Group-Contribution Lattice-Fluid EOS: Prediction of LLE in Polymer Solutions

Byung-Chul Lee and Ronald P. Danner
Center for the Study of Polymer-Solvent Systems, Dept. of Chemical Engineering, Pennsylvania State University,
University Park, PA 16802

The modified group-contribution lattice-fluid equation of state (GCLF − EOS) was applied to predict liquid − liquid equilibria (LLE) in polymer solutions. The modified GCLF − EOS is a group-contribution form of the equation of state by Panayiotou and Vera based on the lattice-hole theory. Group contributions for the interaction energy and reference volume were developed based only on the saturated vapor pressures and liquid densities of low-molecular-weight compounds. For a mixture, group contributions for the binary interaction parameter were developed from the binary vapor − liquid equilibria of low-molecular-weight compounds. This modified GCLF − EOS model can be applied to predict LLE behavior in polymer solutions with the same group-contribution parameters as used for predicting the vapor − liquid equilibria. The only input required for the model is the structure of the molecules in terms of their functional groups.

Introduction

Liquid–liquid equilibrium (LLE) in polymer solutions has not received as much attention as vapor–liquid equilibrium (VLE), although it is of extreme importance for practical applications, such as in the paints and coating industries. The LLE behavior in polymer solutions strongly depends on temperature, pressure, and polymer molecular weight. VLE in polymer–solvent solutions is usually encountered at low concentrations of the solvent, whereas LLE often takes place in the opposite concentration range, that is, at low concentrations of the polymer. The activity of the polymer is a predominant factor in LLE calculations for polymer solutions.

Phase separation in polymer solutions may occur upon cooling to low temperatures—upper critical solution temperature (UCST) behavior—or upon heating to high temperatures—lower critical solution temperature (LCST) behavior. A system containing a poor solvent exhibits both UCST and LCST. UCST behavior is due to an unfavorable energy effect (positive or endothermic heat of mixing) that arises from a difference of chemical nature and of molecular force fields between the components. LCST is detected even for nonpolar or nearly athermal systems, usually at temperatures approaching the solvent critical temperature and at pressures above atmospheric. LCST behavior is due to an unfavorable entropic effect that overcomes the favorable enthalpies of mixing. For a polymer solution the LCST behavior is due to the difference in free volume (degree of thermal expansion) between the polymer and the solvent. This difference is particularly manifested at high temperatures, near the critical temperature of the solvent. Since the polymer is less compressible than the solvent, application of pressure decreases the free-volume difference between the components and increases the polymer–solvent compatibility. LCST behavior tends to be very pressure-dependent, unlike UCST behavior. Usually the LCST lies above the UCST. However, when specific interactions are present (e.g., aqueous polymer solutions), a closed-loop phase behavior is observed. At a temperature below the LCST, a high, energetically favorable interaction causes a single phase to reappear. The LLE phase behavior depends significantly on the molecular weight and the molecular-weight distribution of the polymer.

Traditionally, the solubility parameter approach and the Flory–Huggins (FH) model have been extensively used for phase-equilibrium calculations in polymer solutions. Both approaches, however, have serious limitations; the FH χ-parameter is often a strong function of temperature and composition, specific for each system. Furthermore, the classic FH theory cannot account for the free-volume differences, and consequently cannot predict the LCST behavior. To overcome the problems of traditional approaches, a large number of models, both equations of state and activity coeffi-

---

Correspondence concerning this article should be addressed to R. P. Danner.

cient models, have been proposed for describing the phase behavior of polymer solutions. Most models have been mainly applied to VLE, with good accuracy. However, no reliable thermodynamic model has previously been proposed for correlating or predicting both VLE and LLE in polymer solutions using the same set of adjustable parameters.

The modified group-contribution lattice-fluid equation of state (GCLF-EOS) has been reliably applied to the prediction of the VLE for polymer–solvent systems covering a wide range of polymer and solvent types (Lee and Danner, 1996a,b). In this work we evaluate whether the modified GCLF-EOS, which is successful for the VLE predictions, can be applied to the predictions of the LLE of polymer–solvent solutions. The same group-contribution mixing rules and group parameters as used for the LLE predictions were used for the VLE predictions. All the group parameters have been determined from the vapor–liquid equilibrium properties of the pure components and binary mixtures of low-molecular-weight substances.

Group-Contribution Lattice-Fluid Equation of State

Equation of state and chemical potential

Panayiotou and Vera (1982a,b) developed a lattice-fluid theory. In a lattice structure, vacant holes were allowed to vary the density of the fluid. The total number of sites, N_r, is given by the number of sites occupied by holes (N_h) and the number of sites occupied by the molecules of different types.

$$N_r = N_h + \sum_i r_i N_i. \tag{1}$$

The total number of external contact sites, zN_q, is expressed as

$$zN_q = zN_h + \sum_i zq_i N_i, \tag{2}$$

where z is the coordination number, fixed at 10. The number of contact sites available to a molecule of type i, zq_i, is calculated from

$$zq_i = (z-2)r_i + 2, \tag{3}$$

where r_i is the number of lattice sites (segments) occupied by the molecule i and is defined as

$$r_i = \frac{v_i^*}{v_h}, \tag{4}$$

where v_i^* is the molecular reference (hard core) volume of the molecule i and v_h is the volume of a lattice site (9.75×10^{-3} m^3/kmol).

Using the lattice statistics and quasi-chemical theory of Guggenheim (1952), Panayiotou and Vera (1982a,b) derived a lattice-fluid equation of state that corrects for the nonrandom mixing arising from the interaction energies between molecules. A detailed derivation of the equation of state is given by Lee (1995) and Panayiotou and Vera (1982a,b). The lattice–fluid equation of state for a mixture is

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+(q/r)-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}}, \tag{5}$$

where $\tilde{P}$, $\tilde{T}$, and $\tilde{v}$ are the reduced pressure, temperature, and volume of the mixture, respectively, and are defined by

$$\tilde{P} = \frac{P}{P^*} = \frac{2Pv_h}{z\epsilon^*} \tag{6}$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2RT}{z\epsilon^*} \tag{7}$$

$$\tilde{v} = \frac{v}{v^*} = \frac{v_h(N_h + rN)}{v^* N}, \tag{8}$$

where ϵ^* is the molecular interaction energy of the mixture, v^* is the molecular reference (hard-core) volume of the mixture, given by

$$v^* = \Sigma x_i v_i^*, \tag{9}$$

where x_i is the mole fraction of component i in the mixture. The other parameters in Eq. 5 are calculated from the following simple combining rules:

$$r = \Sigma x_i r_i \qquad q = \Sigma x_i q_i \qquad \theta = \Sigma \theta_i \tag{10}$$

For a binary mixture, ϵ^* is given by

$$\epsilon^* = \bar{\theta}_1 \epsilon_{11} + \bar{\theta}_2 \epsilon_{22} - \bar{\theta}_1 \bar{\theta}_2 \dot{\Gamma}_{12} \Delta\epsilon, \tag{11}$$

where

$$\Delta\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}. \tag{12}$$

ϵ_{ii} is the molecular interaction energy between like molecules of type i and ϵ_{12} is the cross interaction energy between unlike molecules 1 and 2, calculated from

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}(1-\delta_{12}), \tag{13}$$

where δ_{12} is the binary interaction parameter. In Eq. 11, $\bar{\theta}_i$ is the molecular surface fraction of component i on a hole-free basis, given by

$$\bar{\theta}_i = \frac{zq_i N_i}{z\sum_j q_j N_j} = \frac{q_i N_i}{qN} = \frac{x_i q_i}{q}, \tag{14}$$

and θ_i in Eq. 10 is the molecular surface fraction of component i including holes:

$$\theta_i = \frac{zq_i N_i}{z\left(N_h + \sum_j q_j N_j\right)} = \frac{q_i N_i}{N_h + qN}. \tag{15}$$

From Eqs. 14 and 15,

$$\sum_i \bar{\theta}_i = 1 \qquad \text{and} \qquad \theta_i = \bar{\theta}_i \sum_j \theta_j = \bar{\theta}_i \theta. \tag{16}$$

In Eq. 11, $\dot{\Gamma}_{12}$ is the nonrandomness parameter between unlike molecules 1 and 2 and is related with the molecular surface fractions, $\bar{\theta}_i$, by

$$\bar{\theta}_1 \dot{\Gamma}_{11} + \bar{\theta}_2 \dot{\Gamma}_{12} = \bar{\theta}_2 \dot{\Gamma}_{22} + \bar{\theta}_1 \dot{\Gamma}_{12} = 1, \tag{17}$$

where $\dot{\Gamma}_{ii}$ is the nonrandomness parameter between like molecules i. From the quasi-chemical approach (Panayiotou and Vera, 1980; Wilczek-Vera and Vera, 1990)

$$\frac{\dot{\Gamma}_{12}\dot{\Gamma}_{22}}{\dot{\Gamma}_{12}^2} = \exp\left(\theta \frac{\Delta \epsilon}{RT}\right) \equiv \dot{G} \tag{18}$$

we obtain

$$\dot{\Gamma}_{12} = \frac{2}{1 + \sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}}. \tag{19}$$

Panayiotou and Vera (1982a,b) assumed that for a pure component the molecules and holes are randomly placed, while for a mixture the holes are mixed randomly and the molecules are distributed nonrandomly. For the case of random arrangements of molecules, $\Delta \epsilon = 0$ and $\dot{\Gamma}_{11} = \dot{\Gamma}_{22} = \dot{\Gamma}_{12} = 1$.

The change in chemical potentials between the species i in the mixture and the pure component i at the temperature and pressure of the mixture is expressed as

$$\frac{\Delta \mu_i}{RT} = \ln \phi_i + \ln \frac{\tilde{v}_i}{\tilde{v}} + q_i \ln\left(\frac{\tilde{v}}{\tilde{v}-1} \frac{\tilde{v}_i - 1}{\tilde{v}_i}\right) + q_i \left(\frac{2\theta_{i,P} - \theta}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{z q_i}{2} \ln \dot{\Gamma}_{ii}, \tag{20}$$

where the subscript i in $\tilde{T}_i$ and $\tilde{v}_i$ represents a pure component i, and ϕ_i is the volume fraction of component i in the mixture, given by

$$\phi_i = \frac{x_i v_i^*}{\sum_j x_j v_j^*} = \frac{x_i r_i}{\sum_j x_j r_j}. \tag{21}$$

From Eqs. 8, 10, and 15, θ can be expressed as

$$\theta = \frac{q}{q + r(\tilde{v} - 1)}. \tag{22}$$

$\theta_{i,P}$ is the surface area fraction of the pure component i at the same temperature and pressure as the mixture and can be expressed by

$$\theta_{i,P} = \frac{q_i}{q_i + r_i(\tilde{v}_i - 1)}. \tag{23}$$

Group-contribution mixing rules

For a pure component the equation of state (Eq. 5) contains two adjustable parameters: molecular interaction energy, ϵ_{ii}, and molecular reference volume, v_i^*. For a binary mixture, it has one more parameter: binary interaction parameter, δ_{12}. Once these parameters are known at a given temperature, all of the remaining parameters can be determined and properties of a system can be calculated by solving Eq. 5. To make the model predictive, the group-contribution mixing rules for these three parameters have been developed. ϵ_{ii} is determined from the group interaction energies using the following mixing rule:

$$\epsilon_{ii} = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(i)} (e_{kk} e_{mm})^{1/2} \tag{24}$$

where e_{kk} is the group interaction energy between like groups k. The group surface-area fractions, $\Theta_k^{(i)}$, are expressed by

$$\Theta_k^{(i)} = \frac{n_k^{(i)} Q_k}{\sum_n n_n^{(i)} Q_n}, \tag{25}$$

where $n_k^{(i)}$ is the number of groups of type k in component i and Q_k is the surface area of group k, as used in the UNIFAC method (Fredenslund et al., 1977). v_i^* is calculated from the group reference volume parameter, R_k, using the following mixing rule:

$$v_i^* = \sum_k n_k^{(i)} R_k. \tag{26}$$

The characteristic parameters are also a function of temperature. A quadratic form with respect to temperature was found to be adequate. Thus,

$$e_{kk} = e_{0,k} + e_{1,k}\left(\frac{T}{T_0}\right) + e_{2,k}\left(\frac{T}{T_0}\right)^2 \tag{27}$$

$$R_k = \frac{1}{10^3}\left[R_{0,k} + R_{1,k}\left(\frac{T}{T_0}\right) + R_{2,k}\left(\frac{T}{T_0}\right)^2\right], \tag{28}$$

where $e_{i,k}$ and $R_{i,k}$ are constants, T is the system temperature in kelvins, and T_0 was arbitrarily set to 273.15 K.

The binary interaction parameter, δ_{12}, is calculated from the group binary parameter between groups m and n, α_{mn}, from

$$\delta_{12} = \sum_m \sum_n \Theta_m^{(M)} \Theta_n^{(M)} \alpha_{mn}, \tag{29}$$

where $\Theta_m^{(M)}$ is the surface area fraction of group m in the mixture:

$$\Theta_m^{(M)} = \frac{\sum_i n_m^{(i)} Q_m}{\sum_k \sum_i n_k^{(i)} Q_k} \tag{30}$$

All the group parameters (e_{kk}, R_k, α_{mn}) were estimated from properties of low-molecular-weight compounds only. First of all, the molecular parameters, ϵ_{ii} and v_i^*, at various temperatures for each pure compound were simultaneously determined by fitting the experimental saturated-vapor pressure and liquid-density data to the equation of state. The binary interaction parameters, δ_{12}, were estimated from the VLE data of low-molecular-weight binary mixtures. In this work δ_{12} was considered to be independent of temperature. The pure-component properties of low-molecular-weight compounds were obtained from Daubert and Danner (extant 1994), and the binary VLE data were obtained from DECHEMA database (Gmehling et al., 1977–1993). Second, the group parameters (e_{kk}, R_k, α_{mn}) at each temperature were independently estimated from the molecular parameters (ϵ_{ii}, v_i^*, δ_{12}) by nonlinear regression using the mixing rules, Eqs. 24, 26 and 29. Finally, the parameter constants ($e_{i,k}$ and $R_{i,k}$) were determined by fitting the group parameters obtained at the various temperatures to Eqs. 27 and 28. Tables of the group parameters for a variety of functional groups are available from Lee (1995) and Lee and Danner (1996a) or by request. Once the molecular structures of the components in a mixture are known with respect to their functional groups, one can calculate the molecular parameters from the group parameters and then predict the equilibrium behavior of polymer solutions as well as of low-molecular-weight compounds.

Calculation Procedure

The LLE problem in a polymer solution consists of determining if phase separation occurs; and if so, what are the equilibrium compositions (conventionally the polymer-weight fractions) of the phases. The compositions can be determined if pressure and temperature are specified, and they can be calculated by solving equations resulting from the criterion for phase equilibrium. If a configuration of two liquid phases has a lower Gibbs free energy than one liquid phase, separation will occur. The condition for the binodal compositions is that the chemical potentials in two liquid phases must be equal for all the components:

$$\Delta\mu_i'(x_i') = \Delta\mu_i''(x_i''), \qquad \text{for all } i, \tag{31}$$

where

$$\Sigma x_i' = 1 \qquad \text{and} \qquad \Sigma x_i'' = 1. \tag{32}$$

The spinodal compositions are determined by

$$\left(\frac{\partial\Delta\mu_i'}{\partial x}\right)_{T,P} = \left(\frac{\partial\Delta\mu_i''}{\partial x}\right)_{T,P} = 0. \tag{33}$$

The LLE calculations in this work were performed in two successive steps (Wang, 1993). Since all the calculations were purely predictions, initial estimates of the weight fraction of the polymer in each of the coexisting liquid phases were required to start the calculations. In the first step, a search for phase splitting in an extended temperature range was carried out by calculating the chemical potentials of the polymer in the polymer–solvent mixture over the entire concentration range.

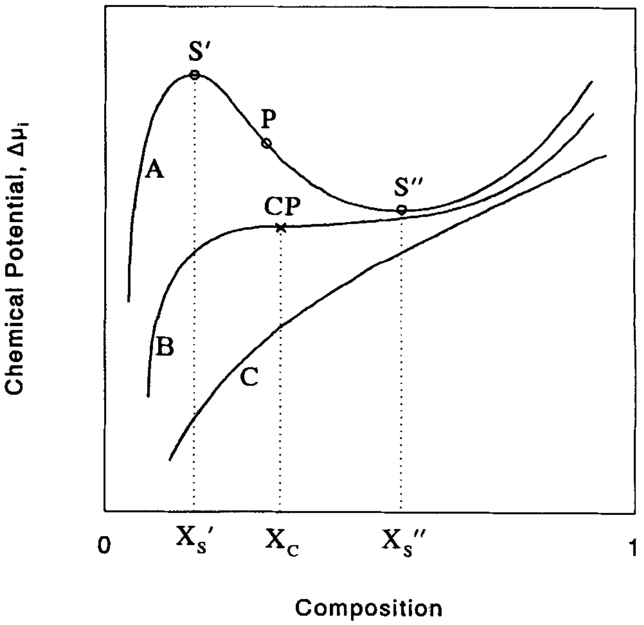

Figure 1. Three different types of chemical potentials as a function of composition in liquid–liquid equilibria.

Figure 1 illustrates three possible types of behavior of the chemical potential of a component (polymer or solvent) as a function of the weight fraction of the component at a fixed temperature and pressure (Michio, 1982). The criterion for phase splitting can be expressed as

$$\left(\frac{\partial\Delta\mu_i}{\partial x_i}\right)_{T,P} < 0. \tag{34}$$

Curve A in Figure 1 has negative values of the derivatives of chemical potential with respect to compositions in a certain range of compositions. The compositions (X_s' and X_s'') corresponding to the maximum and minimum points (S' and S'') represent the spinodal compositions at the two phases, according to Eq. 33. Curve C gives positive slopes at all compositions, and thus it shows complete miscibility and no phase separation. The inflection point (CP) in curve B corresponds to the critical solution point. Therefore, by plotting the chemical potentials with respect to compositions at a given temperature, one can check if phase splitting occurs. The temperature range over which the phase splitting occurs is obtained in this step. The spinodal compositions were determined by calculating the slopes of the chemical potentials with respect to compositions in infinitely small intervals of compositions using the bisection method.

The second step was to calculate the binodal compositions in the two phases at temperatures where the phase separation occurred. The binodal compositions at a fixed temperature and pressure were calculated by solving Eqs. 31 and 32 simultaneously. Figure 2 illustrates the chemical potentials of the two components as a function of the composition of a component. The rectangular construction (*wxyz*) represents

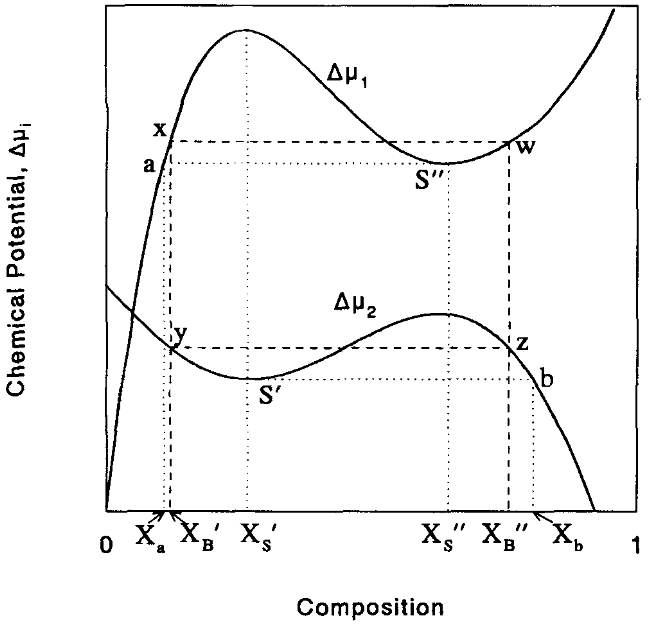

Figure 2. Chemical potentials of each component as a function of composition in a binary system where phase splitting occurs.

Modified from Lacombe and Sanchez, 1976.

the unique solution of the binodal compositions (X_B' and X_B''). At the points w and x, the chemical potentials of component 1 are equal, whereas the chemical potentials of component 2 are identical at the points y and z. The points a and b and their corresponding compositions X_a and X_b are obtained by drawing horizontal lines from the two minima (S', S'') to the chemical potential curves. X_B' is located between X_a and X_s', and X_B'' is between X_s'' and X_b. In order to avoid trivial solutions, this constraint must be employed in the algorithm. The arithmetic average of X_s and X_s' was used as the initial guess for X_B', while the average of X_s'' and X_b provided the initial guess for X_B''. Using these initial guesses, the exact values of the binodal compositions were calculated at each temperature. By repeating the calculations of the spinodal and binodal compositions at various temperatures in the two-phase region, the temperature-composition diagram was obtained. When a step change in the temperature caused a change from the two-phase region to the single-phase region, the calculation terminated. The critical solution temperature was determined by finding the temperature that makes the difference in the binodal compositions of the two phases very close to zero (0.0001). As the critical solution temperature was approached, a very small temperature step (0.01 K or less) was used.

The molecular parameters (ϵ_{ii}, v_i^*, and δ_{12}) in the equation of state (Eq. 5) were calculated from the group parameters (e_{kk}, R_k, and α_{mn}) using the group-contribution mixing rules (Eqs. 24, 26 and 29). The same group parameters as were used for the prediction of the VLE for polymer–solvent systems were used for the LLE predictions (see Lee and Danner, 1996a, for a listing of the parameter values). The chemical potential change ($\Delta\mu_i$) was calculated from Eq. 20 and the liquid reduced volumes of the pure components and the mixture were obtained by solving the equation of state.

Results and Discussion

Predictions of the LLE were performed for a variety of polymer–solvent systems. The spinodal and binodal curves and the critical solution temperature were predicted. All the experimental data were obtained from the database of Danner and High (1993). The experimental data were the cloud-point curves measured using the turbidimetry or the light-scattering turbidimetry method. In most cases, however, data points in only a short range of temperature and concentration were available. Most polymer–solvent systems investigated in this work showed LCST behavior. Some systems showed UCST behavior, both LCST and UCST behavior, or hourglass behavior. The LLE behavior of polymer–solvent systems was found to strongly depend upon the molecular weight of the polymer. Polymers included in this work were mostly monodisperse or slightly polydisperse polymers,and thus the effect of polydispersity on the LLE was not considered.

Figure 3 illustrates the predictions of LCST behavior by the model for the systems containing high-density polyethylene (HDPE) and normal alkanes. Only experimental data near the critical temperature were available. The model gave excellent agreement with the experimental data. Figure 4 shows the predictions of the binodal curves at various molecular weights of the polymer for the HDPE/2,4-dimethylpentane system. The LLE behavior of a polymer solution is significantly affected by the molecular weight of the polymer. In general, as the molecular weight of the polymer increases, the LCST is shifted to a lower temperature and a lower polymer concentration, while the UCST tends to move toward higher temperature and lower polymer concentration. In other words, increasing the molecular weight of the polymer reduces the single-phase region. The model correctly predicted this effect of the molecular weight of the polymer, showing satisfactory agreement with experimental data. At

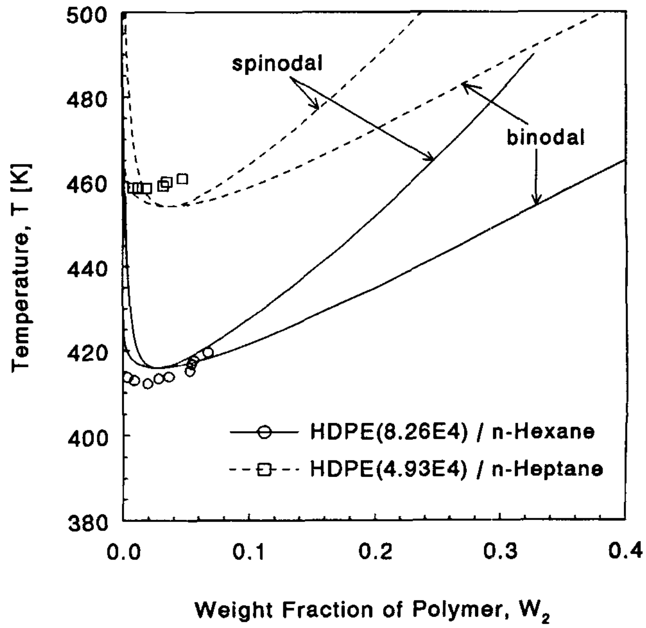

Figure 3. Prediction of LCST behavior for high-density polyethylene/*n*-alkane systems.

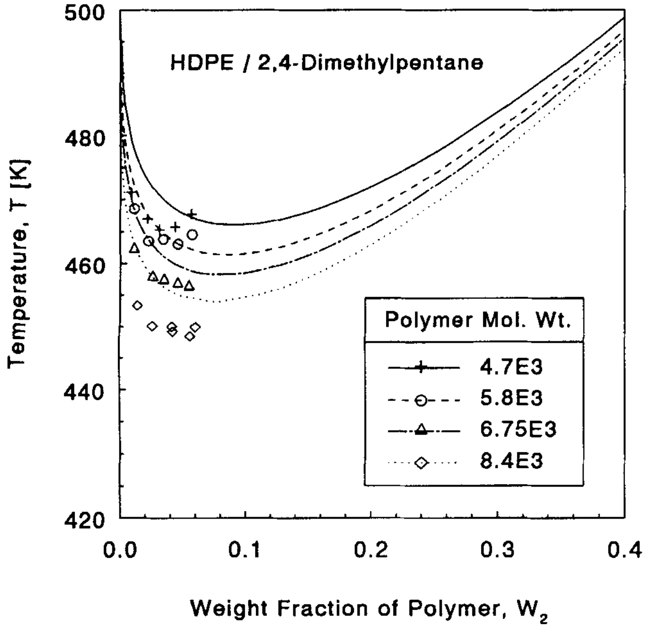

Figure 4. Prediction of binodal curves for high-density polyethylene/2,4-dimethylpentane system: effect of polymer molecular weight.

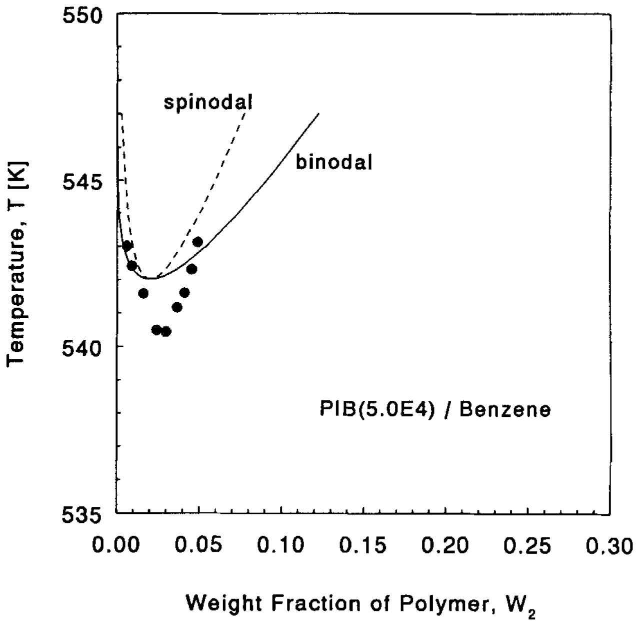

Figure 6. Prediction of LCST behavior for polyisobutylene/benzene system.

higher molecular weights of the polymer, the model predicted a lower LCST and thus a smaller single-phase region.

The prediction of LCST behavior for the butadiene rubber/2-methylhexane system is given in Figure 5. The model gave good predictions over a wide range of concentrations. Figure 6 shows the predictions of the spinodal and binodal curves for the LCST behavior of polyisobutylene/benzene system. The experimental values were observed in a narrow range of concentrations and temperatures. The predicted values by the model were in excellent agreement with the experimental data, considering the small range of temperatures and concentrations. Figure 7 illustrates the experimental and predicted values for the poly(methyl methacrylate)/*tert*-butyl alcohol system. The model predicted well the UCST behavior for this system. In general the model predicts LCST behavior better than UCST behavior.

Figure 8 shows the prediction of the binodal curves for the poly(ethylene glycol)/*tert*-butyl acetate system at various molecular weights of the polymer. This system showed both LCST and UCST behavior, and the polymer molecular weight had a significant influence on the phase behavior. As the

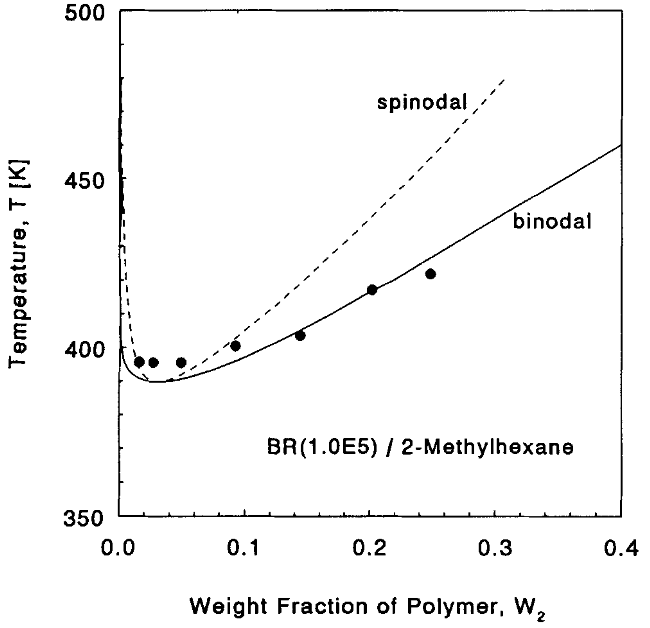

Figure 5. Prediction of LCST behavior for butadiene rubber/2-methylhexane system.

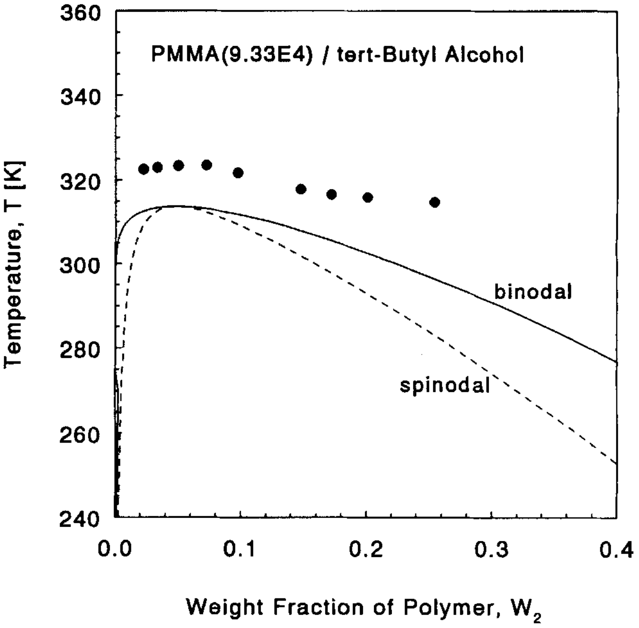

Figure 7. Prediction of UCST behavior for poly(methyl methacrylate)/*tert*-butyl alcohol system.

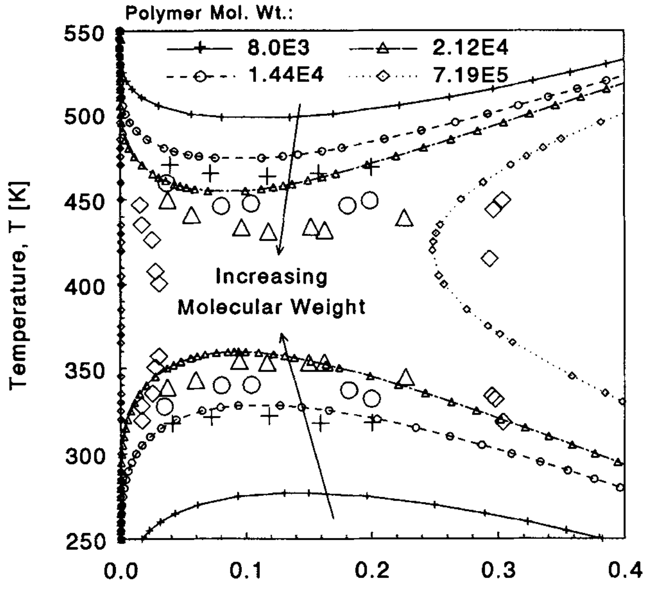

Figure 8. Prediction of binodal curves for poly(ethylene glycol)/*tert*-butyl acetate system: effect of polymer molecular weight.

Large symbols—experimental data; small symbols with lines—predicted results.

polymer molecular weight increased, the LCST curves were shifted to lower temperatures and the the UCST curves moved toward higher temperatures. As the molecular weight of the polymer increased further, the LCST and UCST merged to give an hourglass shape. It was observed that the binary interaction parameters (δ_{12}) increased as the polymer molecular weight increased or as the single-phase region decreased. According to Eq. 13, the interaction energies between unlike molecules or the cross interaction energies (ϵ_{12}) become smaller at higher δ_{12} values. When the ϵ_{12} decreased, the LCST and UCST curves became closer together and then merged to give an hourglass-type phase diagram. (The lefthand side of the predicted hourglass for a molecular weight of 7.19×10^5 falls essentially on the y-axis.) The model took into account the effect of the polymer molecular weight in this system. Using the same group parameters developed for the prediction of the VLE for polymer–solvent systems, the model provided qualitatively good predictions of the LLE for many polymer–solvent systems. The model was able to predict the hourglass-type diagram as well as the LCST and UCST behavior.

The modified GCLF–EOS was applied to the calculation of the polymer–polymer miscibility behavior in polymer blends. The computational procedure was the same as used for the LLE predictions in polymer–solvent systems. Phase behavior of polymer blends depends primarily on the enthalpic interactions between the blend components, since the combinatorial entropic contribution to free energy of mixing is usually quite small for mixtures of large molecules. In polymer blends, UCST behavior, which is common in low-molecular-weight polymer blends, is due to asymmetry in interaction energies between the components. Since the magnitude of the entropy of mixing is very small, small increases in the ratio of pure-component interaction energies can lead to dramatic increases in the UCST. LCST behavior in polymer blends is due to chain-length difference between the polymers, which is related to compressibility difference. The difference in molecular size coupled with the asymmetry in interaction energies can lead to LCST behavior.

Polymer–polymer miscibility calculations by the modified GCLF–EOS were found to be extremely sensitive to the value of the binary interaction parameter (δ_{12}). A very small change in the δ_{12} parameter (as small as 0.0001) gave very different results. For example, the predicted behavior changed from complete miscibility over the entire temperature range to complete immiscibility. For polymer–polymer systems, the model was not able to predict phase behavior using the group binary interaction parameters (α_{mn}). Therefore, the model was used as a correlative tool in terms of the δ_{12} parameter. The molecular interaction energy and reference volume parameters (ϵ_{ii} and v_i^*) were calculated from the group-contribution mixing rules and group parameters (e_{kk} and R_k), as was done for polymer–solvent systems. The δ_{12} parameter for each system was determined by finding an optimum value that gave the best fit to the experimental value of the critical solution temperature. A very small change in the δ_{12} parameter for a polymer–polymer system affects significant changes in the chemical potential functions, and thus can lead to totally different miscibility behavior.

Figure 9 illustrates the correlation of the polymer–polymer miscibility for polystyrene/poly(vinyl methyl ether) system that shows LCST behavior. The correlation of the coexistence curves for a polystyrene/styrene butadiene rubber (50% styrene) is given in Figure 10. This system exhibits the UCST behavior. For each system, the optimum value of the δ_{12} parameter is shown. By adjusting only the binary interaction parameter (δ_{12}), the modified GCLF–EOS was able to correlate the miscibility behavior in polymer blends with good accuracy.

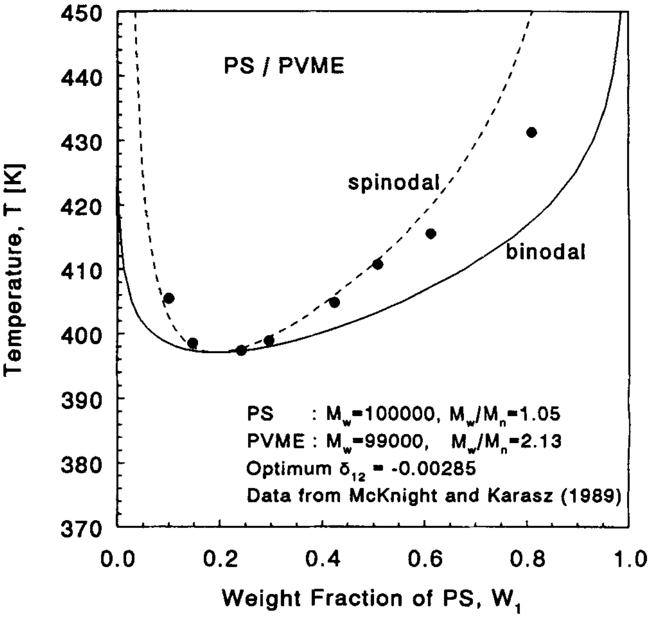

Figure 9. Correlation of polymer–polymer miscibility for polystyrene/poly(vinyl methyl ether) system.

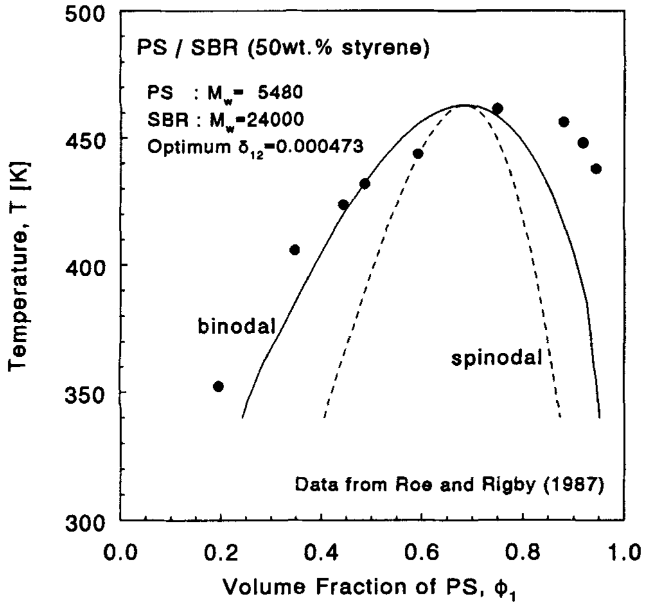

Figure 10. Correlation of polymer-polymer miscibility for polystyrene/styrene butadiene rubber (50% styrene) system.

Conclusions

A modified group-contribution lattice-fluid equation of state (GCLF-EOS) has been developed that is capable of predicting phase equilibria in polymer-solvent solutions. The modified GCLF-EOS was developed by calculating group contributions for the equation-of-state parameters from the equilibrium properties of low-molecular-weight compounds.

The modified GCLF-EOS was applied to the prediction of LLE behavior in polymer solutions. The spinodal and binodal curves were predicted for a number of polymer-solvent systems. The same group-contribution mixing rules and group parameters as were used for vapor-liquid equilibria predictions were used for the LLE predictions. The modified GCLF-EOS gave fairly good predictions for many systems, accounting for the effect of the polymer molecular weight on the phase behavior. By adjusting only the binary interaction parameter, the modified GCLF-EOS was able to correlate the miscibility behavior in polymer blends.

The only information required for the modified GCLF-EOS is the structures of the solvent and polymer repeat unit in terms of their functional groups. No other pure component or mixture properties of the polymer and solvent are needed. The modified GCLF-EOS is useful for engineering purposes and can be applied to predict the phase behavior in polymer solutions that can be constructed from the available group contributions.

Notation

ΔG_{mixing} = Gibbs-free-energy change of mixing, J/mol
M_n = number average molecular weight polymer
M_w = weight average molecular weight of polymer
N = total number of molecules in the mixture; number of data points
N_i = number of molecules of type i
P = pressure, kPa
P^* = characteristic pressure of a mixture, kPa
q = surface area parameters of a mixture
r = number of lattice sites occupied by a mixture
R = gas constant
T^* = characteristic temperature of a mixture, K
v = molar volume, m^3/kmol
x_i = mole fraction of component i
$\Delta\epsilon$ = interaction energy change, J/mol
$\bar{\theta}_i$ = fraction of contacts that involve molecules of type i on a hole-free basis
ϕ_i = volume fraction of component i

Literature Cited

Danner, R. P., and M. S. High, *Handbook of Polymer-Solution Thermodynamics*, Design Institute for Physical Property Data, AIChE, New York (1993).

Daubert, T. E., and R. P. Danner, *Physical and Thermodynamic Properties of Pure Compounds: Data Compilation*, Taylor & Francis, New York (extant 1994).

Fredenslund, Aa., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC*, Elsevier, New York (1977).

Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt, **I**, Parts 1, 2a (1977).

Gmehling, J., U. Onken, and W. Arlt, *Vapor-Liquid Equilibria Data Collection, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt, **I**, Parts 1a (1981), 2b (1978), 2c (1982), 3, 4 (1979), 6a, 6b, 7 (1980), 8 (1984).

Gmehling, J., U. Onken, and P. Grenzheuser, *Vapor-Liquid Equilibria Data Collection, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt, **I**, Part 5 (1982).

Gmehling, J., U. Onken, and B. Kolbe, *Vapor-Liquid Equilibria Data Collection, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt, **I**, Part 6c (1983).

Gmehling, J., U. Onken and J. R. Rarey-Nies, *Vapor-Liquid Equilibria Data Collection, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt, **I**, Parts 1b (1988), 2e (1988), 2f (1990), 3b (1993).

Gmehling, J., U. Onken, and U. Weidlich, *Vapor-Liquid Equilibria Data Collection, DECHEMA Chemistry Data Series*, DECHEMA, Frankfurt, **I**, Part 2d (1982).

Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford (1952).

Lacombe, R. H., and I. C. Sanchez, "Statistical Thermodynamics of Fluid Mixtures," *J. Phys. Chem.*, **80**, 2568 (1976).

Lee, B.-C., *Prediction of Phase Equilibria in Polymer Solutions*, PhD Thesis, The Pennsylvania State Univ., University Park (1995).

Lee, B.-C., and R. P. Danner, "Prediction of Polymer-Solvent Phase Equilibria by a Modified Group-Contribution Lattice-Fluid Equation of State," *AIChE J.*, **42**, 837 (1996a).

Lee, B.-C., and R. P. Danner, "Application of the Group-Contribution Lattice-Fluid Equation of State to Random Copolymer-Solvent Systems," *Fluid Phase Equilibria*, **117**, 33 (1996b).

McKnight, W. J., and F. E. Karasz, "Polymer Blends," *Comprehensive Polymer Science*, Vol. 7, Chap. 4, Pergamon Press, Oxford, p. 111 (1989).

Michio, K., *Thermodynamics of Polymer Solutions*, Harwood Academic Publishers, Chur, Switzerland (1982).

Panayiotou, C., and J. H. Vera, "The Quasi-chemical Approach for Non-randomness in Liquid Mixtures. Expressions for Local Surfaces and Local Compositions with an Application to Polymer Solutions," *Fluid Phase Equilib.*, **5**, 55 (1980).

Panayiotou, C., and J. H. Vera, "An Improved Lattice-Fluid Equation of State for Pure Component Polymeric Fluids," *Poly. Eng. Sci.*, **22**, 345 (1982a).

Panayiotou, C., and J. H. Vera, "Statistical Thermodynamics of r-Mer Fluids and Their Mixtures," *Poly. J.*, **14**, 681 (1982b).

Roe, R.-J., and D. Rigby, "Phase Relations and Miscibility in Polymer Blends Containing Copolymers," *Advances in Polymer Science*, Vol. 82, Springer-Verlag, Berlin, p. 103 (1987).

Wang, W., *Application of Lattice Models in Liquid-Liquid Equilibria*, MS Thesis, Oklahoma State Univ., Stillwater (1993).

Wilczek-Vera, C., and J. H. Vera, "A General Derivation of Thermodynamic Functions from the Quasichemical Theory and Their Use in Terms of Non-Random Factors," *Fluid Phase Equilib.*, **59**, 15 (1990).

Manuscript received Dec. 18, 1995, and revision received May 13, 1996.