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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)
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 $\Delta_{\text{mix}}A$: 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 $\Delta_{\text{mix}}A$ 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 $\Delta_{\text{mix}}A$. In this paper we use the recently-presented new expression for $\Delta_{\text{mix}}A$ for incompressible monomer/r-mer mixture obtained by correlating the Monte Carlo simulation results reported by Lamben 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 Brinle 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 $\epsilon_{ij} + \delta\epsilon_{ij}$ or in a non-specific manner with interaction energy $\epsilon_{ij}$ where $i=1$ or 2 and $j=1$ or 2. Both $\epsilon_{ij}$ and $\delta\epsilon_{ij}$ 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 ($\Delta_{\text{mix}}U$) is given by

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

(1)

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

$$\omega = \epsilon + f_{11}(-\delta\epsilon_{11}) + f_{22}(-\delta\epsilon_{22}) + f_{12}(2\delta\epsilon_{12})$$

(2)

where $\epsilon$ is the interchange energy

$$\epsilon = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$$

(3)

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

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

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

(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

$$f_{ij} = \frac{1}{1 + g_{ij}\exp(\delta\epsilon_{ij}/kT)}.$$  \hspace{1cm} (5)

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

$$\frac{\Delta_{\text{mix}}A}{N_{r}kT} = \int_{0}^{\frac{1}{T}} \Delta_{\text{mix}}U \left(\frac{1}{T}\right) + \frac{\Delta_{\text{mix}}A}{N_{r}kT} f_{T=\infty} \, d\left(\frac{1}{T}\right)$$  \hspace{1cm} (6)

$$\left(\frac{\Delta_{\text{mix}}A}{N_{r}kT}\right)_{f_{T=\infty}} = \frac{\phi_{1}}{r_{1}} \ln \phi_{1} + \frac{\phi_{2}}{r_{2}} \ln \phi_{2} + \frac{2}{\phi_{1}} \left[\frac{\phi_{1}q_{1} \ln \phi_{1} + \phi_{2}q_{2} \ln \phi_{2}}{\phi_{1}}\right]$$  \hspace{1cm} (7)

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

$$\bar{T} = \frac{kT}{\epsilon}.$$  \hspace{1cm} (8)

Here $r_i$, $\phi_i$, and $\theta_i$ are the number of segments per molecule, volume fraction, and surface fraction of component $i$, respectively. $\phi_i$ and $\theta_i$ are defined by

$$\phi_i \equiv \frac{N_ir_i}{N_1r_1 + N_2r_2}.$$  \hspace{1cm} (9)

$$\theta_i \equiv \frac{N_iq_i}{N_1q_1 + N_2q_2}.$$  \hspace{1cm} (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

$$zq_i = r_i(z - 2) + 2$$  \hspace{1cm} (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 ($1/T$) is necessary in Eq. (6), Simpson's rule is used at 101 equally spaced points along the axis of $1/T$.

Our main task is the estimation of $N_{12}$ which, in turn, determines $\Delta_{\text{mix}}U$ 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/mermer mixture in the absence of specific interactions:

$$N_{12} = N_i\phi_1\phi_2\left[A' + B' \left( \phi_2 - \phi_1 \right) + C' \left( \phi_2 - \phi_1 \right)^2 \right]$$  \hspace{1cm} (12)$$

where

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

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

$$a_1(r_2) = -1.2374 - \frac{0.09616(r_2 - 1)}{1 + 0.14585(r_2 - 1)}$$  \hspace{1cm} (15)$$
The numerical coefficients in Eqs. (14) to (17) follow from Monte-Carlo calculations. In the remainder 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, \( \varepsilon \) is replaced by \( \omega \) in Eq. (1). Therefore, as a first approximation it seems reasonable to replace \( \varepsilon \) by \( \omega \) 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:

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

where

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

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

In Model I, \( \Delta_{\text{mix}} U \) is given by

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

$$N_{12} = \Gamma_{12} N_{12}^*$$  \hspace{1cm} (22)

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

$$\Gamma_{12} = 1 - 0.8031 \theta_1 \theta_2 \left[ \exp \left( \frac{1}{T} \right) - 1 \right]$$  \hspace{1cm} (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 ($\phi_c$) and reduced temperature ($T_c$) predicted by this model are 0.875 and 3.681, respectively, while Guggenheim's quasichemical approximation gives $\phi_c = 0.882$ and $T_c = 3.706$. In the presence of specific interactions, the nonrandomness factor is assumed to be given by

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

$$\frac{\Delta_{\text{mix}}A}{N_r kT} = \frac{\phi_1 \ln \phi_1}{r_1} + \frac{\phi_2 \ln \phi_2}{r_2} + \chi \phi_1 \phi_2$$  \hspace{1cm} (25)$$

where \( \chi \) is the Flory interaction parameter

$$\chi = \frac{N_r}{2} \left[ (1 + 2\delta \varepsilon_{12}/\varepsilon) \left( \frac{1}{T_r} \right) + 2 \ln \left( \frac{1 + g_{12}}{1 + g_{12} \exp(\delta \varepsilon_{12}/\varepsilon T)} \right) \right].$$  \hspace{1cm} (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

\[
\frac{\partial^2 (\frac{\Delta_{\text{mix}} A}{N_i kT})}{\partial \phi_1^2} |_{T,V} = 0; \quad \frac{\partial^3 (\frac{\Delta_{\text{mix}} A}{N_i kT})}{\partial \phi_1^3} |_{T,V} = 0
\]  \hspace{1cm} (27)

where the differentiation is at constant temperature (T) and volume (V) of the system. These equations are solved for \( \phi_c \) and \( T_c \).

The coexistence curve is found from the conditions

\[
\Delta \mu_1' = \Delta \mu_1'' \]  \hspace{1cm} (28)

\[
\Delta \mu_2' = \Delta \mu_2'' \]  \hspace{1cm} (29)

where \( \Delta \mu_1 \) 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 \( \Delta_{\text{mix}} A \) by

\[
\Delta \mu_1 = \left( \frac{\partial \Delta_{\text{mix}} A}{\partial N_1} \right)_{T,N_2} \]  \hspace{1cm} (30)

\[
\Delta \mu_2 = \left( \frac{\partial \Delta_{\text{mix}} A}{\partial N_2} \right)_{T,N_1} \]  \hspace{1cm} (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 $\varepsilon$ is determined from the experimental ratio of UCST to LCST, while $\varepsilon$ is calculated from $T_c$ 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 ($M_\eta=2290$)/water ($T_{UCST}/T_{LCST}=1.165$) (Saeki et al., 1976), respectively. Here, $M_\eta$ 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 $\varepsilon$ 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 $\varepsilon$ 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; \( \omega \) is therefore given by

\[
\omega = \varepsilon + f_{11}(-\delta \varepsilon_{11}) + f_{12}(2\delta \varepsilon_{12})
\]

(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 \(M_n=2180\) (\(T_{UCST}/T_{LCST}=1.091\)) [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 \(\epsilon\) and \(\delta\epsilon_{12}\) 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 $r_2 = 1 - 370$.

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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

\( \bar{T} \) = reduced temperature

\( \bar{T}_c \) = reduced critical temperature

\( U \) = internal energy

\( V \) = volume

\( z \) = lattice coordination number, a constant here set equal to 6

Greek letters

\( \Gamma_{12} \) = nonrandomness factor for 1-2 contact

\( \delta \varepsilon_{ij} \) = difference between specific interaction energy and non-specific interaction energy of i-j contact

\( \varepsilon \) = interchange energy excluding specific interactions

\( \varepsilon_{ij} \) = interaction energy of i-j contact

\( \theta_i \) = surface fraction of component i

\( \mu_i \) = chemical potential of component i

\( \phi_c \) = critical volume fraction

\( \phi_i \) = volume fraction of component i

\( \chi \) = Flory interaction parameter

\( \omega \) = 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 ($\Delta_{\text{mix}} U$) is defined as

$$\Delta_{\text{mix}} U \equiv U_{\text{mixture}} - U_{\text{pure 1}} - U_{\text{pure 2}}$$  \hspace{1cm} (A.1)

where $U_{\text{mixture}}$ and $U_{\text{pure i}}$ 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 $\epsilon_{ij} + \delta \epsilon_{ij}$ and that $1 - f_{ij}$ is the fraction of non-specific interactions having interaction energy of $\epsilon_{ij}$, $U_{\text{mixture}}$ is given by

$$U_{\text{mixture}} = (1 - f_{11})N_{11}\epsilon_{11} + f_{11}N_{11}(\epsilon_{11} + \delta \epsilon_{11}) + (1 - f_{22})N_{22}\epsilon_{22} + f_{22}N_{22}(\epsilon_{22} + \delta \epsilon_{22})$$

$$+ (1 - f_{12})N_{12}\epsilon_{12} + f_{12}N_{12}(\epsilon_{12} + \delta \epsilon_{12})$$  \hspace{1cm} (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 $i$ ($z_i N_i$) through the conservation equation given by

$$z_i N_i = 2N_{ii} + N_{12}$$  \hspace{1cm} (A.3)

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

$$U_{\text{mixture}} = \frac{1}{2} \left[ z_i N_1 (\epsilon_{11} + f_{11} \delta \epsilon_{11}) + z_2 N_2 (\epsilon_{22} + f_{22} \delta \epsilon_{22}) + N_{12} \omega \right]$$  \hspace{1cm} (A.4)

Assuming that $f_{ii}$ in the mixture is identical to that in the pure substance containing molecules of component $i$, $U_{\text{pure i}}$ is given by
Thus, substitution of Eqs. (A.4) and (A.5) into Eq. (A.1) gives Eq. (1).

\[ U_{\text{pure } i} = \frac{1}{2} z q_i N_i \left[ (1 - f_{ii}) \epsilon_{ii} + f_{ii} (\epsilon_{ii} + \delta \epsilon_{ii}) \right] = \frac{1}{2} z q_i N_i \left( \epsilon_{ii} + f_{ii} \delta \epsilon_{ii} \right) \]  
\hspace{1cm} (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_\text{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-propanol. 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 represent 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 (Mₙ=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) Mₙ=2190; (b) Mₙ=3350; (c) Mₙ=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 
($M_n=2290$) /Water Systems

<table>
<thead>
<tr>
<th>$g_{12}$</th>
<th>(1a) $r_2=1.241$</th>
<th>(1b) $r_2=105.9$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon$ (kcal/mol)</td>
<td>$\delta\varepsilon_{12}$ (kcal/mol)</td>
</tr>
<tr>
<td>5</td>
<td>1.253</td>
<td>-1.153</td>
</tr>
<tr>
<td>40</td>
<td>0.826</td>
<td>-1.656</td>
</tr>
<tr>
<td>200</td>
<td>0.712</td>
<td>-2.289</td>
</tr>
<tr>
<td>1000</td>
<td>0.663</td>
<td>-3.028</td>
</tr>
<tr>
<td>5000</td>
<td>0.641</td>
<td>-3.823</td>
</tr>
</tbody>
</table>
TABLE II. Parameters for (2) Glycerol/Benzylethylamine, (3) Water/Nicotine, and (4) a) Water/1-Propoxy-Propan-2-ol Systems

<table>
<thead>
<tr>
<th>System and $r_2$</th>
<th>$\varepsilon$ (kcal/mol)</th>
<th>$\delta\varepsilon_{12}$ (kcal/mol)</th>
<th>$\varepsilon$ (kcal/mol)</th>
<th>$\delta\varepsilon_{12}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) $r_2=1.619$</td>
<td>0.801</td>
<td>-4.595</td>
<td>0.612</td>
<td>-4.537</td>
</tr>
<tr>
<td>(3) $r_2=7.054$</td>
<td>0.480</td>
<td>-4.329</td>
<td>0.342</td>
<td>-4.161</td>
</tr>
<tr>
<td>(4) $r_2=5.485$</td>
<td>0.449</td>
<td>-3.956</td>
<td>0.326</td>
<td>-3.808</td>
</tr>
</tbody>
</table>

a) Parameters $\varepsilon$ 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

<table>
<thead>
<tr>
<th>System and ( r_2 )</th>
<th>Model I</th>
<th>Model I</th>
<th>Model III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \varepsilon )</td>
<td>( \delta \varepsilon_{12} )</td>
<td>( \delta \varepsilon_{11} )</td>
</tr>
<tr>
<td>(5) ( r_2 = 3.197 )</td>
<td>0.497</td>
<td>-4.231</td>
<td>0.475</td>
</tr>
<tr>
<td>(6) ( r_2 = 1.264 )</td>
<td>0.600</td>
<td>-3.957</td>
<td>0.573</td>
</tr>
</tbody>
</table>
TABLE IV. Parameters for (7) Poly(propylene glycol)/Water and (8) a) Poly(ethylene glycol)/Water Systems

<table>
<thead>
<tr>
<th>System and $r_2$</th>
<th>Model I</th>
<th>Model III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon$ (kcal/mol)</td>
<td>$\delta\varepsilon_{12}$ (kcal/mol)</td>
</tr>
<tr>
<td>(7) $r_2=23.15$</td>
<td>0.419</td>
<td>-4.074</td>
</tr>
<tr>
<td>(8a) $r_2=100.8$</td>
<td>0.385</td>
<td>-4.933</td>
</tr>
<tr>
<td>(8b) $r_2=154.9$</td>
<td>0.386</td>
<td>-4.928</td>
</tr>
<tr>
<td>(8c) $r_2=370.0$</td>
<td>0.389</td>
<td>-4.903</td>
</tr>
</tbody>
</table>

a) For system 8(c), parameters $\varepsilon$ and $\delta\varepsilon_{12}$ for Model II are 0.308 and -4.672 kcal/mol, respectively.
Figure 1

(a) Mole fraction m-toluidine

(b) Weight fraction PEG

Data from Sorensen and Arlt (1979)

Data from Saeki et al. (1976)
Figure 2

![Graph showing the relationship between temperature (T °C) and mole fraction benzylethylamine. The graph includes a curve with data points labeled as 'Data from Sorensen and Arlt (1979).']
Figure 4

![Graph of T (°C) vs. Mol. fraction 1-propoxy-propane-2-ol with lines representing Model I, Model II, and Model III, and data points from Sorensen and Arlt (1979).]
Figure 5

Data from Sorensen and Arlt (1979)
Figure 7

![Graph showing weight fraction vs. temperature with data points and curves labeled as 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)

Weight fraction PEG

0.0 0.1 0.2 0.3 0.4 0.5 0.6