Phase Behaviors of Binary Polymer Solutions: The Extended Lattice Fluid Model

JEONG GYU JANG, YOUNG CHAN BAE

Department of Industrial Chemistry and Molecular Thermodynamics Laboratory, Hanyang University, Seoul 133-791, S. Korea

ABSTRACT: The generalized lattice–fluid (GLF) model is extended to predict phase behaviors of polymer/solvent systems. The GLF model gives some difficulties in describing liquid–liquid equilibria (LLE) of binary polymer solution systems due to general assumptions on its derivation. An extended lattice–fluid (ELF) model is proposed by introducing a new universal constant (C_0) and a model parameter (κ_{11}). The proposed model is then compared with experimental data for polymer/solvent systems and polymer1/polymer2 systems, which exhibit lower critical solution temperature (LCST) behaviors. Theoretical predictions and experimental results are in good agreement. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1143–1150, 1998

Key words: extended lattice–fluid model; liquid–liquid equilibria

INTRODUCTION

A variety of polymer-solution theories have been developed to understand the phase behavior of polymer/solvent mixtures different from that of ordinary liquid mixtures due to the large molecular size difference of the components. Phase behaviors of many polymer solvent systems have been investigated for the past several decades. There are many different types of phase behaviors for polymer solutions, for example, an upper critical solution temperature (UCST), a lower critical solution temperature (LCST), and both UCST and LCST. For a polymer in a poor solvent, the typical hour-glass type of cloud-point curve is observed.[1] A phase diagram of the closed-loop type with both UCST and LCST follows from an orientation-dependent interaction (or specific interaction), for example, a hydrogen bond.

Molecular-based thermodynamic models for describing liquid–liquid equilibria (LLE) in polymer mixtures can be divided into four categories, each corresponding to a particular statistical mechanical framework: incompressible-lattice models, generalized van der Waals partition function theories, compressible-lattice models, and off-lattice (continuous-space) models of chain fluids.

The most widely used and best known of the incompressible-lattice model is the Flory-Huggins theory,[2,3] which is based on a lattice model for polymer solutions wherein all lattice sites are occupied by segments of molecules. A mean field approximation was used to obtain the Helmholtz energy of mixing ΔA. Much work has been done to improve the mathematical solution of the lattice model, including chain connectivity and nonrandom mixing.[4] The Flory-Huggins model gives too narrow or parabolic a liquid–liquid coexistence curve near the critical region when compared with experimental data.

To obtain a more accurate fit, Koningsveld and Kleintjens[5] derived a closed-form expression for the interaction parameter considering the nearest neighbor site-occupancy probability. Recently,

Lambert et al.[6] reported a new expression of ΔA for incompressible monomer/r-mer mixtures obtained by correlating the Monte-Carlo simulation result using the quasi-chemical model. Bae et al.[7] simplified the model and improved the mathematical approximation defects.

Although these modified models provide some improvements, there still are difficulties to describe phase behaviors of the systems with LCST or with miscibility loops. If strong or oriented interactions from hydrogen bonding or other specific forces exist in the system, LCST or miscibility loops can arise, as first indicated by Hirschfelder et al.[8] for mixtures of ordinary liquids. Barker and Fock[9] developed a quasi-chemical method to account for such specific interactions. ten Brinke and Karasz[10] have developed an incompressible model of binary mixture with specific interactions. Furthermore, Freed et al.[11–13] reported a complicated lattice field theory for polymer solutions that is formally an exact mathematical solution of the Flory-Huggins lattice. Hu et al.[14,15] investigated a double-lattice model based on Freed's theory. Recently, Bae et al.[16] reported on a modified double-lattice model by introducing new universal parameters and simplifying the expression of the Helmholtz energy of mixing.

The above theories are all based on a closed-packed lattice. To account for the compressibility and change in density upon isothermal mixing, free volume theories for polymer solutions were developed by numerous investigations notably by Flory[17] and by Patterson and Delmas.[18] These theories were based on a generalized form of the van der Waals partition function, which is the product of two independent partition functions: one accounts for free volume, and the other for attractive forces.

Heil and Prausnitz[19] and later Brandani,[20,21] Vera,[22] McMaster,[23] and Xie[24] developed a theory taking into account local composition. Bae et al.[25–27] reported on the extended Flory-Huggins theory for binary polymer systems. On the other hand, the Flory-Owoll-Vrij-Eichinger (FOVE) equation of state model[7,28,29] and the lattice fluid (LF) model of Sanchez and Lacombe[30–33] accounted for compressibility and volume changes. However, neither model took into account specific interactions and the associated entropy effect. Using the quasi-chemical approaches to treat the nonrandom character of a solution, Panayiotou and Vera[34] and Renuncio and Prausnitz[35] have improved the FOVE model. Panayiotou[34] and

Sanchez and Balazs[36] generalized the LF model to account for the specific interaction. However, because of the basic assumption, and ignoring the specific interaction between the pure components in the generalized LF model (GLF), it has some difficulties in being applied to a polymer–solvent system. Recently, a group-contribution lattice–fluid equation of state for the prediction of VLE and LLE in polymer solutions was reported by High and Danner[37–39] and was modified by Lee and Danner.[40]

The aim of this study is to establish an expression for the GLF free energy of mixing at zero pressure to predict the phase separation of binary polymer solutions. We modified the generalized lattice–fluid model of Sanchez and Balasz and extended the applicability of our proposed model to the polymer/solvent systems using a universal constant and a new adjustable model parameter.

MODEL DEVELOPMENT

The GLF Free Energy

At zero pressure, the GLF free energy, f per mer of binary mixture, is given by Sanchez and Balazs.[36] For a binary mixture of N_1 molecules of size r_1 and N_2 molecules of size $r_2 \cdot$ the GLF free energy f is

$$f = -\tilde{\rho}\varepsilon^* - T(S_{\text{comb}} + S_{\text{vac}}) \qquad (1)$$

where $\tilde{\rho}$ is the reduced density of the mixture and equals the fraction of occupied sites, ε^* is the mixing interaction energy and is defined as

$$\varepsilon^*(\phi, T) = \frac{z}{2} (\phi_1^2 \varepsilon_{11} + 2\phi_1\phi_2 f_{12} + \phi_2^2 \varepsilon_{22})$$
$$\equiv (\phi_1^2 \varepsilon_{11}^* + 2\phi_1\phi_2 f_{12}^* + \phi_2^2 \varepsilon_{22}^*) \quad (2)$$

where ϕ_i is a volume fraction of the component i and ε_{ij} is the mer–mer interaction energy between mers i and j

$$\varepsilon_{ij}^* \equiv \frac{z}{2} \varepsilon_{ij}, \ f_{12}^* \equiv \frac{z}{2} f_{12} \qquad (3)$$

f_{12} is the free energy parameter that replaces the pure energetic parameter ε_{12}. It includes the specific interaction parameter $\delta\varepsilon/k$ and the entropy effect generated by the specific interaction. f_{12} is defined as

$$f_{12} = \varepsilon_{12} + \delta\varepsilon - kT \ln\left[\frac{1+q}{1 + q\,\exp\left(-\dfrac{\delta\varepsilon}{kT}\right)}\right] \quad (4)$$

where q is the number of ways that the nonspecific 1–2 interaction occurs. The usual combinatorial entropy of mixing (S_{comb}) and the entropy of mixing lattice vacancies with the molecules (S_{vac}) are given by

$$S_{\text{comb}}(\phi) = -k\left(\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right) \quad (5)$$

$$S_{\text{vac}} = -k\left(\frac{1-\tilde\rho}{\tilde\rho}\ln(1-\tilde\rho) + \frac{\ln\tilde\rho}{r}\right) \quad (6)$$

where definitions of r and ϕ_i are as follow:

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2}, \quad rN = r_1 N_1 + r_2 N_2 \quad (7)$$

$$\phi_i = \frac{r_i N_i}{rN} \quad (8)$$

In the derivation of the number of ways Ω for packing molecules on the lattice,[41] Ω can be expressed as

$$\Omega = \Omega_{\text{ends}}\Omega_{r-1} \quad (9)$$

where Ω_{ends} is the number of ways of distributing $N_1 + N_2$ polymer chain ends on a lattice of rN sites; for binary system, it is given by

$$\Omega_{\text{ends}} = \frac{rN!}{N_1! N_2! (rN - N_1 - N_2)!} \quad (10)$$

Using Stirling's approximation, it reduces to

$$\Omega_{\text{ends}} = \left(\frac{r_1}{\phi_1}\right)^{N_1}\left(\frac{r_2}{\phi_2}\right)^{N_2}\left(1 - \frac{1}{r}\right)^{-rN(1-(1/r))} \quad (11)$$

If r_1 and r_2 are both large, r is large for all compositions by Eq. (7), and we can make use of

$$\lim_{r\to\infty}\left(1 + \frac{a}{n}\right)^n = e^a \quad \text{to obtain}$$

$$\left(1 - \frac{1}{r}\right)^{-rN(1-(1/r))} \cong e^{N(1-(1/r))} \cong e^N$$

and it gives

$$\Omega_{\text{ends}} = \left(\frac{r_1 e}{\phi_1}\right)^{N_1}\left(\frac{r_2 e}{\phi_2}\right)^{N_2} \quad (12)$$

Ω_{r-1} is the number of ways that the remaining $r_1 - 1$ mers of each molecule 1 and $r_2 - 1$ mers of each molecule 2 can be placed and is given by[41]

$$\Omega_{r-1} = (\delta_1 \prod_{l=1}^{r_1-1} P_l)^{N_1}(\delta_2 \prod_{k=1}^{r_2-1} P_k)^{N_2} \quad (13)$$

where δ_i is a parameter that is defined as

$$\delta_i = \frac{z}{\sigma}(z-1)^{r_i-2} \quad (14)$$

and p_k is a probability that a nearest-neighbor site is vacant and is available for the continuation of the random walk at kth step. To calculate p_k, the large z or Flory's approximation is used. Then p_k is equal to the fraction of empty sites available at the kth step. At the kth step,

$$kN_2 + lN_1 = \left(\frac{k}{r_2}\right)(r_2 N_2 + r_1 N_1) = \left(\frac{k}{r_2}\right)rN,$$

$$\left(l = \frac{r_1}{r_2}k\right) \quad (15)$$

This means that $(k/r_2)rN$ lattice sites are occupied and $(1 - k/r_2)rN$ sites are vacant. Therefore, the probability p_k is given by

$$P_k = \frac{\left(1 - \dfrac{k}{r_2}\right)rN}{rN} = 1 - \frac{k}{r_2},$$

$$P_l = 1 - \frac{l}{r_1} = 1 - \left(\frac{kr_1/r_2}{r_1}\right) = P_k \quad (16)$$

Using Stirling's approximation, the probabilities reduce to

$$\prod_{k=1}^{r_2-1} P_k = \prod_{k=1}^{r_2-1}\left(1 - \frac{k}{r_2}\right) = \frac{r_2!}{r_2^{r_2}} \cong e^{-r_2} \quad (17.1)$$

$$\prod_{l=1}^{r_1-1} P_l = \prod_{l=1}^{r_1-1}\left(1 - \frac{l}{r_1}\right) = \frac{r_1!}{r_1^{r_1}} \cong e^{-r_1} \quad (17.2)$$

Table I Lattice Fluid Equation of State Parameters[41]

Fluid	T^* (K)	P^* (Mpa)	ρ^* (kg/m³)	r
Methane	224	248	500	4.26
Pentane	441	310	755	8.09
Diethylether	431	363	870	8.62
Cyclohexane	517	391	917	8.14
Tetrahydrofuran	498	479	1019	8.18
Ethyl acetate	468	458	1052	9.87

As listed in Table I, the size parameters r of the most solvents are smaller than 15. If we take Stirling's approximation in the calculation of probability P_k, it will give a serious error, because Stirling's approximation applies only to large $r (r \gg 1)$. Similarly, in calculation of Ω_{ends},

$$\left(1 - \frac{1}{r}\right)^{-rN(1 - (1/r))}$$

cannot be reduced to e^N. Therefore, the model presents a serious problem when we apply it to the polymer/solvent systems. To avoid the defect, we introduce a new universal parameter C_0

$$\bar{r}_1 = C_0 r_1, \quad \frac{1}{\bar{r}} = \frac{\phi_1}{\bar{r}_1} + \frac{\phi_2}{r_2} \quad (18)$$

In a later section, we will discuss how C_0 can be determined as a universal constant. In the GLF model, the effect of a specific interaction between pure components is ignored. To consider the possibility of a specific interaction among pure components, we introduce an adjustable model parameter, κ_{11}, which determines the deviation of the characteristic parameters at low pressure conditions.

The extended lattice fluid (ELF) model is then given by

$$f_E = -\tilde{\rho}\varepsilon^* - T(S_{\text{comb}} + S_{\text{vac}}) \quad (19)$$

$$\varepsilon^*(\phi, T)$$
$$= (\phi_1^2 \varepsilon_{11}^*(1 - \kappa_{11}) + 2\phi_1\phi_2 f_{12}^* + \phi_2^2 \varepsilon_{22}^*) \quad (20)$$

$$S_{\text{comb}}(\phi) = -k\left(\frac{\phi_1}{\bar{r}_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2\right) \quad (21)$$

$$S_{\text{vac}} = -k\left(\frac{1 - \tilde{\rho}}{\tilde{\rho}} \ln(1 - \tilde{\rho}) + \frac{\ln \tilde{\rho}}{\bar{r}}\right) \quad (22)$$

If there is no deviation of the characteristic parameter associated with the interaction energy (i.e., $\kappa_{11} = 0$) and both r_1 and r_2 are large enough (i.e., $C_0 = 1$) (e.g., polymer/polymer system), the ELF model reduces to the GLF model.

The Equilibrium Value of $\tilde{\rho}$

In the GLF model, $\tilde{\rho}$ is considered to be a constant for the calculation of its chemical potential. In the ELF model, the equation of state at zero pressure,

$$\left(\frac{\partial f}{\partial \tilde{\rho}}\right)_\phi = 0,$$

determines the value $\tilde{\rho}$, which can be calculated numerically.

$$\tilde{\rho}^2 \beta \varepsilon^* + \ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{\bar{r}}\right)\tilde{\rho} = 0, \quad \beta = \frac{1}{kT} \quad (23)$$

Correlating Equations

For the prediction of a binary coexistence phase diagram, we need a chemical potential of each component. The chemical potential for component 1 is given by[42]

$$\mu_1 = r_1[f_E + \phi_2(df_E/d\phi_1)] \quad (24)$$

$$\frac{df_E}{d\phi_1} = \frac{\partial f_E}{\partial \phi_1} + \frac{\partial f_E}{\partial \tilde{\rho}} \cdot \frac{\partial \tilde{\rho}}{\partial \phi_1} \quad (25)$$

Because $\tilde{\rho}$ is a function of composition, we can get the value of $(\partial\tilde{\rho}/\partial\phi_1)$ from eq. (23) by taking the partial differential with respect to ϕ_1.

$$\frac{\partial \tilde{\rho}}{\partial \phi_1} = -\frac{\tilde{\rho}^2 \beta \dfrac{\partial \varepsilon^*}{\partial \phi_1} - \left(\dfrac{1}{\bar{r}_1} - \dfrac{1}{r_2}\right)\tilde{\rho}}{2\tilde{\rho}\beta\varepsilon^* + \dfrac{1}{\tilde{\rho} - 1} + \left(1 - \dfrac{1}{\bar{r}}\right)} \quad (26)$$

From eqs. (24), (25), and (26), the chemical potential is expressed by

$$\beta\mu_1 = \ln \phi_1 + \left(1 - \frac{\bar{r}_1}{r_2}\right)\phi_2 - \frac{1}{2}\bar{r}_1\tilde{\rho}\beta\frac{d^2\varepsilon^*}{d\phi_1}\phi_2^2$$

$$+ \bar{r}_1\left[-\tilde{\rho}\beta\varepsilon_{11}(1 - \kappa_{11}) + \frac{1 - \tilde{\rho}}{\tilde{\rho}} \ln(1 - \tilde{\rho}) + \frac{\ln \tilde{\rho}}{\bar{r}_1}\right]$$

$$+ \bar{r}_1\left[-\beta\varepsilon^* - \frac{\ln(1 - \tilde{\rho})}{\tilde{\rho}^2} + \left(\frac{1}{\bar{r}} - 1\right)\frac{1}{\tilde{\rho}}\right] \quad (27)$$

μ_2 is obtained by interchanging index 1 and 2. In the GLF model, $\tilde{\rho}$ is considered as a constant, while in the ELF model, $\tilde{\rho}$ is a function of composition, as first suggested by Sanchez and Balazs.[36]

Critical Point

The critical condition is given by

$$\frac{d\mu}{d\phi_2} = \frac{d^2\mu}{d\phi_2^2} = 0, \quad \text{or} \quad \frac{d^2f_E}{d\phi_2^2} = \frac{d^3f_E}{d\phi_2^3} = 0 \quad (28)$$

$$\frac{d^2f_E}{d\phi_2^2} = \frac{\partial^2 f_E}{\partial \phi_2^2} + \frac{\partial^2 f_E}{\partial \phi_2 \partial \tilde{\rho}} \cdot \frac{\partial \tilde{\rho}}{\partial \phi_2} = 0, \quad \left(\because \frac{\partial f_E}{\partial \phi_2} = 0\right) \quad (29)$$

$$\frac{d^3f_E}{d\phi_2^3} = \frac{\partial^3 f_E}{\partial \phi_2^3} + \frac{\partial^3 f_E}{\partial \phi_2^2 \partial \tilde{\rho}} \cdot \frac{\partial \tilde{\rho}}{\partial \phi_2}$$

$$+ \left(\frac{\partial^3 f_E}{\partial \phi_2^2 \partial \tilde{\rho}} + \frac{\partial^3 f_E}{\partial \phi_2 \partial \tilde{\rho}^2} \cdot \frac{\partial \tilde{\rho}}{\partial \phi_2} \right) \cdot \frac{\partial \tilde{\rho}}{\partial \phi_2}$$

$$+ \frac{\partial^2 \tilde{\rho}}{\partial \phi_2^2} \cdot \frac{\partial^2 f_E}{\partial \phi_2 \partial \tilde{\rho}} = 0 \quad (30)$$

The value of $\partial^2\tilde{\rho}/\partial\phi_2^2$ can be calculated from eq. (26)

$$\frac{\partial^2 \tilde{\rho}}{\partial \phi_2^2} = -\frac{A}{B} \quad (31)$$

$$A = \frac{\partial \tilde{\rho}}{\partial \phi_2} \left(2\tilde{\rho}\beta \cdot \frac{\partial \varepsilon^*}{\partial \phi_2} + 2\beta\varepsilon^* \cdot \frac{\partial \tilde{\rho}}{\partial \phi_2} \right.$$

$$\left. + \frac{1}{(\tilde{\rho}-1)^2} \cdot \frac{\partial \tilde{\rho}}{\partial \phi_2} + \frac{1}{\bar{r}_1} - \frac{1}{r_2} \right) + 2\tilde{\rho}\beta \frac{\partial \varepsilon^*}{\partial \phi_2}$$

$$\times \frac{\partial \tilde{\rho}}{\partial \phi_2} + \tilde{\rho}^2\beta \cdot \frac{\partial^2 \varepsilon^*}{\partial \phi_2^2} + \left(\frac{1}{\bar{r}_1} - \frac{1}{r_2} \right) \frac{\partial \tilde{\rho}}{\partial \phi_2} \quad (31.1)$$

$$B = 2\tilde{\rho}\beta\varepsilon^* + \frac{1}{\tilde{\rho}-1} + \left(1 - \frac{1}{\bar{r}} \right) \quad (31.2)$$

RESULTS AND DISCUSSIONS

In this study, we introduce a new adjustable model parameter, κ_{11}, and a universal constant, C_0, to extend the GLF model to a polymer/solvent system. Our proposed ELF model has three adjustable model parameters, ε_{12}, $\delta\varepsilon$, and κ_{11}.
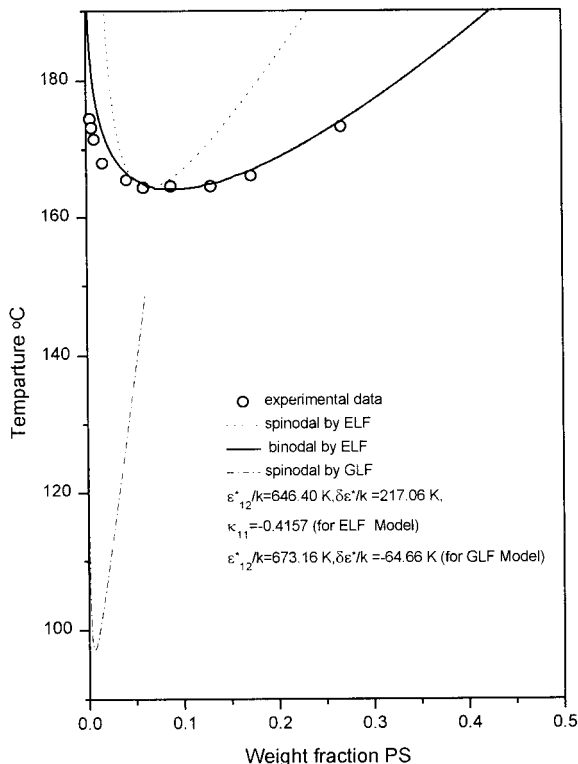
Figures 1 and 2 show a phase diagram of PS (polystyrene, $M_w = 100,000$) in an ethyl acetate
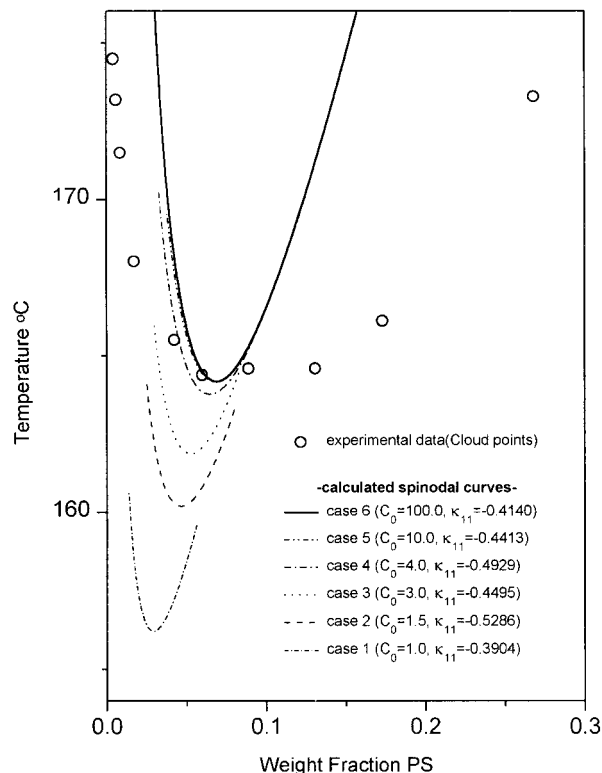
Figure 1 Spinodal curves for the PS (polystyrene, $M_w = 100,000$)/ethyl acetate system. Spinodal curves are calculated from this work in each cases. The open circles are experimental data by Bae et al.[26]

system. Open circles are cloud point data by Bae et al.[26] Figure 1 represents how the universal constant, C_0, can be determined. As we discussed previously, the GLF model is good for polymer blends due to their approximation in eqs. (17.1) and (17.2). As shown in Figure 1, the spinodal curve converges to the expected critical point as C_0 value increases to 100. In this study, we fix C_0 at 100 for any polymer/solvent systems. Though we tested the C_0 value only for the PS/ethyl acetate system, the proposed model with $C_0 = 100$ gives good agreement for the PMMA/solvent systems, as shown in Figures 4 and 5.

Figure 2 represents the comparison of the GLF model, with the ELF model for the PS/ethyl acetate system. The GLF model gives a serious deviation from experimental data, while the ELF model agrees very well with the experimental results. The adjustable model parameter values are $\varepsilon_{12}^*/k = 646.40$ K, $\delta\varepsilon^*/k = 217.09$ K, and $\kappa_{11} = -0.4157$ for the ELF model and $\varepsilon_{12}^*/k = 673.161$ K, $\delta\varepsilon^*/k = -64.66$ K for the GLF model. The GLF model gives a negative values for

Figure 2 Comparison of phase diagrams calculated from this work and the GLF model for the PS (polystyrene, M_w = 100,000)/ethyl acetate system. The solid line is the binodal curve calculated form this work with ε_{12}^*/k = 646.40 K, $\delta\varepsilon^*/k$ = 217.09 K, and κ_{11} = −0.4157. The dotted line is the spinodal by this work. The spinodal by GLF with ε_{12}^*/k = 673.16 K, $\delta\varepsilon^*$ = −64.66 K, showing large deviation from the experimental data.[26]

$\delta\varepsilon^*/k$, while the ELF model gives a positive $\delta\varepsilon^*/k$ value, as we expected. If a value of κ_{11} = −0.4157 is considered, it implies that ε_{11}^* from the GLF model is underestimated by about 41%.

Figure 3 shows coexistence curve for the PS (polystyrene, M_w = 50,000)/PVME (Poly (vinyl methyl ether), M_w = 99,000) system. The system exhibits LCST behavior. The solid line is a binodal curve predicted by this work. Open circles are experimental data by Bae et al.[25] In this system, C_0 is fixed as a unity. The theoretical prediction agrees well with the experimental data. The adjustable model parameter values are ε_{12}^*/k = 670.82 K, $\delta\varepsilon^*/k$ = 156.01 K, and κ_{11} = 0.035. If a value of κ_{11} = 0.035 is considered, ε_{11}^* from the GLF model is very close to a real value. It implies that the GLF model gives excellent agreement for this polymer blend system.

Figure 4 shows the coexistence curve for the PMMA (poly(methyl methacrylate), M_w = 37,109)/

ethyl acetate system. The system also exhibits LCST behavior. The solid line is calculated by this work with C_0 = 100. Open circles are experimental data by Muller.[43] The adjustable model parameter values are ε_{12}^*/k = 566.01 K, $\delta\varepsilon^*/k$ = 892.38 K, and κ_{11} = −0.3936. Considering a value of κ_{11} = −0.3936, ε_{11}^* for the system from the GLF model is underestimated at about 40% less than that of the real value.

Figure 5 shows phase behavior of the PMMA (poly(methyl methacrylate), M_w = 37,109)/THF (tetrahydrofuran) system and it exhibits LCST behavior. The solid line is a binodal curve predicted by this work with C_0 = 100. Open circles are experimental data by Muller.[43] The adjustable model parameter values are ε_{12}^*/k = 402.51 K, $\delta\varepsilon^*/k$ = 2110.97 K, and κ_{11} = −0.1490. If we consider a value of κ_{11} = −0.1490, ε_{11}^* for the system from the GLF model is underestimated by about 15%.

In this study, we considered κ_{11} to take into account the specific interaction among component
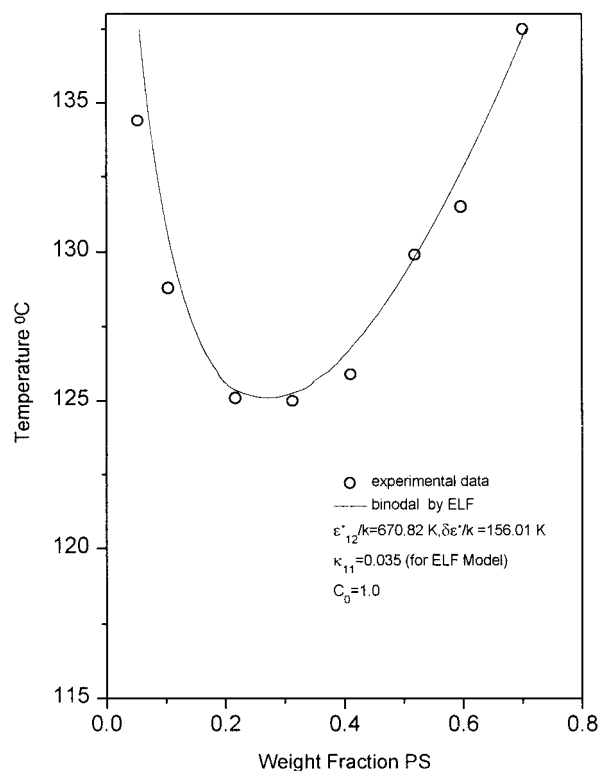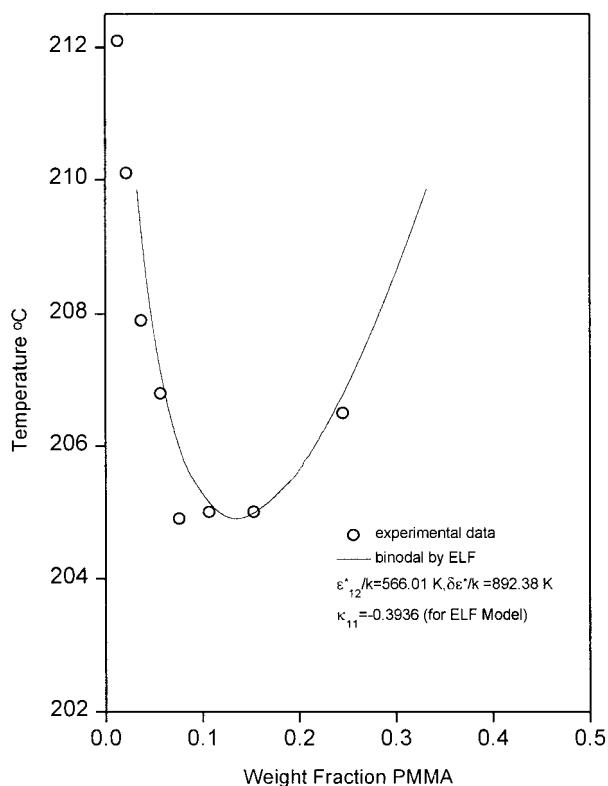

Figure 3 Binodal curves calculated by this work for the poly (vinyl methyl ether) (PVME) (M_w = 99,000)/polystyrene (M_w = 50,000) system. The solid line is the binodal curve calculated by this work with ε_{12}^*/k = 670.82 K, $\delta\varepsilon^*/k$ = 156.01 K, and κ_{11} = 0.035. C_0 = 1 for a polymer1/polymer2 system. Open circles are cloud points from Bae et al.'s experimental data.[26]
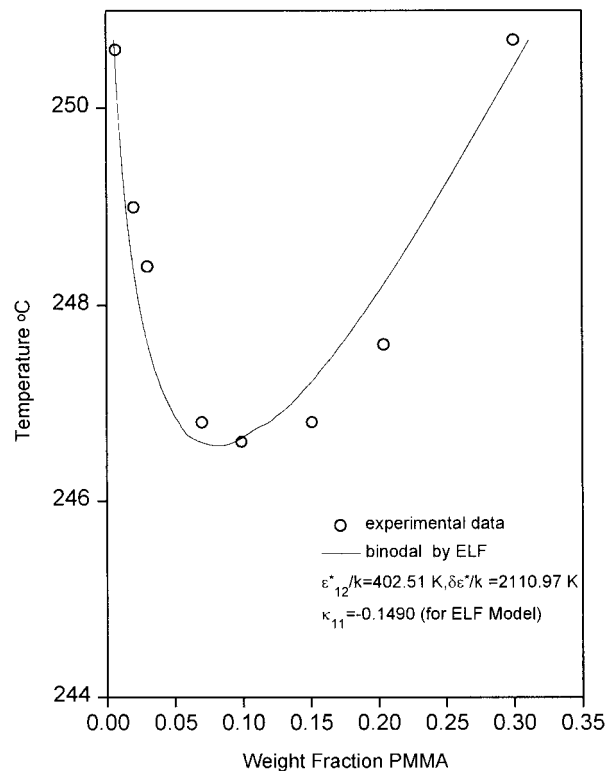
1. This is because ε^*_{11} is much more sensitive in the calculation of critical point than that of ε^*_{22}.

CONCLUSIONS

We proposed an extended lattice fluid (ELF) model by introducing a new universal constant (C_0) and a new model parameter (κ_{11}). The GLF model gives excellent agreement for polymer blend systems. However, it shows a serious deviation for the prediction of polymer/solvent systems. In the ELF model, we fix a universal constant $C_0 = 100$ for polymer/solvent systems and add a new adjustable model parameter κ_{11}. The proposed ELF model predicts and describes phase behaviors of polymer/solvent systems remarkably well. The ELF model reduce to the GLF model when we take $C_0 = 1$ and $\kappa_{11} = 0$. The ELF model presented here is essentially semiempirical. Its advantage follows from its simplicity: a simple

Figure 5 Binodal curve for the PMMA(poly (methyl methacrylate), $M_w = 37,109$)/THF (tetrahydrofuran) system. The solid line is the binodal curve by this work with $\varepsilon^*_{12}/k = 402.51$ K, $\delta\varepsilon^*/k = 2110.97$ K, and $\kappa_{11} = -0.1490$, and the open circles are cloud points from Muller's experimental data.[43]

modification appears to be suitable for representing phase behaviors of polymer/solvent systems.

Figure 4 Binodal curve for the PMMA(poly (methyl methacrylate), $M_w = 37,109$)/ethyl acetate system. The solid line is the binodal curve by this work with $\varepsilon^*_{12}/k = 566.01$ K, $\delta\varepsilon^*/k = 892.38$ K, and $\kappa_{11} = -0.3936$, and the open circles are cloud points from Muller's experimental data.[43]

REFERENCES

1. L. A. Kleintjens, *Fluid Phase Equilib.,* **33,** 289 (1989).
2. P. J. Flory, *J. Chem. Phys.,* **10,** 51 (1942).
3. M. L. Huggins, *J. Phys. Chem.,* **10,** 51 (1942).
4. E. A. Guggenheim, *Mixtures,* Clarendon Press, Oxford, (1952).
5. R. Koningsveld and L. A. Kleintjens, *Macromolecules,* **4,** 637 (1971).
6. S. M. Lambert, D. S. Soane, and J. M. Prausnitz, *Fluid Phase Equilib.,* **83,** 59 (1993).
7. B. H. Chang and Y. C. Bae, *Polymer,* to appear.

8. J. Hirshfelder, D. Stevenson, and H. Erying, *J. Chem. Phys.,* **92,** 6166 (1990).

9. J. A. Backer and W. Fork, *Discuss. Faraday Soc.,* **15,** 188 (1953).

10. G. Ten Brinke and F. E. Karasz, *Macromolecules,* **17,** 815 (1984).

11. K. F. Freed, *J. Physiol. A: Math. Gen.,* **18,** 871 (1985).

12. M. G. Bawendi, K. F. Freed, and U. Mohanty, *J. Chem. Phys.,* **87,** 5534 (1988).

13. M. G. Bawendi, K. F. Freed, and U. Mohanty, *J. Chem. Phys.,* **88,** 2741 (1988).

14. Y. Hu, S. M. Lambert, D. S. Soane, and J. M. Prausnitz, *Macromolecules,* **24,** 4356 (1991).

15. Y. Hu, H. Liu, D. S. Soane, and J. M. Prausnitz, *Fluid Phase Equilib.,* **67,** 65 (1991).

16. J. S. Oh and Y. C. Bae, *Polymer,* to appear.

17. P. J. Flory, *J. Am. Chem. Soc.,* **87,** 1833 (1965); *Discuss. Faraday Soc.,* **49,** 7 (1970).

18. D. Patterson and G. Delmas, *Trans. Faraday Soc.,* **65,** 708 (1969).

19. J. F. Heil and J. M. Prausnitz, *AIChE. J.,* **12,** 678 (1966).

20. V. Brandani, *Macromolecules,* **12,** 883 (1979).

21. V. Brandani, G. Del Re, and F. Di Giacomo, *Macromolecules,* **24,** 2391 (1991).

22. J. H. Vera, *Fluid Phase Equilib.,* **8,** 315 (1982).

23. L. P. McMaster, *Macromolecules,* **6,** 760 (1973).

24. H. Xie, E. Nies, A. Stroeks, and R. Simha, *Polym. Eng. Sci.,* **32,** 1654 (1992).

25. Y. C. Bae, J. J. Shim, D. S. Soane, and J. M. Prausnitz, *J. Appl. Polym. Sci.,* **47,** 1193 (1993).

26. Y. C. Bae, S. M. Lambert, D. S. Soane, and J. M. Prausnitz, *Macromolecules,* **24,** 4403 (1991).

27. Y. C. Bae, *J. Ind. & Eng. Chemistry,* **1,** 18 (1995).

28. P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.,* **86,** 3515 (1964).

29. B. E. Eichinger and P. Flory, *J. Trans. Faraday Soc.,* **64,** 2035 (1968).

30. I. C. Sanchez, *Encyclopedia of Physical Science and Technology,* Academic Press; New York, 1982, p. 59.

31. I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.,* **80,** 2352, 2568 (1976).

32. I. C. Sanchez and R. H. Lacombe, *J. Polym. Sci., Polym. Lett. Ed.,* **15,** 71 (1977).

33. I. C. Sanchez and R. H. Lacombe, *Macromolecules,* **11,** 1145 (1978).

34. C. Panayiotou and J. H. Vera, *Fluid Phase Equilib.,* **5,** 55 (1980).

35. J. A. R. Renuncio and J. M. Prausnitz, *Macromolecules,* **17,** 815 (1984).

36. I. C. Sanchez and A. C. Balazs, *Macromolecules,* **22,** 2325 (1989).

37. M. S. High and R. P. Danner, *Fluid Phase Equilib.,* **53,** 323 (1989).

38. M. S. High, Ph.D thesis, The Pennsylvania State Univ., University Park (1990).

39. M. S. High and R. P. Danner, *AIChE. J.,* **36,** 1625 (1990).

40. B. C. Lee and R. P. Danner, *AIChE. J.,* **42,** 837 (1996).

41. I. C. Sanchez, Ed., *Models for Thermodynamic and Phase Equilibria Calculations,* Marcel Dekker, Inc., New York, 1994.

42. I. C. Sanchez, *Encyclopedia of Physical Science and Technology,* vol. XI, Academic Press, New York, 1987, p. 1.

43. C. Muller, Diploma Thesis, University of Karlsruhe, Germany (1991).