The perturbed hard-sphere-chain (PHSC) equation of state is applied to calculate phase diagrams of ternary mixtures containing polymers. Special attention is given to the effects of polymer molecular weight, pressure, temperature, and various molecular parameters.

KEY WORDS: equation of state; phase diagrams; polymer solution; ternary systems.

1. INTRODUCTION

It has been recognized for some time that thermodynamic properties of polymer mixtures depend on the properties of solvents and polymers and equations of state provide useful tools for correlating and estimating thermodynamic properties of polymer mixtures [1, 2]. For example, the equation-of-state theory has successfully explained both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) phenomena for polymer solutions. The classical Flory-Huggins equation [3] ignores the thermodynamic properties of pure components and completely fails to describe LCST behavior.

In general, an equation-of-state approach to polymer mixtures starts with describing properties of the pure components; extensions to mixtures follow soon after success for pure systems. This approach usually involves using arbitrary mixing and combining rules to obtain parameters from the pure components for mixtures [4]. Recently, there have been an increased interest in developing statistical/mechanical based equations of state for polymer mixtures. Although a rigorous statistical/mechanical treatment for polymers is difficult, because of their asymmetric structure, their large number of internal degrees of freedom, and the strong coupling between...
intra- and intermolecular interactions, a number of equations of state have been developed based on a relatively simple model, hard-sphere chains, in which a molecule is modeled by a series of freely jointed tangent hard spheres [5-12]. Among them is the perturbed hard-sphere-chain (PHSC) equation of state, which takes the hard-sphere chains as its reference system plus a van der Waals term as the perturbation [10-12].

For pure fluids and polymers, the PHSC equation of state is characterized by three molecular parameters: segment number per molecule \( r \), segment size \( \sigma \), and nonbonded segment–segment interaction energy \( e \); they can be obtained from readily available data for thermodynamic properties such as vapor pressures, densities, and compressibilities [10, 12]. For mixtures containing polymers, no mixing rules are required for the hard-sphere-chain contribution. Only the perturbation needs the van der Waals one-fluid mixing theory. The PHSC equation of state can reproduce all types of fluid phase equilibria that have been found experimentally in binary mixtures containing polymers, including the lower critical solution temperature (LCST), the upper critical solution temperature, and the hour glass-shaped phase behavior [11]. For several binary mixtures containing polymers, calculated liquid–liquid coexistence curves are in good agreement with experiment [12].

In this paper, we apply the PHSC equation of state to ternary mixtures containing polymers. We are particularly concerned here with liquid–liquid equilibria of ternary systems because of the variety of observed phase behavior reported in the literature. We present some calculated phase diagrams for ternary mixtures and investigate the effects of polymer molecular weight, pressure, and temperature. Conclusions are summarized in the last section.

2. PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

The derivation of the PHSC equation of state for mixtures follows a rigorous first-order statistical–mechanical perturbation theory based on a mixture of hard-sphere chains as the reference system plus a van der Waals term as the perturbation; details are given in previous publications [10, 12]. Here we reproduce only the main steps necessary for describing the model.

In general, the PHSC equation of state is applicable to fluid mixtures containing any number of components over the entire range of fluid conditions. Its form for pure fluids is [10]

\[
\frac{p}{\rho k_B T} = 1 + r^2 b \rho g(d^+) - (r - 1) g(d^+) - 1 - \frac{r^2 a \rho}{k_B T} \tag{1}
\]