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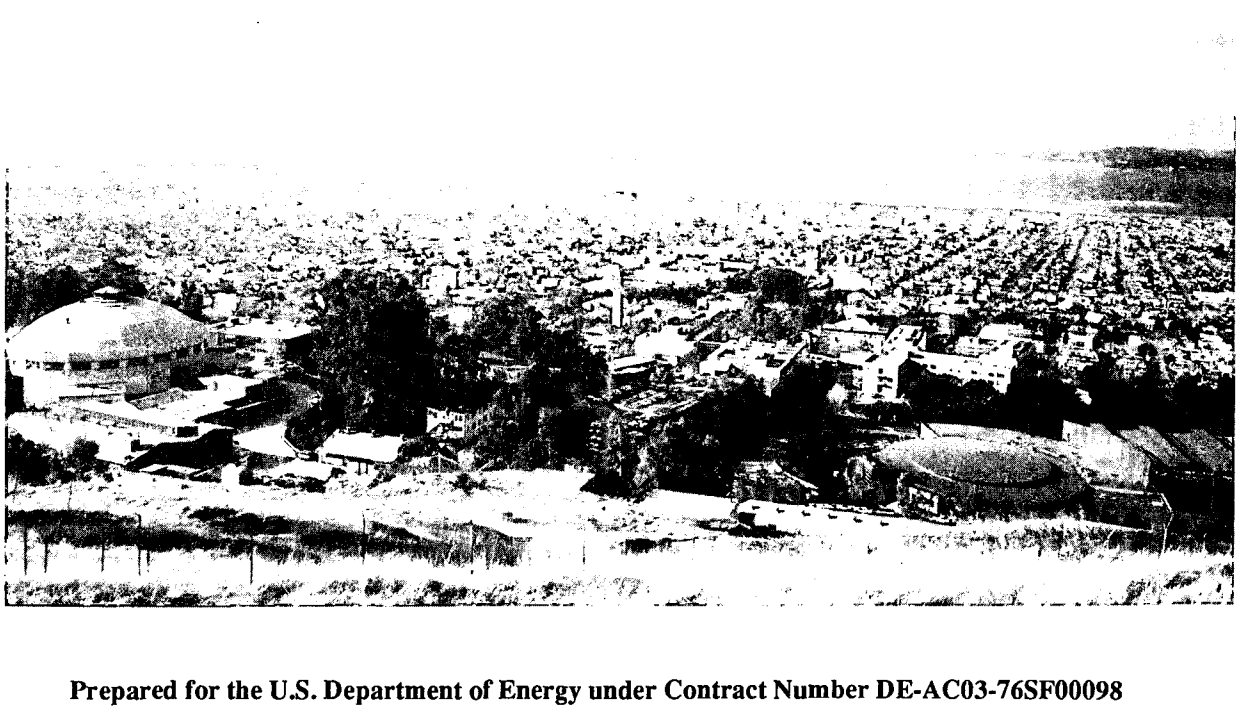

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MOLECULAR THERMODYNAMICS FOR CLOSED-LOOP LIQUID-LIQUID EQUILIBRIA OF BINARY SYSTEMS INCLUDING POLYMER SOLUTIONS

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ABSTRACT

The incompressible lattice-gas model by ten Brinke and Karasz is adopted to introduce the effect of specific interactions into a recently-presented, Monte-Carlo based lattice expression for the Helmholtz energy of nonrandom mixing. While the lattice remains incompressible, intermolecular forces consist of two types: London dispersion and specific (chemical) forces. The specific interactions between similar components as well as those between dissimilar components are incorporated in a systematic manner. Closed-loop temperature-composition phase diagrams are successfully reproduced. The theory is compared with experimental data for several binary systems, including polymer solutions, which exhibit closed-loop coexistence curves. Theoretical and experimental results are in good agreement.

(Keywords: lattice model; lower critical solution temperature; phase equilibria; polymer solution)

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INTRODUCTION

Some binary systems exhibit a closed miscibility loop with both an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST) in the temperature-composition phase diagram such that the UCST lies above the LCST. Classical examples are aqueous solutions of nicotine (Hudson, 1904) and poly(ethylene glycol) (Saeki et al., 1976). A realistic qualitative explanation for this phenomenon was given many years ago by Hirschfelder et al. (1937); closed-loop behavior follows from competition among three contributions to the Helmholtz energy of mixing $\left(\Delta_{mix}A\right)$: dispersion forces, combinatorial entropy of mixing, and highly oriented specific interactions (e.g., hydrogen bonding). While the dispersion forces energetically favor phase separation, the combinatorial entropy of mixing favors mutual miscibility. The specific interactions are energetically favorable but entropically unfavorable because of their highly directional-specific character. Therefore, in the presence of specific interactions between dissimilar components, the mixture could form a single homogeneous phase at low temperatures where the specific interactions are stable. At moderate temperatures, where neither specific interactions and combinatorial entropy of mixing dominates, the effect of dispersion forces become significant and the mixture exhibits phase separation. At higher temperatures, the combinatorial entropy of mixing becomes dominant and a single homogeneous phase reappears.

Within the framework of a lattice model (Guggenheim, 1952), several attempts have been made to develop molecular-thermodynamic models for representing a closed miscibility loop. The essence of these earlier attempts is the extension of conventional lattice models which are suitable only for representing an UCST. However, a molecular-thermodynamic model for a closed miscibility loop must first accurately represent the phase behavior of a simpler system where no specific interactions are present.

Using the quasichemical approximation (Guggenheim, 1952), Barker and Fock (1953) were the first to give a qualitative description of closed-loop coexistence curve for

a binary system of equal-sized molecules. In their model, one or more of the contact points of each molecule are allowed to have an interaction energy different from that of the others. This quasi-chemical method was extended to polymer solutions by Prange et al. (1989). Although the quasichemical approximation accounts for some deviation from random mixing, it is well-known that the calculated coexistence curve is too narrow compared to experiment. In addition, in the quasi-chemical method, the derivation of critical coordinates is extremely tedious.

More rigorous models are the decorated lattice models by Wheeler (1975) and Anderson and Wheeler (1978a, b). The decorated lattice model can be mapped onto a three-dimensional Ising model for which reliable solutions are available (Scesney, 1970). Wheeler et al. obtained qualitative agreement between calculated and experimental coexistence curves for several binary low-molecular-weight systems. Wheeler's theory was later incorporated into the UNIQUAC equation (Abrams and Prausnitz, 1975) by Kim and Kim (1988). The decorated lattice model, however, is very complicated and it is difficult to apply to polymer solutions and multicomponent systems.

Mathematically simple models have also been proposed. Some examples are the solvation model by Matsuyama and Tanaka (1990) and the lattice-gas model by Vause and Walker (1980; Goldstein and Walker, 1983; Goldstein, 1985). The latter model was originally developed as a compressible model for mixtures of low-molecular-weight species and was later applied to polymer blends through an incompressible model by ten Brinke and Karasz (1984). Sanchez and Balazs (1989) also adopted a similar approach using the lattice-fluid model which is able to account for the free-volume effect. Unfortunately, these models are based on the original random-mixing Flory-Huggins theory (Flory, 1953) which is often not accurate to describe the behavior of real mixtures even in the absence of specific forces.

Recently, Hu et al. (1991a, b) developed a secondary lattice model applicable to polymer solutions. In the absence of specific interactions, they first proposed a new

expression for $\Delta_{mix}A$ for binary polymer solutions based on Freed's lattice-field theory (Freed, 1985; Bawendi et al., 1987; Bawendi and Freed, 1988), which is formally an exact mathematical solution of the Flory-Huggins lattice. The effect of specific interactions were then incorporated through a secondary lattice whose essential role was to assign a temperature dependence to the interaction energy parameter. Although Hu's model requires several adjustable parameters and the expression for the Helmholtz energy of mixing for a secondary lattice is somewhat arbitrary, the calculated coexistence curves were found to be in good agreement with experiment. The success of the secondary-lattice and aforementioned decorated-lattice models follows because these models are close to the accurate solutions of a lattice model.

The purpose of this work is to develop a simple molecular-thermodynamic model for closed-loop liquid-liquid equilibria based on a theoretically sound expression for $\Delta_{mix}A$. In this paper we use the recently-presented new expression for $\Delta_{mix}A$ for incompressible monomer/r-mer mixture obtained by correlating the Monte Carlo simulation results reported by Lambert et al. (1992). In that work, computer simulations were carried out by taking into account dispersion forces only. For systems exhibiting UCST, the coexistence curves calculated by this model were found to agree with the experimental data much better than those obtained by existing lattice models, including the Flory-Huggins theory (Flory, 1953) and Guggenheim's quasichemical approximation (Guggenheim, 1952). The effect of specific interactions are here introduced by superimposing on Lambert's work the incompressible lattice-gas model by ten Brinke and Karasz (1984). When we consider the specific interactions between dissimilar components only, our model requires two additional parameters. As shown later, however, one of them can be assigned a constant value. The remaining parameter is determined from the (experimental) ratio of UCST to LCST. The resulting model is conceptually and mathematically simple.

THEORY

1. Internal and Helmholtz Energies of Mixing. Consider a binary mixture of components 1 and 2 which can form specific interactions between similar components as well as between dissimilar components. Each contact point of a molecule is assumed to interact either in a specific manner with the interaction energy of $\varepsilon_{ij} + \delta\varepsilon_{ij}$ or in a non-specific manner with interaction energy ε_{ij} where i=1 or 2 and j=1 or 2. Both ε_{ij} and $\delta\varepsilon_{ij}$ are negative and independent of temperature. We assume that a fraction, f_{ij}, of the i-j interactions are specific and $1 - f_{ij}$ are non-specific. We also assume that f_{ii} in the mixture is identical to that in the pure substance containing molecules of component i. Under these assumptions the internal energy of mixing $(\Delta_{mix}U)$ is given by

$$\Delta_{mix} U = \frac{1}{2} N_{12}\omega \tag{1}$$

where N_{12} is the total number of 1-2 pair-wise contacts and ω is defined by

$$\omega \equiv \varepsilon + f_{11}(-\delta\varepsilon_{11}) + f_{22}(-\delta\varepsilon_{22}) + f_{12}(2\delta\varepsilon_{12}) \tag{2}$$

where ε is the interchange energy

$$\varepsilon \equiv 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \quad . \tag{3}$$

The derivation of Eq. (1) is shown in the Appendix.

We assume that f_{ij} is given by the Boltzmann distribution law

$$\frac{1 - f_{ij}}{f_{ij}} = g_{ij} \exp\left[-\frac{\{\varepsilon_{ij} - (\varepsilon_{ij} + \delta\varepsilon_{ij})\}}{kT}\right] \tag{4}$$

where k is the Boltzmann constant, T is the absolute temperature, and g_{ij} is the ratio of the degeneracy of non-specific i-j interactions to that of specific i-j interactions; f_{ij} is therefore given by

$$f_{ij} = \frac{1}{1 + g_{ij}\exp\left(\delta\varepsilon_{ij}/kT\right)} \quad . \tag{5}$$

The Helmholtz energy of mixing $\left(\Delta_{mix}A\right)$ is obtained by integrating the Gibbs-Helmholtz equation using the Guggenheim's athermal entropy of mixing as the boundary condition:

$$\frac{\Delta_{mix}A}{N_r kT} = \int_0^{\frac{1}{\tilde{T}}} \frac{\Delta_{mix}U}{N_r\varepsilon}\, d\left(\frac{1}{\tilde{T}}\right) + \left(\frac{\Delta_{mix}A}{N_r kT}\right)_{\tilde{T}=\infty} \tag{6}$$

$$\left(\frac{\Delta_{mix}A}{N_r kT}\right)_{\tilde{T}=\infty} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \frac{z}{2}\left[\phi_1\frac{q_1}{r_1}\ln\frac{\theta_1}{\phi_1} + \phi_2\frac{q_2}{r_2}\ln\frac{\theta_2}{\phi_2}\right] \tag{7}$$

where N_r is the total number of lattice sites and $\tilde{T}$ is the dimensionless temperature defined as

$$\tilde{T} \equiv \frac{kT}{\varepsilon} \tag{8}$$

Here r_i, ϕ_i, and θ_i are the number of segments per molecule, volume fraction, and surface fraction of component i, respectively. ϕ_i and θ_i are defined by

$$\phi_i \equiv \frac{N_i r_i}{N_1 r_1 + N_2 r_2} \tag{9}$$

$$\theta_i \equiv \frac{N_i q_i}{N_1 q_1 + N_2 q_2} \tag{10}$$

where N_i and q_i are the number of molecules and the surface area parameter of component i, respectively; q_i is related to the number of surface contacts per molecule, zq_i, defined as

$$zq_i \equiv r_i(z-2)+2 \tag{11}$$

where z is the lattice coordination number. In this study, including computer simulations, a simple cubic lattice (z=6) is used. When numerical integration with respect to the inverse of reduced temperature $(1/\tilde{T})$ is necessary in Eq. (6), Simpson's rule is used at 101 equally spaced points along the axis of $1/\tilde{T}$.

Our main task is the estimation of N_{12} which, in turn, determines $\Delta_{mix}U$ by Eq. (1). In the next section we briefly review two new expressions for N_{12} obtained by correlating the Monte Carlo simulation results.

2. Total Number of 1-2 Pair-Wise Contacts. Based on Monte-Carlo calculations, Lambert et al. (1992) recently proposed the following expression for N_{12} for monomer/r-mer mixture in the absence of specific interactions:

$$N_{12} = N_r\phi_1\phi_2\left[A' + B'(\phi_2-\phi_1) + C'(\phi_2-\phi_1)^2\right] \tag{12}$$

where

$$A' = a_0(r_2) + a_1(r_2)\left[\exp\left(\frac{1}{\tilde{T}}\right)-1\right] \tag{13}$$

$$a_0(r_2) = 6 - \frac{0.9864(r_2-1)}{1+0.8272(r_2-1)} \tag{14}$$

$$a_1(r_2) = -1.2374 - \frac{0.09616(r_2-1)}{1+0.14585(r_2-1)} \tag{15}$$

$$B'(r_2) = \frac{0.8186(r_2 - 1)}{1 + 0.76494(r_2 - 1)} \tag{16}$$

$$C' = 1.20\left[\exp\left(\frac{1}{\tilde{T}}\right) - 1\right] . \tag{17}$$

The numerical coefficients in Eqs. (14) to (17) follow from Monte-Carlo calculations. In the reminder of this paper the above model is Model I. In this model r_1 must be always unity. The temperature dependence of N_{12} is expressed in terms of the dimensionless temperature $\tilde{T}$ defined by Eq. (8). In the presence of specific interactions, ε is replaced by ω in Eq. (1). Therefore, as a first approximation it seems reasonable to replace ε by ω in $\tilde{T}$ in Eqs. (13) and (17) to obtain the expression for N_{12} in the presence of specific interactions. The resulting equations are as follows:

$$N_{12} = N_r\phi_1\phi_2\left[A'' + B'\left(\phi_2 - \phi_1\right) + C''\left(\phi_2 - \phi_1\right)^2\right] \tag{18}$$

where

$$A'' = a_0(r_2) + a_1(r_2)\left[\exp\left(\frac{\omega}{\varepsilon\tilde{T}}\right) - 1\right] \tag{19}$$

$$C'' = 1.20\left[\exp\left(\frac{\omega}{\varepsilon\tilde{T}}\right) - 1\right] . \tag{20}$$

In Model I, $\Delta_{mix}U$ is given by

$$\frac{\Delta_{mix}U}{N_r\varepsilon} = \frac{1}{2}N_r\phi_1\phi_2\left[A'' + B'\left(\phi_2 - \phi_1\right) + C''\left(\phi_2 - \phi_1\right)^2\right]\left(\frac{\omega}{\varepsilon}\right) \tag{21}$$

For comparison, we also consider Model II which is close to Guggenheim's quasichemical approximation (Guggenheim, 1952). In Model II, in the absence of specific interactions, N_{12} is given by

$$N_{12} = \Gamma_{12} N_{12}^{*} \tag{22}$$

where N_{12}^{*} is the number of 1-2 pair-wise interactions for a random mixture and Γ_{12} is the nonrandomness factor defined as

$$\Gamma_{12} \equiv 1 - 0.8031\theta_1\theta_2 \left[\exp\left(\frac{1}{\tilde{T}}\right) - 1\right] \tag{23}$$

Eq. (23) is a generalization of a result derived for a mixture of equal-sized molecules (r_1=r_2=1) by correlating Monte Carlo simulation results for a cubic Ising lattice. Extension to polymer systems was made by simply replacing the mole fraction by the surface fraction. For a monomer/r-mer mixture, the coexistence curves calculated from Model II were found to be very close to those calculated from the Guggenheim's quasichemical approximation. For example, for a r_1=1; r_2=100 system, the critical composition (ϕ_c) and reduced temperature ($\tilde{T}_c$) predicted by this model are 0.875 and 3.681, respectively, while Guggenheim's quasichemical approximation gives $\phi_c = 0.882$ and $\tilde{T}_c = 3.706$. In the presence of specific interactions, the nonrandomness factor is assumed to be given by

$$\Gamma_{12} = 1 - 0.8031\theta_1\theta_2 \left[\exp\left(\frac{\omega}{\varepsilon\tilde{T}}\right) - 1\right] \tag{24}$$

In this model, r_1 can assume any positive number. Model II is assumed to be applicable to polymer blends.

These models are compared to the original model by ten Brinke and Karasz (1984) (Model III) defined by

$$\frac{\Delta_{mix}A}{N_r kT} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2 \tag{25}$$

where χ is the Flory interaction parameter

$$\chi \equiv \frac{z}{2}\left[\left(1 + 2\delta\varepsilon_{12}/\varepsilon\right)\left(\frac{1}{\tilde{T}}\right) + 2\ln\left(\frac{1 + g_{12}}{1 + g_{12}\exp\left(\delta\varepsilon_{12}/\varepsilon\tilde{T}\right)}\right)\right] . \tag{26}$$

CALCULATION PROCEDURE

For phase-equilibrium calculations, we require expressions for the critical coordinate and for the chemical potential. In a binary system, the critical condition is given by

$$\left[\frac{\partial^2\left(\frac{\Delta_{mix}A}{N_r kT}\right)}{\partial\phi_1^2}\right]_{T,V} = 0; \quad \left[\frac{\partial^3\left(\frac{\Delta_{mix}A}{N_r kT}\right)}{\partial\phi_1^3}\right]_{T,V} = 0 \tag{27}$$

where the differentiation is at constant temperature (T) and volume (V) of the system. These equations are solved for ϕ_c and $\widetilde{T}_c$.

The coexistence curve is found from the conditions

$$\Delta\mu_1' = \Delta\mu_1'' \tag{28}$$

$$\Delta\mu_2' = \Delta\mu_2'' \tag{29}$$

where $\Delta\mu_i$ is the change in chemical potential upon isothermally transferring component i from the pure state to the mixture. Superscripts $'$ and $''$ denote the coexisting phases. $\Delta\mu_1$ and $\Delta\mu_2$ are related to $\Delta_{mix}A$ by

$$\Delta\mu_1 = \left(\frac{\partial\Delta_{mix}A}{\partial N_1}\right)_{T,N_2} \tag{30}$$

$$\Delta\mu_2 = \left(\frac{\partial\Delta_{mix}A}{\partial N_2}\right)_{T,N_1} \tag{31}$$

RESULTS AND DISCUSSION

1. Effect of g_{12}. In all calculations performed here, the number of segments per molecule for the smaller molecule (r_1) is set to 1. For mixtures containing low-molecular-weight species, to determine r_2, we use the ratio of UNIQUAC size parameters (Abrams and Prausnitz, 1975; Sorensen and Arlt, 1979), which are proportional to the van der Waals molecular volumes (Bondi, 1968). For aqueous solutions of poly(propylene glycol) (PPG) and poly(ethylene glycol) (PEG) for which UNIQUAC size parameters are not available, r_2 is set to the ratio of molar volumes at room temperature. The densities of PPG and PEG are assumed to be 1.01 and 1.20 g/cm^3, respectively. Size parameter r_2 is therefore not an adjustable parameter but a pre-set physical parameter.

To include specific interactions between dissimilar components, two additional parameters, degeneracy parameter g_{12} and energy parameter $\delta\varepsilon_{12}$, are required. For a given g_{12}, the ratio of $\delta\varepsilon_{12}$ to interchange energy ε is determined from the experimental ratio of UCST to LCST, while ε is calculated from $\tilde{T}_c$ at UCST or LCST. Figures 1(a) and 1(b) compare the theoretical coexistence curves by Model I at different values of g_{12} with experimental data for the systems glycerol/m-toluidine (T_{UCST}/T_{LCST}=1.407) (Sorensen and Arlt, 1979) and PEG (M_η=2290)/water (T_{UCST}/T_{LCST}=1.165) (Saeki et al., 1976), respectively. Here, M_η stands for the average molecular weight of polymer determined from viscosity measurements; T_{UCST} and T_{LCST} denote the upper critical solution temperature and lower critical solution temperature in degrees Kelvin, respectively. Table I gives interaction energy parameters ε and $\delta\varepsilon_{12}$. Figures 1(a) and 1(b) show that the width of the coexistence curves becomes narrower when the value of g_{12} declines.

In the subsequent calculations, g_{12} is set to 5000. Although such a high value of g_{12} implies a strongly directional interaction, Figures 1(a) and 1(b) indicate that this value gives good fits for both small and large r_2. In addition, the magnitudes of ε and $\delta\varepsilon_{12}$ for the above systems are physically reasonable. The strength of hydrogen bonding lies

between 1 and 10 kcal/mole (Prausnitz et al., 1986) and the ratio of specific force to dispersion force ranges from 5 to 50 (Coleman et al., 1991).

2. Comparison with experiment. Figures 2, 3, and 4 compare theoretical coexistence curves by Models I and III with experimental data for the systems glycerol/benzylethylamine (T_{UCST}/T_{LCST}=1.715), water/nicotine (T_{UCST}/T_{LCST}=1.513), and water/1-propoxy-propane-2-ol (T_{UCST}/T_{LCST}=1.446) (Sorensen and Arlt, 1979), respectively. These calculations include specific interactions between dissimilar components. In Figure 4 the theoretical curve by Model II is also shown. Agreement between the theoretical curves by Model I with experimental data is good. Table II gives parameters for these calculations.

Figures 5 and 6 show theoretical coexistence curves by Models I and III along with experimental data for the systems water/tetrahydrofuran (T_{UCST}/T_{LCST}=1.189) and glycerol/guaiacol (T_{UCST}/T_{LCST}=1.140) (Sorensen and Arlt, 1979), respectively. In these systems, those calculated coexistence curves which include only specific interactions between dissimilar components are narrow compared to the experimental data. Also plotted are the theoretical curves including specific interactions between similar components as well as those between dissimilar components. To simplify the problem, in the latter calculation it is assumed that only one component is able to form specific interactions with itself; ω is therefore given by

$$\omega = \varepsilon + f_{11}(-\delta\varepsilon_{11}) + f_{12}(2\delta\varepsilon_{12}) \tag{32}$$

and g_{11} is assumed to be equal to g_{12}. The above simplification may not be serious because in Eq. (2) both the term associated with the specific interactions between molecules of type 1 and that between molecules of type 2 have the same (negative) sign. In this calculation, $\delta\varepsilon_{11}$ (or $\delta\varepsilon_{12}$) can be arbitrarily chosen and $\delta\varepsilon_{12}$ (or $\delta\varepsilon_{11}$) is

determined from the ratio of UCST to LCST. It was found that inclusion of specific interactions between similar components results in wider coexistence curves. Table III gives interaction energy parameters for these calculations.

Figure 7 compares theoretical coexistence curves by Models I and III with experimental data for the PPG/water system (T_{UCST}/T_{LCST}=1.763) (Müller, 1991). The number-average molecular weight of polymer (M_n) is 421. Figures 8(a), 8(b), and 8(c) show theoretical coexistence curves and experimental data for the systems PEG/water of M_η=2180 (T_{UCST}/T_{LCST}=1.091) [2], M_n=3350 (T_{UCST}/T_{LCST}=1.212) (Bae et al., 1991), and M_n=8000 (T_{UCST}/T_{LCST}=1.397) (Bae et al., 1991), respectively. Table IV gives parameters for these calculations. The polydispersity factor, which is the ratio of weight-average molecular weight to number-average molecular weight, of M_n=3350 and M_n=8000 samples is about 1.6. In Figure 8(c) the theoretical curve by Model II is also shown. Although our model cannot account for the effect of polydispersity, the theoretical curves by Model I for polydisperse samples shown in Figures 8(b) and 8(c) compare favorably with the experimental data. In addition, improvement of the theoretical curve by Model I over those by Models II and III is significant. As shown in Table IV, for PEG/water systems, the energy parameters ε and $\delta\varepsilon_{12}$ are slightly molecular-weight dependent.

Finally, we note some inherent limitations in the current model. For specific interactions between similar components, the present model cannot distinguish between intramolecular specific interactions and intermolecular interactions. In addition, the specific interactions are assumed to be formed at any contact points of a molecule with equal probability. This assumption is not correct if specific interactions can be formed only at particular parts of a molecule. Such a restriction, however, might be taken into consideration by viewing a molecule as a copolymer consisting of several chemically different units.

Interpretation of the degeneracy parameter g_{ij} also remains ambiguous. It is not clear how much physical significance can be attached to this ad hoc parameter. However, since it appears that g_{ij} can be assigned a constant value, this ambiguity should impose little restriction on the use of our model for phase equilibrium calculations.

Because of the simplified expression for $\Delta_{mix}A$, our model could be used for the prediction of phase behavior of ternary solvent/solvent/polymer systems, which include specific interactions, from binary information only. The use of Model II for polymer blends including random-copolymers seems promising.

CONCLUSIONS

A simple Monte-Carlo-based lattice model has been developed for closed-loop phase equilibrium calculations based on the incompressible lattice-gas model by ten Brinke and Karasz. A new expression is used for the Helmholtz energy of mixing for monomer/r-mer mixture obtained by correlating Monte Carlo simulation results. Calculated coexistence curves agree well with experimental data over a range of $r_2 \approx 1 \sim 370$.

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Notation

a	=	coefficient in Eqs. (13) and (19)
A	=	Helmholtz energy
A'	=	coefficient in Eq. (12)
A''	=	coefficient in Eq. (18)
B'	=	coefficient in Eqs. (12) and (18)
C'	=	coefficient in Eq. (12)
C''	=	coefficient in Eq. (18)
f_{ij}	=	fraction of i-j interactions which are specific
g_{ij}	=	degeneracy parameter for i-j contact
k	=	Boltzmann constant
N_i	=	number of molecules of component i
N_{12}	=	number of 1-2 contacts
N_{12}^*	=	number of 1-2 contacts for a random mixture
N_r	=	total number of lattice sites
q_i	=	surface parameter for component i
r_i	=	size parameter for component i
T	=	temperature
$\tilde{T}$	=	reduced temperature
$\tilde{T}_c$	=	reduced critical temperature
U	=	internal energy
V	=	volume
z	=	lattice coordination number, a constant here set equal to 6

Greek letters

Γ_{12}	=	nonrandomness factor for 1-2 contact
$\delta\varepsilon_{ij}$	=	difference between specific interaction energy and non-specific interaction energy of i-j contact
ε	=	interchange energy excluding specific interactions
ε_{ij}	=	interaction energy of i-j contact
θ_i	=	surface fraction of component i
μ_i	=	chemical potential of component i
ϕ_c	=	critical volume fraction
ϕ_i	=	volume fraction of component i
χ	=	Flory interaction parameter
ω	=	interchange energy including specific interactions

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APPENDIX: Internal Energy of Mixing Including Specific Interactions

Consider a binary mixture of N_1 molecules of component 1 and N_2 molecules of component 2. The internal energy of mixing $(\Delta_{mix}U)$ is defined as

$$\Delta_{mix}U \equiv U_{mixture} - U_{pure\,1} - U_{pure\,2} \tag{A.1}$$

where $U_{mixture}$ and $U_{pure\,i}$ are the internal energy of the mixture and that of the pure substance containing N_i molecules of component i. If we assume that a fraction f_{ij} of the i-j interactions (i,j = 1,2) is specific, having interaction energy of $\varepsilon_{ij} + \delta\varepsilon_{ij}$ and that $1 - f_{ij}$ is the fraction of non-specific interactions having interaction energy of ε_{ij}, $U_{mixture}$ is given by

$$\begin{aligned} U_{mixture} = {} & (1-f_{11})N_{11}\varepsilon_{11} + f_{11}N_{11}\left(\varepsilon_{11} + \delta\varepsilon_{11}\right) + (1-f_{22})N_{22}\varepsilon_{22} + f_{22}N_{22}\left(\varepsilon_{22} + \delta\varepsilon_{22}\right) \\ & + (1-f_{12})N_{12}\varepsilon_{12} + f_{12}N_{12}\left(\varepsilon_{12} + \delta\varepsilon_{12}\right) \end{aligned} \tag{A.2}$$

where N_{ij} is the number of i-j pair-wise contacts. N_{12} and N_{ii} are related to the total number of contacts of component i (zq_iN_i) through the conservation equation given by

$$zq_iN_i = 2N_{ii} + N_{12} \tag{A.3}$$

In terms of N_i and N_{12}, the internal energy of mixing is expressed as

$$U_{mixture} = \frac{1}{2}\left[zq_1N_1\left(\varepsilon_{11} + f_{11}\delta\varepsilon_{11}\right) + zq_2N_2\left(\varepsilon_{22} + f_{22}\delta\varepsilon_{22}\right) + N_{12}\omega\right] \tag{A.4}$$

Assuming that f_{ii} in the mixture is identical to that in the pure substance containing molecules of component i, $U_{pure\,i}$ is given by

$$U_{\text{pure } i} = \frac{1}{2} z q_i N_i \left[(1 - f_{ii}) \varepsilon_{ii} + f_{ii} \left(\varepsilon_{ii} + \delta\varepsilon_{ii} \right) \right] = \frac{1}{2} z q_i N_i \left(\varepsilon_{ii} + f_{ii} \delta\varepsilon_{ii} \right) \tag{A.5}$$

Thus, substitution of Eqs. (A.4) and (A.5) into Eq. (A.1) gives Eq. (1).

Figure Captions

Figure 1. Temperature-composition coexistence curves for the systems (a) glycerol/m-toluidine and (b) polyethylene glycol (M_η=2290)/water. Points represent experimental data. Curves are calculated using different g_{12}. Specific interactions between dissimilar components only are included.

Figure 2. Temperature-composition coexistence curve for the system glycerol/benzylethylamine. Points represent experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively. Specific interactions between dissimilar components only are included.

Figure 3. Temperature-composition coexistence curve for the system water/nicotine. Points represent experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively. Specific interactions between dissimilar components only are included.

Figure 4. Temperature-composition coexistence curve for the system water/1-propoxy-propane-2-ol. Points represent experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively. The theoretical curve by Model II (–·–·–) is also shown. Specific interactions between dissimilar components only are included.

Figure 5. Temperature-composition coexistence curve for the system water/tetrahydrofuran. Points represent experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively, including specific interactions between dissimilar molecules only. The theoretical curve by Model I (–·–·–) includes specific interactions between similar components as well as those between dissimilar components.

Figure 6. Temperature-composition coexistence curve for the system glycerol/guaiacol. Points represen: experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively, including specific interactions between dissimilar components only. The theoretical curve by Model I (–·–·–) includes specific interactions between similar components as well as those between dissimilar components.

Figure 7. Temperature-composition coexistence curve for the system poly(propylene glycol)/water (M_n=421). Points represent experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively. Specific interactions between dissimilar components only are included.

Figure 8. Temperature-composition coexistence curves for the system poly(ethylene glycol)/water; (a) M_η=2190; (b) M_n=3350; (c) M_n=8000. Points represent experimental data. Solid (——) and broken (------) curves are calculated by Models I and III, respectively. Figure (c) shows the theoretical curve by Model II (–·–·–). Specific interactions between dissimilar components only are included.

TABLE I. Parameters for (1a) Glycerol/m-Toluidine and (1b) PEG (M_η=2290)/Water Systems

	(1a) r_2=1.241		(1b) r_2=105.9	
g_{12}	ε (kcal/mol)	$\delta\varepsilon_{12}$ (kcal/mol)	ε (kcal/mol)	$\delta\varepsilon_{12}$ (kcal/mol)
5	1.253	–1.153	0.953	–1.161
40	0.826	–1.656	0.579	–1.859
200	0.712	–2.289	0.470	–2.726
1000	0.663	–3.028	0.416	–3.773
5000	0.641	–3.823	0.388	–4.931

TABLE II. Parameters for (2) Glycerol/Benzylethylamine, (3) Water/Nicotine, and (4) [a] Water/1-Propoxy-Propane-2-ol Systems

	Model I		Model III	
System and r_2	ε (kcal/mol)	$\delta\varepsilon_{12}$(kcal/mol)	ε (kcal/mol)	$\delta\varepsilon_{12}$(kcal/mol)
(2) r_2=1.619	0.801	–4.595	0.612	–4.537
(3) r_2=7.054	0.480	–4.329	0.342	–4.161
(4) r_2=5.485	0.449	–3.956	0.326	–3.808

[a] Parameters ε and $\delta\varepsilon_{12}$ for Model II are 0.419 and –3.950 kcal/mol, respectively.

TABLE III. Parameters (kcal/mol) for (5) Water/Tetrahydrofuran and (6) Glycerol/Guaiacol Systems

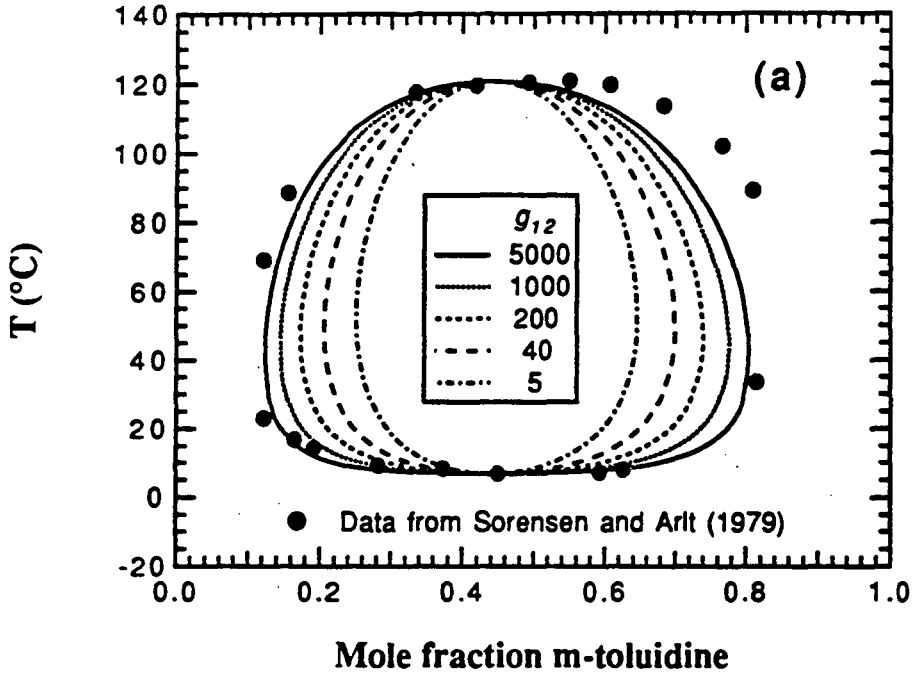
	Model I		Model I			Model III	
System and r_2	ε	$\delta\varepsilon_{12}$	ε	$\delta\varepsilon_{11}$	$\delta\varepsilon_{12}$	ε	$\delta\varepsilon_{12}$
(5) r_2=3.197	0.497	–4.231	0.475	–6.180	–5.632	0.377	–4.065
(6) r_2=1.264	0.600	–3.957	0.573	–5.733	–5.207	0.484	–3.838

TABLE IV. Parameters for (7) Poly(propylene glycol)/Water and (8) [a] Poly(ethylene glycol)/Water Systems

	Model I		Model III	
System and r_2	ε (kcal/mol)	$\delta\varepsilon_{12}$ (kcal/mol)	ε (kcal/mol)	$\delta\varepsilon_{12}$ (kcal/mol)
(7) r_2=23.15	0.419	–4.074	0.275	–3.829
(8a) r_2=100.8	0.385	–4.933	0.237	–4.547
(8b) r_2=154.9	0.386	–4.928	0.233	–4.526
(8c) r_2=370.0	0.389	–4.903	0.227	–4.407

[a] For system 8(c), parameters ε and $\delta\varepsilon_{12}$ for Model II are 0.308 and –4.672 kcal/mol, respectively.

Figure 1


(a)
g_{12}
5000
1000
200
40
5
Data from Sorensen and Arlt (1979)
T (°C)
Mole fraction m-toluidine

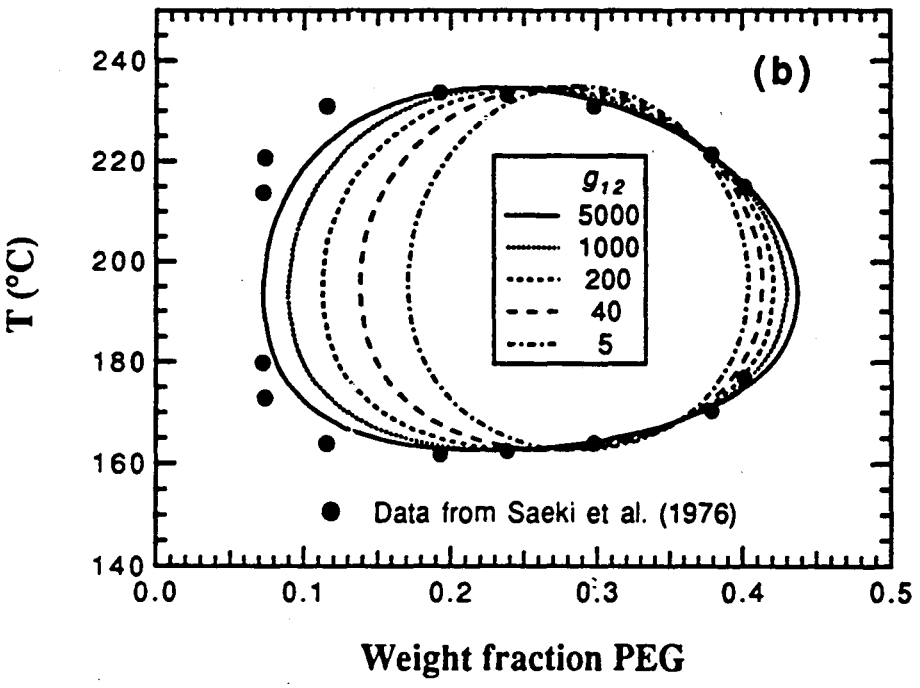
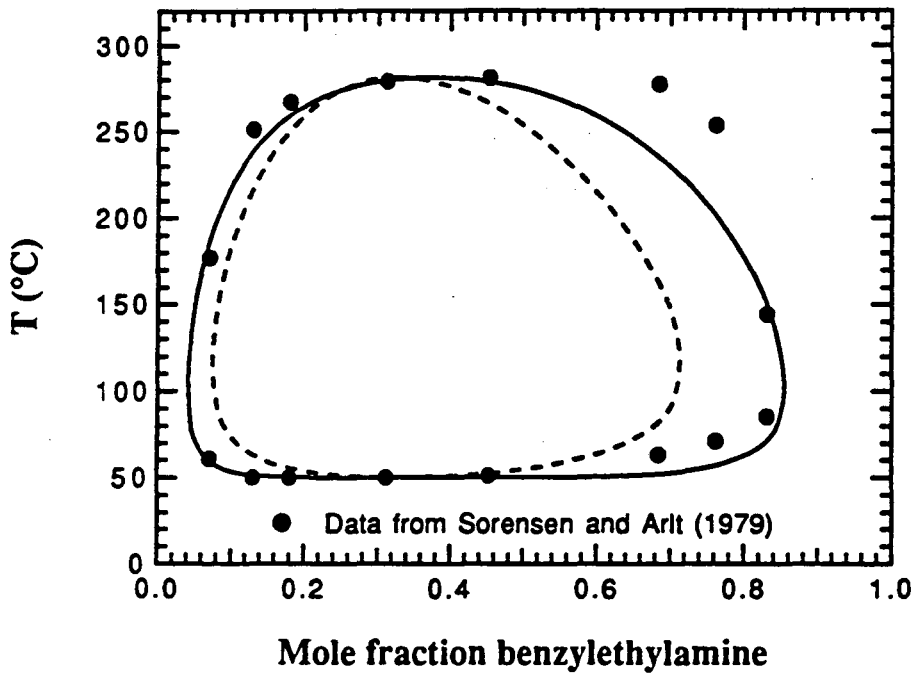

(b)
g_{12}
5000
1000
200
40
5
Data from Saeki et al. (1976)
T (°C)
Weight fraction PEG

Figure 2


300
250
200
150
100
50
0
T (°C)
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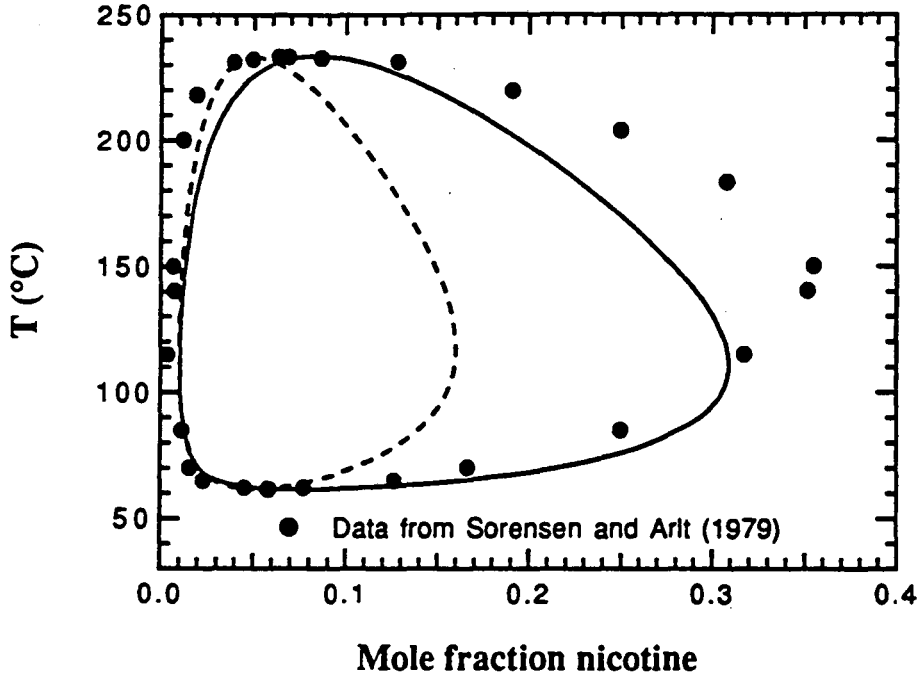
0.2
0.4
0.6
0.8
1.0
Data from Sorensen and Arlt (1979)
Mole fraction benzylethylamine

Figure 3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100
50
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0.2
0.3
0.4
Mole fraction nicotine
Data from Sorensen and Arlt (1979)

Figure 4

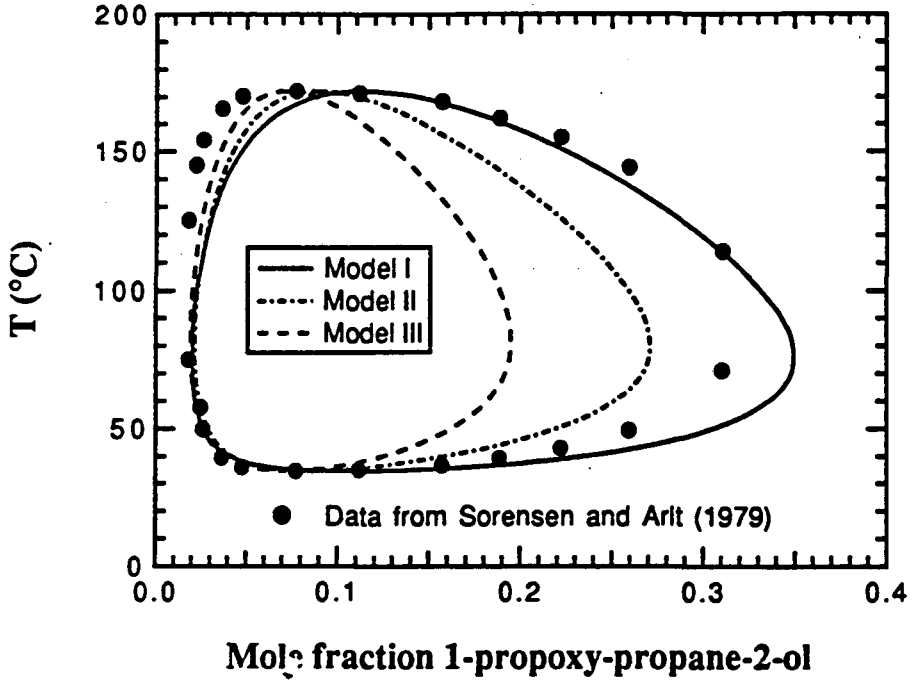
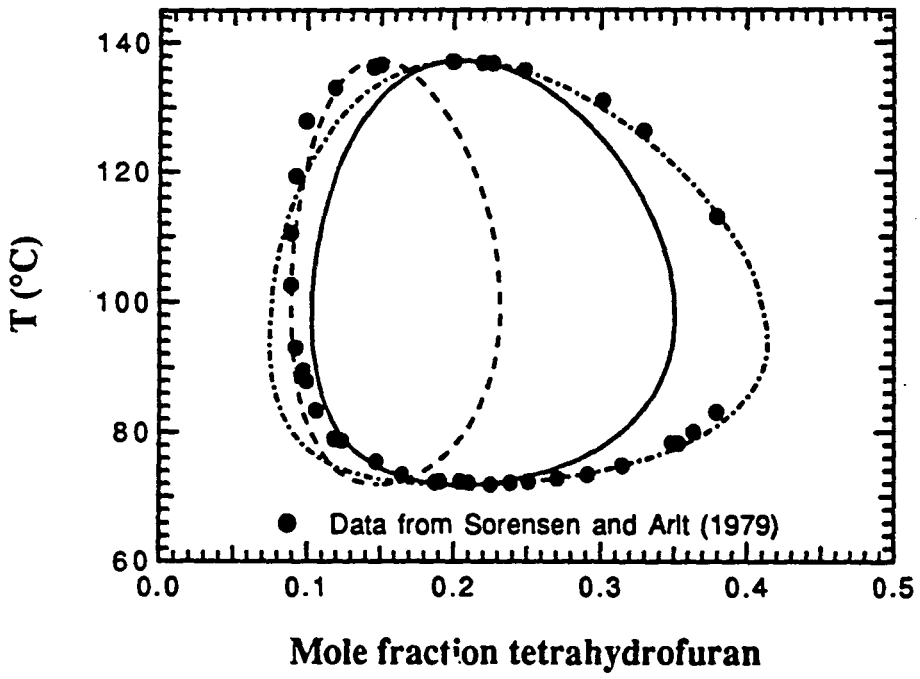

200
150
100
50
0
T (°C)
Model I
Model II
Model III
Data from Sorensen and Arlt (1979)
0.0
0.1
0.2
0.3
0.4
Mole fraction 1-propoxy-propane-2-ol

Figure 5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120
100
80
60
T (°C)
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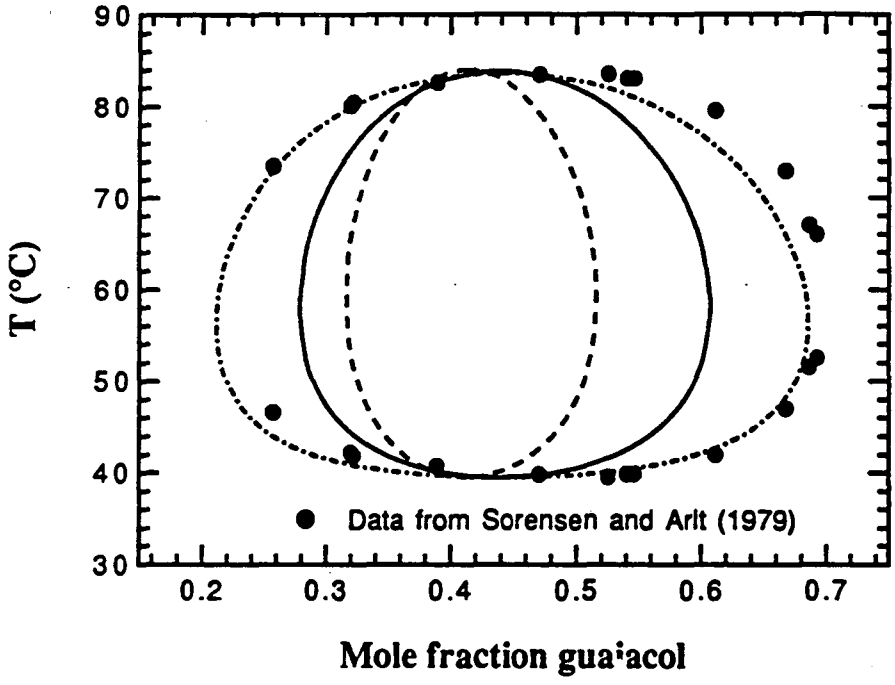
0.2
0.3
0.4
0.5
Data from Sorensen and Arlt (1979)
Mole fraction tetrahydrofuran

Figure 6


90
80
70
60
50
40
30
T (°C)
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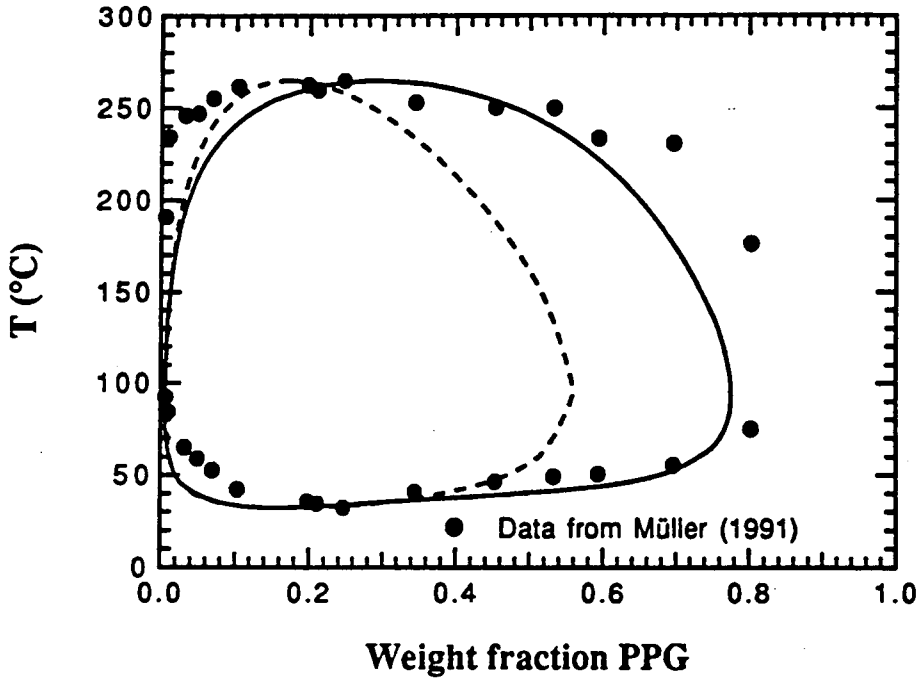
0.4
0.5
0.6
0.7
Mole fraction guaiacol
Data from Sorensen and Arlt (1979)

Figure 7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200
150
100
50
0
T (°C)
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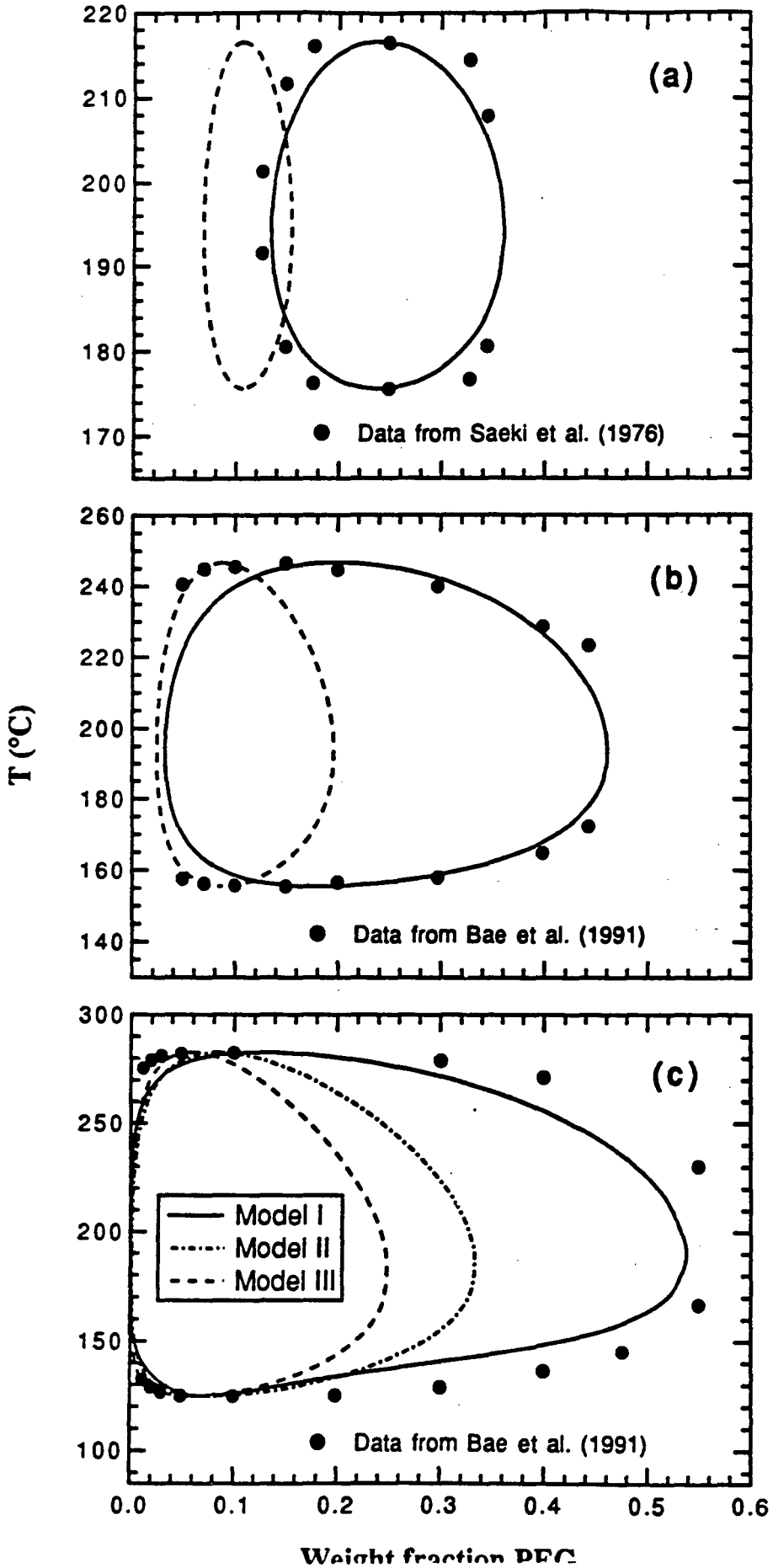
0.4
0.6
0.8
1.0
Weight fraction PPG
Data from Müller (1991)

Figure 8


(a)
Data from Saeki et al. (1976)
(b)
Data from Bae et al. (1991)
(c)
Model I
Model II
Model III
Data from Bae et al. (1991)
T (°C)
Weight fraction PEG

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