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THETA CONDITIONS IN BINARY AND MULTICOMPONENT POLYMER SOLUTIONS USING A PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

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ABSTRACT

Theta conditions in binary and multicomponent polymer solutions are calculated using a perturbed hard-sphere-chain (PHSC) equation of state. Theta conditions are identified by roots of the spinodal criterion in the limit of infinite polymer molecular weight and zero polymer-segment fraction. Because the thermodynamic properties of mixtures are described by an equation of state, both upper and lower theta temperatures can be calculated. For binary systems (one polymer and one solvent), experimentally determined theta conditions and the critical solution temperature for a single polymer molecular weight are used to obtain equation-of-state parameters. Parameters obtained in this manner yield nearly quantitative representation of upper and lower theta temperatures as a function of pressure and upper and lower critical solution temperatures as a function of polymer molecular weight. For ternary systems (two solvents and one polymer), the dependence of the theta temperature on solvent composition can be described using parameters obtained from binary data.

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1. Introduction

Solvent quality, an important quantity characterizing the behavior of a polymer in solution, is often defined with respect to theta conditions. A polymer dissolved in a "better than theta", i.e. a "good" solvent, is stable and will not phase separate at all concentrations and polymer molecular weights. On the other hand, a polymer dissolved in "worse than theta", i.e. a "poor" solvent, *may* phase separate at some concentration or polymer molecular weight[1]. In addition to miscibility, the conformational structure of a polymer molecule in dilute solution can also be related to theta conditions. In a good solvent, an isolated polymer coil is expanded, whereas in a poor solvent, the polymer collapses into a globular structure. At the theta condition, repulsive excluded-volume interactions exactly counter attractive dispersion forces between polymer segments and the polymer behaves as an ideal chain[2,3]. Also, the behavior of complex systems can sometimes be linked to theta conditions; for example, the flocculation conditions of sterically stabilized colloidal dispersions correlate strongly with the theta conditions of the stabilizing polymer moiety[4]. Because theta conditions characterize both the phase behavior and conformational behavior of polymers in solution, an array of experimental techniques is available for their determination; a few techniques are summarized below.

For a binary mixture of a polymer in a single solvent, the "Shultz-Flory" method is based on a relation between the critical solution temperature and polymer molecular weight; this relation is derived from the Flory-Huggins incompressible-lattice model[1,5]:

$$\frac{1}{T_{\mathrm{CST}}} = \frac{1}{\Theta}\left[1+\frac{1}{\psi_1}\left(\frac{1}{\sqrt{r}}+\frac{1}{2r}\right)^n\right] \tag{1}$$

In Eq. (1), T_{CST} is the critical solution temperature, Θ is the theta temperature, ψ_1 is the Flory residual-entropy parameter, and r is the ratio of the molecular volume of the polymer to that of the solvent; r is proportional to the polymer molecular weight. For a reliable estimation of the theta temperature, the Shultz-Flory method requires three or more monodisperse polymer samples of

different molecular weight. For each molecular weight, cloud-point temperatures are measured for several solutions spanning a range of polymer segment fractions of approximately 10^{-3}-10^{-1}. If cloud points appear upon decreasing temperature, the maximum temperature as a function of polymer concentration is the upper critical solution temperature (UCST). If cloud points appear upon increasing temperature, the minimum temperature as a function of polymer concentration is the lower critical solution temperature (LCST). The reciprocals of the critical solution temperatures are plotted vs. $r^{-1/2}+(2r)^{-1}$. Extrapolation to infinite polymer molecular weight (i.e., $r^{-1/2}+(2r)^{-1} = 0$) gives the reciprocal of the theta temperature.

Since there are two types of critical solution temperatures, two types of theta temperatures can exist, one associated with the UCST and the other associated with the LCST. Although the Flory-Huggins model can predict only a UCST because it assumes the mixture is incompressible, Eq. (1) has also been used to correlate the molecular-weight dependence of LCSTs. In the original form of Eq. (1), the exponent n is unity; however, Shultz-Flory plots for some systems can exhibit distinct curvatures. In that event, the *ad hoc* exponent n is adjusted empirically to linearize experimental data to perform a reliable extrapolation to infinite polymer molecular weight[6-8].

The Flory-Huggins model also shows that the polymer segment fraction at the critical consolute point, $\phi_{\text{polymer}}^{\text{CST}}$, asymptotically approaches zero in the limit of infinite polymer molecular weight:

$$\phi_{\text{polymer}}^{\text{CST}} = \frac{1}{1+r^{1/2}} \tag{2}$$

This behavior is observed experimentally, even though the segment fraction at the critical consolute point is difficult to determine accurately from measured cloud-point curves. The behavior of $\phi_{\text{polymer}}^{\text{CST}}$ in the limit of infinite polymer molecular weight plays an important role in devising appropriate criteria which allow the calculation of theta conditions from an equation of state for chain-like fluid mixtures.

Another method for experimental determination of theta conditions is the cloud-point titration method[9-14] and also has theoretical justification from the Flory-Huggins model[4,15]. The cloud-point titration method uses the same type of measurements as the Shultz-Flory method (i.e. turbidimetry), but there are several key differences. First, the cloud-point titration method requires only one molecular-weight polymer sample. Second, smaller polymer concentrations are required, typically in the range of 10^{-5}-10^{-2}. The behavior of cloud-point temperatures in this concentration range is summarized by

$$\frac{1}{T_{CP}} = \frac{1}{\Theta} - B_T \ln \phi_{polymer} \tag{3}$$

where T_{CP} is the cloud-point temperature and B_T is the slope of the cloud-point curve when T_{CP}^{-1} is plotted against $\ln \phi_{polymer}$. According to Eq. (3), extrapolation of a plot of the inverse cloud point temperature vs. the logarithm of the polymer concentration to pure polymer ($\phi_{polymer} = 1$) gives the reciprocal of the theta temperature. The cloud-point method and the Shultz-Flory method have been shown to produce consistent theta temperatures for several systems to within experimental uncertainty[11].

A third difference between these two methods is that the cloud-point titration method can be extended to describe a polymer in a mixed solvent. In this case, a non-solvent (component 2) is added to a mixture of good-solvent (component 1) and polymer (component 3) at constant temperature until a cloud-point is observed. The mixed-solvent composition at the cloud-point (ϕ_2^{CP}) is measured for several dilute-polymer concentrations, again in the range of $10^{-5} < \phi_3 < 10^{-2}$. The behavior is summarized in a manner similar to Eq. (3):

$$\phi_2^{CP} = \phi_2^{\Theta} - B_\phi \ln \phi_3 \tag{4}$$

where B_ϕ is the slope of the cloud-point concentration curve when ϕ_2^{CP} is plotted against $\ln \phi_3$. Extrapolation of ϕ_2^{CP} to pure polymer ($\phi_3 = 1$) gives the "theta-composition" ϕ_2^{Θ}. Performing

titrations at different temperatures gives the dependence of ϕ_2^{Θ} on temperature, or identically, the dependence of Θ on solvent composition.

A third method probes the behavior of another thermodynamic property of dilute polymer solutions: the osmotic second virial coefficient, A_2. Two common experimental techniques for measuring the second osmotic virial coefficient are osmometry[1] and low-angle laser-light scattering[16]. Like the cloud-point titration method, measurement of A_2 requires only a single polymer molecular weight. Theta conditions are determined by scanning temperatures or solvent compositions to find the conditions where the measured value of A_2 is zero.

Additional methods for determining theta conditions examine the molecular-weight dependence of various hydrodynamic properties of polymer solutions. These methods can be generalized by[1,17]:

$$P = KM^a \tag{5}$$

where P is a measured property such as the intrinsic viscosity, sedimentation coefficient or diffusion coefficient, M is the polymer molecular weight and K is a proportionality constant. The temperature or solvent composition where the exponent $a = 1/2$ identifies a theta condition. Like the Shultz-Flory method, this method requires experimental measurements using several molecular weights of a given polymer.

The techniques discussed above probe distinctly different properties (thermodynamic or hydrodynamic) over a wide range of concentration (concentrated vs. dilute). Different experimental methods raises questions concerning consistency. Surveying a compiled list of measured theta conditions for a wide range of polymers, solvents and experimental techniques[17] is inconclusive. In many cases, consistent results are obtained across techniques but for some systems, results from different methods can differ significantly.

Theoretically, this concern is less ambiguous. Models that describe dilute polymer solutions are fundamentally different from those that describe concentrated polymer solutions (such as the Flory-Huggins model or hard-sphere-chain models). In dilute solutions, the non-uniform distribution of polymer segments is important; however, in concentrated solutions, the spatial distribution of segments is properly assumed to be uniform. As discussed by Flory (ref. 1, pg. 532), this distinction between models becomes unimportant at the theta condition. Recently, computer simulations have been performed that probed both phase equilibria and conformational properties of polymers whose segments interact through the Lennard-Jones potential[18]. Simulations which determined phase equilibria were used to construct a "Shultz-Flory" plot for Lennard-Jones chains. Additional simulations which sampled conformational properties were performed to calculate the second virial coefficient. Although simulated polymer chain-lengths were somewhat small, the theta temperature obtained from the Shultz-Flory plot was found to be near the "Boyle" temperature of large chain-length polymers.

This paper has three objectives. First, we present a method for calculating theta conditions using and equation of state for chain-like fluid mixtures. Second, we use experimentally determined theta conditions (and a minimum amount of additional experimental information) for binary systems to extract equation-of-state parameters that yield quantitative representation of upper and lower critical solution temperatures as a function of pressure and polymer molecular weight. Finally, we attempt to represent quantitatively the theta temperature of polymers in a mixed solvent using parameters obtained from binary data.

Although the method presented here for the calculation of theta conditions can be used with any equation of state for chain-like fluids, we perform calculations using the perturbed hard-sphere-chain (PHSC) equation of state[19-21]. Other equations of state which could be used include those derived from lattice-fluid models[22-25] and the statistical associated-fluid theory (SAFT)[26,27]. We begin by summarizing the pertinent thermodynamic functions associated with the PHSC equation of state.

2. Equation of State and Thermodynamic Functions

The perturbed hard-sphere-chain (PHSC) equation of state[21] for an m-component mixture is:

$$\frac{p}{\rho_r k_B T} = 1 + \rho_r \sum_{ij}^{m} \phi_i \phi_j b_{ij} g_{ij}(d_{ij}^+) - \sum_{i}^{m} \phi_i \left(1 - \frac{1}{r_i}\right) g_{ii}(d_{ii}^+) - \frac{\rho_r}{k_B T} \sum_{ij}^{m} \phi_i \phi_j a_{ij} \tag{6}$$

where p is the pressure, $\rho_r = N_r / V$ is the segment density ($N_r = \Sigma_{i=1}^{m} N_i r_i$ is the total number of segments in volume V), $\phi_i = N_i r_i / N_r$ is the segment fraction of component i, k_B is the Boltzmann constant, and T is absolute temperature. In Eq. (6), $g_{ij}(d_{ij}^+)$ is the ij pair radial distribution function of hard-sphere mixtures at contact, b_{ij} is the second virial coefficient of effective hard-sphere mixtures, and a_{ij} reflects the strength of attractive forces between unbonded segments of component i and component j.

According to perturbed hard-sphere-chain theory[20,21], parameters a_{ii} and b_{ii} are functions of temperature:

$$a_{ii}(T) = \frac{2\pi}{3} \sigma_{ii}^3 \varepsilon_{ii} \mathcal{F}_a(k_B T / \varepsilon_{ii}) \tag{7}$$

$$b_{ii}(T) = \frac{2\pi}{3} d_{ii}^3(T) = \frac{2\pi}{3} \sigma_{ii}^3 \mathcal{F}_b(k_B T / \varepsilon_{ii}) \tag{8}$$

where d_{ii} is the effective hard-sphere diameter of a segment of component i at temperature T and constants ε_{ii} and σ_{ii} characterize the intermolecular potential between unbonded segments of component i; ε_{ii} is the depth of the minimum in the pair potential and σ_{ii} is the separation distance between segment centers at this minimum. For brevity, ε_{ii} is referred to as an effective "interaction energy" between non-bonded segments of component i and σ_{ii} is referred to as an

effective "hard-core" segment diameter of component i. Functions $\mathcal{F}_a$ and $\mathcal{F}_b$ in Eqs. (7) and (8) are determined from the thermodynamic properties of simple fluids ($r = 1$) and represented by

$$\mathcal{F}_a(k_BT/\varepsilon_{ij}) = \alpha_1 \exp\left[-\alpha_2(k_BT/\varepsilon_{ij})\right] + \alpha_3 \exp\left[-\alpha_4(k_BT/\varepsilon_{ij})^{3/2}\right] \tag{9}$$

$$\mathcal{F}_b(k_BT/\varepsilon_{ii}) = \beta_1 \exp\left[-\beta_2(k_BT/\varepsilon_{ii})^{1/2}\right] + (1-\beta_1)\exp\left[-\beta_3(k_BT/\varepsilon_{ii})^{3/2}\right] \tag{10}$$

Constants α_i and β_i are listed in Table 1 and are the same for all fluids†.

For each pair of components in the mixture, cross terms a_{ij} and b_{ij} are needed. A simple extension of Eq. (7) is used for a_{ij}:

$$a_{ij}(T) = \frac{2\pi}{3}\sigma_{ij}^3 \varepsilon_{ij} \mathcal{F}_a(k_BT/\varepsilon_{ij}) \tag{11}$$

Eq. (11) requires combining rules to determine ε_{ij} and σ_{ij}:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}\,(1-\kappa_{ij}) \tag{12}$$

$$\sigma_{ij} = (\sigma_{ii}+\sigma_{jj})/2 \tag{13}$$

Eq. (12) introduces binary interaction parameter κ_{ij}. Unlike a_{ij}, b_{ij} is not arbitrary, but is uniquely determined from additivity of effective hard-sphere diameters:

$$b_{ij}(T) = \frac{2\pi}{3} d_{ij}^3(T) = \frac{1}{8}(b_{ii}^{1/3}+b_{jj}^{1/3})^3 \quad ; \quad d_{ij}(T) = \frac{1}{2}\left[d_{ii}(T)+d_{jj}(T)\right] \tag{14}$$

Finally, the PHSC EOS for mixtures uses for $g_{ij}(d_{ij}^+)$ the Boublik-Mansoori extension of the Carnahan-Starling equation to mixtures of hard-spheres[28,29]:

$$g_{ij}(d_{ij}^+) = g_{ij}(\eta,\xi_{ij}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)^3} \tag{15}$$

† A simplified version of the PHSC equation is used here. In previous publications, the temperature dependence of the universal functions were scaled by a parameter s which was a function of chain length, r. In the present model, this scale factor is removed and the universal functions were determined from the thermodynamic properties of argon and methane over a wider temperature range. Removal of $s(r)$ from the universal functions allows use of simpler combining rules. The simpler rules do not sacrifice accuracy in fitting thermodynamic properties of pure (non-associating) fluids to obtain equation-of-state parameters.

where η and ξ_{ij} are packing fractions defined as

$$\eta = \frac{\rho_r}{4}\sum_{i=1}^{m}\phi_i b_{ii} \tag{16}$$

$$\xi_{ij} = \left(\frac{b_{ii}b_{jj}}{b_{ij}}\right)^{1/3}\frac{\rho_r}{4}\sum_{k=1}^{m}\phi_k b_{kk}^{2/3} \tag{17}$$

From the equation of state, Eq. (6), other relevant thermodynamic functions such as the Helmholtz energy and chemical potential are derived using appropriate thermodynamic identities[30]. The Helmholtz energy of the mixture is

$$\begin{aligned}\frac{A}{N_r k_B T} &= \sum_{i=1}^{m}\phi_i\frac{A_i^\circ}{N_i r_i k_B T} + \rho_r\sum_{i,j=1}^{m}\phi_i\phi_j b_{ij}W_{ij} - \sum_{i=1}^{m}\phi_i\left(1-\frac{1}{r_i}\right)Q_{ii} \\ &- \frac{\rho_r}{k_B T}\sum_{i,j=1}^{m}\phi_i\phi_j a_{ij} + \sum_{i=1}^{m}\frac{\phi_i}{r_i}\ln\left(\frac{\phi_i}{r_i}\rho_r k_B T\right)\end{aligned} \tag{18}$$

where A_i° is the Helmholtz energy of pure component i as an ideal gas at temperature T. W_{ij} and Q_{ii} are given by:

$$W_{ij}(\eta,\xi_{ij}) = K_1 + \frac{3}{2}\xi_{ij}K_2 + \frac{1}{2}\xi_{ij}^2 K_3 \tag{19}$$

$$Q_{ii}(\eta,\xi_{ii}) = -\ln(1-\eta)+\frac{3}{2}\frac{\xi_{ii}}{1-\eta}+\frac{1}{4}\frac{\xi_{ii}^2}{(1-\eta)^2} \tag{20}$$

$$K_n = \frac{1}{\eta}\left[-K_{n-1}+\frac{1}{n-1}\frac{1}{(1-\eta)^{n-1}}\right], \qquad K_1 = -\frac{\ln(1-\eta)}{\eta} \tag{21}$$

The chemical potential of component k is

$$\begin{aligned}\frac{\mu_k}{k_B T} &= \frac{\mu_k^\circ}{k_B T} + 2r_k\rho_r\sum_{i=1}^{m}\phi_i b_{ik}W_{ik} + \rho_r\sum_{i,j=1}^{m}\phi_i\phi_j b_{ij}\left(N_r\frac{\partial W_{ij}}{\partial N_k}\right) \\ &- (r_k-1)Q_{kk} - \sum_{i=1}^{m}\phi_i\left(1-\frac{1}{r_i}\right)\left(N_r\frac{\partial Q_{ii}}{\partial N_k}\right) \\ &- \frac{2r_k\rho_r}{k_B T}\sum_{i=1}^{m}\phi_i a_{ik} + \ln\left(\frac{\phi_k}{r_k}\rho_r k_B T\right) + 1\end{aligned} \tag{22}$$

where μ_k° is the chemical potential of pure component i as an ideal gas at temperature T and

$$\left(N_r \frac{\partial W_{ij}}{\partial N_k}\right) = \left(\frac{\partial W_{ij}}{\partial \eta}\right)\left(N_r \frac{\partial \eta}{\partial N_k}\right) + \left(\frac{\partial W_{ij}}{\partial \xi_{ij}}\right)\left(N_r \frac{\partial \xi_{ij}}{\partial N_k}\right) \tag{23}$$

$$\left(N_r \frac{\partial Q_{ii}}{\partial N_k}\right) = \left(\frac{\partial Q_{ii}}{\partial \eta}\right)\left(N_r \frac{\partial \eta}{\partial N_k}\right) + \left(\frac{\partial Q_{ii}}{\partial \xi_{ii}}\right)\left(N_r \frac{\partial \xi_{ii}}{\partial N_k}\right) \tag{24}$$

$$\left(N_r \frac{\partial \eta}{\partial N_k}\right) = \frac{\rho_r}{4} r_k b_k \tag{25}$$

$$\left(N_r \frac{\partial \xi_{ij}}{\partial N_k}\right) = \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho_r}{4} r_k b_k^{2/3} \tag{26}$$

3. Critical Consolute Points

Critical consolute points in liquid mixtures satisfy the following equations which define a critical point for a m-component mixture[31]:

$$X = \begin{vmatrix} -p_\rho & p_{\phi_1} & \cdots & p_{\phi_{m-1}} \\ -p_{\phi_1} & A_{\phi_1\phi_1} & \cdots & A_{\phi_1\phi_{m-1}} \\ \vdots & \vdots & \ddots & \vdots \\ -p_{\phi_{m-1}} & A_{\phi_{m-1}\phi_1} & \cdots & A_{\phi_{m-1}\phi_{m-1}} \end{vmatrix} = 0 \tag{27}$$

$$Y = \begin{vmatrix} -X_\rho & X_{\phi_1} & \cdots & X_{\phi_{m-1}} \\ -p_{\phi_1} & A_{\phi_1\phi_1} & \cdots & A_{\phi_1\phi_{m-1}} \\ \vdots & \vdots & \ddots & \vdots \\ -p_{\phi_{m-1}} & A_{\phi_{m-1}\phi_1} & \cdots & A_{\phi_{m-1}\phi_{m-1}} \end{vmatrix} = 0 \tag{28}$$

where the elements of determinants X and Y are defined as

$$p_\rho = \frac{1}{k_B T}\left(\frac{\partial p}{\partial \rho_r}\right) \tag{29}$$

$$p_{\phi_l} = \frac{1}{\rho_r k_B T}\left(\frac{\partial p}{\partial \phi_l}\right) \tag{30}$$

$$A_{\phi_l \phi_k} = \frac{\partial}{\partial \phi_k \partial \phi_l}\left(\frac{A}{N_r k_B T}\right) \tag{31}$$

$$X_\rho = \rho_r \frac{\partial X}{\partial \rho_r} \tag{32}$$

$$X_{\phi_l} = \frac{\partial X}{\partial \phi_l} \tag{33}$$

The elements of determinants X and Y are expressed as dimensionless quantities.

For consistency, the polymer is always identified as the largest numbered component in the mixture and the solvent having the smallest value of r has the lowest number. For example, in a binary solvent/polymer mixture, the solvent is component 1 and the polymer is component 2. In a ternary mixture of two solvents and a polymer, the polymer is component 3 and the solvents are designated such that $r_1 < r_2$.

An attempt is made here to calculate critical solution temperatures that are consistent with those obtained from experimental cloud-point methods. In most cases, the vessel containing a solvent/polymer mixture also contains vapor space[32,33], unless measurements are performed at an elevated pressure above the saturation pressure of the solution[34-36]. When phase-separation occurs at temperatures approaching the critical temperature of the solvent (i.e., LCSTs), the vapor-pressure above the solution can be significantly greater than one atmosphere.

For consistency with experiment, calculations of critical consolute temperatures of binary mixtures are not at atmospheric pressure, but at the vapor pressure of the solution. For mixtures considered here, the polymer is assumed non-volatile and the vapor pressure of the mixture is determined by equating the chemical potentials of solvent in the liquid (L) to that in the vapor (V):

$$\mu_1^{\mathrm{L}}(\phi_1) = \mu_{\text{pure 1}}^{\mathrm{V}} \tag{34}$$

Therefore, calculation of the critical consolute point of a binary mixture involves four unknowns: the critical consolute temperature T_{CST} (upper or lower), the critical polymer segment fraction ϕ_{2c}, the segment density at the critical consolute point, and the vapor pressure of the mixture p^{sat}. These quantities are determined from four equations: the critical-point conditions Eqs. (27) and (28), the equation of state Eq. (6) and the equality of solvent chemical potential in the liquid to that in the vapor, Eq. (34).

Critical consolute points calculated assuming a fixed low pressure (zero or atmospheric) and those calculated as described above are necessarily different, but the difference is only significant for LCSTs. UCSTs in polymer solutions usually occur at temperatures near the triple-point temperature of the solvent where its vapor pressure is almost always much less than atmospheric.

4. Determination of Theta Conditions

To calculate theta conditions using an equation of state for chain-like fluids, we consider the stability criterion of a binary mixture. Thermodynamic stability at some composition, temperature and pressure can be determined by the sign of the second derivative of the Gibbs energy, G, with respect to the segment fraction of component 1, ϕ_1. If $(\partial^2 G/\partial\phi_1^2)_{T,p} > 0$, the mixture is stable or metastable; otherwise, if $(\partial^2 G/\partial\phi_1^2)_{T,p} < 0$, the mixture is unstable. Therefore, the relation $(\partial^2 G/\partial\phi_1^2)_{T,p} = 0$ provides a convenient criterion for defining the limit of mixture stability.

To apply this criterion to determine the theta temperature of a binary mixture, we make use of some important features of the theta condition that evolve from the Shultz-Flory relation, Eq. (1). First, the theta temperature is identical to the critical consolute temperature of a solution containing a polymer of infinite molecular weight. Second, the critical polymer segment fraction vanishes in this limit. Hence, a theta temperature should correspond to a root of $(\partial^2 G/\partial\phi_1^2)_{T,p}$ in

the limit of infinite polymer molecular weight ($r_2 \to \infty$) and zero polymer segment fraction ($\phi_2 \to 0$). If in contact with its vapor, the pressure of the system is the vapor pressure of the pure solvent.

For a polymer (component m) mixed with $m-1$ solvents, the appropriate criterion is:

$$\begin{vmatrix} G''(1,1) & \cdots & G''(1,m-1) \\ \vdots & \ddots & \vdots \\ G''(m-1,1) & \cdots & G''(m-1,m-1) \end{vmatrix} = 0 \tag{35}$$

where

$$G''(i,j) \equiv \left(\frac{\partial^2 G}{\partial\phi_i \partial\phi_j}\right)_{T,p} \tag{36}$$

The theta temperature of a polymer in a fixed composition of m–1 solvents is determined by the roots of Eq. (35) in the "theta limit" (i.e., $r_m \to \infty$ and $\phi_m \to 0$).

However, evaluation of Eq. (35) is inconvenient because when thermodynamic properties of a mixture are derived from a pressure-explicit equation of state, the derivatives of the Gibbs energy with respect to composition cannot be computed analytically. This problem is circumvented by variable transformations[31] which replaces the determinant in Eq. (35) with determinant X given by Eq. (27). Eq. (27) expresses the stability criterion as derivatives of the Helmholtz energy and pressure with respect to segment-density and composition that can be computed analytically. The two determinants are equivalent except for a difference in sign. In this work, theta conditions are determined by finding the roots of determinant X in the "theta limit," denoted by X^∞. When $X^\infty > 0$, the mixture may phase separate at some concentration and polymer molecular weight. When $X^\infty < 0$, the polymer is miscible in all proportions with the solvent or solvent mixture, regardless of polymer molecular weight.

Determination of theta temperatures for a binary mixture is illustrated in Figure 1 for a hypothetical solvent/polymer mixture where the solvent is composed of four spherical segments.

The ratio of pure-component interaction-energies and that for hard-core segment-diameters are set equal to unity. For three binary interaction parameters κ_{12}, Figure 1 shows X^{∞} as a function of temperature scaled by the critical temperature of the solvent. The pressure of the system is the vapor pressure of the pure solvent.

When $\kappa_{12} = 0$, the solvent is essentially a low-molecular-weight analog of the polymer. Because of compressibility differences which arise from size differences between solvent and polymer as temperature increases, a root of X^{∞}, corresponding to a "lower" theta temperature Θ_L, occurs at a reduced temperature of approximately 0.76. A lower theta temperature signifies that the mixture becomes unstable upon increasing temperature, as illustrated by the change in sign of X^{∞} from negative below Θ_L to positive above Θ_L.

A non-zero value of the binary interaction parameter introduces asymmetry in the pair interactions. When $\kappa_{12} = 0.0075$, a low-temperature root and a high-temperature root are observed. The high-temperature root corresponds again to Θ_L, whereas the low-temperature root corresponds to an upper theta temperature, Θ_U, and the change of sign of X^{∞} indicates that the mixture becomes unstable upon decreasing temperature below Θ_U.

If the binary interaction parameter is increased further to $\kappa_{12} = 0.012$, X^{∞} has a positive sign at all temperatures. Consequently, for some molecular weights and concentrations, the polymer is not completely miscible with the solvent at all temperatures. However, the low molecular weights of the polymer may be miscible at some conditions, as illustrated in Figure 2 which shows the Shultz-Flory plots (reciprocal critical solution temperatures vs. $r^{-1/2}+(2r)^{-1}$ where $r = r_2/r_1$) corresponding to each value of κ_{12} used in Figure 1. In Figure 2(c), the UCST and LCST merge as the molecular weight of the polymer increases, indicating hourglass-type phase diagrams in the temperature-composition plane. For the smaller values of κ_{12}, the intercepts on the vertical axes of Figure 2(a) and (b) correspond to the reciprocal reduced theta temperatures identified from roots of X^{∞} in Figure 1. Finally, the non-linear behavior of the Shultz-Flory plots

commonly observed experimentally is predicted by using an equation-of-state description of the fluid mixture.

Shultz-Flory plots for estimating theta temperatures also provide a convenient means for "mapping" regions of miscibility as a function of temperature and polymer molecular weight. Having established a method for the determination of theta temperatures in binary systems, the next section discusses how Shultz-Flory plots for several binary systems can be quantitatively correlated by using experimental theta temperatures to determine equation-of-state parameters. Parameters determined in this manner are then used to predict critical solutions temperatures as a function of pressure, polymer molecular weight and solvent composition.

5. Determination of Equation-of-State Parameters

Three parameters characterize each pure component in the mixture: the number of effective hard spheres per molecule r_i, the effective segment-segment interaction energy ε_{ii}, and the effective "hard-core" segment diameter, σ_{ii}. In addition, the PHSC equation of state also requires a binary interaction parameter κ_{ij} for each pair of components in the mixture. The number of effective hard-spheres per molecule r_i for a polymer is linearly related to the polymer molecular weight; therefore, a polymer is more conveniently characterized by r_i/M_i, where M_i is the polymer molecular weight. However, when calculating theta conditions, r_i (or r_i/M_i) is not required because the polymer molecular weight is infinite.

For a binary solvent/polymer mixture in the theta limit, some thermodynamic properties of the mixture, for example, the vapor pressure and liquid density, reduce to the thermodynamic properties of the pure solvent, indicating the importance of characterizing the pure solvent. Therefore, equation-of-state parameters r_i, ε_{ii}, and σ_{ii} for solvents are determined by regression of vapor-pressure and saturated liquid-density data at temperatures between $0.5 < T/T_c < 0.9$,

where T_c is the gas-liquid critical temperature of the solvent. Thermodynamic properties for all solvents considered here are obtained from the DIPPR pure-chemical-data compilation[37]. Table 2 gives the PHSC equation-of-state parameters for solvents considered here. The root-mean-square relative deviation between calculated and experimental vapor pressures and saturated liquid densities is 1-6%.

For quantitative correlation of experimental liquid-liquid equilibria, determination of pure-component parameters for polymers is less obvious. A common source of pure-polymer parameters is regression of liquid polymer *PVT* data; however, when used in conjunction with solvent parameters, quantitative correlation of experimental liquid-liquid equilibrium data has been largely unsuccessful regardless of which equation of state is used[23,38,39]. Adjusting binary interaction parameter κ_{ij} or adding a second binary parameter [e.g., relaxing the additivity of hard-sphere diameters constraint, Eq. (12)] does not give the equation of state enough flexibility to correlate LLE. The conventional procedure for using equations of state to correlate LLE is not satisfactory because when pure polymer *PVT* data are used, parameters characterizing the polymer repeat unit differ significantly from the parameters for solvent analog (e.g., the energy parameter for polyethylene is significantly different from that for large molecular weight normal alkanes)[20].

Because polymer parameters obtained from *PVT* data cannot correlate LLE, we determine polymer parameters using judiciously chosen experimental data. First, the polymer segment diameter is set equal to that of the solvent, $\sigma_{22} = \sigma_{11}$. Second, for systems which only exhibit LCST behavior, the polymer-polymer segment interaction energy, ε_{22}, is adjusted to match the experimentally determined lower theta temperature, Θ_L, and the binary interaction parameter, κ_{12}, is set to zero. For systems which exhibit both UCST and LCST behavior, both ε_{22} and κ_{12} are adjusted to match Θ_U and Θ_L. Using the parameters determined from theta conditions, r_2/M_2 is determined by matching the critical solution temperature for a specific polymer molecular weight. If the critical solution temperature for more than one polymer molecular weight is available, the lowest molecular weight is used and the critical solution temperatures at all other polymer

molecular weights are predicted. If a system exhibits both UCST and LCST behavior, the UCST is chosen to determine r_2/M_2, and the LCSTs for systems with finite polymer molecular weights are predicted.

6. Results and Discussion

The binary systems considered first are those showing only LCST behavior. Figure 3 shows the Shultz-Flory plots for polyethylene in normal alkanes (pentane through octane)[40]. For each solvent, Table 3 gives the polyethylene interaction energy determined from the reported Θ_L. Also listed in Table 3 is the value of r_2/M_2 determined from the LCST of the lowest polyethylene molecular weight. For mixtures with pentane, the polyethylene molecular weight range studied was $M_w = 4.9\times10^3 - 14.3\times10^3$; for mixtures with hexane $M_w = 34.9\times10^3 - 4.421\times10^5$; for mixtures with heptane and octane $M_w = 76.8\times10^3 - 2.02\times10^5$. The parameter estimation method used here fixes the two points at each end of the Shultz-Flory plot and predicts points in between. For systems with hexane, heptane, and octane, excellent agreement between calculated and experimental lower critical solution temperatures is observed. For systems with pentane, however, the LCSTs of the two higher polyethylene molecular weights are overestimated by approximately 5 °C. This discrepancy is due to uncertainty in the reported Θ_L since the polyethylene molecular weights used with pentane were much smaller than those used with the other solvents.

Similar results are shown in Figure 4 for polystyrene in benzene[7] which shows only LCST behavior. The equation-of-state parameters for polystyrene in benzene is listed in Table 4.

Shultz-Flory plots for polystyrene in various solvents which exhibit upper and lower critical solution temperatures have been widely studied; Table 4 gives pertinent parameters. The Shultz-Flory plot for polystyrene ($M_w = 43\times10^3$–1.6×10^6) in cyclopentane[41,42] is shown in Figure 5. The polymer-polymer segment interaction energy ε_{22} and the binary interaction

parameter κ_{12} were determined from the upper and lower theta temperatures; r_2/M_2 was determined from the UCST reported for the lowest polystyrene molecular weight. Like the LCST Shultz-Flory plot for benzene, parameters are chosen to fix each end of the UCST Shultz-Flory plot. UCSTs in between are well correlated; the maximum error between calculated and experimental UCST is less than 1.7 °C. However, the lower critical solution temperatures for all finite polystyrene molecular weights are always under-predicted. The error between predicted and calculated LCSTs is 1.3 °C for the largest molecular weight and increases to 4.7 °C for the smallest molecular weight.

Similar results are obtained for polystyrene ($M_w = 20.4 \times 10^3 - 2.7 \times 10^6$) in cyclohexane[6,32] shown in Figure 6 and polystyrene ($M_w = 10.2 \times 10^3 - 2.7 \times 10^6$) in methylcyclohexane[6,43,44] shown in Figure 7. For both solvents the UCSTs are slightly over-predicted by at most 2 °C, and the LCSTs are under-predicted. For cyclohexane the maximum error between predicted and experimental LCSTs is 8.4 °C, whereas for methylcyclohexane the maximum difference is 5.6 °C.

The same behavior is also shown in Figures 8-11 for polystyrene ($M_w = 37 \times 10^3 - 2.7 \times 10^6$) in *n*-propyl acetate, *iso*-propyl acetate, ethyl acetate, and methyl acetate[45] and in Figure 12 for polystyrene ($M_w = 1 \times 10^5 - 3.45 \times 10^6$) in *t*-butyl acetate[32,35]. Except for *t*-butyl acetate, UCSTs are correlated to within 1.5 °C. LCSTs are under-predicted more severely; the maximum errors between calculated and experimental LCSTs are 14.6, 11.2, 10.6, 8.1 and 8 °C, respectively, for *n*-propyl acetate, *iso*-propyl acetate, ethyl acetate, methyl acetate and *t*-butyl acetate.

For *t*-butyl acetate, data for the lowest polystyrene molecular weight from Saeki, et al.[35] were used to determine r_2/M_2, since there appears to be some inconsistency between their results and the results of Bae, et al.[32] for the molecular-weight dependence of the UCST. The UCSTs from Bae, et al.[32] are under-predicted by 9-12 °C. The PHSC equation of state predicts non-linear curves for both the UCST and LCST in good agreement with experiment.

For *t*-butyl acetate/polystyrene mixtures, data for Shultz-Flory plots at elevated pressures have also been measured. These data allow calculation of the effect of pressure on the upper and lower theta temperature[35]. Using equation-of-state parameters determined from the Shultz-Flory plot at low pressure (Figure 12), Figure 13 shows excellent agreement between predicted and experimental upper and lower theta temperatures for pressures up to 50 atm.

Finally, we consider the upper theta temperature of polystyrene in a mixed solvent containing cyclohexane and methylcyclohexane[46]. Because only the upper theta temperature for the solvent mixture at low pressure is considered, calculations are performed assuming zero pressure. Also, polystyrene parameters must be determined. Noting that polymer parameters for each of the corresponding binary mixtures are similar, the polystyrene segment-segment interaction energy and hard-core segment diameter, ε_{33} and σ_{33}, are set to the average of the parameters for two solvents. The two solvent-polymer binary interaction parameters, κ_{13} and κ_{23}, are readjusted to match each binary upper theta temperature, since ε_{33} and σ_{33} have been changed slightly. These parameters are listed in Table 5. An approximate value for the solvent-solvent binary interaction parameter, κ_{12}, can be obtained from analyzing vapor-liquid equilibrium data[47]. It was found that κ_{12} values ranging from 0 to 0.0035 give a nearly identical and quantitative representation of binary VLE data.

Figure 14 examines the effect of the solvent-solvent binary interaction parameter, κ_{12}, on the upper theta temperature. Experimentally determined upper theta temperatures lie between the calculated curves which span the range of κ_{12} values estimated from solvent-solvent VLE data. Also shown is the curve for the value of κ_{12} which provides a quantitative correlation of the dependence of Θ_U on solvent composition. The curve for $\kappa_{12} = 0.01$ is included in Figure 14 to illustrate that the equation of state can predict a situation where Θ_U for the mixture is lower than that for either single-solvent system. In that event the polymer has an increased range of miscibility with the mixed solvent relative to that with either single solvent.

7. Conclusion

By considering the thermodynamic stability criterion of mixtures, a method has been proposed for calculating theta conditions using a perturbed hard-sphere-chain equation of state. This method uses two important results concerning the theta condition which emerge from the Flory-Huggins model of incompressible mixture: 1) that the theta temperature is identical to the critical consolute temperature of a solution containing a polymer of infinite molecular weight and 2) the critical polymer segment fraction asymptotically approaches zero in the limit of infinite polymer molecular weight.

Theta temperatures, in conjunction with thermodynamic data for pure solvents and the critical consolute temperature of one polymer molecular weight, are used to determine equation-of-state parameters for binary mixtures. Parameters obtained in this manner provide a quantitative correlation of upper and lower critical solution temperatures as a function of polymer molecular weight and the upper and lower theta temperatures at elevated pressures. Also, the theta temperature of a polymer in a mixed solvent can be estimated from binary data. Although only one solvent mixture is considered here, we speculate that VLE data could be used to help screen solvent mixtures for desired polymer miscibility characteristics.

Although the method discussed here for determining equation-of-state parameters has the unfortunate consequence of making polymer parameters solvent dependent, it is important to note that the binary data chosen to determine equation-of-state parameters could be obtained even when only one polymer sample is available (albeit, monodisperse and of sufficiently large molecular weight). Theta temperatures (upper and lower), measured using a variety of methods, can be used to estimate two of three equation-of-state parameters for the polymer. A single critical solution temperature, measured from cloud-point measurements, can be used to estimate the remaining polymer parameter.

Finally, we point out some limitations of the current model. First, the version of the PHSC equation of state used here cannot describe systems possessing specific or oriented interactions such as hydrogen bonding. For mixed solvent systems, self-associating solvents (such as alcohols) are often used as precipitating agents for fractionation, where knowledge of theta conditions is very useful. For this reason, the majority of experimental data for theta conditions of polymers in mixed solvents usually contain one self-associating solvent. However, the PHSC equation of state can be extended to include hydrogen-bonding components using the method of Veytsman[48,49]. Second, the PHSC equation of state used here is applicable only to solvent-homopolymer mixtures, but extension to copolymer and solvent-copolymer mixtures is straightforward[19,50,51]. For solvent-copolymer systems, the dependence of theta conditions on copolymer composition can be obtained by extending the framework presented here.

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Table 1. Constants used in Eqs. (9) and (10)

Eq. (9)		Eq. (10)	
α_1	1.8681	β_1	0.7303
α_2	0.0619	β_2	0.1649
α_3	0.6715	β_3	2.3973
α_4	1.7317		

Table 2. PHSC equation-of-state parameters for various solvents

Solvent	r	ε/k_B (K)	σ (Å)
n-pentane	3.149	226.0	3.995
n-hexane	3.446	235.6	4.084
n-heptane	4.255	225.9	3.947
n-octane	5.055	219.6	3.850
benzene	2.727	291.6	3.958
cyclopentane	2.509	277.3	4.090
cyclohexane	2.723	286.7	4.425
methylcyclohexane	2.968	283.7	4.336
methyl acetate	3.804	224.8	3.338
ethyl acetate	4.509	213.5	3.369
n-propyl acetate	4.989	213.9	3.440
iso-propyl acetate	4.779	210.6	3.484
t-butyl acetate	4.485	220.2	3.743

Table 3. PHSC equation-of-state parameters for polyethylene (2) in several alkanes

Solvent (1)	ε_{22}/k_B (K)	r_2/M_2 (mol/g)
n-pentane	225.5	0.03490
n-hexane	232.6	0.02026
n-heptane	222.9	0.02925
n-octane	216.2	0.02090

Table 4. PHSC equation-of-state parameters for polystyrene (2) in several solvents

Solvent (1)	ε_{22}/k_B (K)	κ_{12}	r_2/M_2 (mol/g)
benzene	237.3	0	0.01808
cyclopentane	245.0	0.01450	0.02112
cyclohexane	246.8	0.01458	0.03390
methylcyclohexane	253.7	0.01582	0.01877
methyl acetate	220.1	0.01192	0.01760
ethyl acetate	213.0	0.00678	0.03685
n-propyl acetate	212.5	0.00513	0.07100
iso-propyl acetate	217.1	0.00567	0.02975
t-butyl acetate	226.8	0.00678	0.01458

Table 5. PHSC equation-of-state parameters for polystyrene (3) used to calculate upper theta temperatures in a mixed solvent of cyclohexane (1) and methylcyclohexane (2).

ε_{33}/k_B (K)	250.3
σ_{33} (Å)	4.396
κ_{13}	0.01658
κ_{23}	0.01424

Figure Captions

Figure 1. Calculation of theta temperatures in a hypothetical solvent(1)/polymer(2) mixture. Theta temperatures are identified by roots of the spinodal criterion, Eq. (27), in the limit of infinite polymer molecular weight and zero polymer segment fraction.

Figure 2. Shultz-Flory plots corresponding to the hypothetical solvent(1)/polymer(2) mixtures considered in Figure 1. (a) Only lower critical solution temperatures are observed; the vertical-axis intercept is T_{c1}/Θ_L. (b) Both upper and lower critical solution temperatures are observed; the intercepts on the vertical axis are T_{c1}/Θ_L and T_{c1}/Θ_U. (c) The upper and lower critical solution temperatures merge as polymer molecular weight increases, indicating hourglass-type phase diagrams; theta temperatures do not exist for this system.

Figure 3. Shultz-Flory plots of lower critical solution temperatures of polyethylene in normal alkanes. The symbols on the vertical axis are the reciprocals of the reported theta temperatures. Lines are calculated using the PHSC equation of state.

Figure 4. Shultz-Flory plots of lower critical solution temperatures of polystyrene in benzene. Line is calculated using the PHSC equation of state.

Figure 5. Shultz-Flory plot of lower (left axis) and upper (right axis) critical solution temperatures of cyclopentane/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 6. Shultz-Flory plot of lower (left axis) and upper (right axis) critical solution temperatures of cyclohexane/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 7. Shultz-Flory plot of lower (left axis) and upper (right axis) critical solution temperatures of methylcyclohexane/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 8. Shultz-Flory plot of lower (left axis) and upper (right axis) critical solution temperatures of *n*-propyl acetate/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 9. Shultz-Flory plot of lower (left axis) and upper (right axis) critical solution temperatures of *iso*-propyl acetate/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 10. Shultz-Flory plot of lower (left axis) and upper (right axis) critical solution temperatures of ethyl acetate/polystyrene solutions. Lines are calculated using the PHSC equation of state.

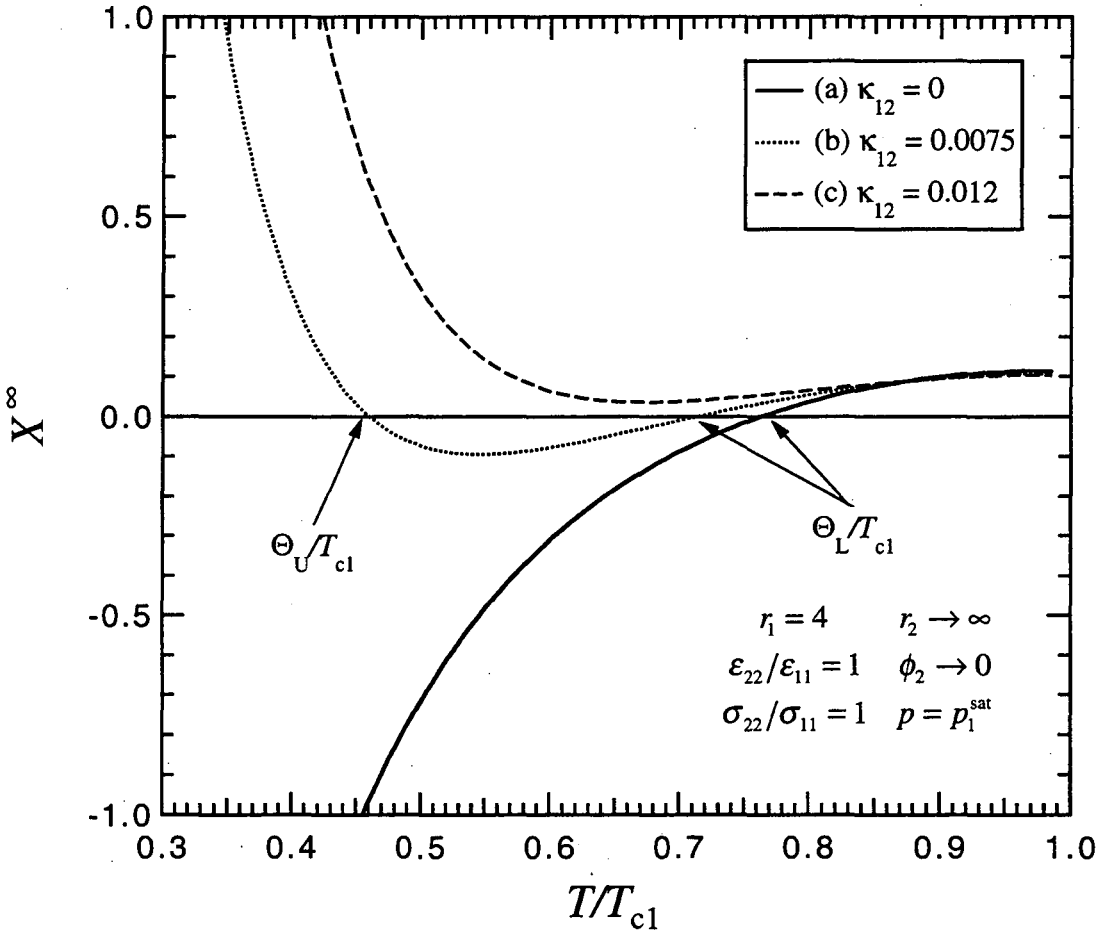
Figure 11. Shultz-Flory plot of lower and upper critical solution temperatures of methyl acetate/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 12. Shultz-Flory plot of lower and upper critical solution temperatures of *t*-butyl acetate/polystyrene solutions. Lines are calculated using the PHSC equation of state.

Figure 13. Pressure dependence of the upper (left axis) and lower (right axis) theta temperatures for *t*-butyl acetate/polystyrene solutions. The lines are predictions using the PHSC equation of state.

Figure 14. Dependence of upper theta temperature on solvent composition for a ternary mixture of cyclohexane(1), methylcyclohexane(2) and polystyrene(3). Solvent-polymer binary interaction parameters (κ_{13} and κ_{23}) were chosen to match Θ_U for each binary. The solid curve and dotted curve represent the range of κ_{12} values which give good representation of VLE for the solvent mixture (without polymer). The dashed curve represents the value of κ_{12} which best represents the solvent composition dependence of Θ_U. The dot-dashed curve represents a hypothetical system where Θ_U of the polymer in a mixed solvent is lower than that for either of the single-solvent/polymer systems.

Figure 1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0.5
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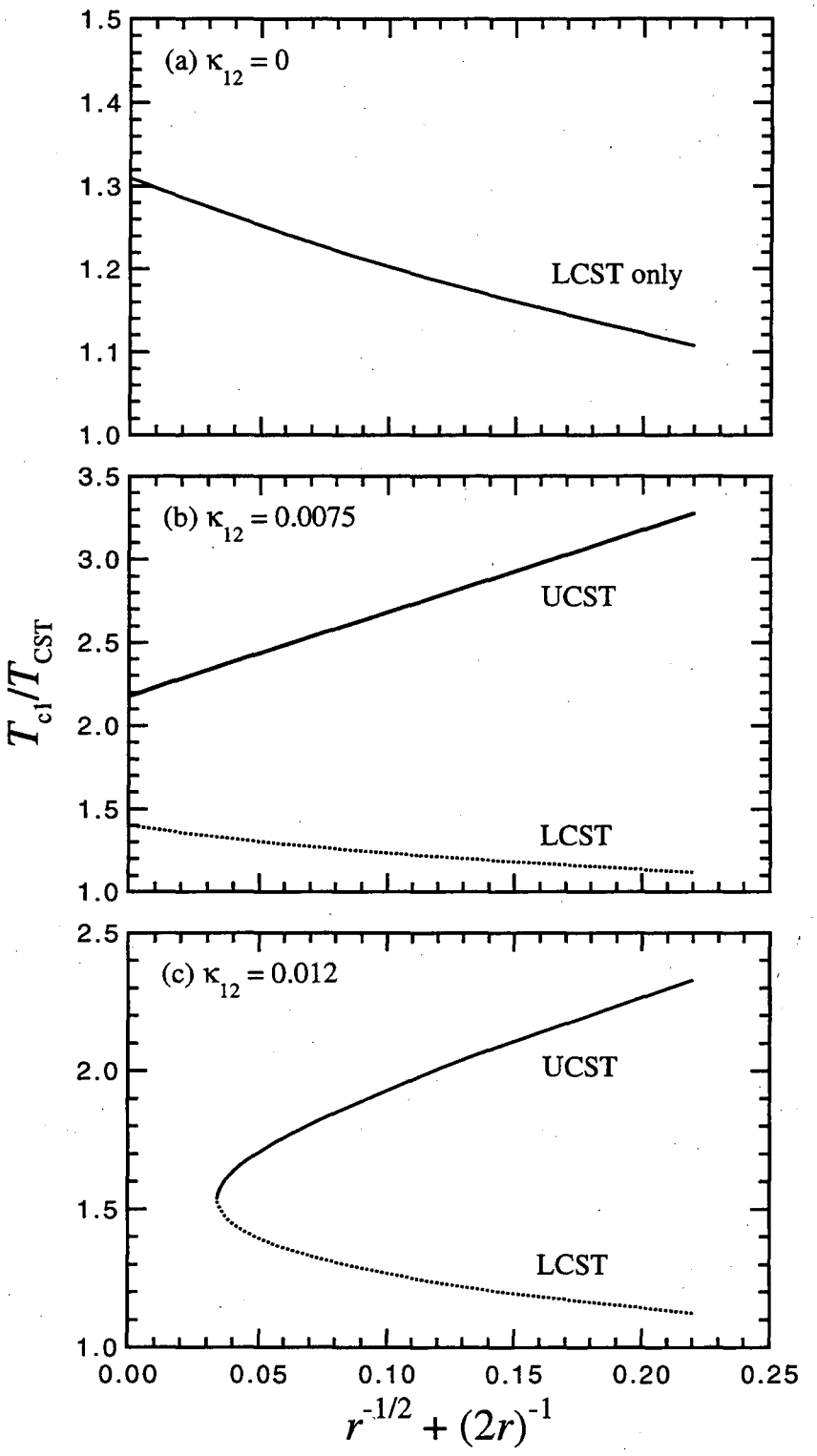
0.9
1.0
χ^{∞}
T/T_{c1}
(a) $\kappa_{12} = 0$
(b) $\kappa_{12} = 0.0075$
(c) $\kappa_{12} = 0.012$
Θ_U/T_{c1}
Θ_L/T_{c1}
$r_1 = 4$ $r_2 \to \infty$
$\varepsilon_{22}/\varepsilon_{11} = 1$ $\phi_2 \to 0$
$\sigma_{22}/\sigma_{11} = 1$ $p = p_1^{sat}$

Figure 2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LCST only
(b) $\kappa_{12} = 0.0075$
UCST
LCST
(c) $\kappa_{12} = 0.012$
UCST
LCST
T_{c1}/T_{CST}
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2.0
2.5
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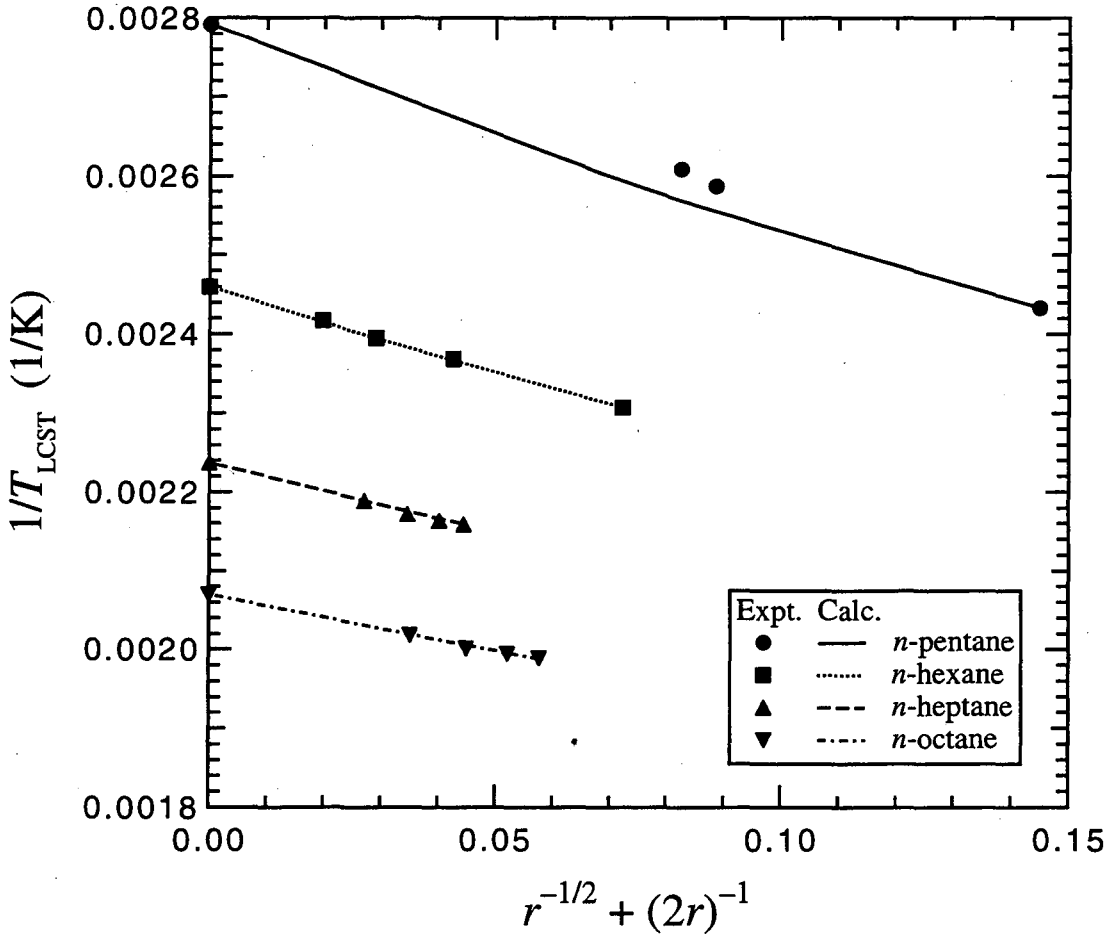
0.05
0.10
0.15
0.20
0.25

Figure 3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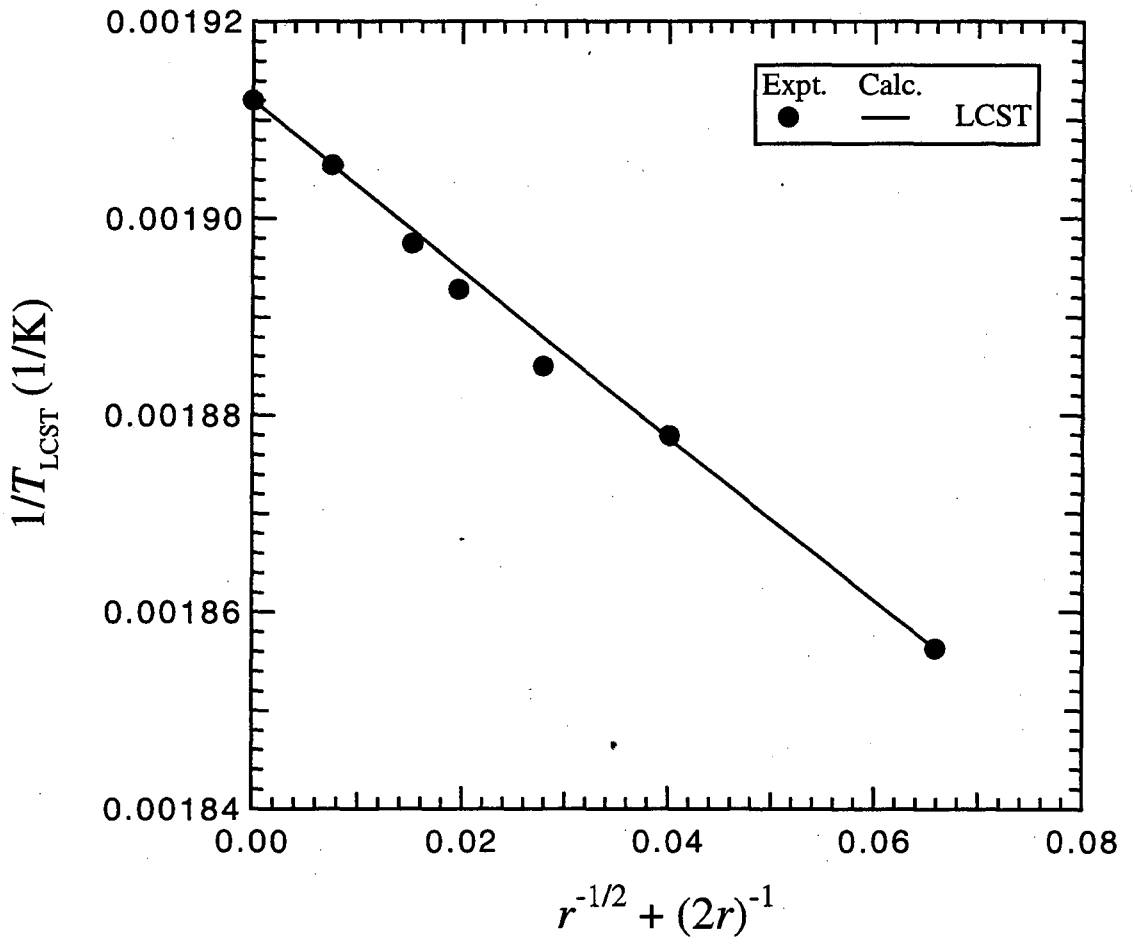
$1/T_{LCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$
Expt. Calc.
n-pentane
n-hexane
n-heptane
n-octane

Figure 4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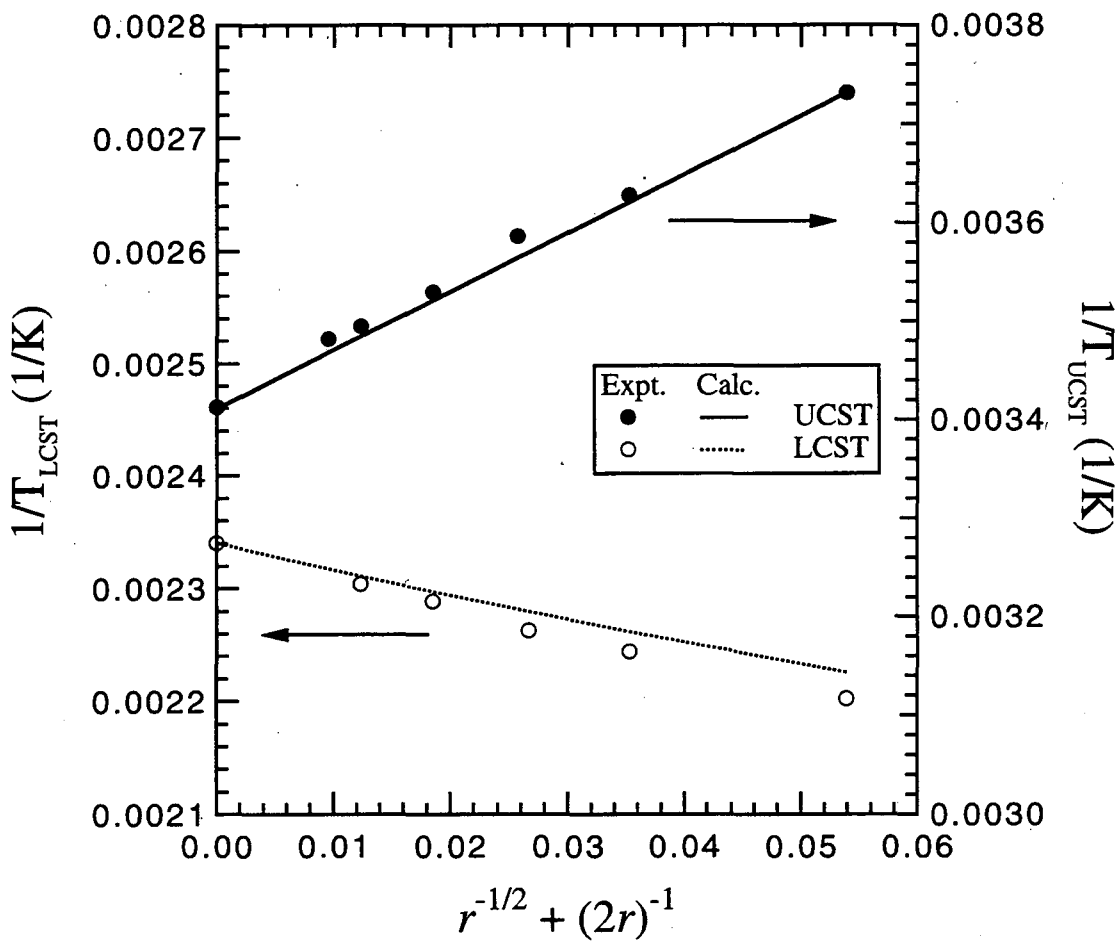
$1/T_{LCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$

Figure 5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0.0038
0.0036
0.0034
0.0032
0.0030
0.00
0.01
0.02
0.03
0.04
0.05
0.06
$1/T_{LCST}$ (1/K)
$1/T_{UCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$
Expt.
Calc.
UCST
LCST

Figure 6

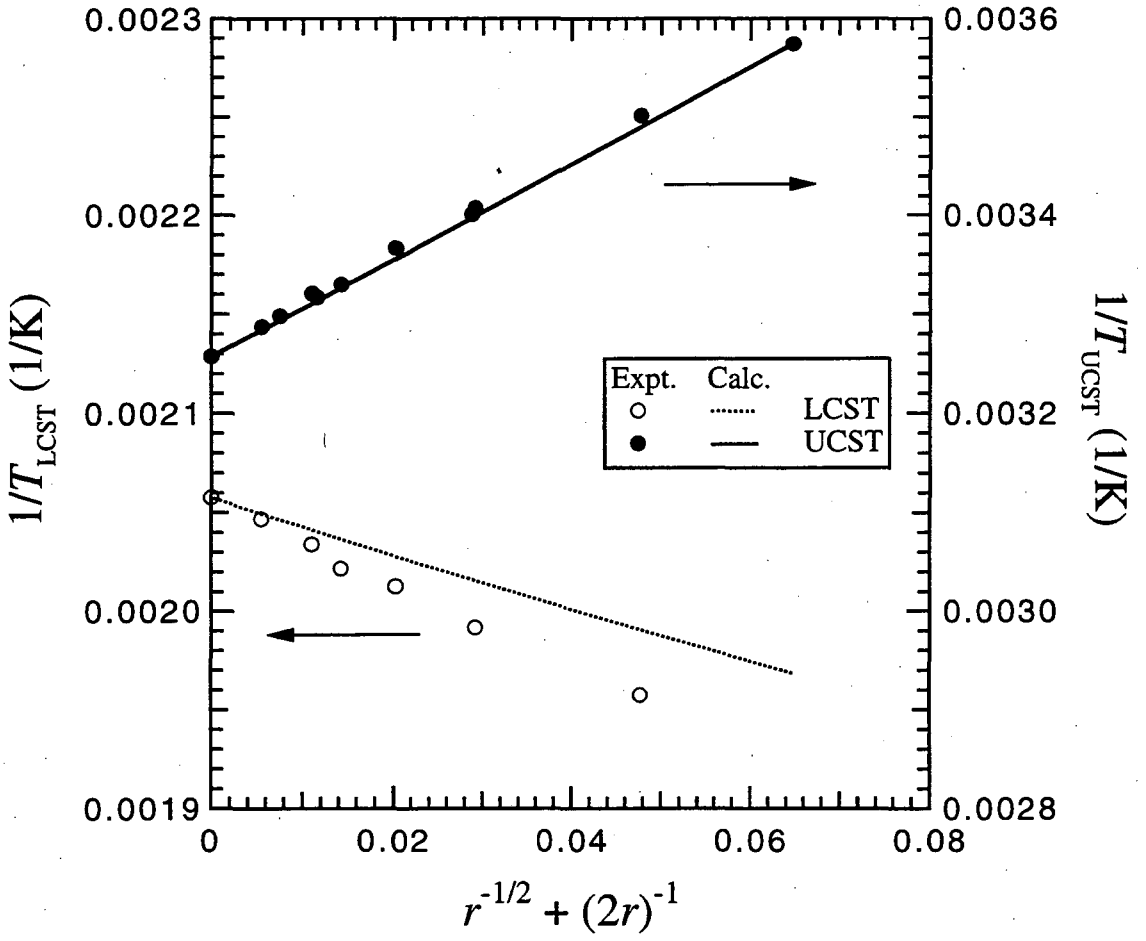

0.0023
0.0022
0.0021
0.0020
0.0019
0.0036
0.0034
0.0032
0.0030
0.0028
0
0.02
0.04
0.06
0.08
$1/T_{LCST}$ (1/K)
$1/T_{UCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$
Expt.
Calc.
LCST
UCST

Figure 7

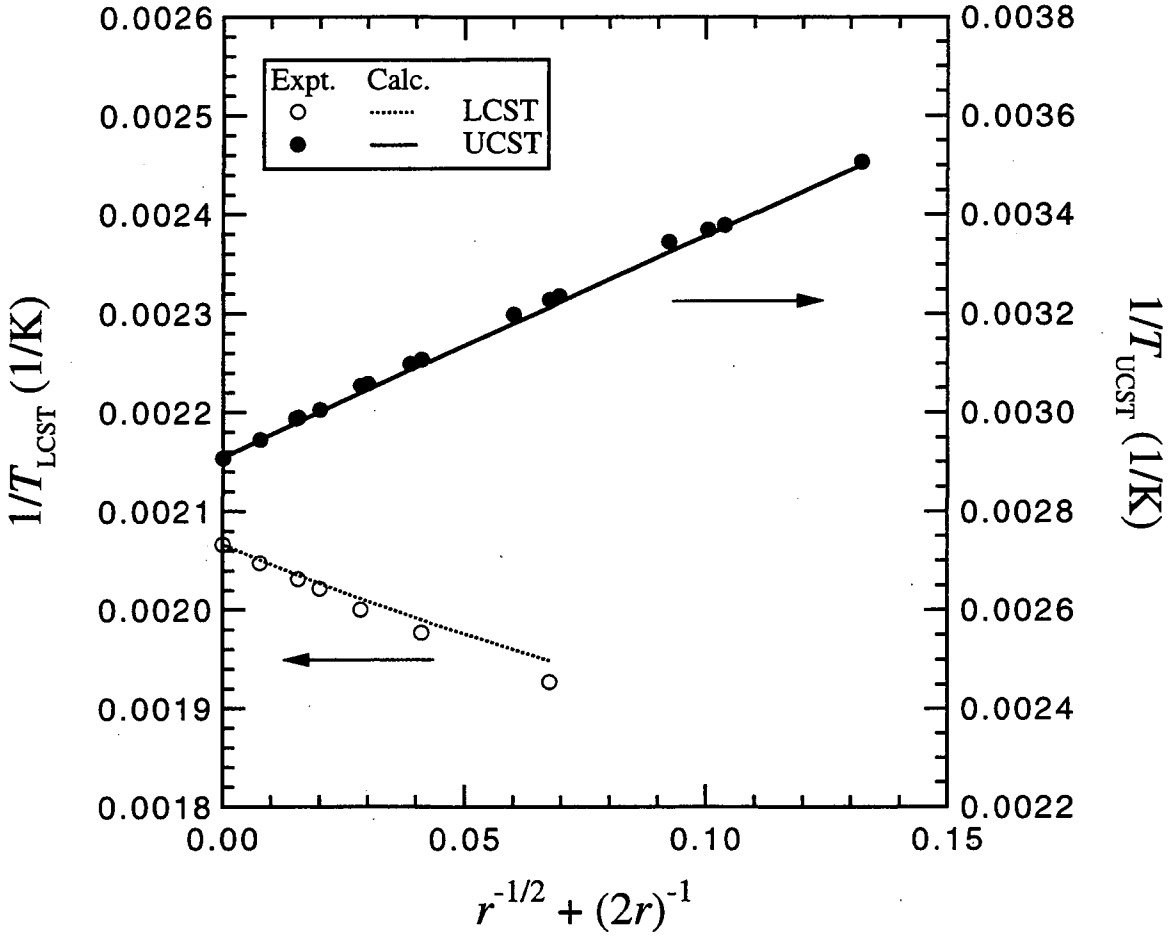

Expt.
Calc.
LCST
UCST
0.0026
0.0025
0.0024
0.0023
0.0022
0.0021
0.0020
0.0019
0.0018
0.0038
0.0036
0.0034
0.0032
0.0030
0.0028
0.0026
0.0024
0.0022
0.00
0.05
0.10
0.15
$1/T_{LCST}$ (1/K)
$1/T_{UCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$

Figure 8

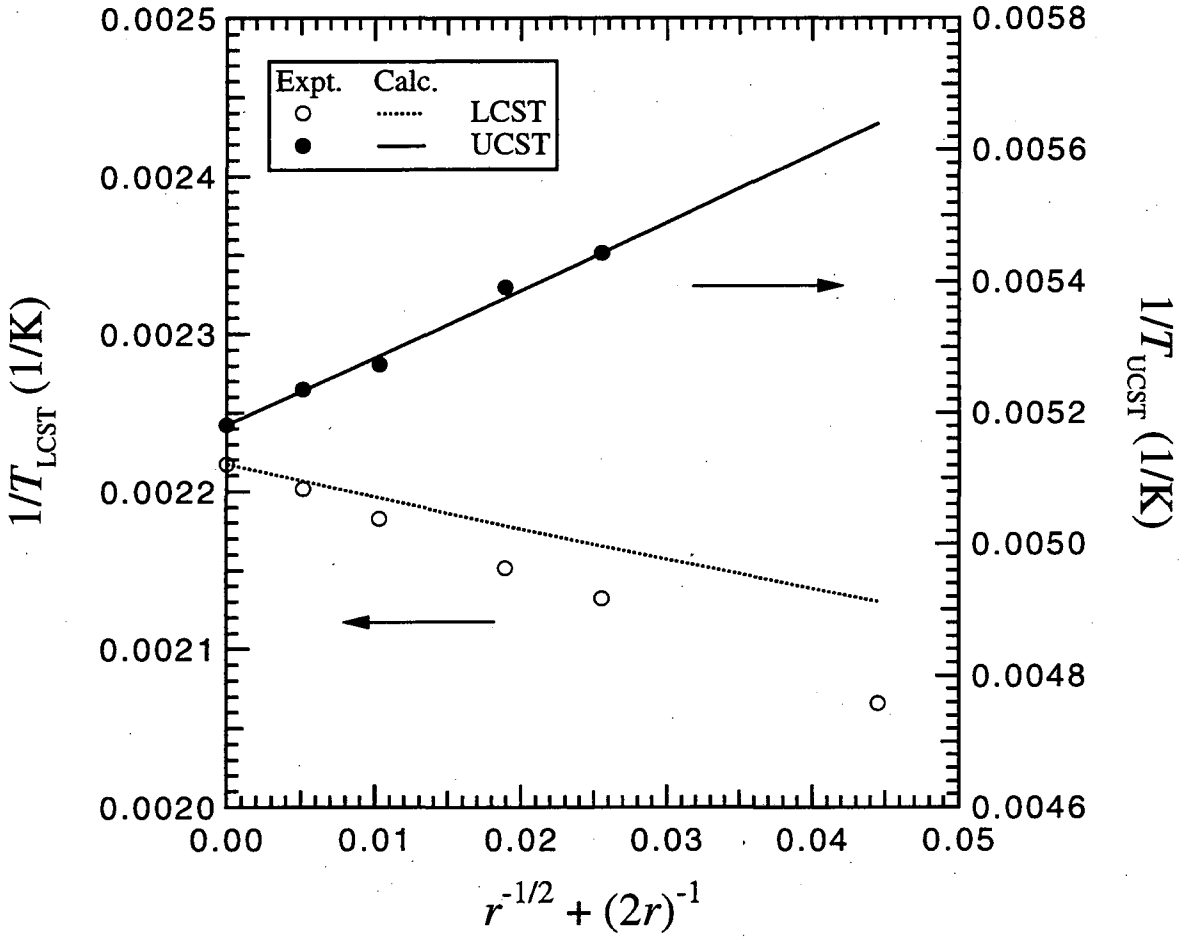

Expt.
Calc.
LCST
UCST
0.0025
0.0024
0.0023
0.0022
0.0021
0.0020
0.0058
0.0056
0.0054
0.0052
0.0050
0.0048
0.0046
0.00
0.01
0.02
0.03
0.04
0.05
$1/T_{LCST}$ (1/K)
$1/T_{UCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$

Figure 9

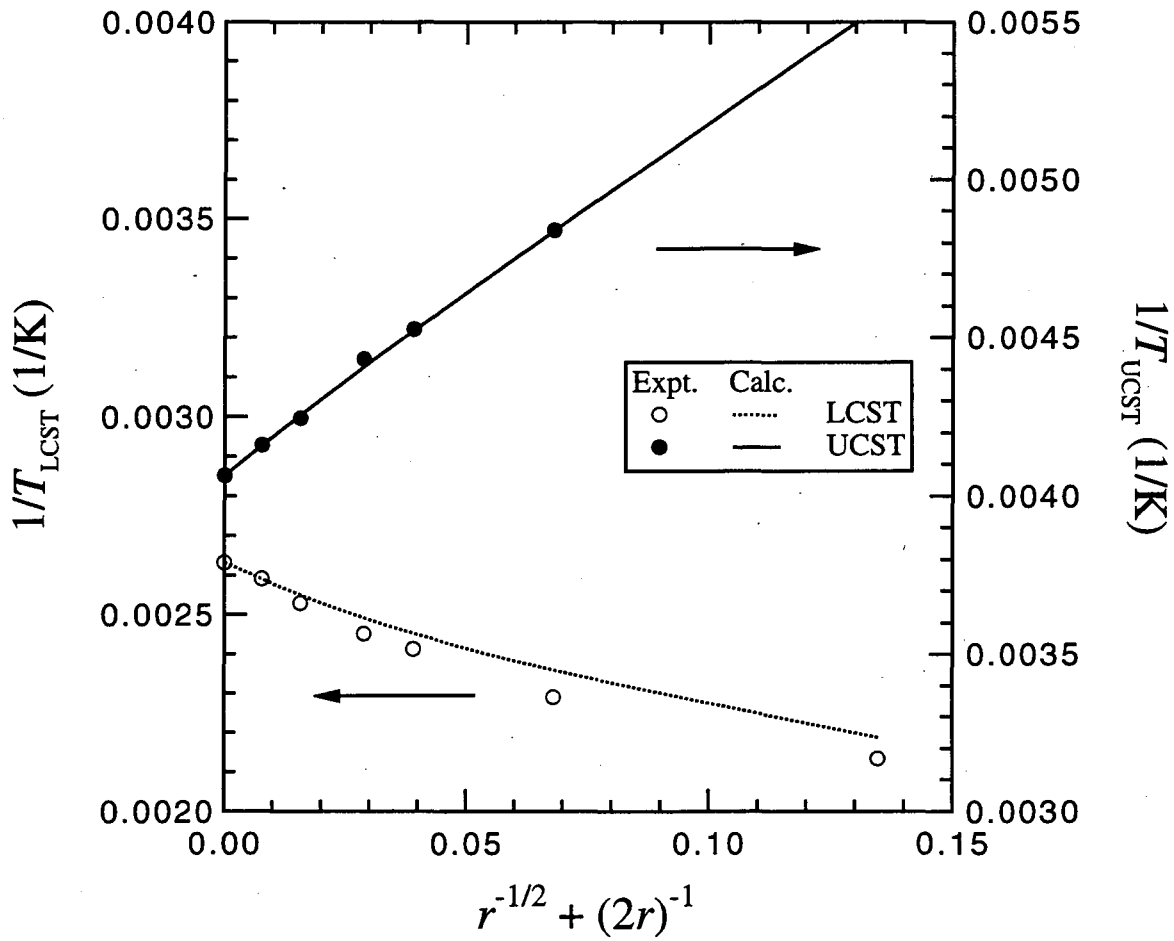

0.0040
0.0035
0.0030
0.0025
0.0020
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.00
0.05
0.10
0.15
$1/T_{LCST}$ (1/K)
$1/T_{UCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$
Expt.
Calc.
LCST
UCST

Figure 10

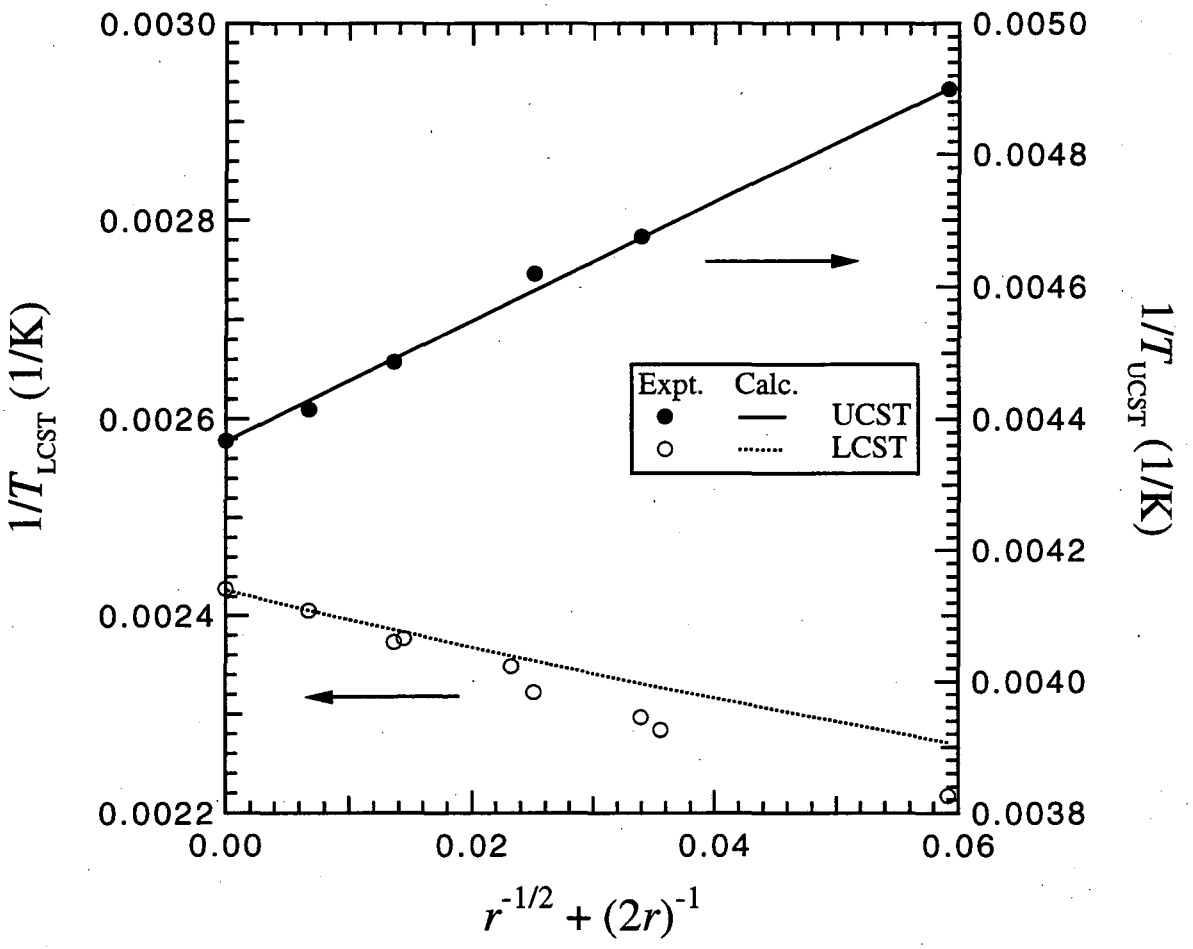

0.0030
0.0028
0.0026
0.0024
0.0022
0.0050
0.0048
0.0046
0.0044
0.0042
0.0040
0.0038
0.00
0.02
0.04
0.06
$1/T_{LCST}$ (1/K)
$1/T_{UCST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$
Expt.
Calc.
UCST
LCST

Figure 11

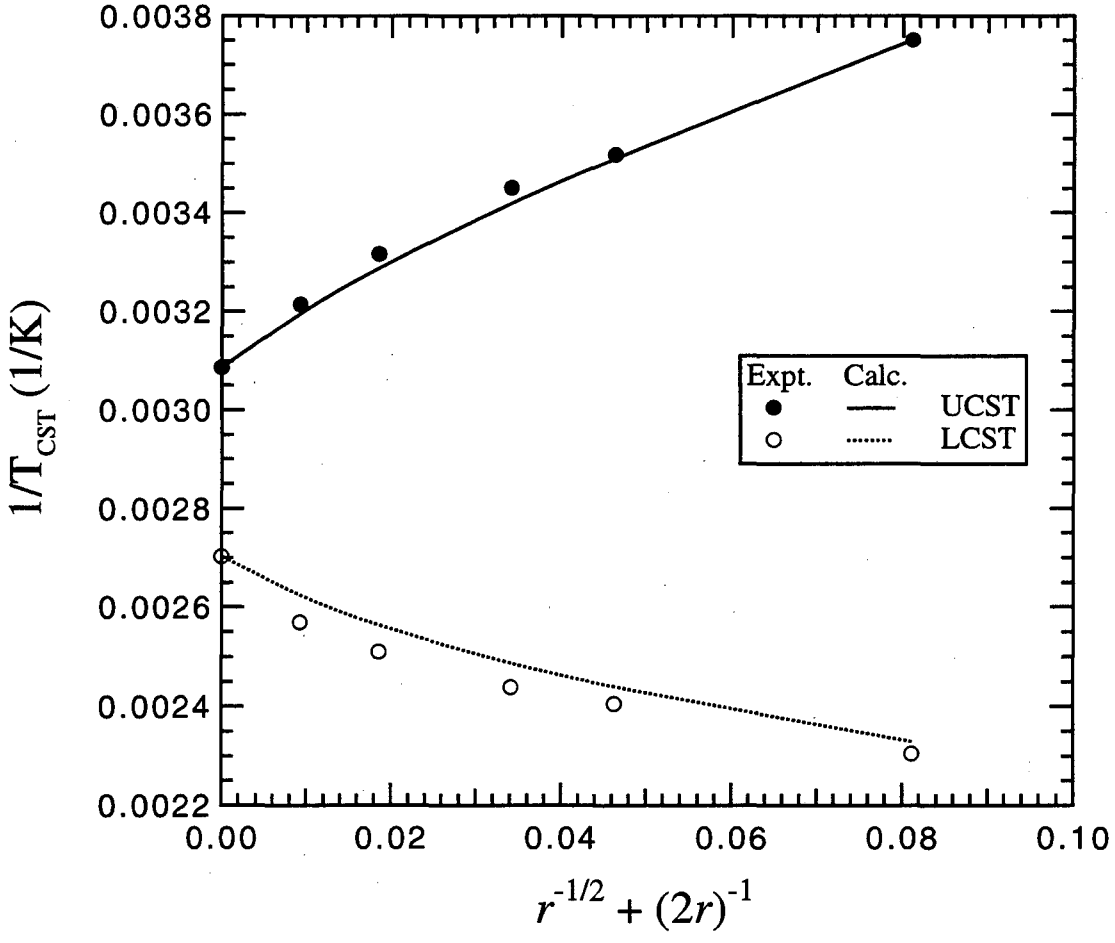

0.0038
0.0036
0.0034
0.0032
0.0030
0.0028
0.0026
0.0024
0.0022
1/T_CST (1/K)
0.00
0.02
0.04
0.06
0.08
0.10
r^-1/2 + (2r)^-1
Expt.
Calc.
UCST
LCST

Figure 12

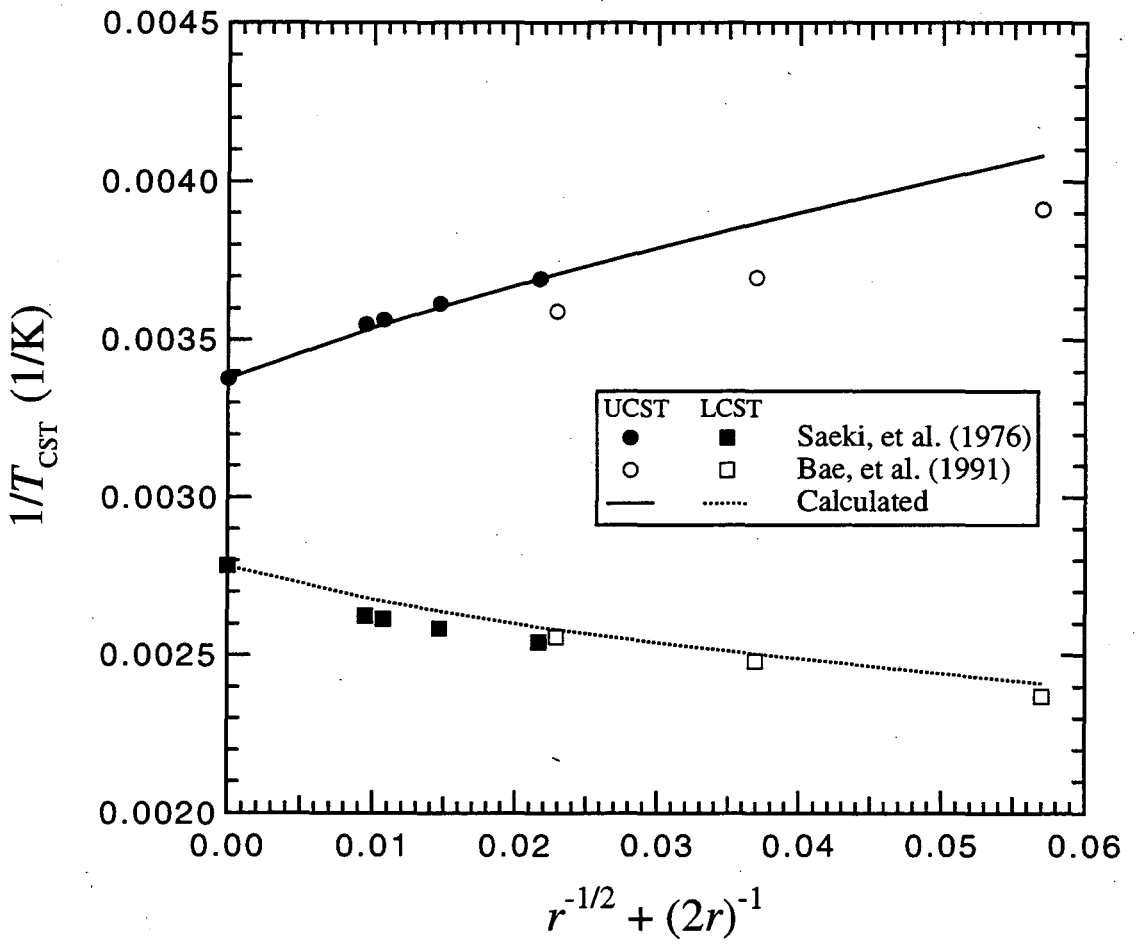

0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.00
0.01
0.02
0.03
0.04
0.05
0.06
$1/T_{CST}$ (1/K)
$r^{-1/2} + (2r)^{-1}$
UCST
LCST
Saeki, et al. (1976)
Bae, et al. (1991)
Calculated

Figure 13

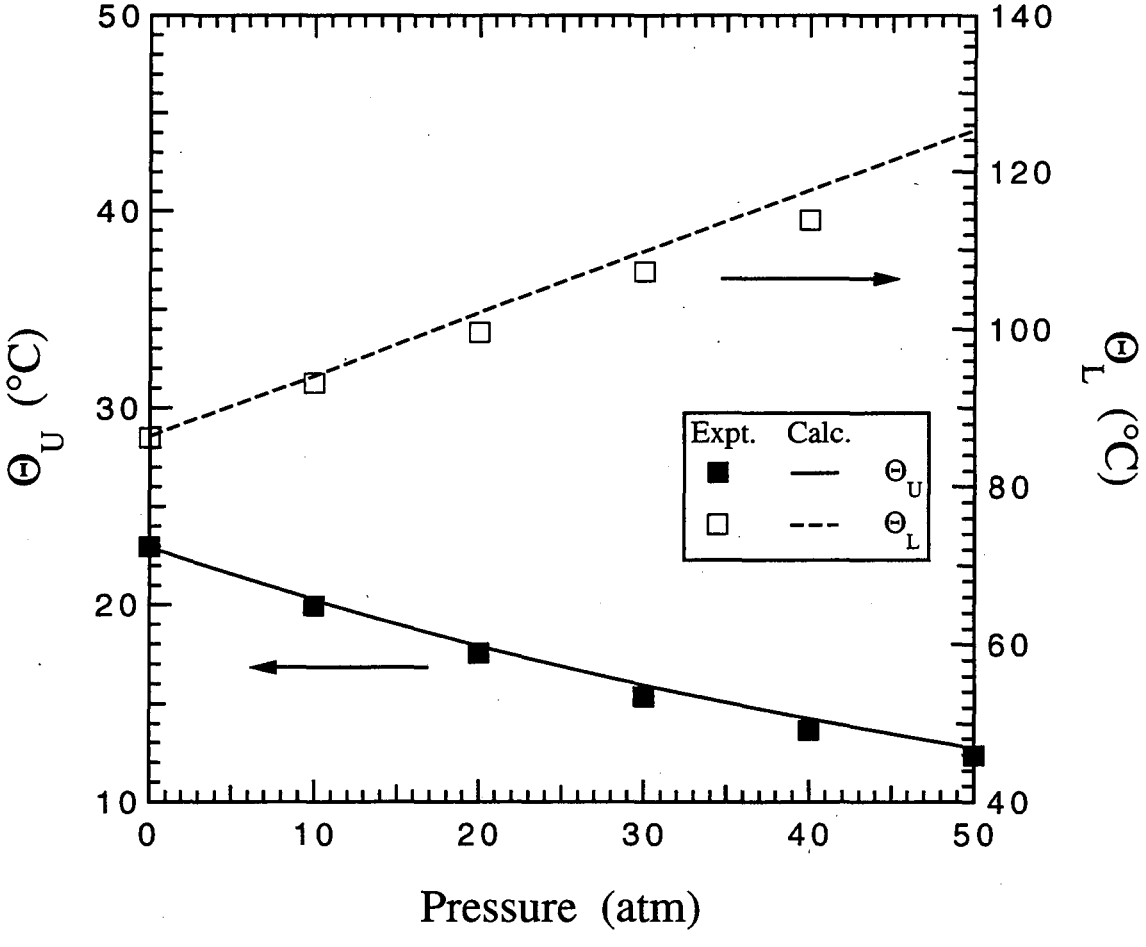
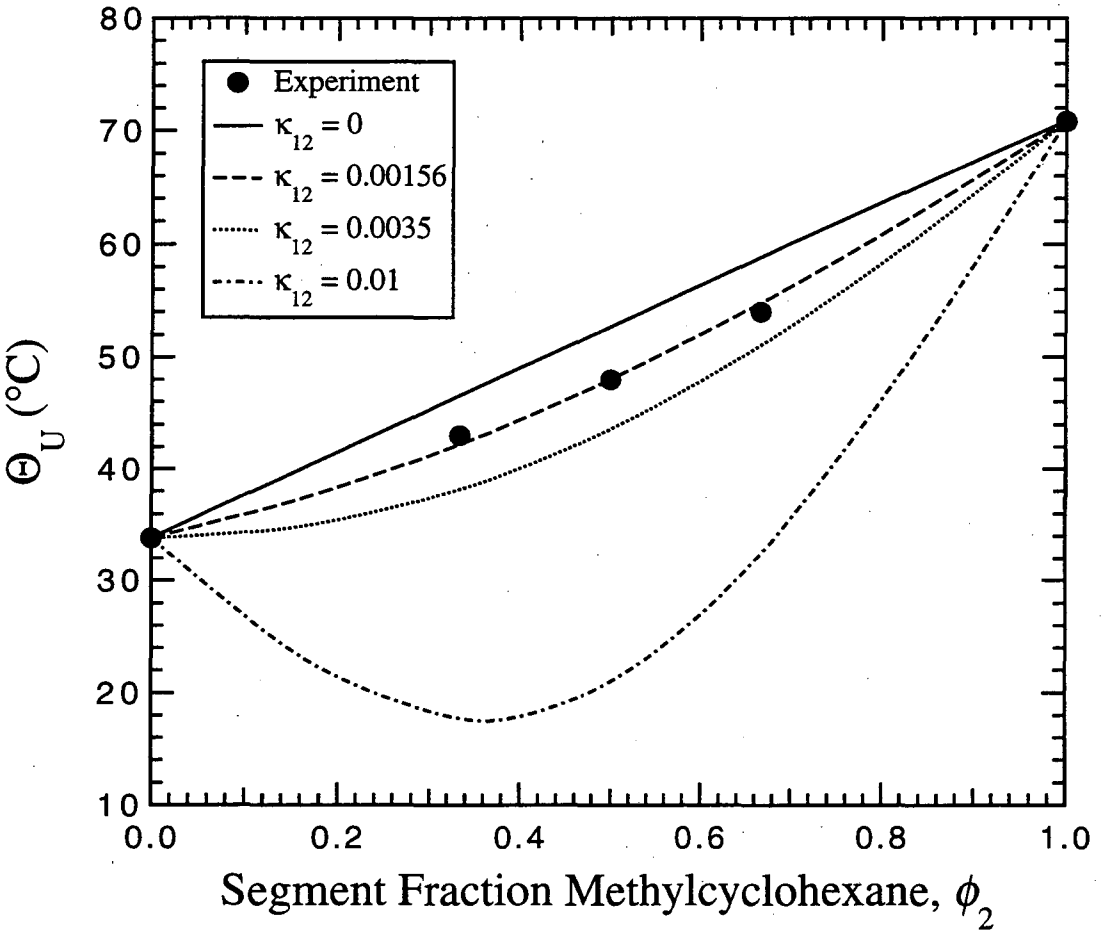

50
40
30
20
10
0
10
20
30
40
50
140
120
100
80
60
40
Θ_U (°C)
Θ_L (°C)
Expt.
Calc.
Θ_U
Θ_L
Pressure (atm)

Figure 14


Experiment
$\kappa_{12} = 0$
$\kappa_{12} = 0.00156$
$\kappa_{12} = 0.0035$
$\kappa_{12} = 0.01$
Θ_U (°C)
80
70
60
50
40
30
20
10
0.0
0.2
0.4
0.6
0.8
1.0
Segment Fraction Methylcyclohexane, ϕ_2

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