean-field theories assume that the immediate environment of each particle in a fluid has the same composition and density as those of the bulk fluid. Mean-field theories neglect density fluctuations that become large near the critical point (Greer and Moldover, 1981; Sengers and Levelt-Sengers, 1986; Fisher, 1998). Levelt-Sengers (1999) gives a detailed historical review of the weaknesses and strengths of mean-field theories.

Although the inability of mean-field theories to describe critical behavior has been known for many years, a method for corrections became available only relatively recently. Taking long-range density fluctuations into account, scaling and crossover theory can correct mean-field theory. The crossover theory developed by Sengers and coworkers (Edison et al., 1998; Anisimov et al., 1999; Povodyrev et al., 1999), by Anisimov et al. (1995) and by Kiselev et al. (1998, 1999a, 1999b) incorporates a crossover from singular thermodynamic behavior at the critical point to regular thermodynamic behavior far away from the critical point. In this way, a common engineering EOS can be modified for use near the critical point and to yield correct critical behavior. However, the necessary modifications are far from trivial; the required calculations are complex and the physical meaning of the many required crossover parameters is not clear in terms of molecular properties.

The optimized random-phase approximation leads to hierarchical reference theory (HRT) (Parola and Reatto, 1984, 1985; Meroni et al., 1990). HRT can be considered as an exact reformulation of Ornstein-Zernike integral theory including density fluctuations at all length scales; it can also be taken as a liquid-state implementation of the renormalization-group (RG) theory. Although HRT has been successfully applied to Lennard-Jones fluids and to binary mixtures (Parola and Reatto, 1991; Pini et al., 1998c), reduction to practice is tedious. A thermodynamically self-consistent Ornstein-Zernike integral theory developed by Stell and coworkers (Pini et al., 1998a, b) provides thermodynamic properties, critical points and coexistence curves for a lattice gas and for a hard-core Yukawa fluid that compare well with computer simulations. But this integral theory, at present restricted to spherical molecules, has not been reduced to practice.

Finally, White and coworkers (White, 1992; White and Zhang, 1993, 1998) developed a global RG theory based on the Nobel-prize winning RG theory of Wilson (1971a, b, 1983). When extended beyond the range of the original RG theory, it can be successfully applied

beyond the critical region. The major advantage of White's work is that only a few parameters are required and these have a molecular basis.

Lue and Prausnitz (1998a,b) extended the accuracy and range of White's RG transformation through an improved Hamiltonian. Good representations of thermodynamic properties and phase equilibria were obtained for pure fluids and their binary mixtures using an analytical formulae for square-well (SW) model fluids (Tang and Lu, 1993, 1994, 1995). Tang (1998), and White and Zhang (1999) have applied White's theory to Lennard-Jones fluids. However, all of these publications are confined to fluids containing simple spherical molecules. Fornasiero et al. (1999) reported a limited attempt to apply White's theory to non-spherical molecules using a cubic EOS.

Based on the work of Lue and Prausnitz (1998a, b), Jiang and Prausnitz (1999a) developed a crossover EOS for pure chain fluids (EOSCF+RG) by incorporating contributions from long-wavelength density fluctuations using RG theory. Outside the critical region, the crossover EOSCF+RG reduces to a classical EOS for chain molecules (Hu et al., 1996, 1999; Liu and Hu, 1998; Jiang et al., 1998) equivalent to the SAFT equation (Chapman et al., 1990; Huang and Radosz, 1990, 1991); inside the critical region, it gives non-classical universal critical exponents. This crossover EOS has been used to determine the critical properties of mixtures (Jiang and Prausnitz, 1999b).

This work concerns vapor-liquid equilibria for mixtures of chain fluids. To illustrate applicability, we calculate VLE as well as critical properties and cricondertherms for asymmetric binary mixtures of n-alkane; we compare calculated and experimental results.

Theoretical Framework

For a mixture of chain fluids, we represent each molecule as a homosegmented chain with number density ρ_i, chain length m_i and segment diameter σ_i. Interaction between nonbonded chain segments is given by a square-well (SW) potential:

$$u_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij} \\ -\varepsilon_{ij} & \sigma_{ij} < r < \lambda_{ij}\sigma_{ij} \\ 0 & r > \lambda_{ij}\sigma_{ij} \end{cases} \tag{1}$$

where σ_{ij} is an additive hard-sphere diameter given by

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{2}$$

Parameters ε_{ij} and λ_{ij}, denoting depth of the SW interaction potential and the reduced width for pair ij, respectively, are related to corresponding parameters for pure components by

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\,(1 - k_{ij}) \tag{3}$$

$$\lambda_{ij} = \frac{\lambda_i \sigma_i + \lambda_j \sigma_j}{\sigma_i + \sigma_j} \tag{4}$$

where cross parameter k_{ij} is obtained from binary experimental data remote from critical conditions. When $k_{ij} = 0$, equations (2) and (3) are the well-known Lorentz (energy)-Berthelot (size) approximation (Rowlinson, 1982).

Without loss of generality, but with a view towards fitting experimental data for alkanes, we assume that ε_i depends on temperature T as proposed by Chen and Kreglewski (1977):

$$\varepsilon_i = \varepsilon_i^0 (1 + e / k_{\mathrm{B}}T) \tag{5}$$

where k_{B} is Boltzmann's constant; e / k_{B} is a constant equal to 5K. Following Barker-Henderson (BH) theory (1967a, b), the temperature dependence of the effective diameter σ_i is

$$\sigma_i = \sigma_i^0 \left[1 - C \exp(-3\varepsilon_i^0 / k_{\mathrm{B}}T) \right] \tag{6}$$

where σ_i^0 is a temperature-independent diameter. C is an integration constant; following Chen and Kreglewski (1977), we set $C = 0.12$.

The Helmholtz energy density f, i.e., the Helmholtz energy per unit volume, is obtained from the general form of the EOSCF,

$$f^{\mathrm{EOSCF}} = f^{\mathrm{id}} + f^{\mathrm{hs}} + f^{\mathrm{sw}} + f^{\mathrm{chain}}. \tag{7}$$

Contributions from ideal-gas, hard-sphere, attractive SW and chain formation are given explicitly in the Appendix.

The equations above constitute the EOS for chain fluids (EOSCF) without RG corrections for a mixture. However, EOSCF performs well only far from the critical region where density fluctuations are very small. Following the work of White (White, 1992; White and Zhang, 1993, 1998), and Lue and Prausnitz (1998a, b), incorporation of contributions from density fluctuations with increasingly longer wavelengths leads to EOSCF+RG. Recursion relations are used to evaluate the Helmholtz energy density:

should be performed until index n approaches infinity; however, we find that $n = 5$ is sufficient. For binary mixtures considered here, we perform the calculations numerically with a density step $6/(\pi m_i \sigma_i^3 500)$ for each component; we then smooth the step-wise Helmholtz energy density with a two-dimensional cubic spline function (Press et al., 1992).

After we calculate the Helmholtz energy density of the system, pressure and chemical potential are obtained from

$$P = -f + \rho \left(\frac{\partial f}{\partial \rho} \right)_{T,N} \tag{18}$$

$$\mu_i = \left(\frac{\partial f}{\partial \rho_i} \right)_{T,V,\rho_{j[i]}} \tag{19}$$

where N is the total number of molecules and V is the total volume.

Results and Discussion

Segment-segment parameters for pure n-alkanes from methane to n-hexatriacontane have been correlated previously (Jiang and Prausnitz, 1999a). The chain length is estimated from a simple empirical relation with carbon number C_i by $m_i = 1 + (C_i-1)/3$. Interaction potential ε_i^0, segment diameter σ_i^0 and square-well width λ_i are optimized to fit experimental data outside the critical region. To incorporate contributions from long-wavelength density fluctuations inside the critical region, we set cut-off length $L = 11.5 \,\text{Å}$ and select a suitable parameter Φ_i to fit the measured pure-component critical properties.

We fit cross-parameter k_{ij} to measured vapor-liquid equilibrium data remote from the critical region for binary n-alkanes mixtures containing CH_4 or C_2H_6. Table 1 gives the optimized k_{ij} and corresponding data sources. Figure 2 shows that parameter k_{ij} rises linearly with low carbon number of the second component, and then rapidly approaches a constant. Triangles are for binary mixtures containing CH_4; circles are for those containing C_2H_6. The trend shown in Figure 2 was observed more than 20 years ago (Donohue and Prausnitz, 1978). Upon increasing the carbon number of the second component, the rising difference between the two components raises k_{ij}. However, upon further increase in carbon number (chain length) of

$$f_n(\rho) = f_{n-1}(\rho) + \delta f_n(\rho) \tag{8}$$

$$\delta f_n(\rho) = -K_n \ln \frac{\Omega_n^s(\rho)}{\Omega_n^l(\rho)}, \quad 0 \le \rho < \rho^{\max}/2 \tag{9.a}$$

$$\delta f_n(\rho) = 0, \quad \rho^{\max}/2 \le \rho < \rho^{\max} \tag{9.b}$$

The zero-order solution f_0 is approximated by Eq.(7); Ω_n^l and Ω_n^s are integrals over the amplitudes of the density fluctuations for long-range attraction and for short-range attraction, respectively; ρ is total number density, $\rho^{\max}$ is the maximum possible density, and

$$K_n = \frac{k_B T}{2^{3n} L^3} \tag{10}$$

$$\Omega_n^\alpha(\rho) = \int_0^{\rho_1} dz_1 \cdots \int_0^{\rho_M} dz_M \exp[-\bar{E}_n^\alpha(\rho, z)/K_n], \quad \alpha = s, l \tag{11}$$

$$\bar{E}_n^\alpha(\rho, z) = \frac{\bar{f}_n^\alpha(\rho + z) + \bar{f}_n^\alpha(\rho - z)}{2} - \bar{f}_n^\alpha(\rho), \quad \alpha = s, l \tag{12}$$

$$\bar{f}_n^l(\rho) = f_{n-1}(\rho) + \sum_i \sum_j b_{ij} \rho_i \rho_j \tag{13}$$

$$\bar{f}_n^s(\rho) = f_{n-1}(\rho) + \sum_i \sum_j b_{ij} \rho_i \rho_j \frac{\Phi_{ij} \xi_{ij}^2}{2^{2n+1} L_{ij}^2}. \tag{14}$$

where z_i ($i = 1, 2, \cdots M$; M is the total number of components) is the integral variable within $[0, \rho_i]$; b_{ij} is the interaction volume and ξ_{ij} refers to the range of the attractive potential. They are related to the parameters of the SW potential by

$$b_{ij} = \frac{2\pi}{3} \varepsilon_{ij} (\lambda_{ij} \sigma_{ij})^3 \tag{15}$$

$$\xi_{ij} = \frac{1}{\sqrt{5}} (\lambda_{ij} \sigma_{ij}) \tag{16}$$

Parameter L_{ij} is the cut-off length; we use the same L for all components. Φ_{ij} is the average gradient of the wavelet function (Battle, 1992, 1994), given by

$$\Phi_{ij} = \frac{\Phi_i \sigma_i + \Phi_j \sigma_j}{\sigma_i + \sigma_j} \tag{17}$$

The above recursion procedure can be interpreted in terms of contributions to the Helmholtz energy density; this procedure gives the ratio of non-mean-field contributions to mean-field contributions at gradually increasing long wavelengths. In principle, the recursion

the second compoent, the first component cannot "see" the increasing difference between itself and the second components; therefore, k_{ij} becomes constant.

Figure 3(a) shows vapor-liquid equilibria for binary mixtures of CH_4 with C_3H_8; Figure 3(b) shows the corresponding equilibrium ratios defined by

$$K_i = y_i / x_i \tag{20}$$

where y and x refer to mole fraction in the vapor phase and liquid phase, respectively. The open points represent experimental data (Knapp et al., 1982); dashed and solid lines are calculated from EOSCF and EOSCF+RG, respectively. The critical points, indicated by solid triangles, are estimated by extrapolation of a K-P plot to $K = 1.0$ as recommended by Sage and others (Sage et al., 1940, 1942; Reamer, et al., 1950; Kahre, 1974). At the critical point, we have

$$\left(\frac{\partial P}{\partial x_1}\right)_T = \left(\frac{\partial P}{\partial y_1}\right)_T = 0 \qquad \text{at } x_1 = y_1 \tag{21}$$

and

$$\left(\frac{\partial P}{\partial K_1}\right)_T = \left(\frac{\partial P}{\partial K_2}\right)_T = 0 \qquad \text{at } K_1 = K_2 = 1. \tag{22}$$

EOSCF is deficient in its description of phase behavior in the critical region; however, EOSCF+RG repairs this deficiency because density fluctuations are reasonably incorporated. Far from the critical region, EOSCF+RG theory reduces to the original EOSCF where the latter is reliable. In general, EOSCF+RG gives good agreement with experiment in both regions.

Figures 4(a) and (b) show vapor-liquid equilibria and equilibrium ratios for binary mixtures of CH_4 with n-C_4H_{10}. Legends are the same as those in Figure 3(a). The solid circle denotes the cricondentherm where

$$\left(\frac{\partial P}{\partial y_1}\right)_T = \infty \tag{23}$$

In a pressure-temperature plot at fixed composition, the cricondentherm condition is

$$\left(\frac{\partial P}{\partial T}\right)_y = \infty \tag{24}$$

Figure 4(c) shows critical and cricondentherm properties for binary mixtures of CH_4 with n-C_4H_{10}. Points represent experimental data (Sage et al., 1940) and lines are calculated from

EOSCF+RG. Triangles and solid lines denote critical properties; circles and dashed lines show cricondentherm properties. Agreement with experiment is good.

Figure 5, similar to Figure 4, gives results for binary mixtures of CH_4 with $n\text{-}C_5H_{12}$. The experimental data for vapor-liquid equilibria are from Knapp et al. (1982); critical and cricondentherm properties are from Sage (1942), and Berry and Sage (1970).

Figures 6 and 7 show vapor-liquid equilibria for binary mixtures of CH_4 with $n\text{-}C_{12}H_{26}$ and $n\text{-}C_{16}H_{34}$, respectively. The points show experimental data (Rijkers et al., 1992; Glaser et al., 1985); dashed and solid lines are calculated from EOSCF and EOSCF+RG, respectively. EOSCF+RG provides much improvement because it takes into account the contribution from density fluctuations in the critical region.

Figure 8 shows the bubble-point curve for three binary mixtures of CH_4 with $n\text{-}C_{20}H_{42}$, $n\text{-}C_{28}H_{58}$, and $n\text{-}C_{36}H_{74}$. Points show experimental data (Darwish et al., 1993; Huang et al., 1987, 1988a, b); solid lines are calculated from EOSCF+RG. Good agreement is obtained.

Finally, Figure 9 shows vapor-liquid equilibria for binary mixtures of C_2H_6 with $n\text{-}C_{20}H_{42}$. Experimental data are from Peters et al. (1987, 1988). Similar to binary mixtures containing CH_4, remote from the critical region, both EOSCF and EOSCF+RG give almost the same results; however, in the critical region, EOSCF+RG is significantly superior.

Conclusion

A recently developed crossover equation of state for pure chain fluids, EOSCF+RG, has been extended to mixtures of chain fluids. This EOSCF+RG is able to describe the phase equilibria of mixtures both far-from and near-to the critical region. Far from the critical region, where density fluctuations are small and RG corrections are negligible, EOSCF+RG reduces to the classical EOSCF. However, near-to and in the critical region where density fluctuations are large, EOSCF fails due to its mean-field nature. Incorporating the essential contribution from density fluctuations, EOSCF+RG significantly improves agreement with experiment.

For the binary mixtures of n-alkanes illustrated here, we use the square-well segment-segment parameters for pure components from our previous work; in addition, we use cross-parameter k_{ij} optimized by fitting equilibria data remote from the critical region. We find that all parameters vary smoothly with the carbon numbers of the components. Therefore, for those binary n-alkanes systems where experimental data are not available, we can with confidence

predict phase equilibria for a wide range of conditions, including the critical region. We can also model n-alkanes as Lennard-Jones chains and optimize the Lennard-Jones segment-segment parameters (Blas and Vega, 1997, 1998a, 1998b).

In general, EOSCF+RG gives good results, much better than those from EOSCF in the critical region. However, we also observe some deviations for EOSCF+RG from experiment. These deviations are not primarily due to RG theory; rather, they result from inadequacies in the classical equation of state remote from critical conditions. Because the classical EOSCF is a first-order perturbation theory, higher-order correlations between the segments in the chain are neglected; also, a crude approximation is used here to subtract contributions from long-wavelength density fluctuations in EOSCF; perhaps, some deviation is due to neglect of many-body interactions (Elrod and Saykally, 1994; Adidharma, and Radosz, 1998; Sadus, 1998a, b; Marcelli and Sadus, 1999) that may be important at high densities.

To use the crossover equation of state described here, the first task is to evaluate numerically the Helmholtz energy density through the recursion relations. We perform these calculations with a suitable density step ρ_i^{max} / N_{step} for each component. In our studies for pure components and binary mixtures, we use $N_{step} = 500$ to achieve good accuracy with reasonable computational time. However, for ternary mixtures, with $N_{step} = 500$, there is not enough memory in our PC to perform the calculations. To maintain accuracy, we cannot significantly reduce N_{step}. The severity of this computational problem increases worse as the number of components in the mixture rises. We are currently making efforts toward solving this computational problem.

While this work discusses the VLE for mixtures of n-alkanes, it can also be used to describe VLE for fluid mixtures containing a polymer like polyethylene (Folie and Radosz, 1995; Luettmer-Strathmann, et al., 1998; Orbey, et al., 1998); for liquid-liquid equilibria of mixtures of small molecules (Greer, 1978; Hölscher, et al., 1986) or polymer with solvent (Hino and Prausnitz, 1997; Liu and Hu, 1998; Vetere, 1998) and for solid-fluid equilibria in natural-gas systems (Won, 1986; Suleiman and Eckert, 1995a, b; Flöter, et al., 1997, 1998; Sun and Teja, 1998; Teja, et al., 1998; Coutinho, 1998) or for the solubility of a solid polymer in dense fluids (O'Neill, et al., 1998; Pan and Radosz, 1998, 1999).

Acknowledgment

Notation

b_{ij} = interaction volume for ij pair

A = Helmholtz energy

C = integration constant in Barker-Henderson theory

f = Helmholtz energy density

$g_{ij}(r)$ = pair correlation function for ij pair

k_B = Boltzmann constant

k_{ij} = cross-parameter for binary mixture ij pair

K_i = equilibrium ratio

L = cut-off length

m_i = chain length of molecule i

M = total number of components

n_i = mole number of component i

N = total number of molecules

N_{step} = step of density

P = pressure

P^c = critical pressure of mixture

r = center-to-center distance

SW = square-well potential

T^c = critical temperature of mixture

u = interaction potential

V = total volume of the system

x_i = mole fraction of component i in the liquid phase

y_i = mole fraction of component i in the vapor phase

$y_{ij}(r)$ = cavity correlation function for ij pair

z = integral variable for density

Greek letters

ρ_i = number density of molecule i

σ_i = segment diameter of molecule (or segment) i

ε_i = SW interaction well-depth of molecule (or segment) i

λ_i = SW interaction range of molecule (or segment) i

Λ_i = de Broglie thermal wavelength of molecule i

μ_i = chemical potential of component i

Φ_i = average gradient of wavelet function for component i

Literature Cited

Adidharma, H., and M. Radosz, "Prototype of an Engineering Equation of State for Heterosegmented Polymers," *Ind. Eng. Chem. Res.*, **37**, 4453 (1998).

Andrews T., *Philos. Trans.*, **159**, 575 (1869).

Anisimov, M. A., V. A. Rabinovich and V. V. Sychev, *Thermodynamics of the Critical State of Individual Substances*, CRC Press, Boca Raton (1995).

Anisimov, M. A., A. A. Povodyrev, and J. V. Sengers, "Crossover Critical Phenomena in Complex Fluids," *Fluid Phase Equil.*, **158/160**, 537 (1999).

Barker, J. A., and D. Henderson, "Perturbation Theory and Equation of State for Fluids: The Square Well Potential," *J. Chem. Phys.*, **47**, 2856 (1967a).

Barker, J. A., and D. Henderson, "Perturbation Theory and Equation of State for Fluids: II. A Successful Theory of Fluids," *J. Chem. Phys.*, **47**, 4714 (1967b).

Battle, G., "Wavelets: A Renormalization Group Point of View," in *Wavelets and Their Applications*, B. Ruskai et al. eds., Bartlett and Jones, Boston (1992).

Battle, G., "Wavelet Refinement of the Wilson Recursion Formula," in *Recent Advances in Wavelet Analysis*, L. L. Schumaker and G. Webb, eds., Academic Press, Boston (1994).

Berry, V. M., and B. H. Sage, "Phase Behavior in Binary and Multicomponent Systems at Elevated Pressures: *n*-Pentane and Methane-*n*-Pentane," NSRDS-NBS, **32** (1970).

Blas F. J., and L. F. Vega, "Thermodynamic Behavior of Homonuclear and Heteronuclear Lennard-Jones Chains with Association Sites from Simulation and Theory," *Mol. Phys.*, **92**, 135 (1997).

Blas F. J., and L. F. Vega, "Prediction of Binary and Ternary Diagrams Using the Statistical Associating Fluid Theory (SAFT) Equation of State," *Ind. Eng. Chem. Res.*, **37**, 660 (1998a).

Blas F. J., and L. F. Vega, "Critical Behavior and Partial Miscibility Phenomena in Binary Mixtures of Hydrocarbons by the Statistical Associating Fluid Theory," *J. Chem. Phys.*, **109**, 7405 (1998b).

Boublik, T., "Hard-Sphere Equation of State," *J. Chem. Phys.*, **53**, 471 (1970).

Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, "New Reference Equation of State for Associating Liquids," *Ind. Eng. Chem. Res.*, **29**, 1709 (1990).

Chao, K. C., and J. D. Seader, "A General Correlation of Vapor-Liquid Equilibria in Hydrocarbon Mixtures," *AIChE, J.*, **7**, 598 (1961).

Chen, S. S., and A. Kreglewski, "Applications of the Augmented van der Waals Theory of Fluids. I. Pure Fluids," *Ber. Bunsen-Ges. Phys. Chem.*, **81**, 1048 (1977).

Coutinho, J. A. P., "Predictive UNIQUAC: A New Model for the Description of Multiphase Solid-Liquid Equilibria in Complex Hydrocarbon Mixtures," *Ind. Eng. Chem. Res.*, **37**, 4870 (1998).

Darwish, N. A., J. Fathikalajahi, K. A. M. Gasem, and R. L. Robinson Jr., "Solubility of Methane in Heavy Normal Paraffins at Temperatures from 323 to 423 K and Pressures to 10.7 Mpa," *J. Chem. Eng. Data.*, **38**, 44 (1993).

Dastur, S. P., and G. Thodos, "Vapor-Liquid Equilibrium Constants of Binary Methane Systems for the Sub-Critical, Critical, and Retrograde Regions," *AIChE, J.*, **9**, 524 (1963).

Dohrn, R., and G. Brunner, "High-Pressure Fluid-Phase Equilibria: Experimental Methods and Systems Investigated (1988-1993)," *Fluid Phase Equil.*, **106**, 213 (1995).

Donohue, M. D., and J. M. Prausnitz, "Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," *AIChE J.*, **24**, 849 (1978).

Duhem, P., "On the Liquefaction of a Mixture of Two Gases," *J. Phys. Chem.*, **1**, 273 (1896).

Duhem, P., "On the Liquefaction of a Mixture of Two Gases. Composition of the Liquid and of the Vapor," *J. Phys. Chem.*, **5**, 91 (1901).

Edison, T. A., M. A. Anisimov, and J. V. Sengers, "Critical Scaling Laws and an Excess Gibbs Energy Model," *Fluid Phase Equil.*, **150/151**, 429 (1998).

Elrod, M. J., and R. J. Saykally, "Many-body Effects in Intermolecular Forces," *Chem. Rev.*, **94**, 1975 (1994).

Fisher, M. E., "Renormalization Group Theory: Its Basis and Formulation in Statistical Physics," *Rev. Mod. Phys.*, **70**, 653 (1998).

Flöter E., Th. W. de Loos, and J. de Swaan Arons, "High Pressure Solid-Fluid and Vapor-Liquid Equilibria in the System (Methane + tetracosane)," *Fluid Phase Equil.*, **127**, 129 (1997).

Flöter E., B. Hollanders, Th. W. de Loos, and J. de Swaan Arons, "The Effect of the Addition of Water, Propane, or Docosane on the Vapor-Liquid and Solid-Fluid Equilibria in Asymmetric Binary *n*-Alkane Mixtures," *Fluid Phase Equil.*, **143**, 185 (1998).

Folie B., and M. Radosz, "Phase Equilibria in High-Pressure Polyethylene Technology," *Ind. Eng. Chem. Res.*, **34**, 1501 (1995).

Fornasiero, F., L. Lue, and A. Bertucco, "Improving Cubic EOSs Near the Critical Point by a Phase-Space Cell Approximation," *AIChE J.*, **45**, 906 (1999).

Galindo A., L. A. Davies, A. Gil-Villegas, and G. Jackson, "The Thermodynamics of Mixtures and the Corresponding Mixing Rules in the SAFT-VR Approach for Potentials of Variable Range," *Mole. Phys.*, **93**, 241 (1998).

Gasem, K. A. M., B. A. Bufkin, A. M. Raff, and R. L. Robinson Jr., "Solubility of Ethane in Heavy Normal Paraffins at Pressure to 7.8 Mpa and Temperatures from 348 to 423 K," *J. Chem. Eng. Data.*, **34**, 187 (1989).

Gasem, K. A. M., and R. L. Robinson Jr., "Evaluation of the Simplified Perturbed Hard Chain Theory (SPHCT) for Prediction of Phase Behavior of *n*-Paraffins and Mixtures of *n*-Paraffins with Ethane," *Fluid Phase Equil.*, **58**, 13 (1990).

Gil-Villegas, A., A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, and A. N. Burgess, "Statistical Associating Fluid Theory for Chain Molecules with Attractive Potentials of Variable Range," *J. Chem. Phys.*, **106**, 4168 (1997).

Glaser, M., C. J. Peters, H. J. Van der Kool, and R. N. Lichtenthaler, "Phase Equilibria of (Methane + *n*-Hexadecane) and (*p*, V_m, *T*) of *n*-Hexadecane," *J. Chem. Thermodynamics*, **17**, 803 (1985).

Goede, R. de, C. J. Peters, H. J. Van der Kool, and R. N. Lichtenthaler, "Phase Equilibria in Binary Mixtures of Ethane and *n*-Hexadecane," *Fluid Phase Equil.*, **50**, 305 (1989).

Greer, S. C., "Liquid-Liquid Critical Phenomena," *Acc. Chem. Res.*, **11**, 427 (1978).

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

Hino, T., and J. M. Prausnitz, "A Perturbed Hard-Sphere Chain Equation of State for Normal Fluids and Polymers Using the Square-Well Potential of Variable Width," *Fluid Phase Equil.*, **138**, 105 (1997).

Hölscher, I. F., G. M. Schneider, and J. B. Ott, "Liquid-Liquid Equilibria of Binary Mixtures of Methanol with Hexane, Nonane and Decane at Pressures up to 150 MPA," *Fluid Phase Equil.*, **27**, 153 (1986).

Hu, Y., H. Liu, and J. M. Prausnitz, "Equation of State for Fluids Containing Chainlike Molecules," *J. Chem. Phys.*, **104**, 396 (1996).

Hu, Y., H. L. Liu, and W. C. Wang, "Molecular Thermodynamics for Chain-like Molecule Systems," *Fluid Phase Equil.*, **160**, 59 (1999).

Huang, S. H., H. M. Lin, and K. C. Chao, "Solubility of Methane, Ethane, and Carbon Dioxide in *n*-Hexatriacontane," *J. Chem. Eng. Data.*, **32**, 467 (1987).

Huang, S. H., H. M. Lin, and K. C. Chao, "Solubility of Carbon Dioxide, Methane, and Ethane in *n*-Octacosane," *J. Chem. Eng. Data.*, **33**, 143 (1988a).

Huang, S. H., H. M. Lin, and K. C. Chao, "Solubility of Carbon Dioxide, Methane, and Ethane in *n*-Eicosane," *J. Chem. Eng. Data.*, **33**, 145 (1988b).

Huang, S. H., and M. Radosz, "Equation of State for Small, Large, Polydisperse and Associating Molecules," *Ind. Eng. Chem. Res.*, **29**, 2284 (1990).

Huang, S. H., and M. Radosz, "Equation of State for Small, Large, Polydisperse and Associating Molecules: Extension to Fluid Mixtures," *Ind. Eng. Chem. Res.*, **30**, 1994 (1991).

Jiang, J., H. Liu, Y. Hu, and J. M. Prausnitz, "A Molecular-Thermodynamic Model for Polyelectrolyte Solutions," *J. Chem. Phys.*, **108**, 708 (1998).

Jiang, J., and J. M. Prausnitz, "Equation of State for Thermodynamic Properties of Chain Fluids Near-to and Far-from the Vapor-Liquid Critical Region," *J. Chem. Phys.* **111**, 5964 (1999a).

Jiang, J., and J. M. Prausnitz, "Critical temperatures and pressures for hydrocarbon mixtures from an equation of state with renormalization-group-theory corrections," *Fluid Phase Equil.*, (1999b), submitted.

Kahre, L. C., "Low-Temperature K Data for Methane-*n*-Butane," *J. Chem. Eng. Data*, **19**, 301 (1974).

Kiselev, S. B., "Cubic Crossover Equation of State," *Fluid Phase Equil.*, **147**, 7 (1998).

Kiselev, S. B., and D. G. Friend, "Cubic Crossover Equation of State for Mixtures," *Fluid Phase Equil.*, **162**, 51 (1999).

Kiselev, S. B., and J. F. Ely, "Crossover SAFT Equation of State: Application for Normal Alkanes," *Ind. Eng. Chem. Res.*, in press (1999).

Knapp, H., R. Döring, L. Oellrich, U. Plöcker, and J. M. Prausnitz, *Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances*, Chemistry Data Series, Vol. VI, DECHEMA (1982).

Kuenen, J. P., "Versuche über die Kondensation und die kritischen Erscheinungen von Gemischen zweier Stoffe," *Z. Phys. Chem.*, **11**, 38 (1893).

Kuenen, J. P., "Messungen über die Oberfläche von van der Waals für Gemische von Kohlensäure und Chlomethyl," *Z. Phys. Chem.*, **24**, 661 (1897).

Lee, K. H., and J. P. Kohn, "Heterogeneous Phase Equilibrium in the Ethane–*n*-Dodecane System," *J. Chem. Eng. Data*, **14**, 292 (1969).

Levelt Sengers, J. M. H., "Mean-Field Theories, Their Weaknesses and Strength," *Fluid Phase Equil.*, **158/160**, 3 (1999).

Liu H., and Y. Hu, "Equation of State for Systems Containing Chainlike Molecules," *Ind. Eng. Chem. Res.*, **37**, 3058 (1998).

Lue, L., and J. M. Prausnitz, "Renormalization-Group Theory Corrections to an Approximation Free-Energy Model for Simple Fluids Near to and Far from the Critical Region," *J. Chem. Phys.*, **108**, 5529 (1998a).

Lue, L., and J. M. Prausnitz, "Thermodynamics of Fluid Mixtures Near to and Far from the Critical Region," *AIChE J.*, **44**, 1455 (1998b).

Luettmer-Strathmann J., J. A. Schoenhard, and J. E. G. Lipson, "Thermodynamics of *n*-Alkanes Mixtures and Polyethylene– *n*-Alkanes Solutions: Comparison of Theory and Experiment," *Macromolecules*, **31**, 9231 (1998).

Ma, S.-K., *Modern Theory of Critical Phenomena*, Benjamin/Cummings, Reading, MA (1976).

Mansoori, G. A., N. F. Carnahan, K. E. Starling, and T. W. Leland, "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, **54**, 1523 (1971).

Marcelli, G., and R. J. Sadus, "Molecular Simulation of the Phase Behavior of Noble Gases Using Accurate Two-Body and Three-Body Intermolecular Potentials," *J. Chem. Phys.*, **111**, 1533 (1999).

McCabe, C., A. Galindo, A. Gil-Villegas, and G. Jackson, "Predicting the High-Pressure Phase Equilibria of Binary Mixtures of Perfluoro-*n*-Alkanes + *n*-Alkanes Using the SAFT-VR Approach," *J. Phys. Chem. B*, **102**, 8060 (1998).

McCabe, C., A. Gil-Villegas, and G. Jackson, "Gibbs Ensemble Computer Simulation and SAFT-VR Theory of non-Conformal Square-Well Monomer-Dimer Mixtures," *Chem. Phys. Lett.*, **303**, 27 (1999).

McCabe, C., and G. Jackson, "SAFT-VR Modelling of the Phase Equilibrium of Long-Chain *n*-Alkanes," *Phys. Chem. Chem. Phys.*, **1**, 2057 (1999).

Meroni, A., A. Parola, and L. Reatto, "Differential approach to the theory of fluids," *Phys. Rev. A*, **42**, 6104 (1990).

O'Neill, M. L., Q. Cao, M. Fang, K. P. Johnston, S. P. Wilkinson, C. D. Smith, J. L. Kerschner, and S. H. Jureller, "Solubility of Homopolymers and Copolymers in Carbon Dioxide," *Ind. Eng. Chem. Res.*, **37**, 3067 (1998).

Orbey, H., C. P. Bokis and C. Chen, "Equation of State Modeling of Phase Equilibrium in the Low-Density Polyethylene Process: The Sanchez-Lacombe, Statistical Associating Fluid Theory, and Polymer-Soave-Redlich-Kwong Equation of State," *Ind. Eng. Chem. Res.*, **37**, 4481 (1998).

Pan, C., and M. Radosz, "Copolymer SAFT Modeling of Phase Behavior in Hydrocarbon-Chain Solutions: Alkane Oligomers, Polyethylene, Poly(ethylene-*co*-olefin-1), polystyrene and Poly(ethylene-*co*-styrene-1)," *Ind. Eng. Chem.Res.*, **37**, 3169 (1998).

Pan, C., and M. Radosz, "Modeling of Solid-Liquid Equilibria in Naphthalene, Normal-Alkane and Polyethylene Solutions," *Fluid Phase Equil.*, **155**, 57 (1999).

Parola, A., and L. Reatto, "Liquid-State Theory for Critical Phenomena," *Phys. Rev. Lett.*, **53**, 2417 (1984).

Parola, A., and L. Reatto, "Hierarchical reference theory of fluids and the critical point," *Phys. Rev. A*, **31**, 3309 (1985).

Parola, A., and L. Reatto, "Microscopic approach to critical phenomena in binary fluids," *Phys. Rev. A*, **44**, 6600 (1991).

Peng, D., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Peters C. J., J. L. de Roo, and R. N. Lichtenthaler, "Measurements and Calculations of Phase Equilibria of Binary Mixtures of Ethane + Eicosane. Part I: Vapor-Liquid Equilibria," *Fluid Phase Equil.*, **34**, 287 (1987).

Peters C. J., J. de Swaan Arons, J. M. H. Levelt Sengers, and J. S. Gallagher, "Global Phase Behavior of Mixtures of Short and Long n-Alkanes," *AIChE J.*, **34**, 834 (1988).

Pini, D, G. Stell, and J. S. Hoye, "Self-Consistent Approximation for Fluids and Lattice Gases," *Int. J. Thermophys.*, **19**, 1029 (1998a).

Pini, D., G. Stell, and N. B. Wilding, "A Liquid-state Theory that Remains Successful in the Critical Region," *Mol. Phys.*, **95**, 483 (1998b).

Pini, D., A. Parola, and L. Reatto, "A comprehensive approach to critical phenomena and phase transitions in binary mixtures," *Int. J. Thermophys.*, **19**, 1545 (1998c).

Povodyrev, A. A., Anisimov, M. A., and J. V. Sengers, "Crossover Flory Model for Phase Separation in Polymer Solutions," *Physica A*, **264**, 345 (1999).

Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN 77: The Art of Scientific Computing*, 2nd ed., Cambridge University Press, New York (1992).

Reamer, H. H., B. H. Sage and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: Volumetric and Phase Behavior of the Methane-Propane System," *Ind. Eng. Chem.*, **42**, 534 (1950).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions. V An Equation of State. Fugacities of Gaseous Solutions," *Chem. Rev.*, **44**, 233 (1949).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hiill, New York (1987).

Rijkers, M. P. W. M., V. B. Maduro, C. J. Peters, and J. de Swaan Arons, "Measurements on the Phase Behavior of Binary Mixtures for Modeling the Condensation Behavior of Natural Gas. Part II. The System Methane + Dodecane," *Fluid Phase Equil.*, **72**, 309 (1992).

Rijkers, M. P. W. M., C. J. Peters, and J. de Swaan Arons, "Measurements on the Phase Behavior of Binary Mixtures for Modeling the Condensation Behavior of Natural Gas. Part III. The System Methane + Hexadecane," *Fluid Phase Equil.*, **85**, 335 (1993).

Rowlinson, J. S., and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed., Butterworths, London (1982).

Sadus, R. J., *High Pressure Phase Behavior of Multicomponent Fluid Mixtures*, Elsevier Science, Netherlands (1992).

Sadus, R. J., "Effect of Three-Body Interactions Between Dissimilar Molecules on the Phase Behavior of Binary Mixtures: The Transition from Vapor-Liquid Equilibria to Type III Behavior," *Ind. Eng. Chem. Res.*, **37**, 2977 (1998a).

Sadus, R. J., "The Effect of Three-Body Interactions on the Liquid-Liquid Phase Coexistence of Binary Fluid Mixtures," *Fluid Phase Equil.*, **151**, 63 (1998b).

Sage, B. H., W. N. Lacey, and J. G. Schaafsma, "Phase Equilibria in Hydrocarbon Systems II. Methane-Propane System," *Ind. Eng. Chem.*, **26**, 214 (1934).

Sage, B. H., B. L. Hicks and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: The Methane-*n*-Butane Systems in the Two-Phase Region," *Ind. Eng. Chem.*, **32**, 1085 (1940).

Sage, B. H., H. H. Reamer, R. H. Olds and and W. N. Lacey, "Phase Equilibria in ydrocarbon Systems: Volumetric and Phase Behavior of Methane-*n*-Pentane System," *Ind. Eng. Chem.*, **34**, 1108 (1942).

Sengers, J. V., and J. M. H. Levelt Sengers , "Thermodynamic Behavior of Fluids near the Critical Point," *Ann. Rev. Phys. Chem.*, **37**, 189 (1986).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Stevens, W. F., and G. Thodos, "Estimation of Enthalpies: Multicomponent Hydrocarbon Mixtures at Their Saturated Vapor and Liquid States," *AIChE, J.*, **9**, 293 (1963).

Suleiman, D., and C. A. Eckert, "Phase Equilibria of Alkanes in Natural Gas Systems. 1. Alkanes in Methane," *J. Chem. Eng. Data*, **40**, 2 (1995a).

Suleiman, D., and C. A. Eckert, "Phase Equilibria of Alkanes in Natural Gas Systems. 1. Alkanes in Ethane," *J. Chem. Eng. Data*, **40**, 572 (1995b).

Sun, T., A. S. Teja, "Vapor-Liquid and Solid-Fluid Equilibrium Calculations Using a Lennard-Jones Equation of State," *Ind. Eng. Chem. Res.*, **37**, 3151 (1998).

Tang, Y., and B. C.-Y. Lu, "A New Solution of the Ornstein-Zernike Equation from the Perturbation Theory," *J. Chem. Phys.*, **99**, 9828 (1993).

Tang, Y., and B. C.-Y. Lu, "An Analytical Analysis of the Square-Well Fluid Behaviors," *J. Chem. Phys.*, **100**, 6665 (1994).

Tang, Y., and B. C.-Y. Lu, "Analytical Solution of the Ornstein-Zernike Equation for Mixtures," *Mol. Phys.*, **84**, 89 (1995).

Tang, Y., "Outside and Inside the Critical Region of the Lennard-Jones Fluid," *J. Chem. Phys.*, **109**, 5935 (1998).

Teja, A. S., V. S. Smith, and T. Sun, "Solid-Fluid Equilibria in Natural Gas Systems," *Fluid Phase Equil.*, **150/151**, 393 (1998).

van der Waals, J. D., Thesis, University of Leiden (1873); English translation and introductory essay by Rowlinson, J. S., *On the Continuity of Gaseous and Liquid States*, Studies in Statistical Mechanics, Vol.14, North Holland, Amsterdam (1988).

Van Horn, L. D., and R. Kobayashi, "The Correlation of Vapor-Liquid Equilibria of Light Hydrocarbons in Paraffinic and in Aromatic Solvents at Low Temperatures and Elevated Pressures," *AIChE, J.*, **14**, 92 (1968).

Vetere, A., "An Empirical Method to Predict the Liquid-Liquid Equilibria of Binary Polymer Systems," *Ind. Eng. Chem. Res.*, **37**, 4463 (1998).

White, J. A., "Contribution of Fluctuations to Thermal Properties of Fluids with Attractive Forces of Limited Range: Theory Compared with $P \rho T$ and C_V Data for Argon," *Fluid Phase Equil.*, **75**, 53 (1992).

White, J. A., and S. Zhang, "Renormalization Group Theory for Fluids," *J. Chem. Phys.*, **99**, 2012 (1993).

White, J. A., and S. Zhang, "Renormalization Group Theory for Fluids to Greater Density Distances from the Critical Point," *Int. J. Thermophys.*, **19**, 1019 (1998)

White, J. A., and S. Zhang. "Lennard-Jones as a Model for Argon and Test of Extended RG Calculations," *J. Chem. Phys.*, in press (1999).

Wilson, K. G., "Renormalization Group and Critical Phenomena. I. Renormalization Group and the Kadanoff Scaling Picture," *Phys. Rev. B*, **4**, 3174 (1971a).

Wilson, K. G., "Renormalization Group and Critial Phenomena. II. Phase-Space Cell Analysis of Critical Behavior," *Phys. Rev. B*, **4**, 3184 (1971b).

Wilson, K. G., "The Renormalization Group and Critical Phenomena," *Rev. Mod. Phys.*, **55**, 583 (1983).

Won, K. W., "Thermodynamics for Solid Solution-Liquid-Vapor Equilibria: Wax Phase Formation from Heavy Hydrocarbon Mixtures," *Fluid Phase Equil.*, **30**, 265 (1986).

Yelash, L. V., and T. Kraska, "Investigation of a Generalized Attraction Term of an Equation of State and its Influence on the Phase Behavior," *Fluid Phase Equil.*, **162**, 115 (1999).

Appendix: Helmholtz Energy Density for a Mixture of Square-Well Chain Fluids

The Helmholtz energy density for the mixture of square-well chain fluids has four contributions:

$$f^{EOSCF} = f^{id} + f^{hs} + f^{sw} + f^{chain} \tag{A.1}$$

The contribution from the ideal gas is

$$f^{id} = k_B T \sum_i [\rho_i \ln(\rho_i \Lambda_i^3) - \rho_i] \tag{A.2}$$

where ρ_i is the number density for component i; Λ_i denotes the de Broglie thermal wavelength of molecule i.

The hard-sphere interaction, given by Boublik (1970) and Mansoori et al. (1971), is the so-called BMCSL equation

$$f^{hs} = k_B T \left[(\zeta_2^3 / \zeta_3^2 - \zeta_0) \ln \Delta + \frac{\pi \zeta_1 \zeta_2 / 2 - \zeta_2^3 / \zeta_3^2}{\Delta} + \frac{\zeta_2^3 / \zeta_3^2}{\Delta^2} \right] \tag{A.3}$$

where $\zeta_l = \sum_i m_i \rho_i \sigma_i^l$ and $\Delta = 1 - \pi \zeta_3 / 6$.

The contribution from the SW attractive potential is estimated by the second-order Baker-Henderson perturbation theory (Barker and Henderson, 1967a, b)

$$f^{sw} = \frac{1}{\zeta_0} \sum_i \sum_j m_i m_j \rho_i \rho_j (a_1^{ij} + a_2^{ij} / k_B T) . \tag{A.4}$$

The mean-attractive energy a_1^{ij} is given by a compact expression from the mean-value theorem (Gil-Villegas et al., 1997; Galindo et al., 1998; McCabe et al., 1998, 1999; McCabe and Jackson, 1999)

$$a_1^{ij} = -2/3 \pi \zeta_0 \sigma_{ij}^3 \varepsilon_{ij} (\lambda_{ij}^3 - 1) g_{ij}^{hs} (\sigma_{ij}, \zeta_3^{eff}) \tag{A.5}$$

where the pair correlation function of hard-spheres at contact is evaluated at an effective ζ_3^{eff},

$$g_{ij}^{hs} (\sigma_{ij}) = \frac{1}{\Delta} + \frac{\pi \sigma_i \sigma_j \zeta_2}{4 \Delta^2 \sigma_{ij}} + \frac{\pi^2 \sigma_i^2 \sigma_j^2 \zeta_2^2}{72 \Delta^3 \sigma_{ij}^2} \tag{A.6}$$

with

$$\zeta_3^{eff} = c_1 \zeta_3 + c_2 \zeta_3^2 + c_3 \zeta_3^3 . \tag{A.7}$$

Coefficients c_n are calculated by the matrix (Gil-Villegas et al., 1997; Galindo et al., 1998; McCabe et al., 1998, 1999; McCabe and Jackson, 1999)

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_{ij} \\ \lambda_{ij}^2 \end{pmatrix} \tag{A.8}$$

The second perturbation term a_2^{ij} describing fluctuations of the attractive energy is given by

$$a_2^{ij} = \frac{\varepsilon_{ij} \zeta_0^2 \Delta^4}{2(\zeta_0 \Delta^2 + \pi \zeta_1 \zeta_2 \Delta + \pi^2 \zeta_2^3 / 4)} \frac{\partial a_1}{\partial \zeta_0} . \tag{A.9}$$

The contribution from chain formation is

$$f^{\text{chain}} = k_B T \sum_i \rho_i (1 - m_i) \ln y_{ii}^{\text{sw}} (\sigma_i) . \tag{A.10}$$

where cavity correlation function $y_{ij}^{\text{sw}} (\sigma_{ij})$ at contact is defined by

$$y_{ij}^{\text{sw}} (\sigma_{ij}) = g_{ij}^{\text{sw}} (\sigma_{ij}) \exp(-\varepsilon_{ij} / k_B T) \tag{A.11}$$

with

$$g_{ij}^{\text{sw}} (\sigma_{ij}) = g_{ij}^{\text{hs}} (\sigma_{ij}) + \frac{1}{2\pi k_B T \sigma_{ij}^3} \left(3 \frac{\partial a_1^{ij}}{\partial \zeta_0} - \frac{\lambda_{ij}}{\zeta_0} \frac{\partial a_1^{ij}}{\partial \lambda_{ij}} \right) . \tag{A.12}$$

Table 1. Cross-Parameter k_{ij} for Binary Mixtures of CH_4 Series and C_2H_6 Series, Respectively, Evaluated from Experimental Data Remote from Critical Conditions

Component j	k_{ij} ($i = CH_4$)	data source	k_{ij} ($i = C_2H_6$)	data source
C_2H_6	0.0048	Knapp et al. (1982)		
C_3H_8	0.0150	Knapp et al. (1982)	0.0095	Knapp et al. (1982)
n-C_4H_{10}	0.0255	Knapp et al. (1982)	0.0163	Knapp et al. (1982)
n-C_5H_{12}	0.0381	Knapp et al. (1982)	0.0220	Knapp et al. (1982)
n-C_6H_{14}	0.0490	Knapp et al. (1982)	0.0263	Knapp et al. (1982)
n-C_7H_{16}	0.0584	Knapp et al. (1982)	0.0312	Knapp et al. (1982)
n-C_8H_{18}	0.0704	Knapp et al. (1982)	0.0375	Knapp et al. (1982)
n-C_9H_{20}	0.0801	Knapp et al. (1982)		
n-$C_{10}H_{22}$	0.0874	Knapp et al. (1982)	0.0455	Knapp et al. (1982)
n-$C_{12}H_{26}$	0.0910	Rijkers et al. (1992)	0.0485	Lee et al. (1969)
n-$C_{16}H_{34}$	0.0920	Glaser et al. (1985)	0.0495	Goede et al. (1989)
n-$C_{20}H_{42}$	0.0932	Darwish et al. (1993)	0.0489	Peters et al. (1987)
		Huang et al. (1988b)		Peters et al. (1988)
n-$C_{28}H_{58}$	0.0930	Darwish et al. (1993)	0.0487	Gasem et al. (1989)
		Huang et al. (1988a)		Huang et al. (1988a)
n-$C_{36}H_{74}$	0.0937	Darwish et al. (1993)	0.0490	Gasem et al. (1989)
		Huang et al. (1987)		Huang et al. (1987)

Figure captions:

Figure 1. Schematic illustration of retrograde-condensation (vaporization) phenomena. (solid curve: bubble point; dashed curve: dew point. point C: critical point; A: cricondenbar; B: cricondentherm. line 1: isothermal retrograde condensation; line 2: isobaric retrograde vaporization.

Figure 2. Dependence of cross-parameter k_{ij} on the carbon number of the second component. (triangles: CH_4 series; circles: C_2H_6 series).

Figure 3(a). Vapor-liquid equilibria for $CH_4(1)-C_3H_8(2)$ mixtures. (open points: experiment; dashed lines: EOSCF; solid lines: EOSCF+RG; solid triangles: critical points)

Figure 3(b). Equilibrium ratios for $CH_4(1)-C_3H_8(2)$ mixtures. Legend as in Figure 3(a).

Figure 4(a). Vapor-liquid equilibria for $CH_4(1)-n$-$C_4H_{10}(2)$ mixtures. (open points: experiment; dashed lines: EOSCF; solid lines: EOSCF+RG; solid triangles: critical points; solid circles: cricondentherms).

Figure 4(b). Equilibrium ratios for $CH_4(1)-n$-$C_4H_{10}(2)$ mixtures. Legend as in Figure 3(a).

Figure 4(c). Critical properties and cricondentherm properties for $CH_4(1)-n$-$C_4H_{10}(2)$ mixtures. (triangles and solid lines: critical properties; circles and dashed lines: cricondentherm properties).

Figure 5(a). Vapor-liquid equilibria for $CH_4(1)-n$-$C_5H_{12}(2)$ mixtures. Legend as in Figure 4(a).

Figure 5(b). Equilibrium ratio for $CH_4(1)-n$-$C_5H_{12}(2)$ mixtures. Legend as in Figure 4(b).

Figure 5(c). Critical properties and cricondentherm properties for $CH_4(1)-n$-$C_5H_{12}(2)$ mixtures. Legend as in Figure 4(c).

Figure 6. Vapor-liquid equilibria for $CH_4(1)-n-C_{12}H_{26}(2)$ mixtures at 303.15K. Legend as in Figure 3(a).

Figure 7. Vapor-liquid equilibria for $CH_4(1)-n-C_{16}H_{34}(2)$ mixtures at 320.0K. Legend as in Figure 3(a).

Figure 8. Bubble pressures at 373.15K for $CH_4(1)-n-C_{20}H_{42}(2)$, $CH_4(1)-n-C_{28}H_{58}(2)$ and $CH_4(1)-n-C_{36}H_{74}(2)$, respectively. (points: experimental data; lines: EOSCF+RG).

Figure 9. Vapor-liquid equilibria for $C_2H_6(1)-n-C_{20}H_{42}(2)$ mixtures at 350.0K. Legend as in Figure 3(a).
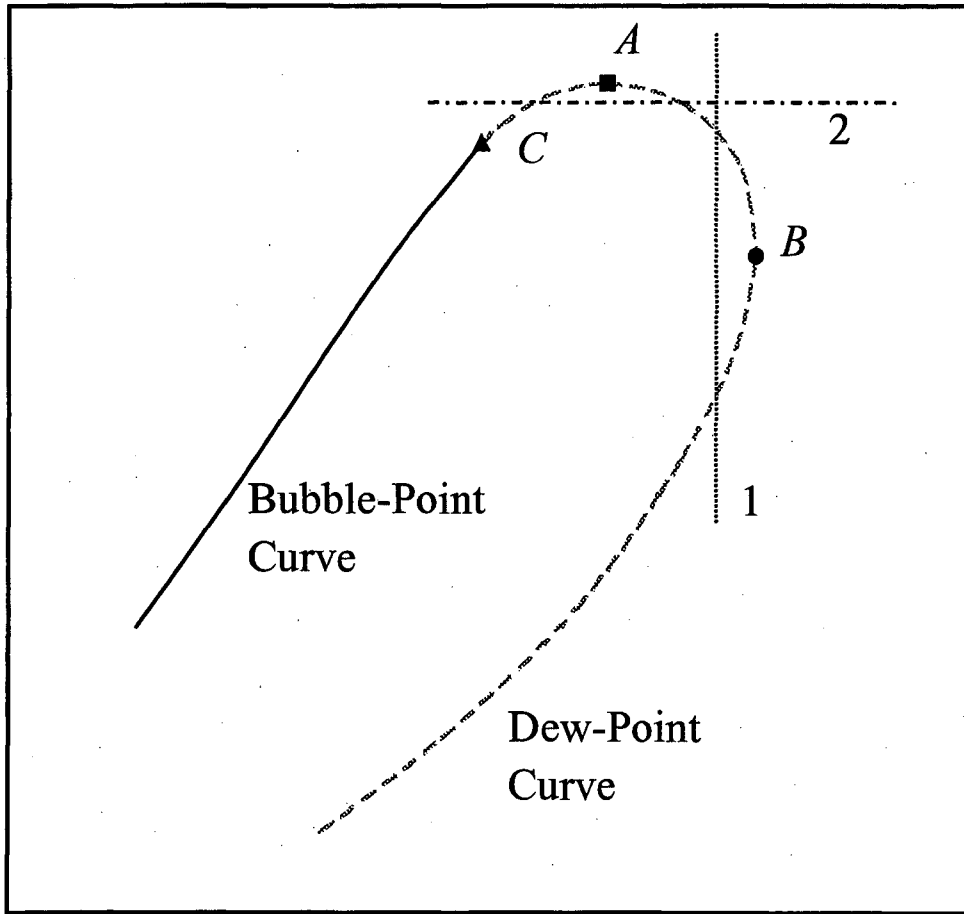
Fig.1

Pressure

A

C

2

B

Bubble-Point
Curve

1

Dew-Point
Curve

Temperature

Carbon Number of Second Component

Fig 3(a)

360.93K

327.59K

294.26K

P (MPa)

x_1, y_1

Fig 4(a)

Fig 4(c)

Fig 5(b)

Fig 3

Fig.6

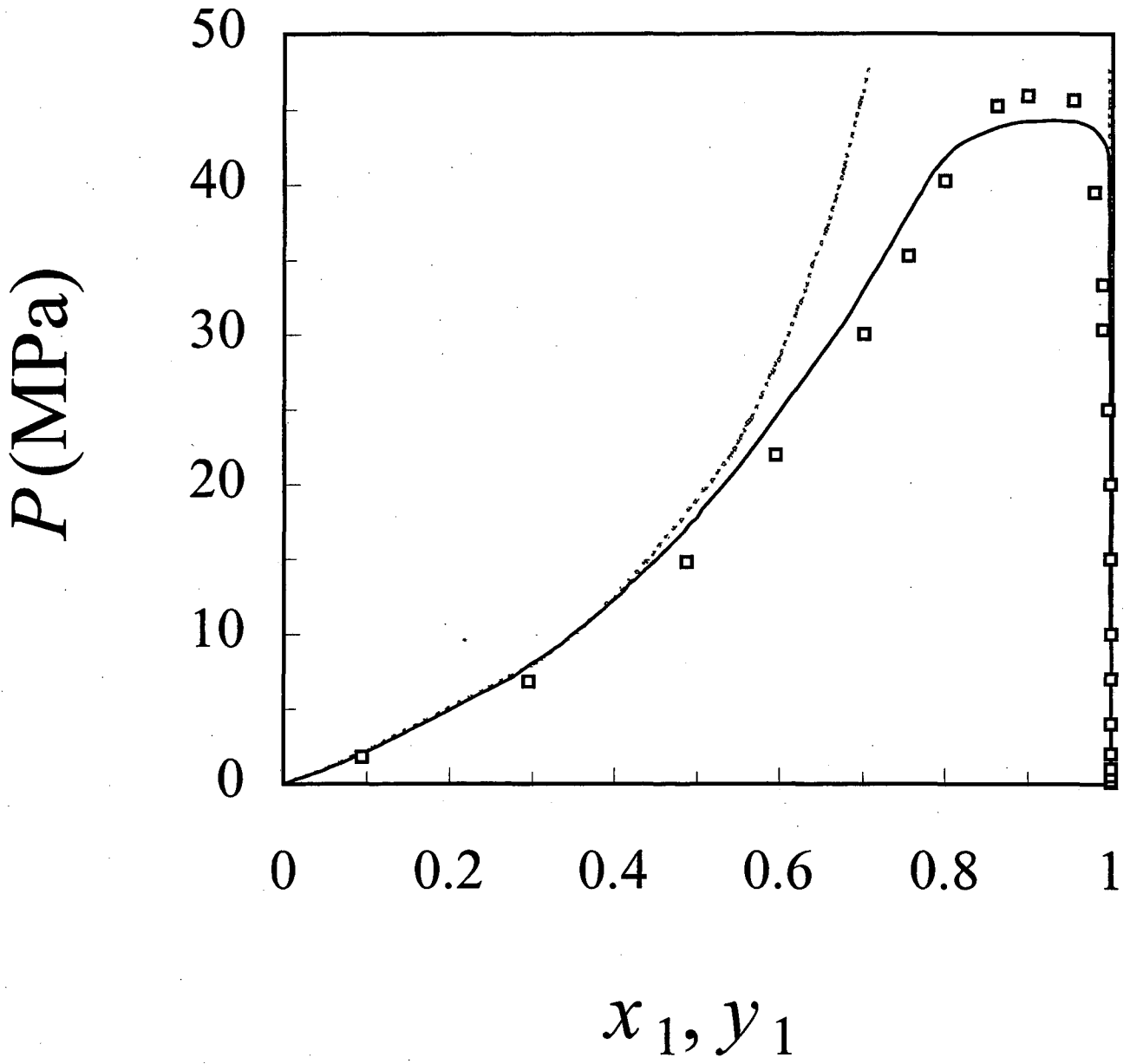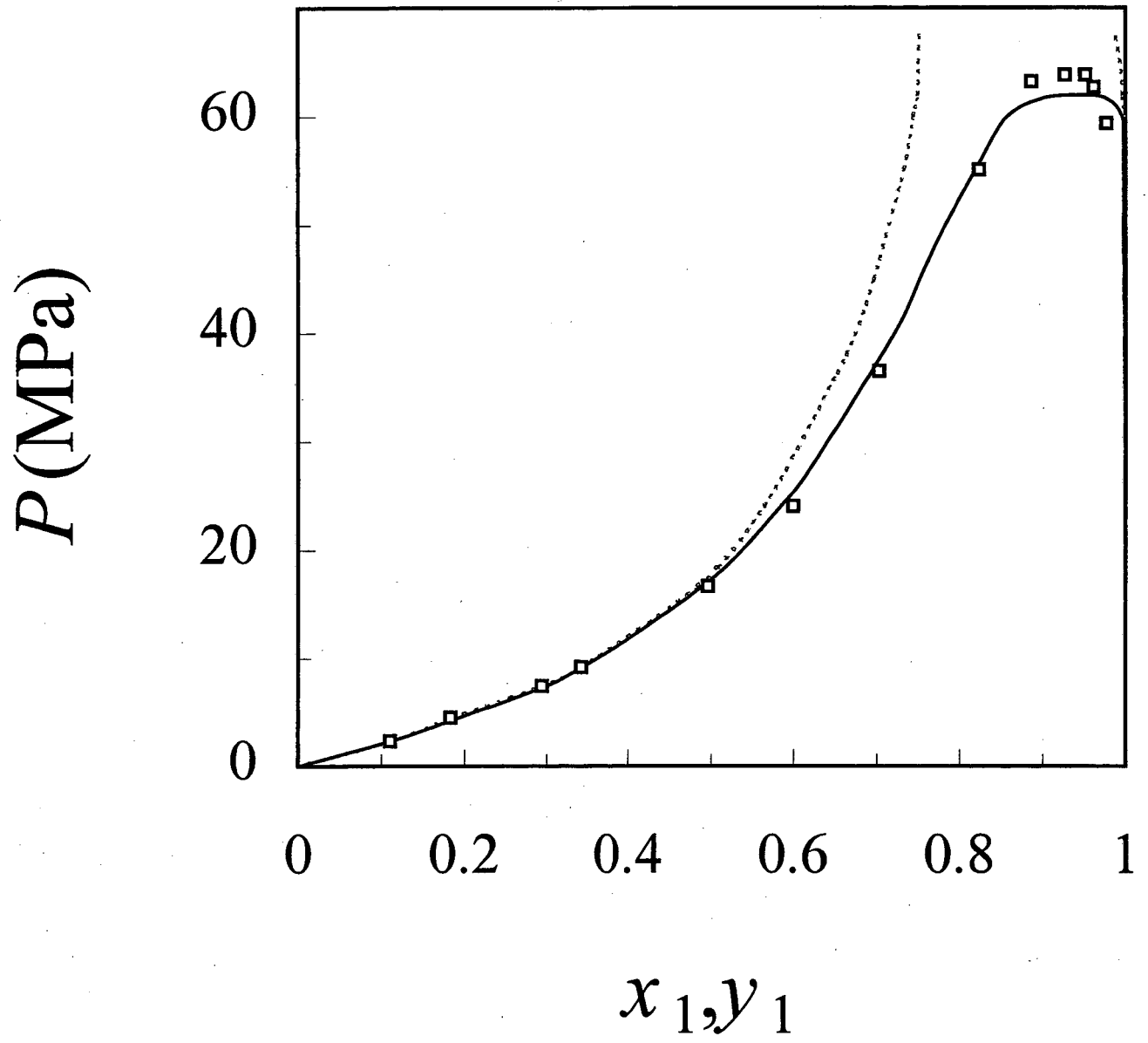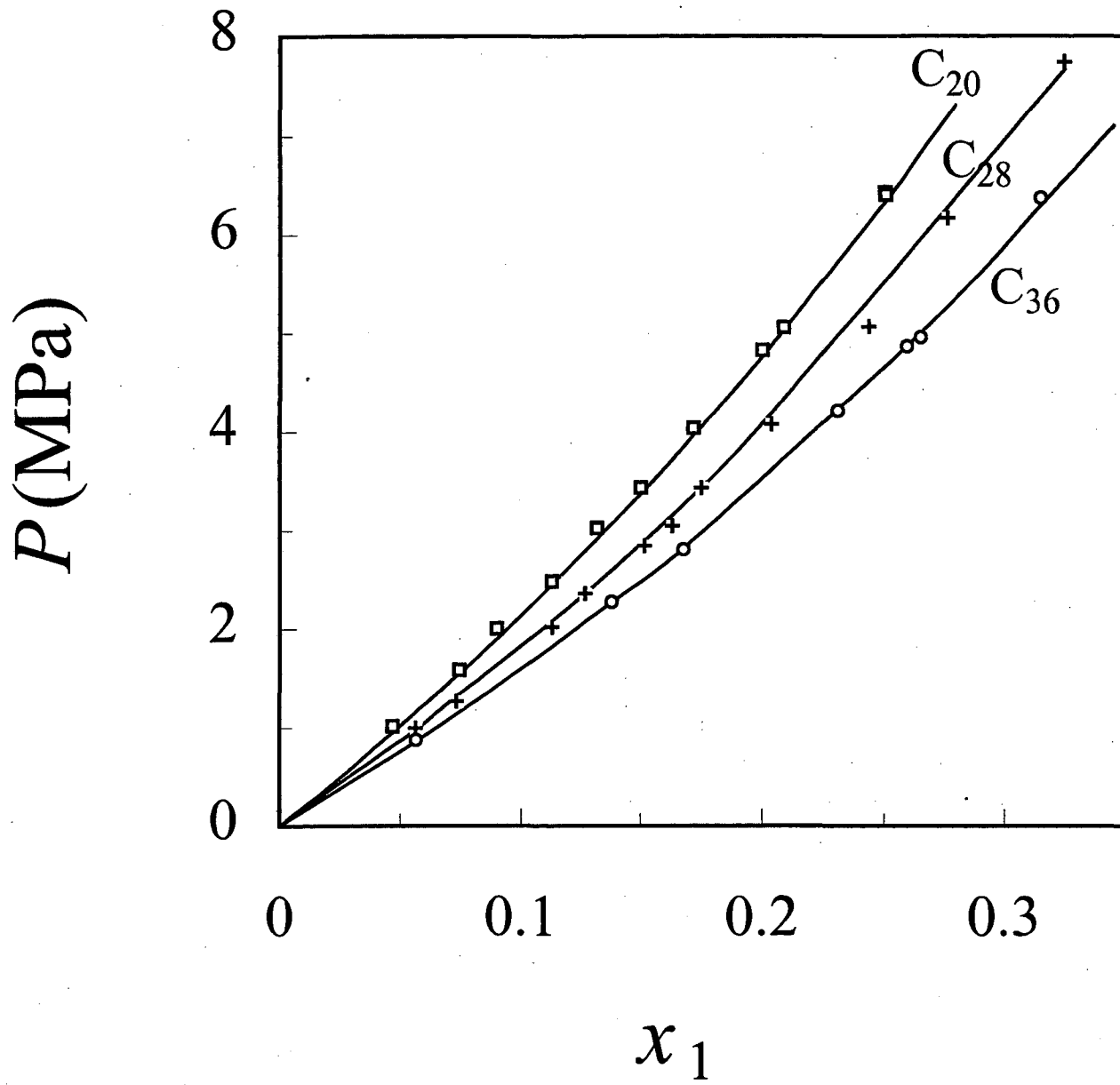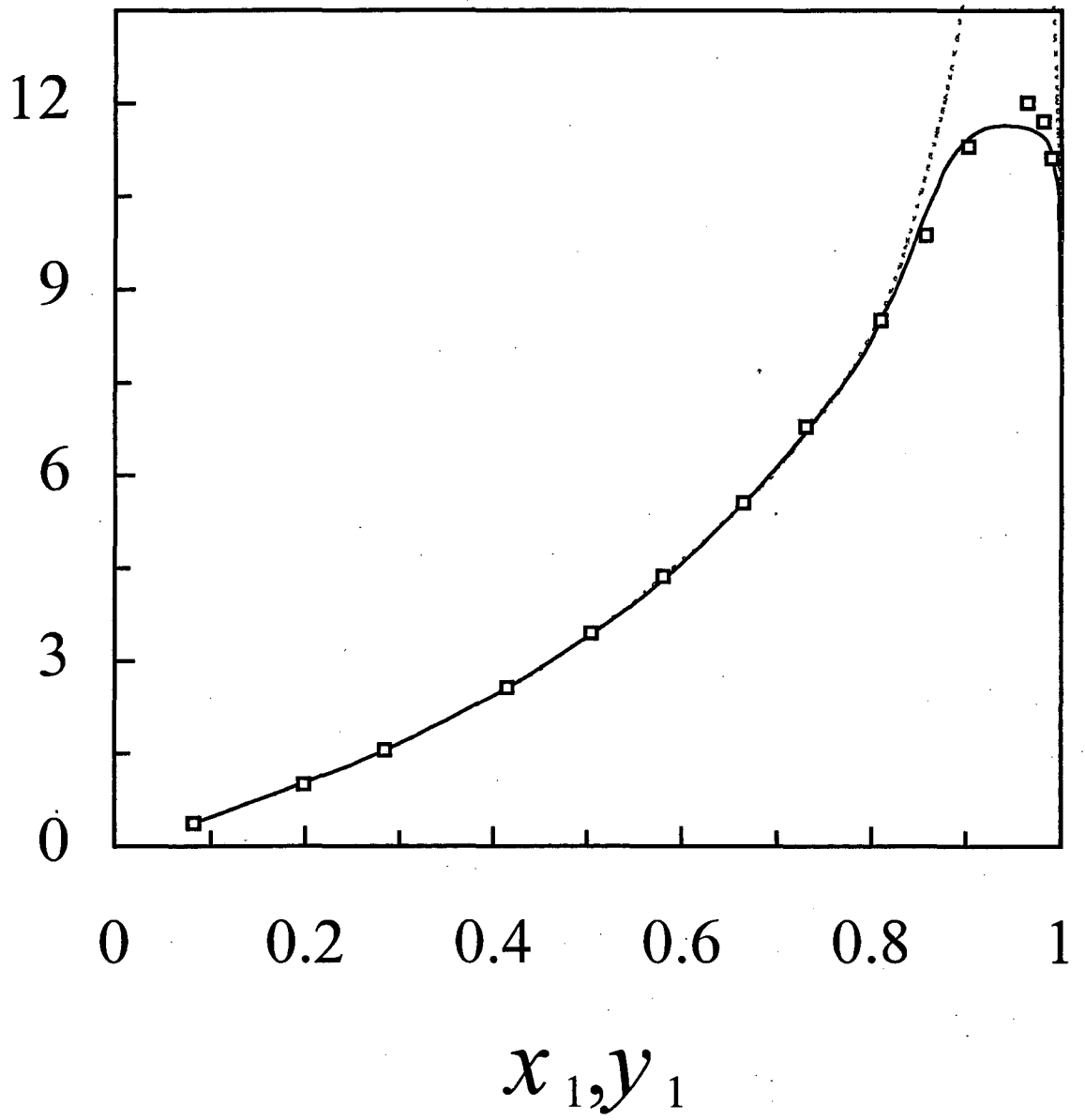Fig. 8
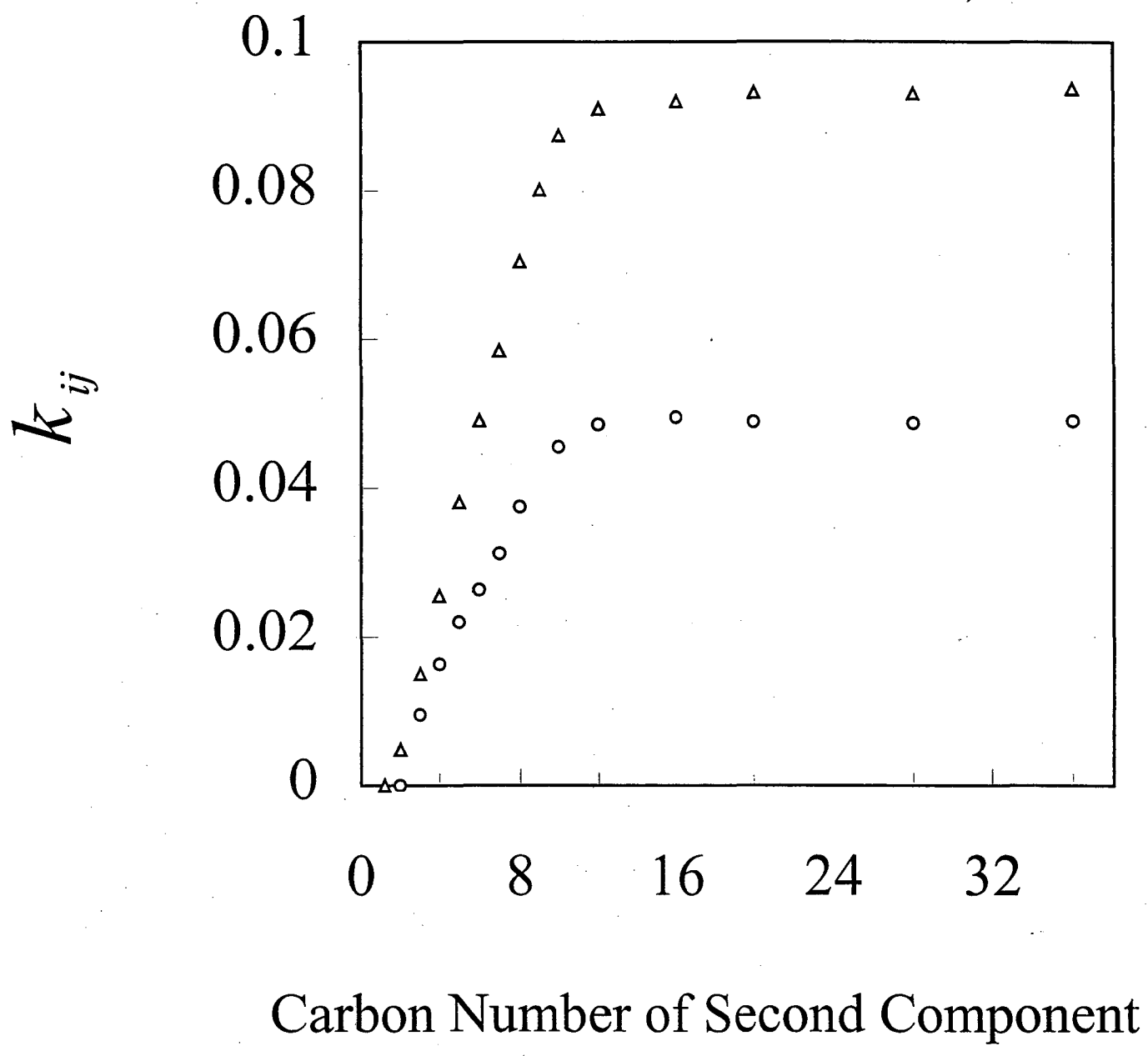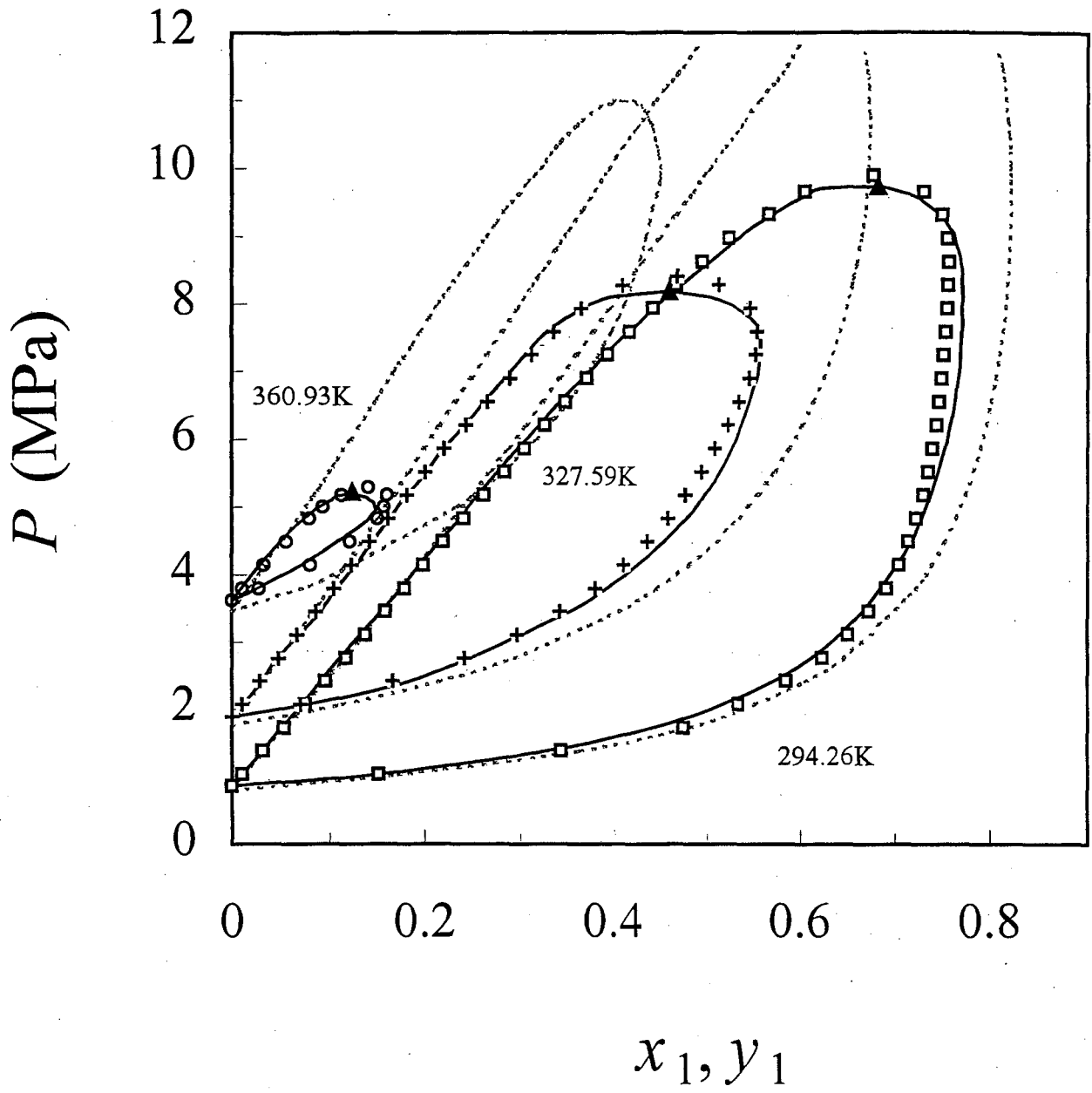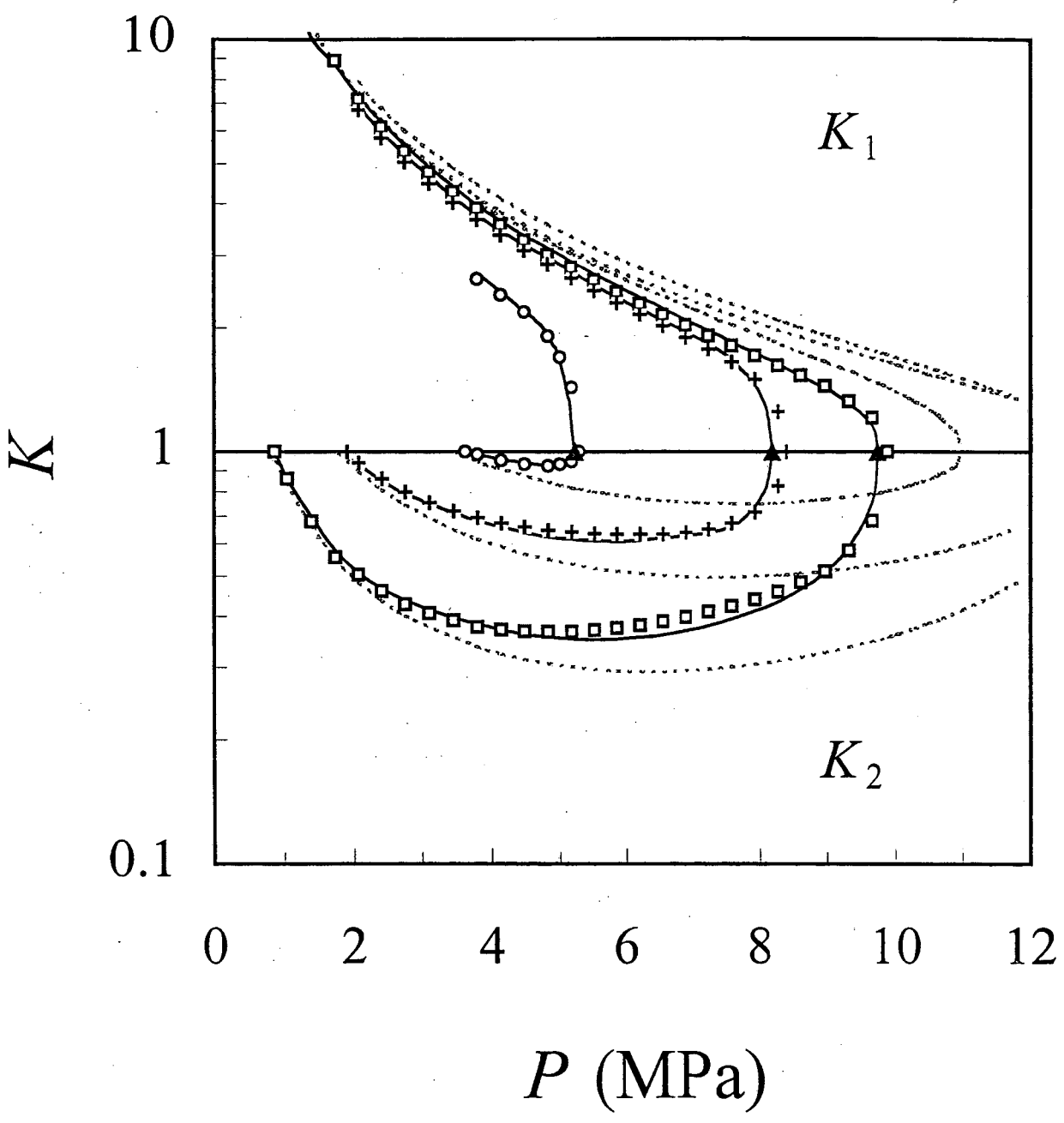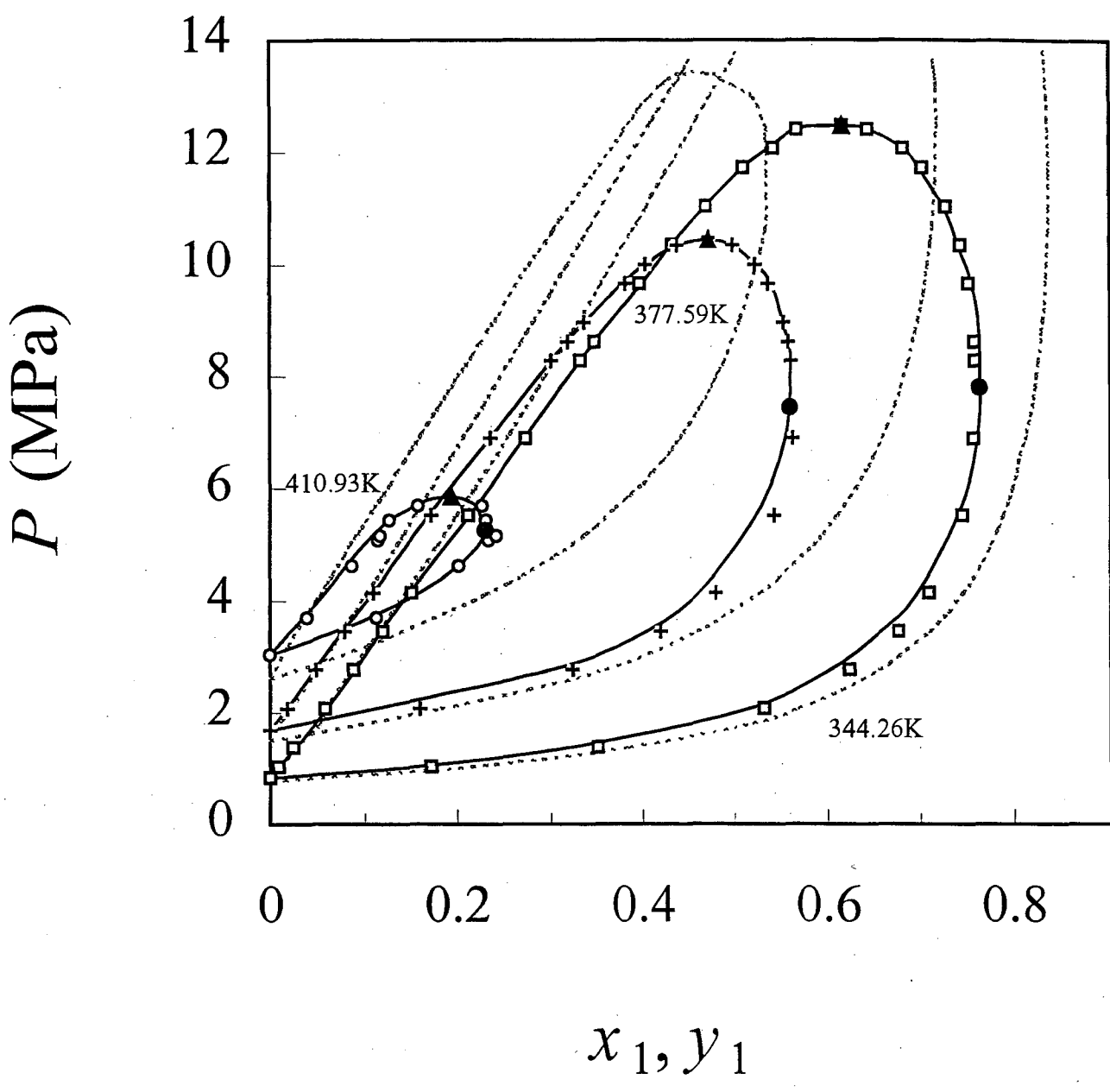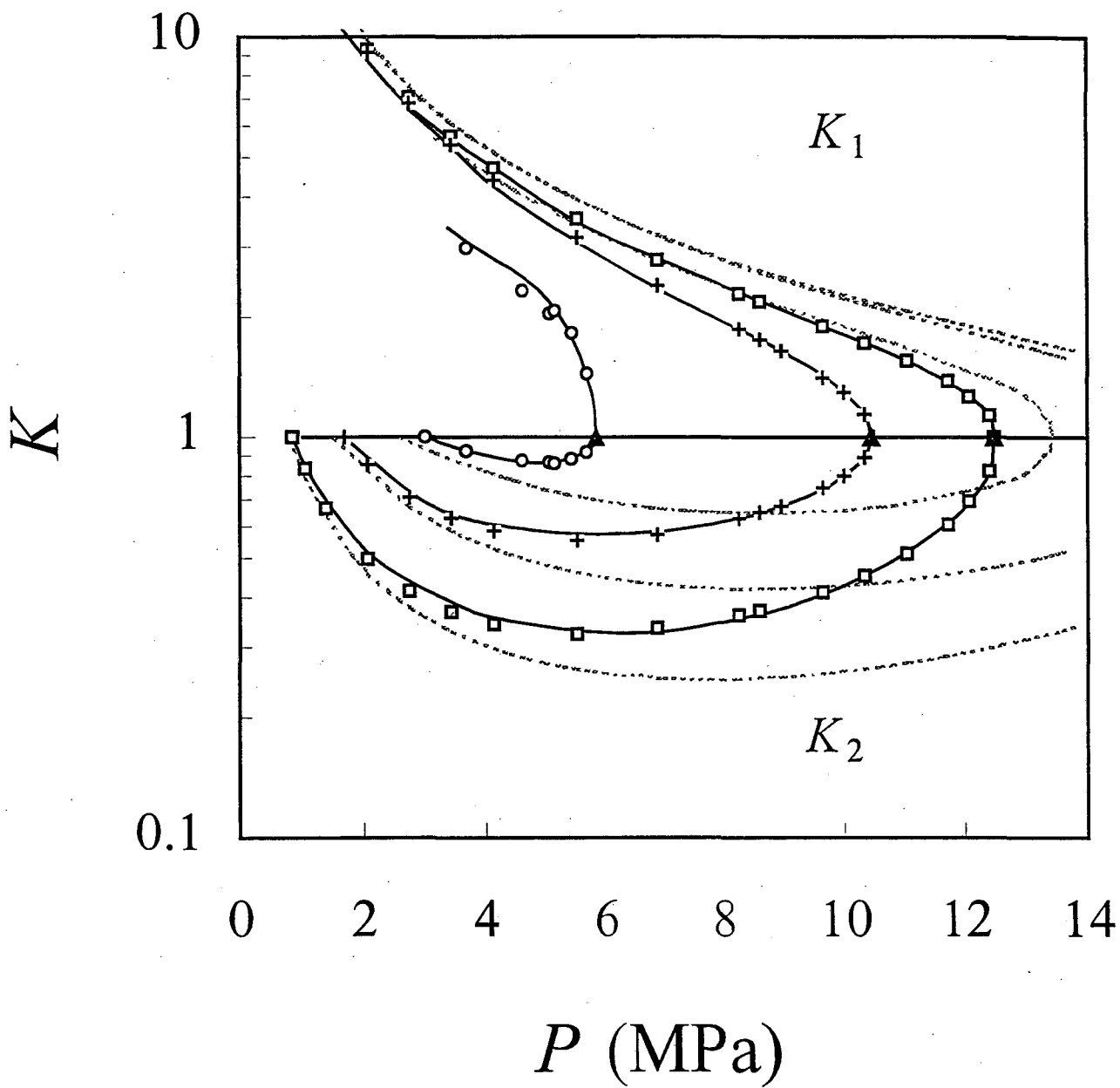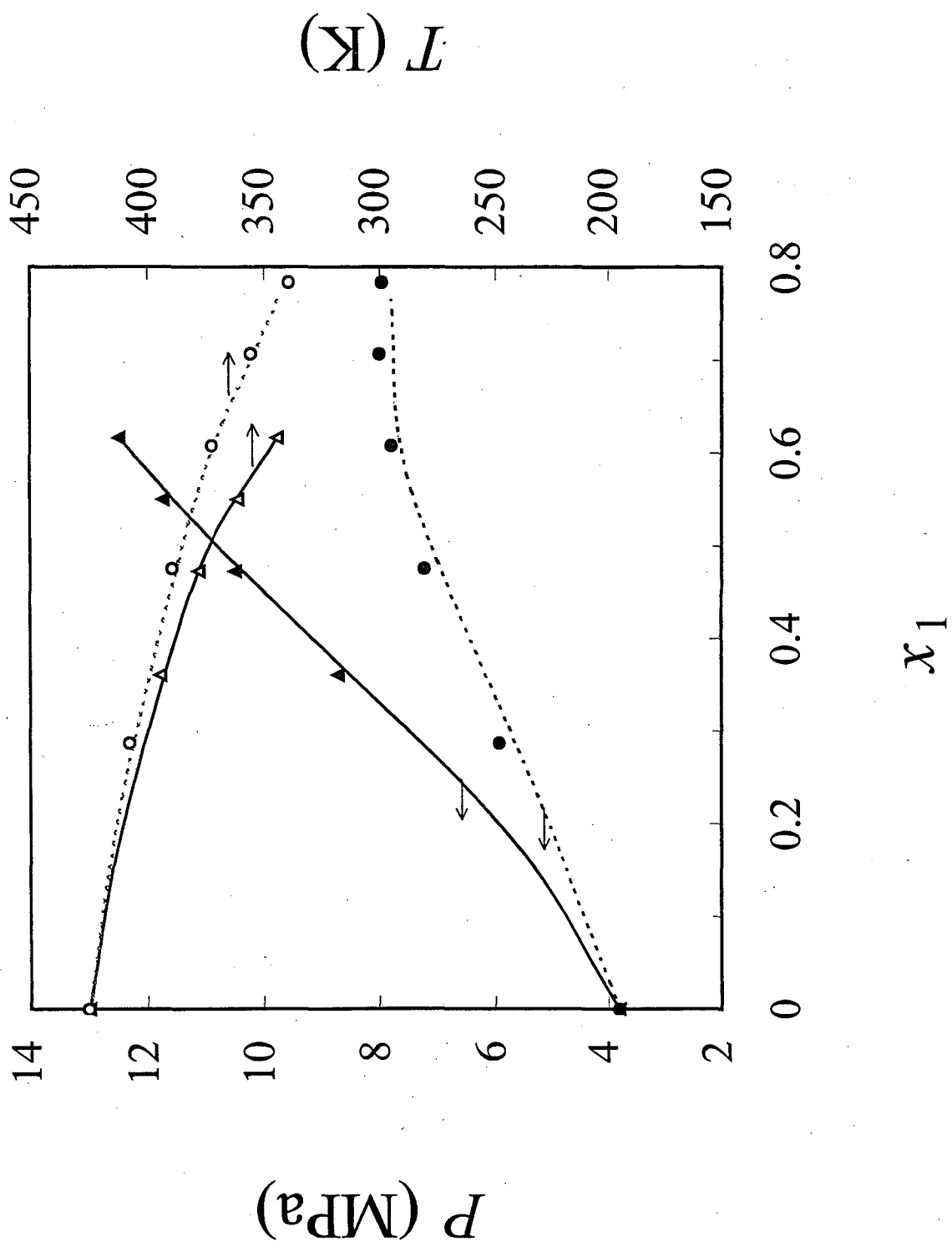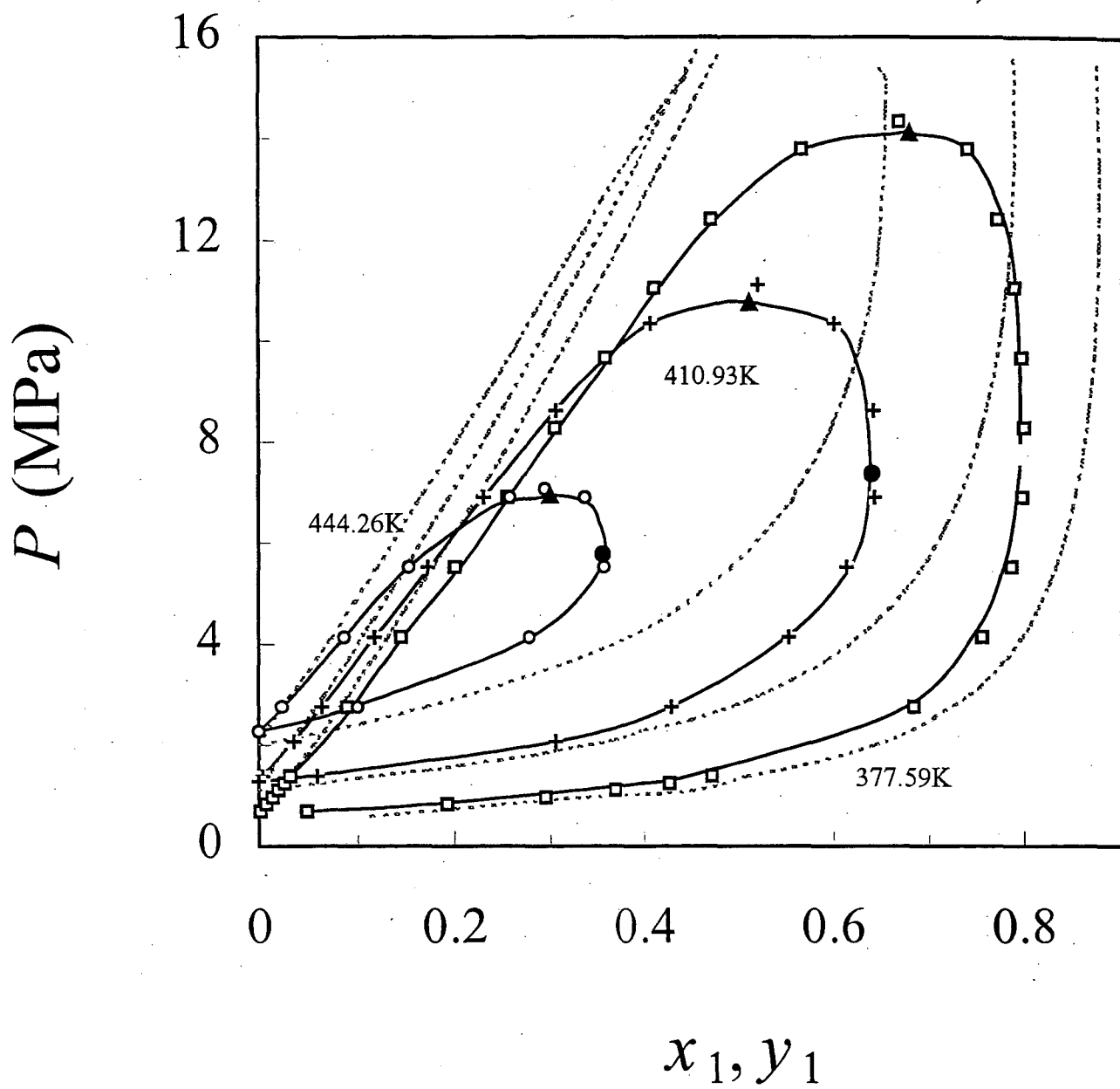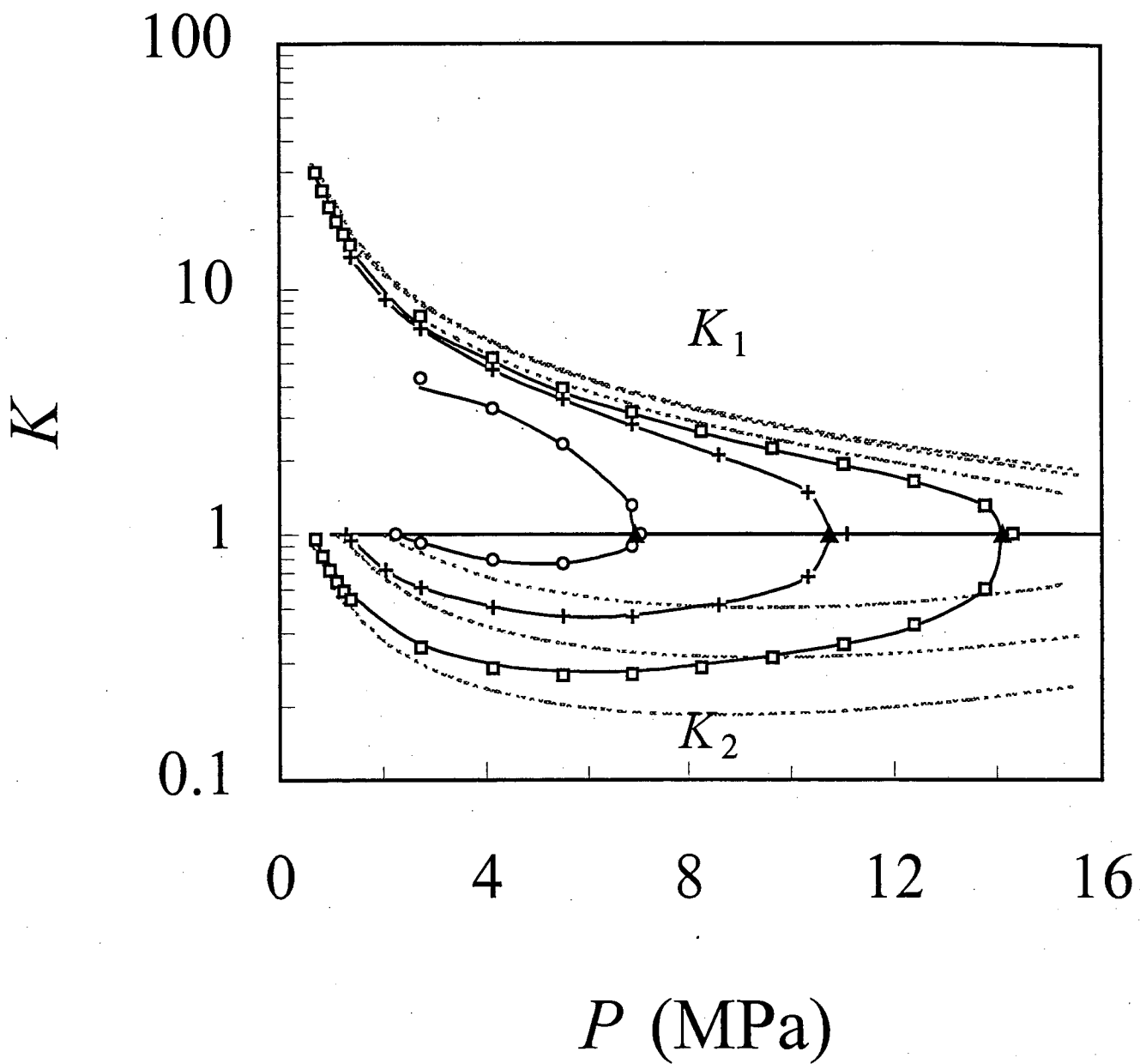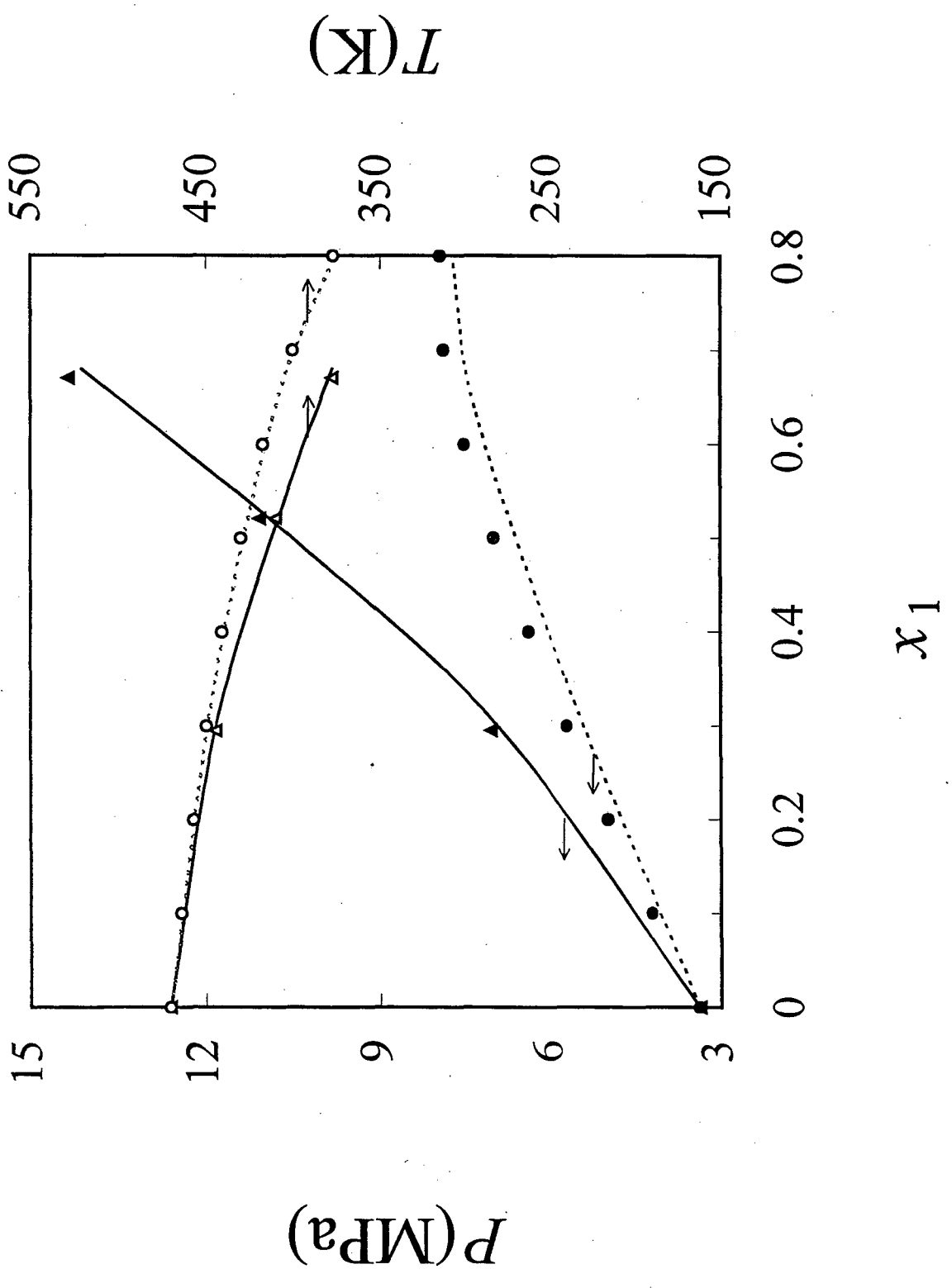
ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720