Understanding phase behaviors of multicomponent polymer mixtures based on a molecular thermodynamic framework combined with molecular simulation

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ABSTRACT

A new molecular thermodynamic model based on a closed-packed lattice model is developed for multicomponent systems. Based on Monte-Carlo (MC) simulation results, we introduce new universal functions to consider the chain length dependence of polymers, and are able to obtain more accurate critical volume fraction results in liquid–liquid equilibrium (LLE) calculations. In associated blend systems, specific interactions are used to characterize strongly interacting polymer mixtures with a secondary lattice. To minimize the number of adjustable model parameters, chain length parameters are calculated in a conventional way using molecular weight and specific volume. Our proposed model successfully describes binary LLE for polymer-solvent systems. Furthermore, the model parameters obtained from these binary systems are directly used to predict corresponding LLE ternary systems, and the results were in good agreement with experimental data.

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1. Introduction

The phase behavior of polymer systems containing multiple components is important in a broad range of industrial processes and research. As such, many chemical engineers have made an effort to understand their mixing behavior. There are many types of LLE diagrams for polymer/solvent systems such as upper critical solution temperature (UCST), lower critical solution temperature (LCST), "hour-glass" shaped and closed-miscibility loop phase diagrams (both UCST and LCST). Owing to the importance of this topic to the practice of chemical engineering, a variety of polymer solution thermodynamic models have been developed to explain phase equilibria during the last few decades.

Many lattice models have been used to predict the thermodynamic properties of polymer systems. Most of them are revisions of the Flory-Huggins (F−H) theory [1−3], which is based on the incompressible-lattice model for polymer solutions wherein all lattice sites are occupied by segments of molecules. The F−H theory illustrates the competition between the entropy of mixing and the attractive forces that produce liquid−liquid phase separation at low temperatures with an UCST. A mean-field approximation was used to formulate the Helmholtz energy of mixing. Scott [4] used two approximate methods including the "single liquid approximation"

and "complete immiscibility approximation" for calculating the phase diagrams in ternary systems. These methods made the calculations easier but restricted their generality. Tompa [5] interpreted the phase relationships in polymer (1)/polymer (2)/solvent systems. Based on this approach, Tompa [5] proposed a power-series expansion in concentration and calculated the phase diagrams of immiscible polymer pairs and a solvent with empirical coefficients for χ_{ij} parameters obtained by various techniques, such as cloud point and glass transition measurements, with good agreement [6−12].

Plenty of theoretical improvements to the F−H theory have been developed including chain connectivity and nonrandom mixing. Despite these improvements, F−H theory and Guggenheim's quasi-chemical model [13] show methodical deviations including too narrow and parabolic liquid−liquid coexistence curves near the critical region when compared with experimental data or computer simulation data. To overcome these limitations associated with the mean-field theory and to pursue an exact formal mathematical solution to the F−H lattice with a complete and systematic analysis, Freed and co-workers [14−20] developed a lattice cluster theory (LCT). This theory begins with a strict formulation of the partition function of the lattice and includes a double expansion in the reciprocal powers of the interchange energy parameter and the coordination number. However, the theory was limited in its application to engineering due to enormous algebraic complexity and inevitable truncation. To make the accuracy of Freed's LCT sufficient for practical applications, Hu et al. [21−23] revised the

Freed theory (RFT) and developed a simple double lattice (DL) model by taking into account specific interactions such as hydrogen bonding. Oh and Bae [24] proposed a modified double lattice model (MDL) by introducing a new interaction parameter and simplifying the Helmholtz energy of mixing expression. Recently, Yang et al. [25] introduced a new molecular thermodynamic model for the multicomponent Ising lattice based on a generalized nonrandom factor, and Liu et al. [26,27] developed a new model for ternary polymer systems. Furthermore, Xu et al. [28,29] proposed a new thermodynamic model based on the lattice fluid theory by considering volume effect on incompressible-lattice model and applied it to the various binary vapor–liquid equilibria(VLE) and LLE systems containing polymer. At the same time, various EoS's have been established by means of molecular thermodynamic theories suitable for complex systems.

In this work, we propose a new molecular thermodynamic model for multicomponent systems based on the lattice model, taking the chain-length dependence of the polymer and oriented interactions into account. We describe various binary LLE phase behaviors using binary polymer-solvent or polymer–polymer miscibility data. To apply this method to ternary polymer systems, we fix the identical interaction energy parameters from these corresponding binary systems and the chain length parameters calculated using the specific volume and molecular weight.

2. Model development

2.1. Helmholtz function of mixing

We derive the multicomponent lattice model to describe the phase behaviors of ordinary polymer solutions starting with a simple cubic lattice (coordination number $Z = 6$) containing a total number of $N_r(= \sum_{i=1}^{K} N_i r_i)$ sites composed of K components.

N_i and r_i represent the number of molecules and chain length of the i th component, respectively. The term $r_i = 1$ signifies that the i th component is solvent. The Helmholtz function of mixing for closed-packed lattice consists of the entropy and energy contribution,

$$\frac{\Delta_{mix}A}{N_r kT} = -\frac{\Delta_{mix}S}{N_r k} + \frac{\Delta_{mix}U}{N_r kT} \tag{1}$$

where, T is the absolute temperature and k is Boltzmann's constant.

Hu et al. [23] applied chain-insertion probability to the derivation of the entropy term to improve the mean-field approximation of the F–H lattice. Following Hu's work, we employ new universal constants to consider chain length dependence of polymers in a solvent.

$$-\frac{\Delta_{mix}S}{N_r k} = \sum_{i=1}^{K} \frac{\phi_i}{r_i}\ln\phi_i + \frac{1}{2}\sum_{i=1}^{K}\sum_{j=1}^{K} \xi_1 \phi_i \phi_j \left(\frac{1}{r_i} - \frac{1}{r_j}\right)^2 \tag{2}$$

where ϕ_i $(=N_i r_i/N_r)$ is the volume fraction of specie i and ξ_1 is a universal constant to consider the chain length dependence of a polymer that revises the degree of asymmetry among the molecules.

A series expansion was adopted to account for interaction in clusters of different sizes. We consider only the nearest−neighbor interactions in this model as follows:

$$\frac{\Delta_{mix}U}{N_r kT} = \sum_{i=1}^{K}\sum_{j=1}^{K} a_{ij}\phi_i\phi_j - \left(\sum_{i=1}^{K}\sum_{j=1}^{K} a_{ij}^*\phi_i\phi_j\right)^2 \tag{3}$$

where a_{ij} and a_{ij}^* are generalized functions of chain lengths r_i, r_j. We adopt Hu's [21] model as a reference standard for determining the coefficients a_{ij} and a_{ij}^*, then the best set of these functions are

$$a_{ij} = \frac{\tilde{\varepsilon}_{ij}}{2}\left(\zeta_1 - \left(\frac{\phi_i}{r_i} + \frac{\phi_j}{r_j}\right) + \left(\frac{1}{r_i} + \frac{1}{r_j}\right)\right) \tag{4}$$

$$a_{ij}^* = \tilde{\varepsilon}_{ij}\sqrt{\zeta_2/4} \tag{5}$$

where ζ_1 and ζ_2 are universal constants to consider the chain length dependence of the polymer, and the reduced interchange energy, $\tilde{\varepsilon}_{ij}$, between the i -j pairs given by

$$\tilde{\varepsilon}_{ij} = \varepsilon_{ij}^*/kT = (\varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij})/kT \tag{6}$$

where ε_{ij}^* is the exchange interaction energy between segments i and j, and ε_{ij} is the interaction energy between segments i and j.

By substituting Eq. (2) and Eq. (3) into Eq. (1), a simple closed-packed lattice model expression for the Helmholtz energy of mixing is given by the following equation:

$$\frac{\Delta_{mix}A}{N_r kT} = \sum_{i=1}^{K} \frac{\phi_i}{r_i}\ln\phi_i + \frac{1}{2}\sum_{i=1}^{K}\sum_{j=1}^{K} \xi_1 \phi_i \phi_j \left(\frac{1}{r_i} - \frac{1}{r_j}\right)^2 + \sum_{i=1}^{K}\sum_{j=1}^{K} a_{ij}\phi_i\phi_j$$
$$- \left(\sum_{i=1}^{K}\sum_{j=1}^{K} a_{ij}^*\phi_i\phi_j\right)^2 \tag{7}$$

2.2. Correlation of Monte-Carlo simulation data

The universal constants ξ_1, ζ_1 and ζ_2 only depend on the polymer chain length in our proposed model. These constants are not adjustable parameters and are determined by comparison with MC simulation data in a binary system ($K = 2$). Fig. 1 shows the configurational bias vaporization method simulation results obtained by Yan et al. [30] for various chain lengths of component 2 from $r_2 = 2$ to 200. The solid lines are the fit from our proposed model with a best-fit value of $\zeta_1 = 1.5998$, which is virtually a constant value because it is a very weak function of chain length. Fig. 2 shows the chain length dependence of ξ_1 and ζ_2 fitted from the results in Fig. 1. The following equations represent the r-mer dependence of ξ_1 and ζ_2 :
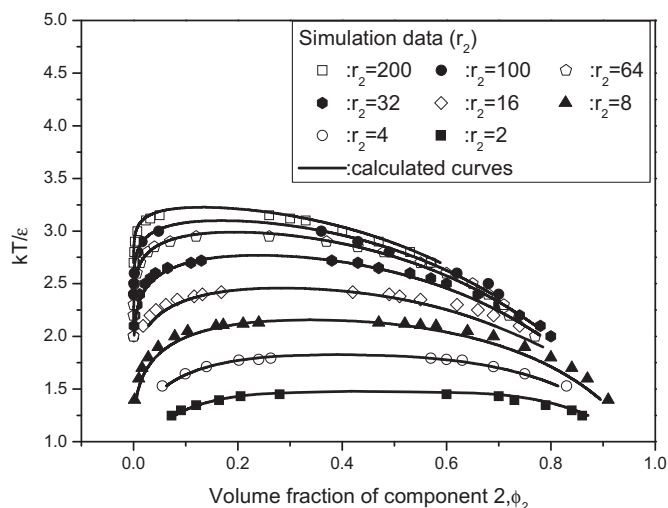

Fig. 1. Phase diagram of lattice-polymer systems with various chain lengths. The lines were generated using Eq. (5).