

# Comparison of thermodynamic lattice models for multicomponent mixtures



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## ABSTRACT

Liquid–liquid equilibrium (LLE) phase behaviors for twenty ternary systems are examined by four lattice-based thermodynamic models, the Flory–Huggins model (F-H), the modified double lattice model (MDL), the modified double lattice model–chain length dependent (MDL-CL) and the Xin model, and compared with experimental data. Ternary systems are composed of simple molecule and polymer solutions, and are described according to Treybal classifications of Type 0, 1, 2 or 3. These types of phase behaviors can be influenced by the nature of the solvent or temperature, and accurate predictions are important in the separation process and to recover residual oils. The interaction energy parameters directly obtained from the LLE binary systems are used to predict the ternary systems. Applicable types of binary phase behavior and adjustable parameters for each model are tabulated. The vapor–liquid equilibrium (VLE) for polymer/solvent systems and the swelling equilibrium of the hydrogel system are described and the same interaction energy parameters from the LLE binary systems were also used. The MDL-CL and Xin models provide better agreement with experimental data than other models.

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## 1. Introduction

Accurate prediction of the phase behavior for multicomponent systems over a wide range of temperature and pressure is important for the optimization of existing processes and the design of new chemical processes, including the separation and purification of fluid mixtures. However, compared with pure compounds and binary systems, the experimental data on multicomponent systems are limited. As such, thermodynamic models have been developed to calculate the thermodynamic property and phase equilibria of these systems.

The system is not appropriate for the separation process if all three components compositionally mix to form homogeneous solutions. Those where immiscibility occurs can be classified by the number of separation pairs. According to the Treybal classification [1], the phase behavior of a ternary system can be categorized as Type 0, 1, 2 and 3.

Types 1 and 2, in which one and two separate regions are exhibited, respectively, are shown in Fig. 1(a) and (b). Numerous examples of real experimental data from small molecule systems

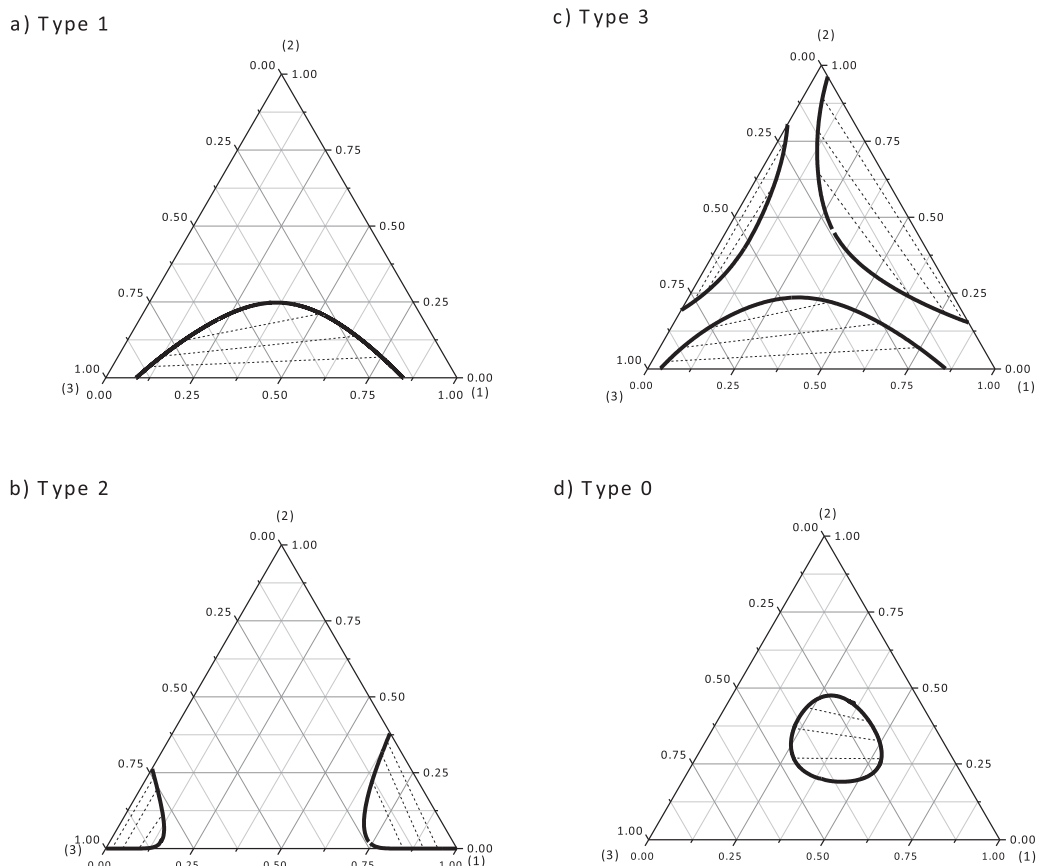
to polymer solutions can be found in literature. Types 0 and 3 are very scarce and only of interest in industrial applications.

Type 3 exhibits three separated regions as shown in Fig. 1 (c). Type 3 can appear in mixtures of water, oil, and nonionic surfactants, and these systems are important in numerous industrial fields [2], especially for the petroleum industry for the recovery of residual oils [3–5]. Type 0 (island), which has three completely miscible binary systems, is represented in Fig. 1(d). Experimental data for Type 0 systems are rare and have a tendency of appearing for ternary systems with two polymers and a low molecular weight solvent [6].

As experimental data of more than two component systems have been limited to binary systems, a suitable multicomponent model would be a useful tool for understanding and predicting the phase equilibrium phenomena. Historically, the prediction of phase behavior has relied on empirical methods, but more realistic thermodynamic models are being developed with various concepts. There are two types of approaches to a theory of liquids as the liquid state is intermediate of the crystalline and gaseous states [7].

The first approach considers liquids to be gas-like and the equation of state description is an example. Wertheim's first order perturbation theory (TPT1) [8–11] and its implementation as an equation of state in statistical associating fluid theory (SAFT) [12,13] have established as a major advancement toward a theoretical framework for modeling multicomponent systems. The SAFT

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**Fig. 1.** Types of phase diagrams for ternary liquid-liquid equilibria categorized by the Treybal classification [1]: (a) Type 1, (b) Type 2, (c) Type 3, and (d) Type 0.

assumes that there are three major contributions to the total intermolecular potential of a given molecule: the contribution due to the segment-segment repulsion and dispersion interactions, the contribution due to the formation of bonds between segments, and the contribution due to association. The most widely applied version of SAFT is developed by Huang and Radosz (SAFT-HR) [14,15]. In the SAFT-HR the dispersion interactions are described by the equation of Chen and Kreglewski [16], which was fitted to the thermodynamic property data of argon. Various papers have reported improvements and applications of SAFT [17–20]. Though there are many versions of SAFT that have been applied to describe the phase behaviors of pure fluid and fluid mixtures, none are superior.

The second approach considers a liquid to be solid-like, where the molecules tend to stay in a small area. The quasi-crystalline picture of the liquid state assumes the molecules sit in a regular array in space, which is called a lattice. Liquid and liquid mixture models based on this simplified picture are called lattice models, and this approach is particularly useful for describing solutions of polymers in liquid solvents.

One of the most widely known lattice models is the Flory-Huggins (F-H) [21,22] theory. The F-H model simply illustrates the competition between the entropy of mixing and the attractive interaction forces. However, the original F-H model deviates from the experimental data or the computer simulation data, especially near the critical point. Some other lattice theories developed to overcome these limitations are associated with mean-field theory. Freed and coworkers [23–25] developed a complicated lattice-cluster theory (LCT) for polymer solutions, which is formally an exact mathematical solution of the F-H model using advanced statistical and mechanical methods. However, the enormous algebraic complexity and inevitable truncation of LCT limit engineering

applications. Hu et al. [26–28] revised Freed's theory and developed the double lattice model (DL) by considering these specific interactions. In a DL model, the polymer solutions are described by the primary lattice and a secondary lattice is introduced as a perturbation to account for the oriented interactions. Oh et al. [29] reported a modified double lattice (MDL) model by introducing new interaction parameters and simplifying the expression of the Helmholtz energy of mixing. Recently, Ryu et al. [30] added simple universal functions to the MDL model to consider the chain length dependence of polymers based on Monte-Carlo simulation results. By comparing with experimental data, the MDL model with a chain length dependence term (MDL-CL) can describe the phase behaviors of the multicomponent systems. Based on the Zhou-Stell [31–33] theory and a mixing Helmholtz function model for a multicomponent Ising lattice [34–36], Xin et al. [37] developed a molecular thermodynamic model of multicomponent chainlike fluid mixtures (Xin).

This work describes various types of binary and ternary LLE phase behaviors through the F-H model and improved closed-packed lattice models: MDL, MDL-CL and Xin. Nineteen ternary systems were composed of simple molecule solution systems and polymer solution systems and are arranged according to the Treybal [1] classification: Type 0, 1, 2 or 3. The interaction energy parameters obtained from the LLE binary systems were applied directly to the ternary systems, which are not dependent on the molecular weight or polymer chain length. VLE is also described for polymer/solvent systems and the swelling equilibrium of a hydrogel system using parameters from binary LLE calculations. For gel swelling equilibrium calculations, the Flory-Rehner chain model [38] was employed as the elastic contribution. The results from each model were compared with the experimental data.

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