

APPLICATION OF LATTICE MODELS IN
LIQUID-LIQUID EQUILIBRIUM

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. GENERAL THERMODYNAMIC BACKGROUND	5
Thermodynamic Framework	5
Criteria for Phase Equilibrium	6
Thermodynamic Formalism	7
Gibbs Energy	7
Chemical Potential	8
Activity Coefficient	8
Liquid-Liquid Equilibrium	9
Liquid-Liquid Phase Behavior	9
Criteria for Phase Splitting	12
Polymer Solution Models	16
Lattice Theory	16
Flory-Huggins Model	18
Modifications of the Flory-Huggins Model	19
Local Composition and Group Contribution	21
Other Lattice Models	23
III. LATTICE MODELS AND GENERAL THERMODYNAMIC ALGORITHM	25
Statistical Mechanics and Lattice-Fluid Theory	25
Sanchez-Lacombe Model	28
Mixing Rules	28
Equation of State and Chemical Potential Expression	30
Group Contribution Lattice-Fluid Model	31
Pure-Component Equation of State	31
Equation of State for Mixture	35
Group Contribution Technique	38
Summary	39
IV. STABILITY ANALYSIS	41
Stability Conditions	41

Chapter	Page
Stability Analysis Using the Sanchez-Lacombe Equation of State	43
Stability Analysis Using the GCLF Equation of State	47
Summary	50
 V. EVALUATION OF SANCHEZ-LACOMBE AND GCLF MODELS	 52
General Thermodynamic Algorithm	52
Problem Formulation	53
Computation Scheme	53
Some Observation from the Application of the Sanchez-Lacombe EOS	 58
Low Molecular Weight Systems	59
Polymer-Solvent Systems	65
Polyisobutylene-Solvent Systems	67
HDPE-Solvent Systems	67
Polystyrene-Solvent Systems	73
Poly(ethylene glycol)-Solvent Systems	78
Molecular Weight Dependence of Critical Solution Temperatures	78
Pressure Dependence of Critical Solution Temperatures	83
Polymer-Polymer Miscibility	83
 VI. CONCLUSIONS AND RECOMMENDATIONS	 86
Conclusions	86
Recommendations	87
 BIBLIOGRAPHY	 90
 APPENDIXES	
APPENDIX A- COMPUTER PROGRAM FOR CALCULATING BINODAL CURVE USING THE GCLF EOS	 94
APPENDIX B- COMPUTER PROGRAM FOR CALCULATING BINODAL CURVE USING THE SANCHEZ- LACOMBE EOS	 112
APPENDIX C- COMPUTER PROGRAM FOR CALCULATING SPINODAL CURVE USING THE SANCHEZ- LACOMBE EOS	 120

Chapter	Page
APPENDIX D- COMPUTER PROGRAM FOR OPTIMIZING THE BINARY INTERACTION PARAMETERS	123
APPENDIX E- INPUT INFORMATION FOR CALCULATIONS USING THE SANCHEZ-LACOMBE AND GCLF EQUATIONS OF STATE	129
APPENDIX F- EXPRESSIONS FOR STABILITY CONDITIONS USING THE GCLF EQUATION OF STATE	132

LIST OF TABLES

Table	Page
I. Molecular Parameters of Solvents for the Sanchez-Lacombe Equation of State	32
II. Molecular Parameters of Polymers for the Sanchez-Lacombe Equation of State	33
III. Group Contributions for the Group Contribution Lattice-Fluid Equation of State	40

LIST OF FIGURES

Figure	Page
1. Schematic Liquid-Liquid Composition-Temperature Phase Diagram For Various Mixtures	11
2. Gibbs Energy of Mixing Versus Mole Fraction in a Binary System	13
3. Typical Temperature-Composition Phase Diagram For a Binary System	15
4. Diagram of Chemical Potentials Versus Molar Composition Representing Phase Transition	42
5. Stability Analysis in the HDPE/n-Pentane System (P=1 atm, T=380 K)	45
6. Stability Analysis Using Sanchez-Lacombe Model on a Temperature-Composition Plane	46
7. Stability Analysis in the PS/Acetone System (P=20 bar, T=350 K)	49
8. Stability Analysis Using GCLF Model on a Temperature-Composition Plane	51
9. Chemical Potentials (μ_1 and μ_2) As Functions of Composition x_1 In a Binary System Undergoing Phase Splitting	55
10. Diagram of Chemical Potentials Versus Concentration in the PIB/n-Pentane System	60
11. Comparison of Theoretical Binodal Curves in the Methanol/Cyclohexane System with Experimental Data	61
12. Comparison of Theoretical Binodal Curves in the Methanol/n-Heptane System with Experimental Data	62
13. Comparison of Theoretical Binodal Curves in the Acetic acid/Decane System with Experimental Data	63
14. Comparison of Theoretical Binodal Curves in the Acetic acid/Dodecane System with Experimental Data	64

Figure	Page
15. Comparison of Theoretical Binodal Curves in the Stearic acid/Propane System with Experimental Data	66
16. Theoretical Binodal Curve of the PIB/n-Pentane System Compared with Experimental Data	68
17. Theoretical Binodal Curve of the PIB/Isopentane System Compared with Experimental Data	69
18. Theoretical Binodal Curve of the PIB/n-Hexane System Compared with Experimental Data	70
19. Theoretical Binodal Curve of the HDPE/n-Pentane System Compared with Experimental Data System	71
20. Theoretical Binodal Curve of the HDPE/n-Hexane System Compared with Experimental Data	72
21. Theoretical Binodal Curve of the HDPE/n-Butyl Acetate System Compared with Experimental Data	74
22. Theoretical Binodal Curve of the PS/Toluene System Compared with Experimental Data	75
23. Theoretical Binodal Curve of the PS/Benzene System Compared with Experimental Data	76
24. Theoretical Binodal Curves of the PS/Cyclohexane System Compared with Experimental Data	77
25. Theoretical Binodal Curves of the PS/Acetone System Compared with Experimental Data	79
26. Comparison of Theoretical Binodal Curves of the PEG/Water System with Experimental Data	80
27. Effect of the Molecular Weight of Polyisobutylene on LCST's in the PIB/n-Pentane System	81
28. Effect of the Molecular Weight of HDPE on LCST's in the HDPE/n-Pentane System	82

Figure	Page
29. Effect of Pressure on Critical Solution Temperatures in the PS/Acetone System	84
30. Effect of Pressure on LCST's in the PIB/Isopentane System	85
31. Comparison of Theoretical Binodal Curve of a PS/PVME Blend with Experimental Data	86

NOMENCLATURE

a_i	activity of component i in a mixture (dimensionless).
A	Helmholtz energy (kJ).
E	energy of a lattice (kJ).
f	fraction of lattice sites occupied by molecular segments in the Sanchez-Lacombe model (dimensionless).
f_0	fraction of lattice sites occupied by holes in the Sanchez-Lacombe model (dimensionless).
f_i	fugacity of component i (dimensionless).
g_c	athermal Guggenheim combinatorial factor (dimensionless).
g_{nr}	nonrandom Guggenheim combinatorial factor (dimensionless).
$g(T, \phi_2)$	new interaction parameter in Flory-Huggins equation (dimensionless).
G	Gibbs energy (kJ).
ΔG	Gibbs energy of mixing (kJ).
G^E	excess Gibbs energy in the mixture (kJ).
k	Boltzman constant ($1.3806 \times 10^{-23} \text{ J K}^{-1}$); interaction parameter in Group Contribution Lattice-Fluid model (dimensionless).
n_i	number of moles of component i (kmol).
N	number of molecules in the ensemble (dimensionless).
N_h	number of holes in the lattice (dimensionless).
N_q	number of interaction sites available to component i (dimensionless).

N_r	total number of lattice sites (dimensionless).
\bar{N}_i	number of contacts between the molecules of the same type in case of nonrandom mixing (dimensionless).
\bar{N}_{ij}	number of contacts between the molecules of different types in case of nonrandom mixing (dimensionless).
\bar{N}_i^o	number of contacts between the molecules of the same type in case of random mixing (dimensionless).
\bar{N}_{ij}^o	number of contacts between the molecules of different types in case of random mixing (dimensionless).
P	pressure (Pa).
\tilde{P}	reduced pressure (dimensionless).
P^*	characteristic pressure (Pa).
q_i	effective chain length of surface area parameter for component i (dimensionless).
q_{int}	internal canonical partition function (dimensionless).
q_{tr}	translational partition function (dimensionless).
Q	canonical partition function (dimensionless).
Q_k	surface area parameter for group k (dimensionless).
r_i	number of segments in a molecule of type i (dimensionless).
r	average number of segments in the mixture in Sanchez-Lacombe model (dimensionless).
R	gas constant ($8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1}$).
ΔS	entropy of mixing (kJ K^{-1}).
T	temperature (K).
\tilde{T}	reduced temperature (dimensionless).

T^*	characteristic temperature (K).
v_i	molar volume of component i ($\text{m}^3 \text{ kmol}^{-1}$); volume per segment of component i (m^3).
v_h	volume of a lattice site ($\text{m}^3 \text{ kmol}^{-1}$).
\tilde{v}_i	reduced volume of component i (dimensionless).
\tilde{v}_m	reduced volume of the mixture in UNIFAC-free volume activity coefficient model (dimensionless).
v^*	characteristic volume per segment in the Sanchez-Lacombe model (m^3); characteristic molar volume in the GCLF-EOS model ($\text{m}^3 \text{ kmol}^{-1}$).
V	volume (m^3).
ΔV	volume change of mixing (m^3).
x_i	mole fraction of component i (dimensionless).
Z	configurational partition function (m^{3N}).
z	coordination number (dimensionless); interaction parameter in Sanchez-Lacombe model (dimensionless).

Greek Symbols

β	$1/kT$ (J^{-1}).
γ_i	mole fraction activity coefficient of component i (dimensionless).
Γ_{ii}	nonrandomness parameters of component i in the Group Contribution Lattice-Fluid model (dimensionless).
Γ_{ij}	nonrandomness parameters between different components in the Group Contribution Lattice-Fluid model (dimensionless).
δ	flexibility parameter (dimensionless).
δ_i	solubility parameter of component i (J m^{-3}) ^{1/2} .
δ_d	contribution to the solubility parameter from dispersive forces (J m^{-3}) ^{1/2} .

δ_p	contribution to the solubility parameter from polar forces (J m^{-3}) ^{1/2} .
δ_h	contribution to the solubility parameter from hydrogen bonding forces (J m^{-3}) ^{1/2} .
ε	energy of interaction per unit of surface area (kJ m^{-2}).
ε^*	interaction energy in the Sanchez-Lacombe model (kJ).
ε_{ij}	characteristic interaction energy between a segment of molecule i and a segment of molecule j (kJ).
θ_i	surface area fraction of component i (dimensionless).
Λ_{ij}	Wilson model nonrandomness parameter for i-j contacts (dimensionless).
μ_i	molar chemical potential of species i (kJ kmol^{-1}).
$\Delta\mu_i$	change in chemical potential upon mixing for species i (kJ kmol^{-1}).
$v_k^{(m)}$	number of groups of type k in molecule m (dimensionless).
$\bar{\rho}$	reduced density (dimensionless).
σ	symmetry parameter (dimensionless).
ϕ_i	volume or segment fraction of species i (dimensionless); fugacity coefficient of component i (dimensionless).
χ	Flory-Chi parameter for the residual term in the Flory-Huggins theory (dimensionless).
Θ_m	functional group surface area fraction (dimensionless).
ω	number of configurations to one molecule in the Sanchez-Lacombe partition function (dimensionless).
Ω	number of configurations in the pressure ensemble in the Sanchez-Lacombe model (dimensionless).

CHAPTER I

INTRODUCTION

Phase equilibrium thermodynamics is the key to the success of the processes that produce useful chemicals with specific, desirable properties in the chemical and pharmaceutical industries. These processes rely on the ability to efficiently and economically separate the desired species from a mixture containing a variety of products. Furthermore, development of new and more powerful separation processes rely upon advances in the separation sciences. The purpose of this research is to improve the understanding of phase equilibrium thermodynamics of polymer solutions.

The usefulness of thermodynamic information gleaned from polymer solutions has long been recognized. Thermodynamic information is a necessity in predicting the behavior of a polymer system in the initial polymerization process, through the removal of possibly toxic volatile materials, to its performance as an end-product. Phase equilibrium properties of polymer solutions affect how these processing steps can be carried out. An appropriate design of each specific operation requires the knowledge of the thermodynamic properties of the polymers, solvents, plasticizers, diluents, etc. involved in a mixture. Another application arises in the processing of polymer blends. Polymer compatibility has been the subject of considerable interest, and thermodynamic models are needed to predict the compatibility of two polymers. Phase equilibrium information is also frequently applied in biochemical engineering for purification operations. One such separation technique is to use aqueous-polymer two-phase systems to separate a wide variety of biomaterials, such as proteins, nucleic acids, fragile subcellular particles, microorganisms, etc. Classical solution theories have been used to correlate the

partitioning of biomolecules. Phase equilibrium thermodynamics in polymer solutions is an underlying key to development of separation and purification techniques applicable to biological materials. Phase equilibrium thermodynamics is an essential element in most non-mechanical separation processes.

Early interest in polymer solutions concerned measurements such as osmotic pressure. Not until the 1960's was it appreciated that liquid-liquid phase separation upon changing temperature (or pressure) is a general phenomenon in polymer solutions, and that a polymer is fractionated by differential partitioning of its species between the two phases (Kennedy, 1978). These observations inspired the growth of interest in polymer solution thermodynamics.

Phase equilibrium thermodynamics provides two approaches to correlate the thermodynamic properties at equilibrium. One is the equation-of-state method and the other is the activity coefficient method. Activity coefficient models have been the primary method to deal with polymer solutions. However, activity coefficient models are typically applicable to the condensed phase, and it is not convenient to use activity coefficient models in systems containing supercritical components because in this case hypothetical standard states have to be assumed. The equation-of-state methods overcome these shortcomings, but the difficulty has been finding a general equation of state applicable to a wide variety of molecules (i.e. large or small; polar or nonpolar) in both the vapor and dense phases. However, as pointed out by High (1990), the benefits of an equation of state outweigh the liabilities. If possible, equations of state are preferred over activity coefficient models for calculation of phase equilibria.

Any successful model, either an activity coefficient model or an equation of state model, requires a good understanding of the nature of intermolecular forces. The case of polymer solutions is necessarily more complicated because consideration must be given not only to interaction between similar and unlike molecules, but also to the configuration of a long molecular chain of polymer. It has been customary to apply statistical mechanics

to relate the phase behavior of macroscopic systems to the properties of small particles such as atoms, molecules, etc. The partition function Q can be related to the Helmholtz energy A by:

$$A = -RT \ln Q. \quad (1)$$

Other thermodynamic functions of interest, such as enthalpy, entropy, and chemical potential μ_i for the i th component of the mixture, can be related to the partition functions by means of classical thermodynamic functions.

The object of statistical mechanics is to determine the macroscopic properties as a function of molecular properties. The problem has been that of expressing Q in terms of molecular and state variables. As a rule, polymers are mixtures of macromolecules varying in chain branching, sequence of monomer units, stereoregularity, and molecular weight. These differences make the study of polymer properties a difficult matter. It has been common to interpret a polymer molecule as an "assemblage of small segments" connected together in some way and more or less free to interpenetrate other such assemblies (Kennedy, 1978). A variety of statistical mechanical models have been proposed to deal with the combinatorial problem of counting the number of ways in which the polymers and solvents in the system can be arranged and estimating the energy assigned to each such arrangement. The problem has been approached in several ways leading to a variety of statistical mechanical models.

Equations can be made predictive through knowledge of the intermolecular potentials of the systems of interest. The group contribution approach assumes that the interaction energy between groups will be constant regardless of the overall structure of the molecule, it offers an efficient way to calculate the intermolecular properties so as to make the equation of state predictive. The group contribution method has been proven to be successful in various activity coefficient models, but equations of state based on group contributions are less common. Holten-Andersen (1985) proposed a group contribution equation of state for polymer solutions. High and Danner (1989, 1990a) developed a new

group contribution lattice fluid equation of state, which is a modification of the EOS derived by Panayiotou and Vera (1982a,b). The GCLF equation of state is based on lattice statistics and has proven to accurately predict solvent activities in various polymer-solvent systems. One objective of this thesis is to extend the GCLF model to applications in polymer-solvent liquid-liquid equilibria.

The subject of this thesis is liquid-liquid equilibrium. The GCLF equation of state has been extended to liquid-liquid equilibrium in low molecular weight systems and polymer-solvent systems, and subsequent testing with experimental data was performed. The GCLF model is compared with the Sanchez-Lacombe equation of state (1974, 1976a,b, 1978). The majority of the discussion is related to the behavior of the two models in liquid-liquid equilibrium.

The content of this thesis is as follows. Chapter 2 provides a general thermodynamic background. The common phenomenon in liquid-liquid systems is described and how phase behavior is related to thermodynamic representation is discussed. A brief review of the most common liquid solution models is given.

Chapter 3 mainly describes the Sanchez-Lacombe and the GCLF equations of state, which are the equations of state we are investigating in liquid-liquid equilibria.

Chapter 4 discusses the stability analysis in liquid mixtures using the Sanchez-Lacombe and the GCLF equations of state. The objective of this chapter is to evaluate the abilities of the two equations of state in the prediction of phase separation.

Chapter 5 discusses the general algorithm for the calculation of liquid-liquid equilibrium. The abilities of the Sanchez-Lacombe and the GCLF equations of state in predicting liquid-liquid equilibria are compared, including upper critical solution temperature (UCST) and lower critical solution temperature (LCST) behavior and the pressure dependence and molecular weight dependence of these critical conditions.

Chapter 6 serves as the conclusion, with the purpose of summarizing what was learned in this research. Suggestions are also provided for future work in this area.

CHAPTER II

GENERAL THERMODYNAMIC BACKGROUND

This chapter seeks to provide the general thermodynamic background necessary for the understanding of the phase behavior in polymer solutions and the evaluation of the application of the models for liquid-liquid equilibrium. First, the basics of solution thermodynamics and some essential quantities in phase equilibrium are discussed. Then, the common behavior of liquid-liquid systems and their thermodynamic representation are discussed.

The objective of this research is to extend the Group Contribution Lattice-Fluid (GCLF) equation of state to the prediction of liquid-liquid equilibrium and compare it with the Sanchez-Lacombe (S-L) model. Detailed derivations of the GCLF model and the Sanchez-Lacombe model can be found in previous work (Sanchez-Lacombe, 1976a,b, 1978; Panayiotou and Vera, 1982a,b; High, 1990). Only a brief review of the lattice models is given in this chapter, a more detailed description of the GCLF EOS and Sanchez-Lacombe models and their application in polymer solutions will be covered in the next chapter.

Thermodynamic Framework

The objective in solution thermodynamics is to determine accurate relationships among physical properties such as temperature, pressure, and composition between different phases. The criteria for phase equilibrium are discussed, then several important thermodynamic functions in solution theories are introduced.

Criteria for Phase Equilibrium

Basically, there are two approaches to correlate the properties of different phases at equilibrium. The first criterion is the equality of T and P for each phase and of the chemical potential, μ_i , for each component in each phase.

$$P^I = P^{II} = \dots = P^N \quad (2)$$

$$T^I = T^{II} = \dots = T^N \quad (3)$$

$$\mu_i^I = \mu_i^{II} = \dots = \mu_i^N \quad (4)$$

where the superscripts represent the number of phases at equilibrium.

In a closed, heterogeneous system the equality of chemical potentials can be replaced by the equality of fugacities:

$$\hat{f}_i^I = \hat{f}_i^{II} = \dots = \hat{f}_i^N. \quad (5)$$

The general expression for calculating binary liquid-liquid equilibrium using activity coefficients is given as:

$$\gamma_i^I x_i^I f_i^{0,I} = \gamma_i^{II} x_i^{II} f_i^{0,II}. \quad (6)$$

In the case when the standard states in both phases are the same, the equation becomes:

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II}. \quad (7)$$

There is a second criterion for stable equilibrium, which is that the Gibbs energy of the system must be at a minimum. Any closed system in stable equilibrium is characterized by the condition that, at constant pressure and temperature, its free energy of mixing is a minimum. In partially miscible liquid systems, when equilibrium is obtained, the system separates into a number of phases and the components are distributed over the phases so that the total Gibbs energy is at a minimum.

All of the expressions described above are general, exact, and can be applied to small molecules, polymers or any other solution systems. What is required are accurate equations of state and activity coefficient models.

Thermodynamic Formalism

In phase equilibrium, the most useful thermodynamic functions are the Gibbs free energy, chemical potential, and activity coefficient. In polymer solution models, microscopic properties are frequently related to two quantities: chemical potential and activity coefficient. These quantities will be used in the ensuing discussion and must be discussed first.

Gibbs Energy. The Gibbs energy is a state function defined as the thermodynamic potential in terms of the independent variables P, T, n. The fundamental equation for an open system is given as:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (8)$$

where,

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \equiv \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} \equiv \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j} \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} \quad (9)$$

The quantity μ_i is the partial molar Gibbs energy, but not the partial molar enthalpy, Helmholtz energy or internal energy. Because the independent variables are T and P, which are arbitrarily chosen in defining partial molar quantities, are also the independent variables for the Gibbs energy, G.

Gibbs energy is also the most useful thermodynamic function to apply in statistical mechanics. Microscopic properties can be easily related to the Gibbs energy by:

$$G = -RT \left[\ln Q - \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N} \right] \quad (10)$$

where,

$$Q = \sum_i e^{-\beta E_i(V,N)}. \quad (11)$$

where Q is called the canonical partition function. $E_i(V,N)$ is the energy of that system of the ensemble which is in energy state i , the term in parentheses (V,N) indicates the canonical ensemble. For a liquid or solid, the second term in the brackets in Equation (10) is negligible, therefore, the Gibbs energy is practically indistinguishable from the Helmholtz energy in Equation (1).

Chemical Potential. Chemical potential is defined as partial molar Gibbs energy. Many models used in polymer solution systems are expressed in terms of chemical potentials. When equilibrium is obtained, the chemical potential of each component in each phase should be equal. An absolute value of the chemical potential cannot be assigned. Hence, we are forced to calculate the changes of chemical potentials or the differences between the state of interest and a reference state. The difference between the chemical potential at the state of interest and the standard state is called the relative chemical potential (Benge, 1986). The choice of a standard state is arbitrary, but it is quite common that the pure components at the temperature and pressure of the system is chosen as the standard state.

The relation between the relative chemical potential of component i and the Gibbs energy of mixing in a multicomponent system is given as:

$$\Delta\mu_i = \mu_i - \mu_i^o = \left[\frac{\partial \Delta G_{mixing}}{\partial n_i} \right]_{T,P,n_j} \quad (12)$$

Activity Coefficient. The activity coefficient is defined as the activity divided by mole concentration. Activity coefficient has the physical significance of being the ratio of actual fugacity to the fugacity of an ideal solution at the same conditions. That is:

$$\gamma_i \equiv \frac{a_i}{x_i} = \frac{\hat{f}_i}{x_i f_i^o} \quad (13)$$

Activity coefficients are readily obtained from expressions for the excess Gibbs energy. The relation between the activity coefficient of an individual component and excess Gibbs energy is given by:

$$\ln \gamma_i = \frac{\bar{g}_i^E}{RT} = \left[\frac{\partial(n_T g^E / RT)}{\partial n_i} \right]_{T, P, n_j} \quad (14)$$

Excess functions are thermodynamic properties of solutions in excess of those of an ideal solution at the same temperature, pressure and composition. The excess Gibbs energy is defined by:

$$g^E \equiv \Delta g_{mixing} - \Delta g_{mixing}^{id} \equiv g_{mixture} - g_{ideal} \quad (15)$$

Liquid-Liquid Equilibrium

Phase equilibrium involves two or more phases in contact. This research work applies to liquid-liquid systems; therefore, an introduction to phase behavior in liquid-liquid systems is necessary. An understanding of how this phase behavior is represented by thermodynamic functions is also discussed.

Liquid-Liquid Phase Behavior

Some polymer solutions have been observed to display a lower critical solution temperature, an upper critical solution temperature, and some display both an upper and lower critical solution temperature. An adequate theory for polymer solutions should be able to predict these behaviors. Here, the characteristics of phase behavior are discussed.

Any synthetic polymer is a mixture of molecules of different molecular weights. It is itself a multicomponent system and its solution is a multicomponent system as well. Hence, a solution of polydisperse polymer and a single solvent is actually a multicomponent system. However, it can be viewed as a binary system if the heterogeneity index is small. In the present work, like the Flory and Holten-Andersen

equations of state, the polymers are considered to be monodisperse. The effects of polydispersity on the calculation results have been reviewed by High (1990). The present polymer solution theories have not been able to deal with the polydisperse polymer solutions with a high degree of accuracy. In the present work, all experimental data are of low degree of dispersity ($M_w/M_n < 1.06$) except for the system of HDPE (high density polyethylene) and hexane, the heterogeneity index of HDPE in this system is 1.37.

The critical solution behavior of polymer solutions is classified into two types by the shape of the cloud-point curve in the temperature-concentration diagram. The cloud point curve of the upper critical solution temperature (UCST) is convex upward in the temperature-composition diagram with a maximum, where the mutual solubility increases with increasing temperature. The temperature of this maximum point is called the upper critical solution temperature. The cloud point curve of the lower critical solution temperature (LCST) is concave upward with a minimum, which is known as the lower critical solution temperature. Partial miscibility occurs at the temperatures above the LCST or below the UCST. The existence of the UCST or LCST is a very common phenomenon in polymer solutions. Upper and lower critical states may exist in the same system. A few examples of closed regions of immiscibility have been observed, as shown in Figure 1b. In the polymer-poor solvent system, the two regions of miscibility are merged to give an "hourglass" shape, as shown in Figure 1c.

The molecular weight of the polymer affects the upper and lower critical solution temperatures. The maximum point of UCST is shifted to a higher temperature and a lower concentration with increasing molecular weight of the polymer; while the minimum point of LCST tends to move toward lower temperature and lower concentration as the molecular weight of the polymer increases. By increasing the molecular weight of the polymer, the UCST is raised and the LCST is lowered, thus enlarging the region of immiscibility. The pressure also affects the UCST and LCST phenomena, it has been observed that the UCST decreases and LCST increases as the pressure increases.

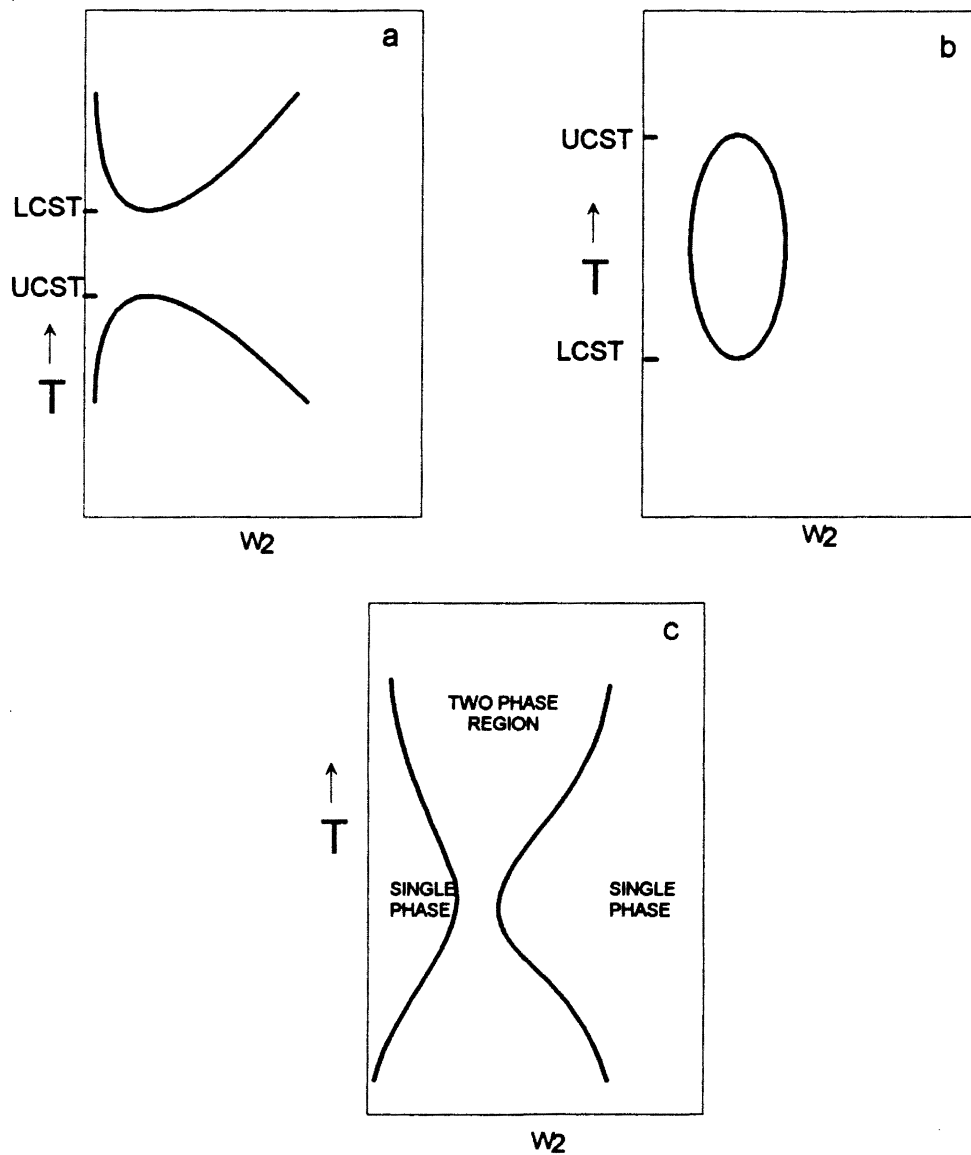


Figure 1. Schematic Liquid-Liquid Temperature-Composition Phase Diagram for Various Mixtures. (a) A Mixture with a LCST Above a UCST; (b) A Mixture with a UCST Above a LCST (Closed-loop Diagram); (c) A Mixture with a Tendency Toward Greater Miscibility at Intermediate Temperature (Hourglass Diagram).

Criteria for Phase Splitting

Many liquid systems exhibit partial miscibility, which is usually termed phase splitting. The most convenient criterion to evaluate phase splitting is the Gibbs energy of mixing. In a binary system, if the formation of additional phase can lower the Gibbs energy of the system, then the mixture splits into two phases.

The phase splitting can be represented by a diagram of the Gibbs energy of mixing versus mole fraction where the curve is partly concave downward, as shown in Figure 2. Notice that Curve 1 has a positive second derivative of the Gibbs energy everywhere, thus, the system is a homogeneous phase for all compositions. Curve 2 is partly concave downward having a common tangent enclosing the region of the curve exhibiting immiscibility. The Gibbs energy within this area is minimized by splitting into two phases having the concentration x' and x'' , respectively. A set of these tie-line points yields the binodal or phase boundary curve. The region of instability corresponds to area between x'_{sp} and x''_{sp} . The two inflection points, x'_{sp} and x''_{sp} , where the second derivative of excess Gibbs energy with respect to composition is zero, are called spinodal points. The locus of these points is called the spinodal curve.

The criterion for phase splitting for a binary liquid mixture is:

$$\left(\frac{\partial^2 \Delta g_{mixing}}{\partial x^2} \right)_{T,P} < 0. \quad (16)$$

Phase splitting can also be evaluated via the excess Gibbs energy. In a binary solution, the excess Gibbs energy can be expressed as:

$$g^E \equiv g_{mixture} - x_1 g_1 - x_2 g_2 - RT[x_1 \ln x_1 + x_2 \ln x_2]. \quad (17)$$

The criterion for phase splitting can be rewritten as:

$$\left(\frac{\partial^2 g^E}{\partial x_1^2} \right)_{T,P} + RT \left(\frac{1}{x_1} - \frac{1}{x_2} \right) < 0. \quad (18)$$

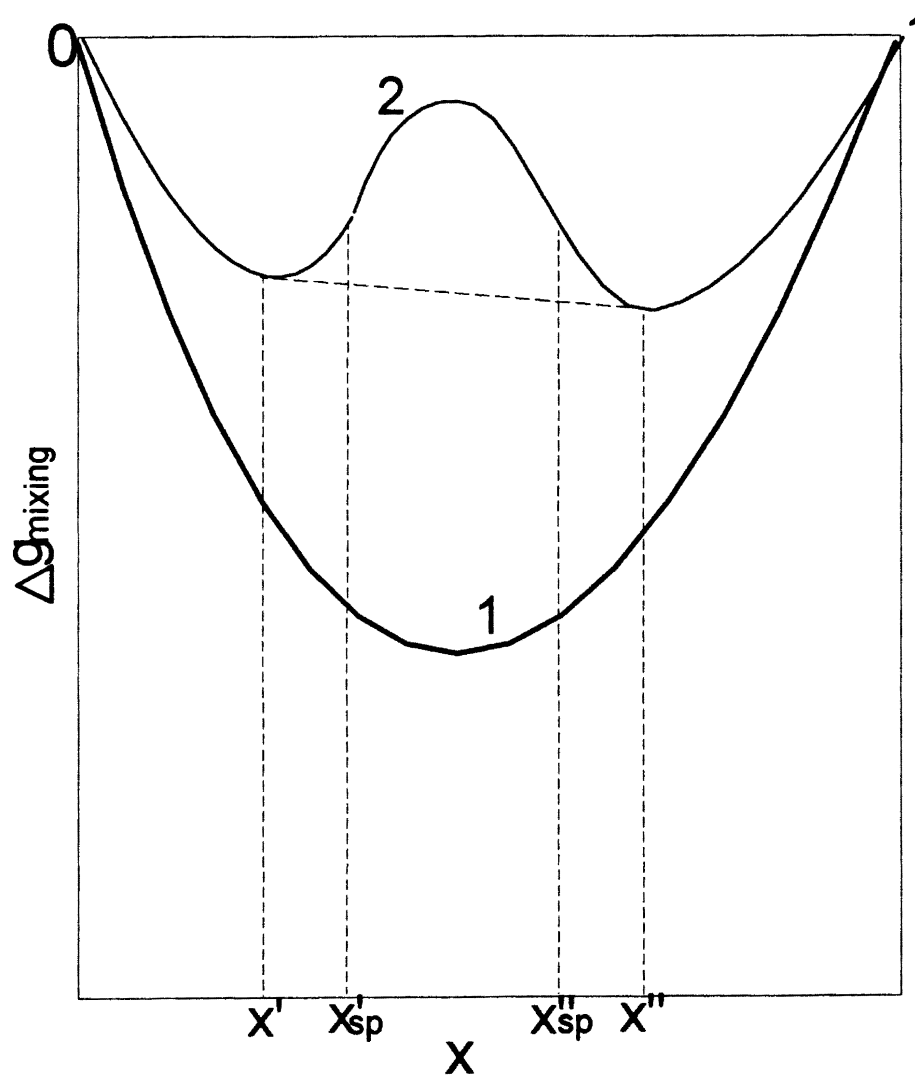


Figure 2. Gibbs Energy of Mixing Versus Mole Fraction in a Binary System.
Curve 1 Corresponds to a System Exhibiting Complete Miscibility;
Curve 2 Represents Partial Miscibility.

In the case of an ideal solution, Gibbs energy of the mixture is equal to zero, so the ideal solution cannot exhibit phase splitting. Mixtures of real fluids do not form ideal solutions. It is noted from Equation (18) that the excess Gibbs energy must be negative for the system to phase split.

Figure 3 illustrates the binodal and spinodal curve on a temperature-composition plane. The region between the two spinodal points is an unstable region, so a total system with a composition in this region leads to spontaneous phase separation. The region between a binodal and spinodal point is a metastable region. A system with a composition in this region does not spontaneously separate. In this situation an activation energy is necessary for phase splitting.

The first three derivatives of the Gibbs energy of mixing are very helpful in analysis of phase separation. The first derivative of the Gibbs energy of mixing is identical to the relative chemical potential, which is expressed by Equation (12). The binodal curve, which is the locus of the phase boundary between the one-phase and two-phase regions of the binary mixture, can be determined by the following relations:

$$\mu_i^\alpha = \mu_i^\beta \quad (19)$$

or,

$$\Delta\mu_i^\alpha = \Delta\mu_i^\beta. \quad (20)$$

The second derivative of Gibbs energy of mixing is the stability condition. It predicts phase separation and spinodal curve, which is the boundary between unstable region and metastable region of the mixture.

$$\left(\frac{\partial^2 \Delta g_{mixing}}{\partial x_i^2} \right)_{P,T} = \left(\frac{\partial \Delta \mu_i}{\partial x_i} \right)_{P,T} < 0. \quad (21)$$

The third derivative of Gibbs energy of mixing, in a binary mixture, is used to find the critical or plait point. That is the point of incipient instability or incipient phase

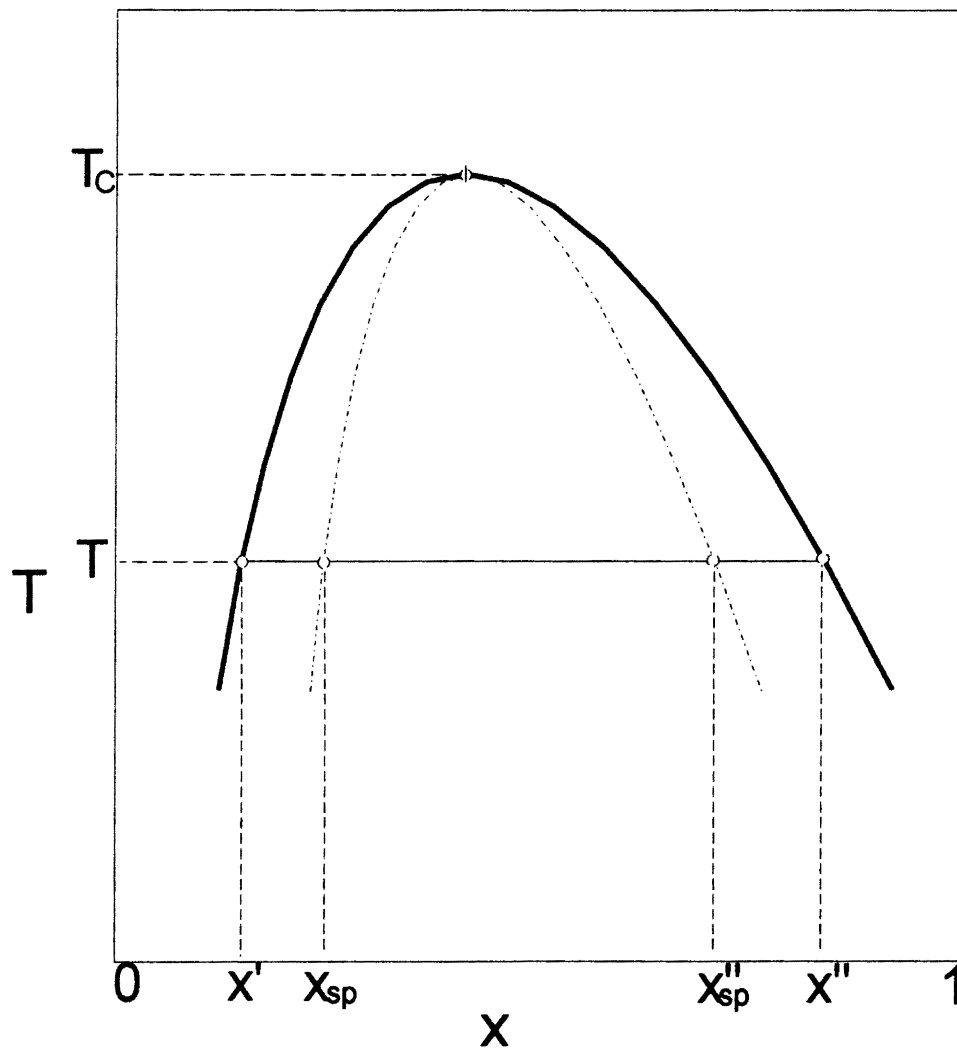


Figure 3. Typical Temperature-Composition Phase Diagram for a Binary System. The Solid and Dashed Curves Are the Binodal and Spinodal Curves, Respectively.

separation. The binodal and spinodal curves both pass through the plait point, the second and third derivatives of Gibbs energy of mixing must be zero at this point.

Polymer Solution Models

Polymer solutions are characterized as liquid mixtures wherein the molecules of one component are very much larger than those of the other one. High (1990) commented that all of the present models applied in polymer solutions can be classified into two categories: lattice models and van der Waals models. Our major concern is the application of lattice models to liquid-liquid equilibrium, the van der Waals-type models are only briefly introduced in the section.

Lattice Theory

In both the lattice models and van der Waals type models, the thermodynamic functions are related to the microscopic properties of the molecules by the canonical partition function. Generally, the canonical partition function is split into a translational contribution and an internal contribution:

$$Q = Q_{tr}Q_{int} = Q_{kin}ZQ_{int}. \quad (22)$$

The translational partition function, Q_{tr} , depends upon the positions and motions of the centers of mass of the molecules in the mixture. It is usually split into a product of two factors, one is the kinetic partition function, Q_{kin} , arising from the kinetic energy, the other factor, Z , is called the configurational partition function which arises from the potential energy. The internal partition function Q_{int} accounts for rotational, vibrational and electronic effects in the fluids. The van der Waals models use a radial distribution function to evaluate the translational partition function. The radial distribution function accounts for the probability of finding the center of another molecule as a function of the distance from the center of the first molecules. The Flory equation of state and Holten-Anderson equation of state are the examples of van der Waals type models. For lattice

models, Guggenheim (1952) stated that on comparing a mixture with its pure constituents all contributions to the free energy of mixing from the internal partition function Q_{int} will cancel out.

From a molecular viewpoint, deviations from ideal behavior in liquid solutions mainly come from two effects. First, forces of attraction between unlike molecules are qualitatively different from those between like molecules, giving rise to a nonvanishing enthalpy of mixing. Second, the differences in size or shape between unlike molecules cause a different molecular arrangement in the mixture from that for the pure liquids, giving rise to a nonideal entropy of mixing. Therefore, it is convenient to describe the behavior of the molecules in terms of these two contributions. The first contribution considers only the size and shape of the molecules; no interactions between the molecules are assumed. This contribution is the combinatorial or the athermal term. The second contribution is commonly referred to as the residual term or attractive energy term. This contribution is calculated by a product of a characteristic energy of interaction per contact and the number of contacts in the system.

Prausnitz et al. (1986) gave an insightful comment on the rule of studies of thermodynamics: "The history of modern science has shown repeatedly that a quantitative description of nature can often be achieved most successfully by first idealizing natural phenomena, i.e., by setting up a simplified model, either physical or mathematical, which crudely describes the essential behavior while neglecting details. The behavior of nature is then related to the idealized model by various correction terms which were neglected in the process of idealization."

The development of lattice models is a typical example. The last forty years have witnessed great improvement in lattice theories. In the 1940's, the Flory-Huggins model was introduced, which is a simple model based on the regular solution theory. It was only useful for mixtures of molecules which are chemically similar and which differ only in size. In the 1960's, the concept of local compositions was used to improve the results from

these "idealized" models. Without considering the intermolecular interactions the molecules in the system tend to be evenly distributed. However, the differences of intermolecular interactions tend to make the molecules segregate either with the like molecules or the unlike ones. The concept of local compositions was used to correct the combinatorial term for the nonrandomness that results from intermolecular forces, which led to a nonrandom combinatorial expression. Later, the introduction of group contributions made it possible to use the available equilibrium data to predict phase equilibria of unknown systems.

Flory-Huggins Model

The first lattice model, known as Flory-Huggins model, was independently developed by Flory (1941) and Huggins (1941, 1942). They gave a solution to the combinatorial arrangement problem for a binary system comprising a polymer and solvent. In this lattice model, one lattice site is occupied by a solvent molecule or polymer segment of similar size. No heat of mixing is assumed, and the entropy of mixing arises only from the configurational consideration disregarding the effects due to molecular interactions. The result is an expression for the athermal, configurational entropy of mixing:

$$\frac{\Delta S}{R} = \frac{\Delta G}{RT} = -n_1 \ln \phi_1 - n_2 \ln \phi_2 \quad (23)$$

where n_1 and n_2 are the number of moles of solvent and polymer molecules, respectively. Φ_1 and Φ_2 are the volume fraction of solvent and polymer, respectively.

The resulting expression for activity of the solvent is given by:

$$\ln a_1 = \ln(1 - \phi_2) + (1 - 1/r)\phi_2 \quad (24)$$

where r is the number of segments occupied by a chain of polymer molecule.

However, the assumption of no enthalpy of mixing is invalid for most solvent-polymer solutions. To correct for energetic effects, Flory (1942) suggested adding a

enthalpy term to account for interactions between lattice sites, which led to the following expression for the solvent activity:

$$\ln a_1 = \ln(1 - \phi_2) + (1 - 1/r)\phi_2 + \chi\phi_2^2 \quad (25)$$

where χ is the interaction parameter or the Flory- χ parameter. As first proposed by Flory (1942), χ is a dimensionless parameter independent of composition. For an athermal solution, χ equals zero. The solubility of the solvent can be estimated from the value of χ . A "good" solvent has a negative χ , while the solubility decreases as the value of χ increases. The critical value of χ is approximately 0.5.

The Flory-Huggins model implies that the major contribution to the Gibbs energy of mixing and, hence, the activity in polymer solutions, is entropic in nature. As has been widely recognized, there are deficiencies with the Flory-Huggins model. The most serious deficiency is the assumption of no volume change on mixing. Since the total volume that can be occupied in the lattice is fixed and no vacancy is allowed, volume changes cannot affect the thermodynamic potential functions such as the Gibbs energy.

Modifications of the Flory-Huggins Model

The Flory-Huggins model continues to be the starting point for most developments in statistical mechanical interpretation of polymer solutions and mixtures. Much of the progressive development of the classical Flory-Huggins model is in the interaction parameter term.

The interaction parameter for non-polar systems can be estimated using Hildebrand-Scott solubility parameters:

$$\chi = \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \quad (26)$$

where v_1 is the liquid molar volume of the solvent, δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively. The solubility parameter, δ_i is defined as the

square root of the cohesive energy density, which is the energy change upon isothermal vaporization of one mole of saturated liquid to ideal-gas state.

Conventionally, only dispersive forces are involved in the definition of the cohesive energy density. Hansen (1969) suggested that the cohesive energy be divided into contributions due to dispersion forces, dipole-dipole forces, and hydrogen bonding forces, so that the polar molecules or the molecules having hydrogen bonds can be modeled.

Recalling that χ is a constant in the Flory-Huggins model, no entropic contribution is associated with it. Blanks and Prausnitz (1964) extended the definition to account for the configurational contributions:

$$\chi = \chi_s + \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \quad (27)$$

where the entropic contribution to the Flory- χ , χ_s , is equal to $1/z$, z is the coordination number of the lattice.

Other modifications to the Flory-Huggins theory stem from considering the temperature, composition, or even molecular weight effect on the interaction parameter. An expression of the Gibbs energy of mixing with concentration-dependent and temperature-dependent interaction parameters for polymer solutions was independently developed by several authors (Guggenheim, 1952; Maron, 1959; Koningsveld, 1968a,b,c). The expression can be written in the following form (Koningsveld and Staverman, 1968a,b,c):

$$\frac{\Delta G_{mixing}}{RT} = \phi_1 \ln \phi_1 + \frac{\phi_2}{r} \ln \phi_2 + g(T, \phi_2) \phi_1 \phi_2 \quad (28)$$

where χ is replaced by a concentration-dependent interaction parameter $g(T, \phi_2)$.

Several forms of the new interaction parameter, $g(T, \phi_2)$, have been suggested. Koningsveld and Staverman (1968b,c) suggested using a truncated power series expansion in ϕ_2 :

$$g = g_0(T) + g_1\phi_2 + g_2\phi_2^2 \quad (29)$$

$$g_0(T) = g_{0,1} + g_{0,2} \frac{1}{T} + g_{0,3} T + g_{0,4} \ln T. \quad (30)$$

Casassa (1977) stated that the classical lattice treatment of Flory and Huggins has proven to be quite useful for modeling liquid-liquid equilibrium in solvent-polymer systems exhibiting UCST behavior. If UCST systems were the only systems of interest, minor modifications could be made to the classic theory to render it sufficient for modeling these UCST systems.

Local composition and Group contribution

The development of lattice models has been a process of adding correction terms to various features. In the 1960's, the concept of "local compositions" has allowed great progress in the development of polymer solution theories. The Flory-Huggins model does not account for the probability of overlapping chains and for the density differences between polymer and solvent. Wilson (1964) proposed a new activity coefficient correlation derived from the Flory-Huggins theory. He suggested using the "local composition" concept, which accounts for the local composition effects caused by the differences in intermolecular forces. Wilson presented the following expressions for the activities in a binary solution:

$$\ln a_1 = \ln x_1 - \ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_1} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (31)$$

$$\ln a_2 = \ln x_2 - \ln(x_2 + \Lambda_{21}x_1) + x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_1} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (32)$$

where Λ_{12} and Λ_{21} are binary adjustable parameters which are related to characteristic energy differences. The Wilson equation can be readily extended to multicomponent systems using only parameters obtained from binary systems. The main deficiency of the Wilson equation is its inability to predict partial miscibility.

The introduction of group contributions made the application of solution theory more practical in industrial applications. The basic idea of this approach is to regard the real solution as the combination of various functional groups, i.e., an acetone molecule is constructed from a methyl group and a CH_3CO group. Real solutions are composed of countless number of chemical compounds, while the number of function groups which constitute these compounds is much smaller. The basic assumption of group contributions is that a physical property of a fluid is the sum of contributions of individual functional groups in the molecules. The contribution made by one group is independent of the other group present. Thus, it is possible to predict the properties of a large variety of unknown solutions from experimental data obtained from functional group contributions.

Derr and co-workers (1959, 1962) used the group contribution approach to develop an activity coefficient expression. Derr and Deal (1969) expanded this idea to develop the Analytical-Solution-Of-Groups (ASOG) method for liquid solutions (Fredenslund et al., 1975). Abrams and Prausnitz (1975) extended Guggenheim's quasichemical treatment to the systems containing molecules of different size. The resulting UNIQUAC (Universal Quasi-Chemical) equation is composed of two parts: combinatorial and residual terms. Staverman's (1950) combinatorial entropy is used in UNIQUAC equation for athermal mixtures and the residual term is determined by Guggenheim's quasichemical theory. UNIQUAC method provides a satisfactory description for many typical mixtures in vapor-liquid equilibria and liquid-liquid equilibria, and only two adjustable parameters are required. Fredenslund et al. (1975) developed a predictive activity coefficient model based on UNIQUAC method using the concept of group contributions. The parameters reflecting the sizes and surface areas in the combinatorial term are treated as the sum of contributions from individual groups. The residual activity coefficient is calculated by contributions of constituent functional groups through combining rules. The method provided a useful tool for solving practical phase equilibrium problems as encountered in chemical process design.

Group contribution has proven to be helpful in engineering applications. It is a useful complement for solution theories because the present theoretical knowledge has not yet reached a stage where any experimental data can be predicted with high accuracy without empirical parameters.

Other Lattice Models

Oishi and Prausnitz (1978) extended the UNIFAC model to polymer solutions by including a contribution to the free volume differences between the polymer and solvent molecules, which was suggested by Flory's equation-of-state theory. For mixtures of ordinary liquids, free volume makes only a negligibly small contribution. However, for mixtures of solvents and polymers, Oishi and Prausnitz reported that it is often significant. The expression for the activity coefficient of a solvent in a polymer is given by:

$$\ln a_1 = \ln a_1^{comb} + \ln a_1^{res} + \ln a_1^{fv} \quad (33)$$

where the free volume contribution is given by:

$$\ln a_1^{fv} = -3c_1 \ln \left[\frac{\bar{v}_1^{1/3} - 1}{\bar{v}_m^{1/3} - 1} \right] - c_1 \left(\frac{\bar{v}}{\bar{v}_m} - 1 \right) \left(\frac{\bar{v}^{1/3}}{\bar{v}_m^{1/3} - 1} \right). \quad (34)$$

The Oishi-Prausnitz approach was compared with the present model in the application of vapor-liquid equilibrium in the previous work, the present model is generally as accurate or slightly more accurate than the Oishi-Prausnitz method (High, 1990). The application of the Oishi-Prausnitz method requires the densities of the pure solvent and pure polymer at the temperature of the mixture of interest and the structure of the solvent and polymer. But since polymer densities data are rare, as pointed out by High (1990), it is a serious weakness of the Oishi-Prausnitz method.

There is growing interest in what have been called "lattice fluid" models. In these models, the assumption is made that a fluid is a mixture of molecules and holes. In essence, they are lattice models in which some of the lattice sites are occupied while others

remain empty (holes). This approach was introduced by Sanchez and Lacombe (1974). They developed a lattice-fluid model in terms of an equation-of-state approach. Panayiotou and Vera (1982a,b) also developed an equation of state based on lattice-fluid theory. In this model nonrandomness of the arrangement of molecules is taken into account. High and Danner (1989, 1990a) modified the Panayiotou-Vera equation of state and combined it with a group contribution technique to make the equation of state predictive. The model is known as the GCLF model (Group Contribution Lattice-Fluid model). The development of the GCLF model is based on the Panayiotou-Vera model in the same manner as the UNIFAC method is based on the UNIQUAC model. The Sanchez-Lacombe and GCLF equations of state will be described in more detail in the next chapter, and their prediction ability for pure components and liquid-liquid equilibrium will be compared.

CHAPTER III

THE SANCHEZ-LACOMBE AND THE GROUP CONTRIBUTION LATTICE-FLUID MODELS

The purpose of this chapter is to describe the two lattice models: the Sanchez-Lacombe (S-L) and the Group Contribution Lattice Fluid (GCLF) models. Both the Sanchez-Lacombe and the GCLF models are based on the Lattice-fluid theory and well-developed Guggenheim's quasichemical theory. Before discussing the two models the basics of statistical mechanics and lattice-fluid theory will be introduced.

Statistical Mechanics and Lattice-Fluid Theory

Statistical mechanics describes the behavior of macroscopic systems in terms of microscopic properties of particles such as atoms, molecules, etc. The bridge linking the microscopic properties and the macroscopic world is the partition function. The Helmholtz energy is related to the partition function by Equation (1).

Instead of the commonly used canonical ensemble, Sanchez and Lacombe (1976) started from a pressure ensemble to develop an equation of state. The Gibbs energy and the configurational partition function are related by:

$$G = -kT \ln Z(T, P) \quad (35)$$

where,

$$Z(T, P) = \sum_V \sum_E \Omega(E, V, N) \exp[-\beta(E + PV)] \quad (36)$$

where $\Omega(E, V, N)$ is the number of configurations in a system of N molecules having a configurational energy E and volume V . In the Sanchez-Lacombe equation of state, the

number of configurations, Ω , is evaluated by Guggenheim's expression (Guggenheim, 1952) for random mixing:

$$\Omega = \left[\prod_i \left(\frac{\delta_i}{\sigma_i} \right)^{N_i} \right] \frac{N_r!}{N_h! \prod N_i!} \left(\frac{N_q!}{N_r!} \right)^{z/2} \quad (37)$$

At the limit of infinitely large coordination number, the number of configurations is approximated as:

$$\Omega \cong (1/f_o)^{N_o} (\omega/f)^N \quad (38)$$

where ω is the number of configurations available to one molecule in the close-packed state, $f_o = N_o / (N_o + rN)$ and $f = rN / (N_o + rN)$ are fraction of empty sites and fraction of occupied sites, respectively. The expression above with the large z limit is called "Flory approximation" because a similar formula was first obtained by Flory (Sanchez and Lacombe, 1976b).

The GCLF model is based on the canonical ensemble, Guggenheim's expression (1952) for nonrandom mixing is used for the canonical partition function:

$$Q = \left[\prod_i \left(\frac{\delta_i}{\sigma_i} \right)^{N_i} \right] g_c g_{nr} \exp\left(-\frac{E}{kT}\right) \quad (39)$$

where δ_i and σ_i are the flexibility parameter and symmetry number of molecule i , respectively. These parameters are used to characterize the configuration of a molecule. In a binary system, the random combinatorial, g_c , and the nonrandomness combinatorial, g_{nr} , are given by (Guggenheim, 1952):

$$g_c = \frac{N_r!}{N_h! \prod N_i!} \left(\frac{N_q!}{N_r!} \right)^{z/2} \quad (40)$$

$$g_{nr} = \frac{\bar{N}_{11}^o! \bar{N}_{22}^o! \left(\frac{\bar{N}_{12}^o!}{2} \right)}{\bar{N}_{11}! \bar{N}_{22}! \left(\frac{\bar{N}_{12}!}{2} \right)} \quad (41)$$

where \bar{N}_{ij}^o , \bar{N}_{ij}^c are the numbers of contacts between the molecules of the same type and that of different types in the case of random mixing, respectively. \bar{N}_{ii} , \bar{N}_{ij} are the numbers of contacts between the molecules of the same type and that of different types in the case of nonrandom mixing, respectively.

Unlike the Flory-Huggins model, the volume occupied by one segment, or one "mer", is not necessarily equal to the volume of the solvent. Holes are allowed to exist in lattice fluid models. The assumptions and description of lattice-fluid model in an square lattice square are introduced as below:

1. A lattice consists of N_i molecules containing r_i mers and N_h empty sites, the total number of lattice sites can be expressed as:

$$N_r = r_i N_i + N_h. \quad (42)$$

2. The number of interaction sites available to a molecule containing r segments (a r -mer) is the sum of neighboring sites adjacent to each site along the chain, excluding the sites occupied by bonded neighbors. The number of these interactions can be represented by zq_i , where z is the coordination number and q_i is the effective chain length, which is related to the molecule's surface area. The parameter q_i is defined by the expression:

$$zq_i = (r_i - 2)(z - 2) + 2(z - 1) = r_i(z - 2) + 2. \quad (43)$$

3. The total number of nearest neighbor pairs in the system is $(z/2)N_r$, but the interactions occur only between the nearest neighbors. Thus, the total number of interaction sites available in the system is:

$$zN_q = z(N_h + q_i N_i). \quad (44)$$

4. In the lattice-fluid models, there are two types of lattice sites: "holes" and "mers". The interactions between hole-hole, hole-mer and bonded mer-mer pairs are assigned a zero energy, the only nonzero interaction energy occurs between nonbonded mer-mer interactions.

Sanchez-Lacombe Model

Sanchez and Lacombe (1974) developed a new equation of state based on the lattice-fluid theory. In the Sanchez-Lacombe model, random mixing of molecules and holes are assumed. Mixing rules for the volume of the molecules are necessary because the volume of one mer of a pure component in pure state is not identical to that in the mixture.

Mixing Rules

One characteristic of the volume change upon mixing is that the volume occupied by one molecule, which is termed close-packed volume, is conserved. If a molecule i occupies r_i^0 sites in the pure state and has a close-packed molecular volume $r_i^0 v_i^*$, it will occupy r_i sites in the mixture and have the same average closed-packed volume V^* .

$$r_i^0 v_i^* = r_i v^* = V^*. \quad (45)$$

v^* is the average close-packed molecular volume in the mixture. A close packed mass density is defined so that:

$$\rho_i^* = M_i / V^* = M_i / (r_i^0 v_i^*) \quad (46)$$

where M_i is the molecular weight of component i .

Another characteristic is that the total number of pair interactions in the close-packed mixture is equal to the sum of the pair interactions of the components in their close-packed pure states.

$$rN = r_1^0 N_1 + r_2^0 N_2 = r_1 N_1 + r_2 N_2. \quad (47)$$

The calculation of the total energy of a lattice is based on the assumption of random mixing. The total energy in a lattice is expressed in terms of the characteristic interaction energy, ε^* :

$$E = -(z\varepsilon/2)N_r f^2 = -\varepsilon^* N_r f^2. \quad (48)$$

the derivation of Equation (48) involves the assumption that the coordination number z is infinite, the probability of the pair mer-mer interaction, f , equals $(r_i N_i / N_r)^2$. ϵ is the mer-mer interaction energy, and ϵ^* , defined as the total interaction energy per mer, characterizes the interaction energy between two mers of the same component.

The parameters, r_i^o and v_i^* , characterize the size of the molecules of the pure components. For the molecular parameters v^* and r in the mixtures, mixing rules are required to obtain these quantities:

$$r = \sum r_i^o x_i = \sum r_i x_i \quad (49)$$

$$v^* = \sum \phi_i^o v_i^* \quad (50)$$

where,

$$\phi_i^o = \frac{r_i^o N_i}{\sum r_i^o N_i} = \frac{r_i^o x_i}{\sum r_i^o x_i}, \quad (51)$$

$$x_i = N_i / \sum N_i. \quad (52)$$

The mixing rule for evaluating ϵ^* in the mixtures assumes that the characteristic interaction energy is pairwise additive:

$$\epsilon^* = \sum \sum \phi_i \epsilon_{ii}^* - kT \phi_i \phi_j \chi \quad (53)$$

where the molecular volume fraction in close-packed state, ϕ_i , is defined as:

$$\phi_i = \frac{r_i N_i}{\sum r_i N_i} = \frac{r_i N_i}{rN}, \quad (54)$$

$$\chi = (\epsilon_{ii}^* + \epsilon_{jj}^* - 2\epsilon_{ij}^*) / kT. \quad (55)$$

A geometric mean formula has been used to evaluate ϵ_{ij}^* , however, as already pointed out by Sanchez and Lacombe (1976b), an adjustable parameter is necessary in the determination of interaction energy between unlike molecules:

$$\epsilon_{ij}^* = z(\epsilon_{ii}^* \epsilon_{jj}^*)^{1/2}. \quad (56)$$

the next two chapters will show the adjustable parameter affect the phase behavior predicted significantly.

The reduced volume, which is used in the Sanchez-Lacombe equation of state, is defined as:

$$\tilde{v} \equiv V / rNv^* = (N_h + rN)v^* / rNv^* = 1 / \tilde{\rho}. \quad (57)$$

Equation of State and Chemical Potential Expression

Based on the Flory's approximation, the Gibbs energy is obtained, then the equation of state can be found by minimization of the Gibbs energy with respect to reduced volume \tilde{v} , which yields:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0. \quad (58)$$

the equation of state for pure components and the mixtures are identical. The reduced parameters in Equation (58) are given by:

$$\tilde{T} = T / T^*, \quad (59)$$

$$T^* = \varepsilon^* / k, \quad (60)$$

$$\tilde{P} = P / P^*, \quad (61)$$

$$P^* = \varepsilon^* / v^*. \quad (62)$$

The chemical potential μ_1 in a binary mixture is:

$$\begin{aligned} \mu_1 = kT \{ \ln \phi_1 + (1 - r_1 / r_2) \phi_2 + r_1^o \tilde{\rho} [\chi + (1 - v_1^* / v_2^*) \lambda_{12}] \phi_2^2 \} + \\ r_1^o kT \{ -\tilde{\rho} / \tilde{T}_1 + \tilde{H}_1 \tilde{v} / \tilde{T}_1 + \tilde{v} [(1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r_1^o} \ln \tilde{\rho}] \} \end{aligned} \quad (63)$$

where,

$$\lambda_{12} = 1 / \tilde{T}_1 - 1 / \tilde{T}_2 + (\phi_1 - \phi_2) \chi = -\lambda_{21}, \quad (64)$$

$$\tilde{T}_i = T / T_i^*, \quad \tilde{P}_i = P / P_i^*. \quad (65)$$

The equation of state has at most three density roots depending on the conditions of the system. If three roots are found, the highest root corresponds to a liquid root; the lowest root corresponds to a vapor root; the middle root corresponds to a maximum in the Gibbs energy of the system (Sanchez-Lacombe, 1976a). In the liquid-liquid equilibrium

calculations, the liquid root is used to calculate the chemical potentials of the components in the liquid phases.

In the Sanchez-Lacombe model, a fluid is characterized by three molecular parameters: v^* , r and ϵ^* . Sanchez-Lacombe (1976a,b) determined these parameters by fitting saturated vapor pressure and liquid density data. First, the close packed mass density is estimated from crystalline densities of the components, thus T^* and P^* can be defined as functions of ϵ^* and r . The fitting procedure is performed by satisfying the equation of state and the equations of equality of chemical potentials. For polymer liquids, the molecular parameters are determined by a nonlinear least-square regression of liquid density data. The molecular parameters are listed in Tables I and II.

Group Contribution Lattice Fluid Model

Panayiotou and Vera (1982) developed an equation of state based on a constant lattice site volume for all molecule segments and a finite coordination number. High and Danner (1989, 1990a) modified the Panayiotou-Vera equation of state and combined it with a group contribution technique to make the equation of state predictive, which led to the Group Contribution Lattice-Fluid equation of state (GCLF EOS).

Pure-Component Equation of State

Both Panayiotou-Vera and High-Danner equations of state are based on the canonical partition function which is given by Equation (39). Panayiotou and Vera (1982b) showed that nonrandomness does not increase the accuracy of the prediction of pure component properties and set the nonrandomness factor to unity. Therefore, a random arrangement of molecules is assumed for pure components.

The assumptions of the lattice arrangement in the GCLF and the Panayiotou-Vera models are identical to that in Sanchez-Lacombe's model, however, there are differences in the definition of lattice volume and coordination number. In the Sanchez-Lacombe model,

TABLE I
MOLECULAR PARAMETERS OF SOLVENTS FOR
THE SANCHEZ-LACOMBE EQUATION OF STATE*

	P^* (atm)	T^* (k)	v^* $\text{cm}^3 \text{mol}^{-1}$	ρ^* g cm^{-3}	r^0
Methane	2450	224	7.52	0.50	4.26
Ethane	3230	315	8.00	0.64	5.87
Propane	3090	371	9.84	0.69	6.50
n-Butane	3180	403	10.40	0.736	7.59
n-Pentane	3060	441	11.82	0.755	8.09
Isopentane	3040	424	11.45	0.765	8.24
Cyclopentane	3750	491	10.53	0.867	7.68
n-Hexane	2940	476	13.28	0.775	8.37
Cyclohexane	3780	497	10.79	0.902	8.65
n-Heptane	3050	487	13.09	0.800	9.57
n-Octane	3040	502	13.55	0.815	10.34
n-Decane	3000	530	14.47	0.837	11.75
n-C ₁₁ H ₂₄	2990	542	14.89	0.846	12.40
n-C ₁₂ H ₂₆	2970	552	15.28	0.854	13.06
n-C ₁₇ H ₃₆	2830	596	17.26	0.88	15.83
Benzene	4380	523	9.80	0.994	8.02
Toluene	3970	543	11.22	0.996	8.50
H ₂ O	26520	623	1.93	1.105	8.46
Methanol	11860	468	3.24	0.922	10.72
Ethyl acetate	4520	468	8.49	1.052	9.87
n-Butyl acetate	3890	498	10.50	1.003	11.03
Diethyl ether	3580	431	9.88	0.870	8.62
Acetone	5260	484	7.54	0.917	8.40
Methyl ethyl ketone	4410	513	9.54	0.913	8.28
Acetic acid	8500	562	5.43	1.164	9.51
n-Stearic acid	2710	691	20.92	0.912	14.91

* The parameters are calculated by Sanchez and Lacombe (1976a).

TABLE II
 MOLECULAR PARAMETERS OF POLYMERS FOR
 THE SANCHEZ-LACOMBE EQUATION OF STATE*

	P^* (MPa)	T^* (K)	v^* $\text{cm}^3 \text{mol}^{-1}$	ρ^* kg m^{-3}
PDMS	320	476	13.1	1104
PVAC	590	509	9.64	1283
PIB	643	354	15.1	974
HDPE	649	425	12.7	904
PMMA	696	503	11.5	1269
PS	735	357	17.1	1105

* The parameters are calculated by Sanchez and Lacombe (1978).

the volume of a lattice is an adjustable parameter and varies from the pure state to the mixture. Mixing rules are necessary for the volume for lattice sites in mixtures. In the Panayiotou-Vera theory, the volume of a lattice site is arbitrarily fixed to be equal to the volume of a methylene group in polyethylene (v_h equals $9.75 \times 10^{-3} \text{ m}^3/\text{kmol}$).

Unlike the Sanchez-Lacombe model, the number of lattice sites occupied by a molecule is not regressed from experimental data, it is a function of the molecular reference volume.

$$r_i = v_i^* / v_h. \quad (66)$$

therefore, only one parameter, v_i^* , is used to characterize the size of the molecule in the present model, compared to two parameters in the Sanchez-Lacombe model.

In the GCLF model, the coordination number, z , is assumed to be 10 for normal fluids, while the Sanchez-Lacombe theory assumes infinite coordination number. Therefore, the calculation of the number of molecule-molecule interactions, and hence the total energy of the system, is different. In a lattice, the total number of interaction sites available is $(z/2)N_r$, the pair probability of nonbonded, molecule-molecule interaction is $(q_i N_i)^2 / N_r N_q$. The number of interactions between like molecules is denoted by N_{ii}^o .

$$E = N_{ii}^o \epsilon_{ii} = \frac{z(q_i N_i)^2}{2 N_q} \epsilon_{ii}. \quad (67)$$

The equation of state in reduced variables is:

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln \frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{z}{2} \ln \frac{\tilde{v}_1 + q_1 / r_1 - 1}{\tilde{v}_1} - \frac{\theta_1^2}{\tilde{T}_1} \quad (68)$$

where r_1 and q_1 can be calculated by Equation (66) and Equation(43), the fraction of interaction sites available to a molecule, θ_1 , is defined as:

$$\theta_1 = q_1 N_1 / N_q. \quad (69)$$

The reduced parameters in the equation of state are given by:

$$\tilde{T}_1 = \frac{2RT}{z\epsilon_{11}}, \quad (70)$$

$$\tilde{A}_1 = \frac{2Pv_h}{z\varepsilon_{11}}, \quad (71)$$

$$\tilde{v}_1 = \frac{v}{v_1^*} = \frac{v_h(N_h + \eta N_1)}{v_1^*} \quad (72)$$

where the characteristic interaction energy, ε_{11} , is the segment-segment average interaction energy over the length of the molecule.

The chemical potential expression for pure component is given as:

$$-\frac{\mu_1}{RT} = \ln \frac{\delta_1}{\sigma_1} + \ln q_1 + \ln \frac{(1-\theta_1)^\eta}{\theta_1} + \frac{\theta_1}{\tilde{I}_1} (q_1 + \eta \tilde{v}_1 \theta_1) \quad (73)$$

where the flexibility parameter δ_1 and the symmetry number σ_1 are independent of composition, temperature and density, therefore they can be canceled out in the equilibrium calculation.

The equation of state for pure component is characterized by two adjustable parameters: a characteristic molecular interaction energy ε_{11} , and a characteristic molecular volume v^* .

Equation of State for Mixtures

In the equation of state for mixtures, the nonrandom combinatorial is added to account for the effect of the nonrandom distribution of the molecules; however, the holes are assumed to be randomly distributed. Notice in Equation (41), \bar{N}_{ii} and \bar{N}_{ij} are used to account for the numbers of contacts between segments of molecules of the same type and that of different type, respectively. These parameters are determined from:

$$\bar{N}_{ii} = \bar{N}_{ii}^o \dot{\Gamma}_{ii} = \frac{zq_i N_i}{2} \bar{\theta}_i \dot{\Gamma}_{ii} \quad (74)$$

$$\bar{N}_{ij} = \bar{N}_{ij}^o \dot{\Gamma}_{ij} \quad (75)$$

where the molecular surface fraction on a hole free basis, $\bar{\theta}_i$, is defined as:

$$\bar{\theta}_i = \frac{zq_i N_i}{zqN} \quad (76)$$

where $\dot{\Gamma}_{ij}$ and $\bar{\Gamma}_{ij}$ are nonrandomness parameters. $\dot{\Gamma}_{ij}$ represents the nonrandomness between unlike molecules, and is calculated through the quasichemical expression. The nonrandomness parameter in a binary system is given by:

$$\dot{\Gamma}_{12} = \frac{2}{1 + \sqrt{1 - 4\bar{\theta}_1\bar{\theta}_2(1 - \dot{G})}} \quad (77)$$

where,

$$\dot{G} = \exp\left[\frac{\theta(\epsilon_{11} + \epsilon_{22} - \epsilon_{12})}{RT}\right] = \exp\left[\theta\frac{\Delta\epsilon}{RT}\right], \quad (78)$$

and

$$\theta = \sum_i \theta_i = 1 - \theta_h. \quad (79)$$

In a binary system, the nonrandomness parameters must satisfy the conservation of number of contact sites in the mixture, as given by Panayiotou and Vera (1982a):

$$\bar{\theta}_1\dot{\Gamma}_{11} + \bar{\theta}_2\dot{\Gamma}_{12} = \bar{\theta}_2\dot{\Gamma}_{22} + \bar{\theta}_1\dot{\Gamma}_{12} = 1. \quad (80)$$

The equation of state for mixtures in reduced variables is identical to that for the pure component case.

$$\frac{\tilde{P}}{\tilde{T}} = \ln \frac{\tilde{v}}{\tilde{v}-1} + \frac{z}{2} \ln \frac{\tilde{v}_1 + q/r - 1}{\tilde{v}} - \frac{\theta^2}{\tilde{T}} \quad (81)$$

where,

$$\tilde{T} = \frac{2RT}{z\epsilon^*}, \quad (82)$$

$$\tilde{P} = \frac{2Pv_h}{z\epsilon^*}, \quad (83)$$

$$v^* = \sum x_i v_i^*, \quad (84)$$

$$r = \sum x_i r_i, \quad (85)$$

$$q = \sum x_i q_i, \quad (86)$$

$$\theta = \sum \theta_i. \quad (87)$$

In a binary mixture, the characteristic reference volume is calculated by Equation (84), the characteristic interaction energy is calculated by:

$$\varepsilon^* = \bar{\theta}_1 \varepsilon_{11} + \bar{\theta}_2 \varepsilon_{22} - \bar{\theta}_1 \bar{\theta}_2 \bar{\Gamma}_{12} \Delta \varepsilon, \quad (88)$$

$$\Delta \varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2 \varepsilon_{12}. \quad (89)$$

In the application of this model to vapor-liquid equilibrium, a geometric mean is used to calculate ε_{12} . However, in this research of liquid-liquid equilibrium, it is of limited utility.

The parameter ε_{12} is calculated by the following expression:

$$\varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}} (1 - k) \quad (90)$$

where k is sometimes called the Prausnitz's k factor. It is observed that k significantly affects the phase behavior in the liquid-liquid equilibrium calculation.

The relative chemical potential of component 1 is given:

$$\begin{aligned} \frac{\Delta \mu_1}{RT} = & \ln \frac{v_1^*}{v^*} + \ln \frac{\tilde{v}_1}{\tilde{v}} + q_1 \ln \left(\frac{\tilde{v}}{\tilde{v} - 1} \frac{\tilde{v}_1 - 1}{\tilde{v}_1} \right) \\ & q_1 \left(\frac{2 \theta_{1,p} - \theta_1}{\bar{T}_1} - \frac{\theta}{\bar{T}} \right) + \frac{zq}{2} \ln \bar{\Gamma}_{11} \end{aligned} \quad (91)$$

where $\theta_{1,p}$ is the surface area fraction of pure component 1 at the same temperature and pressure as the mixture. The quantities with index 1 are calculated from the equation of state for pure component at the same temperature and pressure. The expression for μ_2 is easily obtained by interchanging the indices 1 and 2.

The procedure for liquid-liquid equilibrium calculation using the GCLF EOS is similar to that using the Sanchez-Lacombe EOS, liquid root obtained from the equation of state for mixture is used to calculate the component chemical potentials by Equation (91). It is also required that the reduced volume, reduced temperature, and surface area fraction for the pure component are calculated from the pure-component equation of state before the calculation of chemical potentials.

The molecular parameters are calculated from the group contribution method. Besides the characteristic molecular interaction energy, ϵ_{ii}^* and molecular reference volume, v_i^* , one more adjustable parameter, k , which is used to adjust the binary molecular interaction energy, is introduced in liquid-liquid equilibrium calculation.

Group Contribution Technique

High and Danner (1989, 1990a) calculated molecular parameters for each compound by fitting the saturated liquid density and the vapor pressure data using the equation of state and chemical potential expression at several temperatures. The molecular parameters are expressed in terms of functional group parameters. A second regression can be performed to calculate functional group parameters from molecular parameters. High and Danner (1989, 1990a) formulated the following correlations for determining the group contributions of reference volume and interaction energy parameters.

$$\epsilon_{ii,T} = \sum_k \sum_m \Theta_k \Theta_m \sqrt{e_{kk,T} e_{mm,T}} \quad (92)$$

$$v_{i,T}^* = a_T + \sum_k v_k^{(i)} R_{k,T} \quad (93)$$

where e_{kk} is the group interaction energy, and v_k is the number of the functional group. The group surface area fractions, Θ_k , is calculated from the UNIFAC dimensionless surface area parameters, Q_k :

$$\Theta_k^{(i)} = \frac{v_k^{(i)} Q_k}{\sum_m v_m^{(i)} Q_m} \quad (94)$$

R_k in Equation (93) is the group volume parameter. The molecular reference volume can be determined by linearly interpolating with the group values at 300 and 400 K, where a_{300} is 0.02123 and a_{400} is 0.02237.

The molecular parameters ϵ_{ij} and v^* are determined from a series of n-alkanes, branches, cycloalkanes, arenes, ethers, ketones, monochlorinated alkanes and water evaluated at 300 K and 400 K. The temperature dependence of the molecular parameters can be determined by linearly interpolated using values at 300 K and 400 K. Parameters for 23 function groups are available from previous work (High, 1990; Parekh, 1991) and are listed in Table III. The calculation of molecular parameters requires only the structures of molecules.

Summary

Both the Sanchez-Lacombe and the GCLF equations of state are based on the lattice-fluid model. The assumption of holes in the lattice, enable the models to describe both the gas phase and condensed phase. The main differences between the Sanchez-Lacombe and GCLF models are summarized as follows:

First, an important feature in the Sanchez-Lacombe model is that the Flory approximation is applied, which states that the coordination number is assumed to be infinite; In the GCLF model, the coordination number is assumed, somewhat arbitrarily, to be 10. Second, random mixing of the component molecules and holes is assumed in Sanchez-Lacombe model; The randomness assumption is also applied in the pure component state in GCLF model. In the mixture, nonrandomness of component molecules is accounted for, but the effects of nonrandomness of the holes are ignored. Third, in the Sanchez-Lacombe model, a lattice site of one component has a different volume in the pure state and in the mixture, thus mixing rules for lattice sites are necessary. The requirement can be eliminated by fixing the volume of a lattice, based on these considerations. In the GCLF model all lattices are assumed to have the same fixed volume.

TABLE III
GROUP CONTRIBUTIONS FOR THE GROUP
CONTRIBUTION LATTICE FLUID EQUATION OF STATE

	$e_{kk,300}$ (kJ/kmol)	$e_{kk,400}$ (kJ/kmol)	$R_{k,300}$ (m ³ /kmol)	$R_{k,400}$ (m ³ /kmol)	Q_k
CH ₃	640.87	640.79	0.01596	0.01628	0.848
CH ₂	943.33	987.68	0.01524	0.01498	0.540
CH	2209.38	2708.76	0.01311	0.01175	0.228
C	5378.38	7731.24	0.01071	0.08463	0.150
cy-CH ₂	895.44	911.40	0.01260	0.01256	0.540
cy-CH	1727.56	2043.28	0.01255	0.01199	0.228
cy-C	4069.49	5993.67	0.01242	0.01126	0.150
AC-H	975.38	971.62	0.01059	0.01073	0.400
AC-CH ₃	994.41	1022.68	0.02465	0.02456	0.968
AC-CH ₂	1471.59	1581.80	0.02351	0.02302	0.660
AC-CH	2780.93	3281.53	0.02220	0.02060	0.348
AC-C	5452.73	6771.48	0.01985	0.01700	0.270
-O-	868.47	679.56	0.00760	0.00798	0.240
H ₂ O	949.12	1154.31	0.07611	0.07544	1.400
CH ₃ =O-	1237.10	1171.50	0.03117	0.03254	1.488
-CH ₂ C=O-	1542.00	1509.50	0.02968	0.03039	1.180
-CHCl-	1364.400	1387.30	0.04865	0.05036	0.952
-CH=CH- *	1054.480	1110.63	0.02412	0.02390	0.867
-COO- *	1341.670	1308.80	0.02236	0.02327	1.200
-OH- *	1867.920	1466.87	0.00685	0.00752	1.200
-CH ₂ NH- *	1280.830	1215.76	0.02490	0.02443	0.936
>SiO< *	1064.430	1343.84	0.03376	0.03285	0.4657
AC-CO- *	2181.980	2275.41	0.02105	0.02263	0.760

The parameters are calculated by High (1990a) and Parekh* (1991).

CHAPTER IV

STABILITY ANALYSIS

The objective to evaluate the capabilities of the two models in liquid-liquid equilibria can be separated into two steps. The first step is to evaluate the abilities of the two models in predicting phase separation. If the models are able to describe the phase behavior, then the second step is to compute the compositions in the coexisting phases at equilibrium. In this chapter, the abilities of the two models in predicting phase separations were investigated by performing stability analysis. Another reason to perform stability analysis first is that the region for performing calculations of compositions in the two coexisting phases is not known a priori. Therefore, stability analysis is necessary to perform phase equilibrium calculation more effectively.

Stability Conditions

The thermodynamic criterion for a stable, single-phase, binary mixture is that the second derivative of the Gibbs energy of mixing with respect to concentration must be positive. The stability conditions can also be expressed in terms of chemical potentials, the stability of a homogeneous phase in a binary mixture requires:

$$\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,p} > 0, \left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,p} > 0 \quad (\text{spinodal}). \quad (95)$$

When the equations above are violated, the system phase splits. Referring to Figure 4, a system with a μ_1 versus x_1 like Curve 1 is stable over the entire range of composition, since $(\partial\mu_1/\partial x_1)_{T,P} > 0$ for all x_1 from 0 to 1. In the case of Curve 2, the system is unstable between two spinodal points S' and S'', and thus phase separation occurs. If the

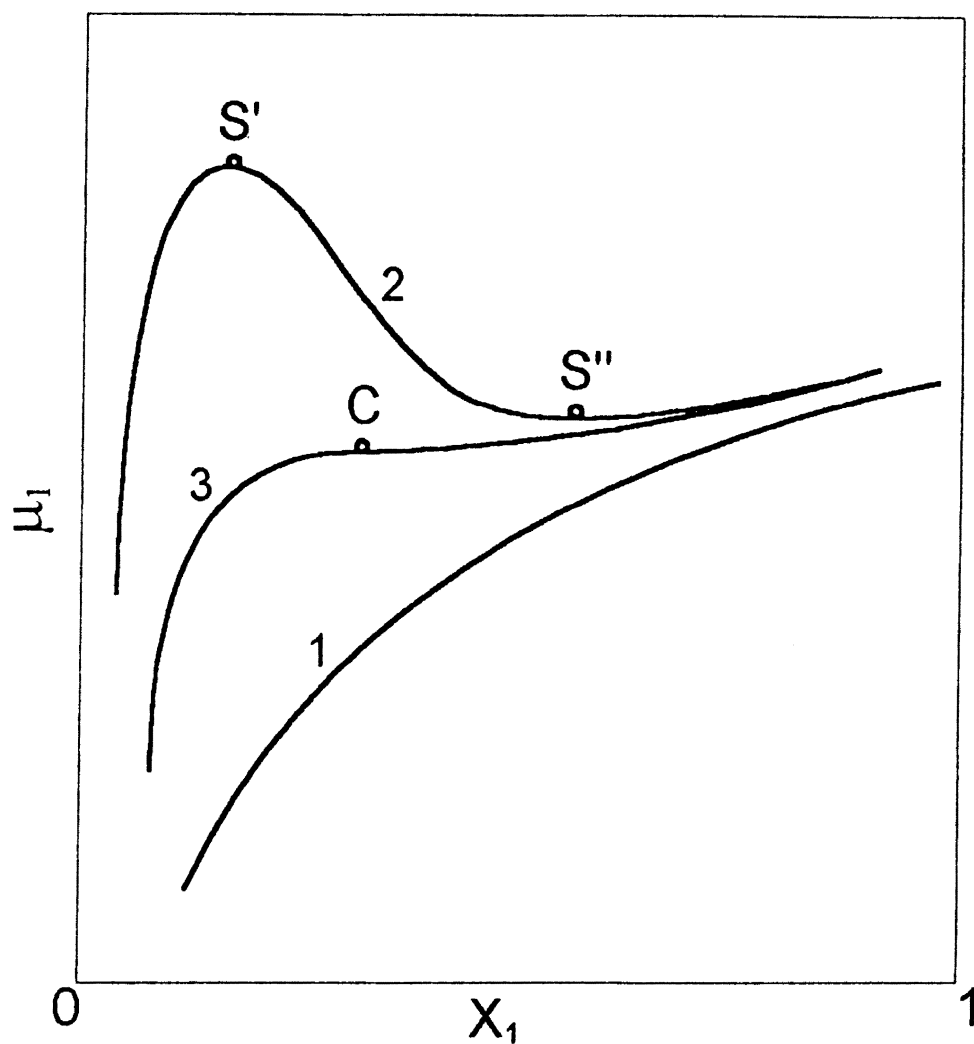


Figure 4. Diagram of Chemical Potentials Versus Molar Composition Representing Phase Transition. Curves 1, 2, 3 Represent Complete Miscibility, Partial Miscibility and Incipient Phase Separation, Respectively. (Reprinted from Michio, 1982)

temperature is varied at a fixed pressure, the curve of μ_1 undergoes a change from a shape like Curve 1 to one like Curve 2. In the course of this change the system should pass through a stage represented by Curve 3 at a certain intermediate temperature. The inflection point C on Curve 3 is the critical point. At point C, the first two derivatives of chemical potential are zero. The chemical potentials can be plotted against compositions in all regions (temperature and pressure) of interest, and the regions of instability can be determined graphically by studying the shapes of chemical potentials.

Stability Analysis Using the Sanchez-Lacombe Equation of State

In the application of the Sanchez-Lacombe and GCLF models in liquid-liquid equilibrium, the geometric mean mixing rule for estimating the binary interaction energy is of limited usefulness. The binary interaction energy needs to be adjusted to give an adequate representation for phase separation. This chapter shows how adjustable parameters affects the phase behavior by performing a stability analysis.

The stability conditions for a homogeneous phase in a binary mixture are given by Equation (95). In the Sanchez-Lacombe equation of state, Sanchez and Lacombe (1976b) stated that the stability conditions are satisfied if:

$$\frac{\partial^2 g}{\partial \phi_1^{\sigma^2}} > 0 \quad \text{or} \quad \frac{\partial^2 g}{\partial \phi_2^{\sigma^2}} > 0. \quad (96)$$

For a binary mixture, this stability condition reduces to:

$$\tilde{p} \left\{ 2 \frac{\phi_1 \phi_2}{\phi_1^{\sigma} \phi_2^{\sigma}} \left[\frac{\phi_1 \phi_2}{\phi_1^{\sigma} \phi_2^{\sigma}} \chi - \left(\frac{\phi_1}{\phi_1^{\sigma}} - \frac{\phi_2}{\phi_2^{\sigma}} \right) \lambda_{12} \right] + \tilde{T} \Psi^2 P^* \beta \right\} < \left(\frac{\phi_2}{\phi_2^{\sigma}} \right)^2 \left(\frac{1}{r_1^{\sigma} \phi_1^{\sigma}} \right) + \left(\frac{\phi_1}{\phi_1^{\sigma}} \right)^2 \left(\frac{1}{r_2^{\sigma} \phi_2^{\sigma}} \right) \quad (97)$$

where χ is given by Equation (55), and where,

$$\lambda_{12} = \frac{1}{\tilde{T}_1} - \frac{1}{\tilde{T}_2} + (\phi_1 - \phi_2)\chi = -\lambda_{21}, \quad (98)$$

$$\psi = \tilde{\rho} \frac{\phi_1 \phi_2}{\phi_1^o \phi_2^o} \lambda_{12} - \left(\frac{1}{r_1^o} - \frac{1}{r_2^o} \right) + \frac{P\tilde{v}}{kT} (v_1^* - v_2^*), \quad (99)$$

$$P^*\beta = \tilde{v}^2 / \left\{ \tilde{T}\tilde{v} \left[1/(\tilde{v} - 1) + 1/r \right] - 2 \right\}. \quad (100)$$

Sanchez and Lacombe (1976b, 1978) termed the left hand side of Equation (97) as a combination of an energetic contribution and an entropic contribution from the equation of state, and the right hand side as the combinatorial entropy contribution. The behavior of the two terms in stability analysis of the HDPE/n-pentane system is shown in Figure 5, the combinatorial entropy term is not a function of adjustable parameter z , while the curve of the left hand side term moves up or down as the z varies. As the value of z changes, the region of instability which satisfy Equation (97) enlarges or shrinks.

It can be shown how the adjustable parameters affect the phase behavior if we perform the stability analysis in a three-dimensional diagram. The LHS's and RHS's of the Equation (97) can be viewed as the surfaces over the temperature-composition plane, as shown in Figure 6. Figure 6 shows the stability analysis using the Sanchez-Lacombe EOS. Any cross section at a specific temperature will be reduced to the equivalent of Figure 5. The surface representative of the LHS in Equation (97) is a curved surface convex downward with low and high temperature ends at higher levels. The surface slopes from the dilute polymer side to the dilute solvent side. The RHS surface represents the combinatorial entropy, which is convex downward, with dilute polymer and dilute solvent ends at high levels. The LHS surface moves up or down as the value of z varies, while the RHS surface remain constant. The two surfaces do not intersect at high z values. As the value of z decreases, the LHS surface moves up and intersects with RHS surface. The overlapping area is the region of instability because the Equation (97) is violated. The curves that the two surfaces intersect are the spinodal curves. For example, in the liquid-

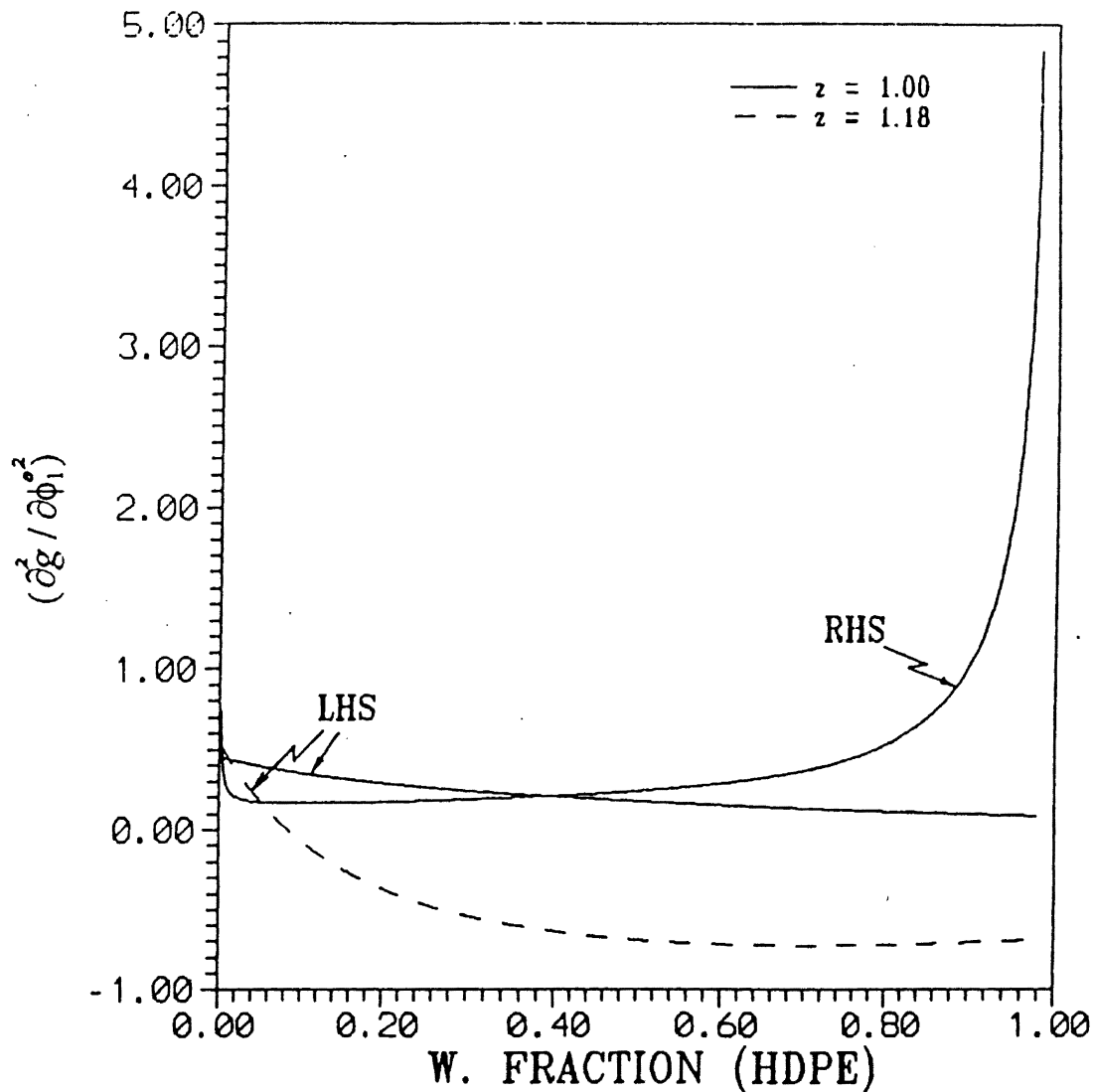


Figure 5. Stability Analysis in the HDPE/n-Pentane system ($P=1\text{atm}$, $T=380\text{K}$). The RHS of Equation (97) is Not a Function of z , the Curve of the LHS Moves Up As the Value of z Decrease. The Portion Where the LHS is Larger Than the RHS is the Region of Instability.

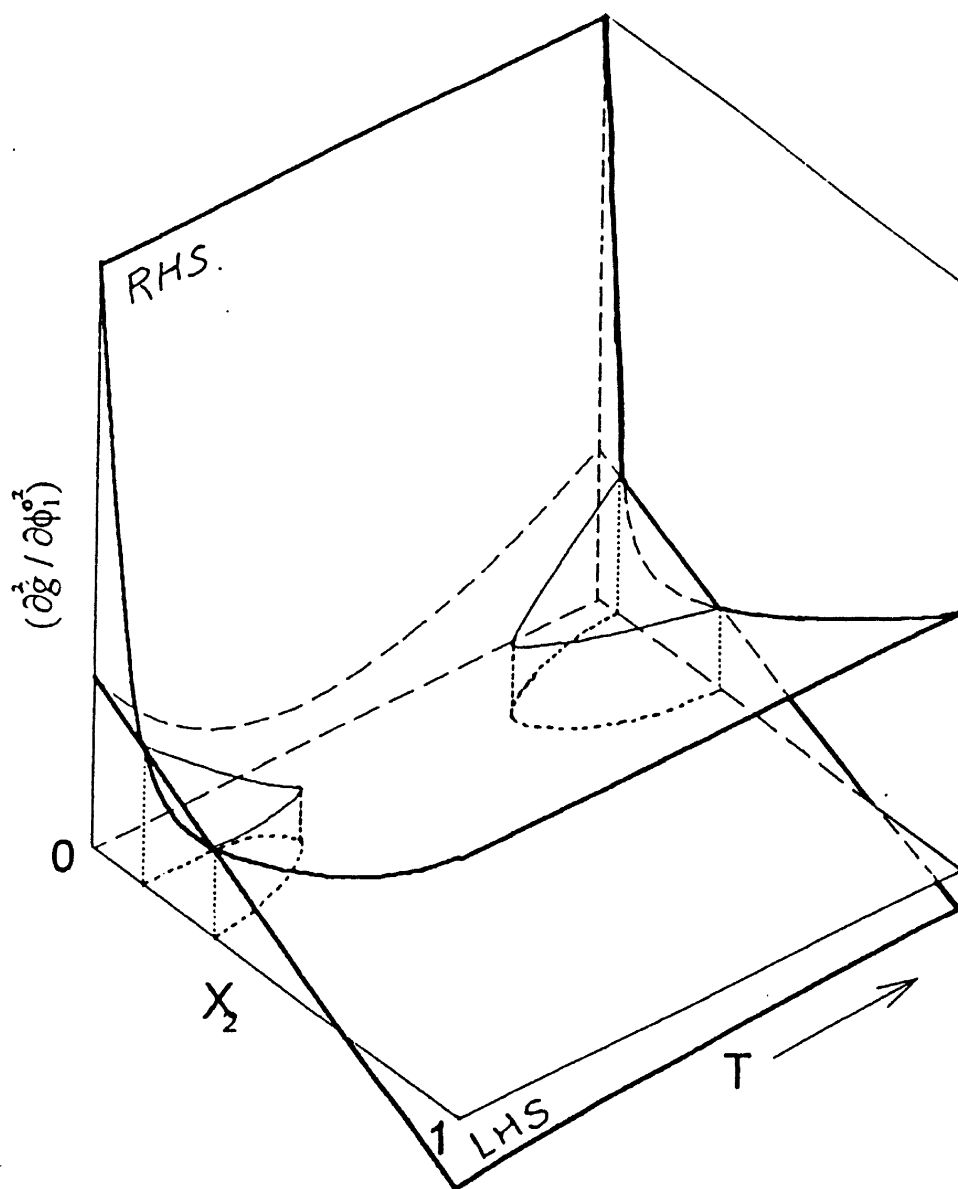


Figure 6. Stability Analysis Using Sanchez-Lacombe Model on A Temperature-Composition Plane. The Upper and Lower Surfaces Represent RHS and LHS Surfaces, Respectively. The LHS Surface Moves Up As the Value of z Decreases. In This Case the LHS Surface Intersects the RHS Surface At Lower and Higher Temperature Regions, Which Implies LCST and UCST Exist in One System.

liquid equilibrium of the PS/cyclohexane system at atmospheric pressure, for the z values smaller than 1 and larger than 0.96, LHS surface touches the RHS surface at high temperature, and thus a LCST results. The LCST decreases as the value of z decreases. At a z of 0.96, the LHS surface touches the RHS surface at the low temperature region, and therefore, both LCST and UCST are observed in one system. A one percent change in z causes more than a 10 K change of critical solution temperature. As the value of z decreases further, at about z equals 0.959, the LCST and UCST merge to form an hourglass curve. Figure 6 shows only the case where both LCST and UCST exist in the system.

Stability Analysis Using GCLF Equation of State

A similar stability analysis can be obtained in the GCLF equation of state. In the GCLF model, a nonrandom distribution of molecules is assumed. The chemical potential expression has one term sensitive to the interaction energy and one term which is weak a function of the interaction energy. The derivative of $\Delta\mu_2$ with respect to x_2 can be obtained and yields:

$$-\frac{zq_1q_2^2}{2q^2\dot{\Gamma}_{22}} \left[\frac{\dot{\Gamma}_{12} - 1}{\theta_2^2} - \frac{\bar{\theta}_1}{\theta_2} \left(\frac{\partial \dot{\Gamma}_{12}}{\partial \theta_2} \right) \right] < \frac{v_1^*}{x_2 v^*} - \frac{1}{\bar{v}} \frac{\partial \bar{v}}{\partial x_2} - \frac{q_2}{\bar{v}(\bar{v}-1)} \left(\frac{\partial \bar{v}}{\partial x_2} \right) - q_2 \left(\frac{1}{\bar{T}_2} + \frac{1}{\bar{T}} \right) \frac{\partial \theta}{\partial x_2} - \frac{zq_2\theta}{2RT} \frac{\partial \varepsilon^*}{\partial x_2} \quad (101)$$

where $\partial \bar{v} / \partial x_2$ can be evaluated from the equation of state,

$$\frac{\partial \bar{v}}{\partial x_2} = \left[\frac{z}{2} \zeta - \frac{zq_1q_2\theta^2}{2RTq^2} \psi + \frac{z\theta}{2RT} (\alpha\theta + 2\varepsilon^*) \chi \right] \bigg/ \left[\frac{1}{\bar{v}(\bar{v}-1)} + \frac{z(q/r-1)}{\bar{v}(\bar{v}+q/r-1)} - \frac{z\theta}{2RT} (\alpha\theta + 2\varepsilon^*) \frac{v^*q}{v_h N_q^2} \right] \quad (102)$$

where,

$$\frac{\partial \theta}{\partial x_2} = -\frac{v^* q}{v_h N_q} \left(\frac{\partial \tilde{v}}{\partial x_2} \right) - \chi, \quad (103)$$

$$\frac{\partial \varepsilon^*}{\partial x_2} = \frac{q_1 q_2}{q^2} \psi + \alpha \frac{\partial \theta}{\partial x_2}, \quad (104)$$

$$\frac{\partial \dot{\Gamma}_{12}}{\partial \bar{\theta}_2} = \frac{\dot{\Gamma}_{12}^2 \left[(1 - \dot{G})(\bar{\theta}_1 - \bar{\theta}_2) - \bar{\theta}_1 \bar{\theta}_2 \left(\frac{\partial \dot{G}}{\partial \bar{\theta}_2} \right) \right]}{\sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}}, \quad (105)$$

$$\frac{\partial \dot{G}}{\partial \bar{\theta}_2} = \frac{q^2}{q_1 q_2} \frac{\dot{G} \Delta \varepsilon_{12}}{RT} \left(\frac{\partial \theta}{\partial x_2} \right), \quad (106)$$

$$\alpha = \frac{\bar{\theta}_1^2 \bar{\theta}_2^2 \Delta \varepsilon_{12}^2 \dot{\Gamma}_{12}^2 \dot{G}}{RT \sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}}, \quad (107)$$

$$\beta = \frac{\dot{\Gamma}_{12}^2 (1 - \dot{G})(\bar{\theta}_1 - \bar{\theta}_2)}{\sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}}, \quad (108)$$

$$\psi = -\varepsilon_{11} + \varepsilon_{22} + \dot{\Gamma}_{12} \Delta \varepsilon_{12} (\bar{\theta}_2 - \bar{\theta}_1) - \bar{\theta}_1 \bar{\theta}_2 \Delta \varepsilon_{12} \beta, \quad (109)$$

$$\chi = \frac{(v_2^* - v_1^*) \tilde{v} q / v_h + (\eta_1 - \eta_2) q + (q_1 - q_2) N_h}{N_q^2}, \quad (110)$$

$$\zeta = \frac{(q_2 - q_1) r - (\eta_2 - \eta_1) q}{(\tilde{v} + q / r - 1) r^2}. \quad (111)$$

Figure 7 shows that the right hand side of Equation (101) is a weak function of k while the left hand side is quite sensitive to the k . As the k values increase, the miscibility region enlarges, and the spinodal and binodal moves up or down in the temperature-composition phase diagram.

Similar phenomena are observed if the stability analysis for the GCLF EOS is extended to three-dimensional diagram. The LHS surface is concave downward and slants from the dilute polymer and low temperature side to dilute solvent and high temperature side. At the limit of dilute solvent, the LHS term reduces to zero. The RHS is convex

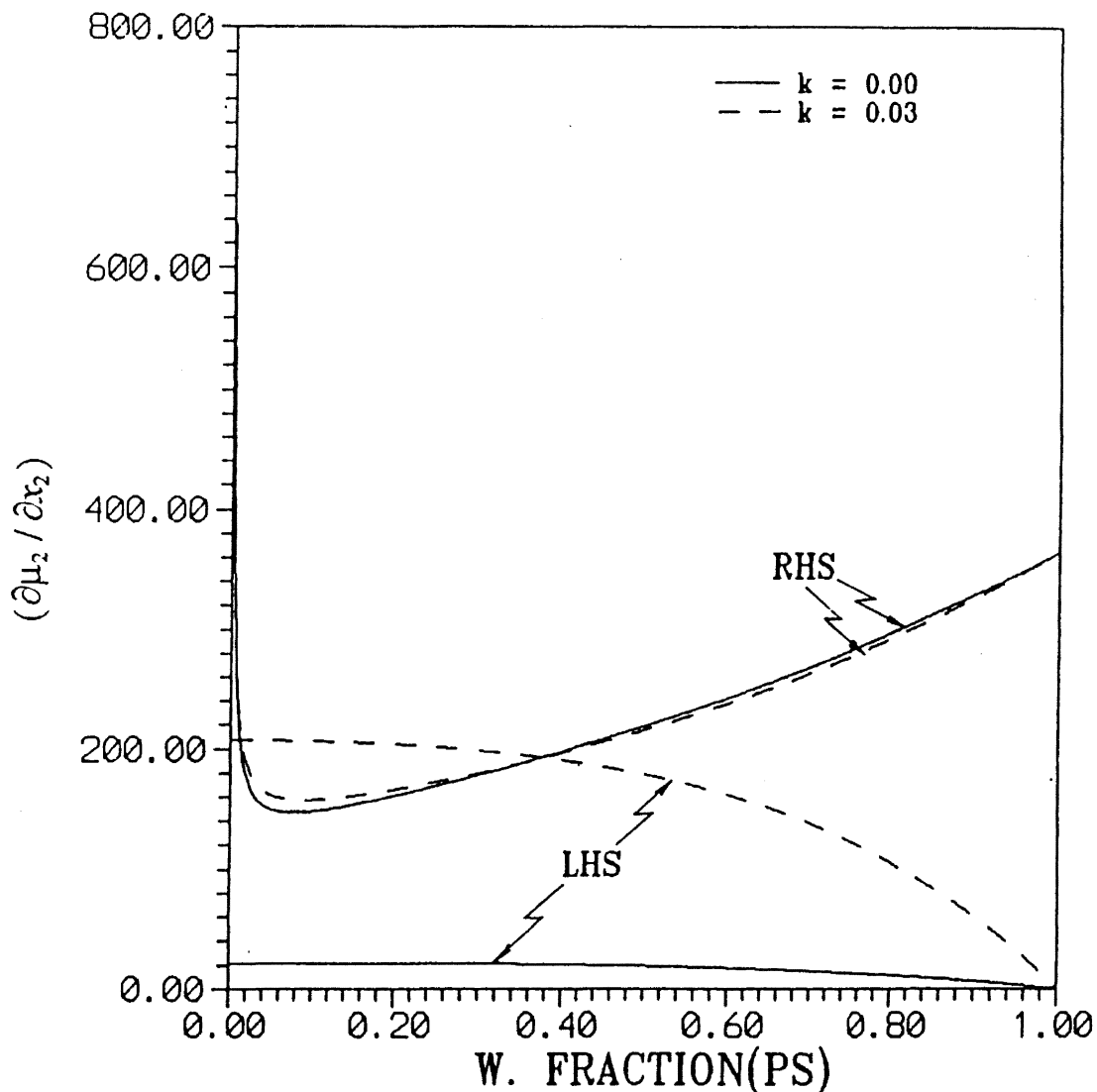


Figure 7. Stability Analysis in PS/Acetone system ($P=20$ bar, $T=350K$). The RHS of Equation (102) is a Weak Function of k . The LHS is Sensitive to the Value of k and Its Curve Moves Up As k Increases. At $k=0.00$ No Phase Splitting Occurs Because Equation (102) is Satisfied. At $k=0.03$ One Portion of The Curve of the LHS is Larger Than the RHS, Phase Separation Occurs.

downwards and slants from low temperature to high temperature, as shown in Figure 8. For example, in the liquid-liquid equilibrium of the PS/cyclohexane system, for k equal to zero, no phase splitting is observed. As the value of k increases, the LHS surface moves up while the RHS surface is almost unchanged, the two surfaces cross at high temperature region which implies a lower critical solution temperature. As the k increases, the LCST decreases in the temperature axis. At about 0.004 the LHS and RHS surfaces intersect at both low and high temperature regions, thus both UCST and LCST are observed. At a k of 0.0055, the hourglass diagram is observed. Figure 8 illustrates the case when both LCST and UCST are present in one system.

Summary

Both models are able to predict LCST and UCST by adjusting the cross interaction energy term, but small changes in adjustable parameters dramatically affect the prediction of phase behavior.

Stronger interaction energies between unlike molecules (higher z value or lower k value) will likely predict only LCST. Note from Equations (56) and (90), as the z value decreases or k value increases, the interaction energies between unlike molecules decrease. As the cross interaction energies decrease, both LCST and UCST are observed in one system. As the interaction energies between unlike molecules decrease further, LCST and UCST curves merge and an hourglass phase diagram is predicted. No closed-loop phase diagram is predicted based on the systems investigated.

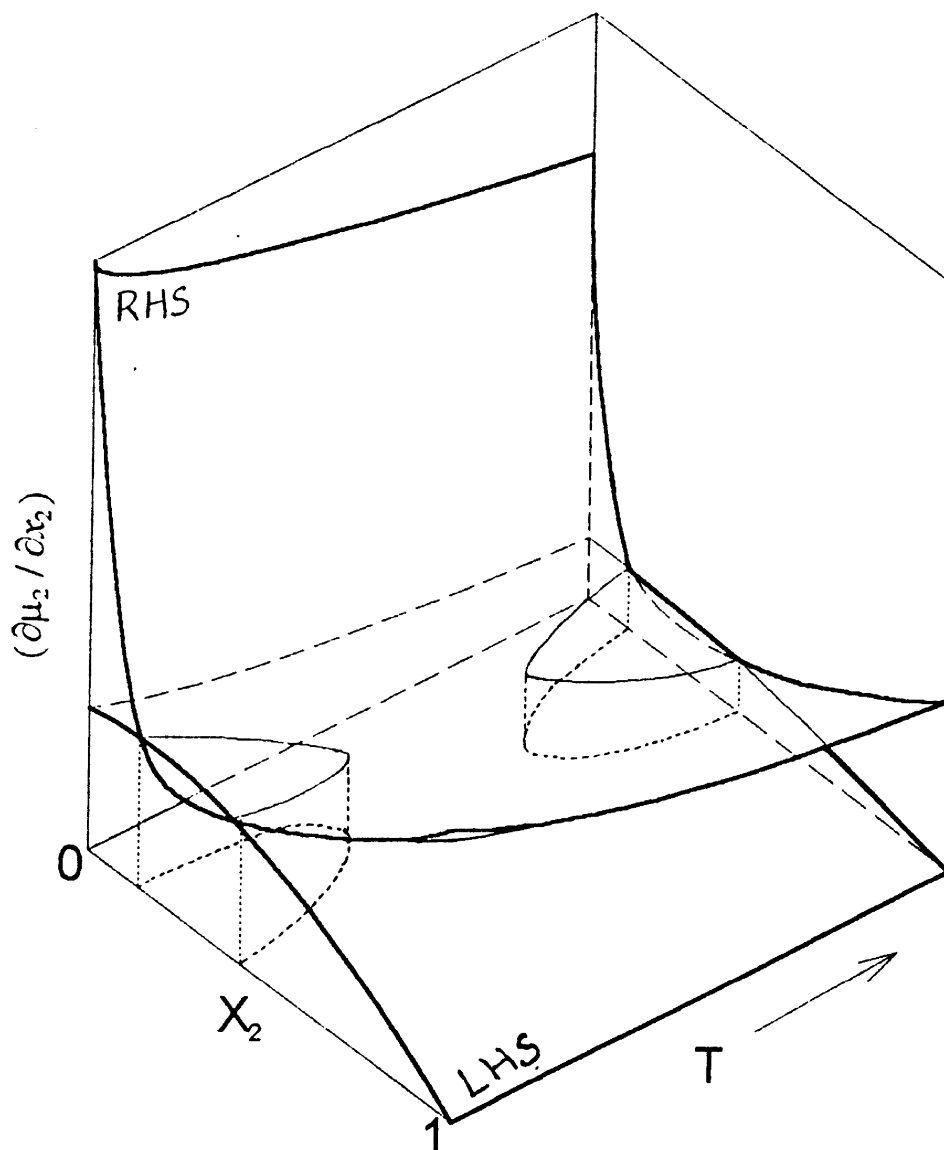


Figure 8. Stability Analysis Using GCLF Model on A Temperature-Composition Plane. The Upper and Lower Surfaces Represent the RHS and LHS Surfaces, Respectively. The LHS Surface Moves Up As the Value of k Increases. In This Case the LHS Surface Intersects the RHS Surface At Lower and Higher Temperature Regions, Which Implies LCST and UCST Exist In One System.

CHAPTER V

EVALUATION OF THE SANCHEZ-LACOMBE
AND GCLF MODELS

Chapter 4 has already investigated the abilities of the Sanchez-Lacombe and the GCLF equations of state in predicting phase separation in binary mixtures. The objective of this chapter is to calculate the compositions in the coexisting phases using the two equations of state. The pure component properties have already been investigated in previous works (Sanchez-Lacombe, 1976a; High, 1990; High and Danner, 1990a). The comparison of the two models is somewhat difficult because of the lack of data for liquid-liquid equilibria. Moreover, it is hard to find a system in which the molecular parameters are available for both the Sanchez-Lacombe and the GCLF equations of state. First, the general thermodynamic algorithm is provided. Then, the predictions of upper and lower critical solution temperatures in the low molecular weight system with the two models are discussed. The abilities of describing the critical solution temperatures in polymer-solvent systems are discussed, the evaluation of the two equations of state in polyisobutylene-solvent, HDPE-solvent, poly(ethylene glycol)-water and polystyrene-solvent systems are given. The capabilities of describing the pressure dependence and the molecular weight dependence of the critical solution temperatures are also discussed.

General Thermodynamic Algorithm

The main interest in this research work is to extend the GCLF model to liquid-liquid equilibria and compare with the Sanchez-Lacombe model and experimental data. In this

section, the general algorithm for calculating the binodal curve, spinodal curve and critical temperature is discussed.

Problem Formulation

By the phase rule, two degrees of freedom are allowed in a binary two-phase system. Thus, the compositions in the phases are fixed if the pressure and temperature are specified. By specifying the pressure and temperature, the composition can be found by solving equations originating from the criterion for phase equilibrium. As already described in Chapter 2, two criteria for phase equilibrium are given: Gibbs energy minimization criterion and equality of fugacity (chemical potential) criterion. Considering the characteristics of the equations of state, and hence the computational complexity, the equality of chemical potential criterion is chosen for development of the phase equilibrium algorithm. The relations can be expressed as:

$$\mu_1^I(x_1^I) = \mu_1^{II}(x_1^{II}), \quad (112)$$

$$\mu_2^I(x_2^I) = \mu_2^{II}(x_2^{II}). \quad (113)$$

The indices 1 and 2 represent solvent and polymer, respectively. It is also required that the sum of the concentrations be unity:

$$x_1^I + x_2^I = 1, \quad (114)$$

$$x_1^{II} + x_2^{II} = 1. \quad (115)$$

Equations (114) and (115) can be integrated into Equations (112) and (113). Equations (112) and (113) can be expressed as functions of the solvent concentrations in the two phases (x_1^I , x_1^{II}). Therefore, there are two equations and two unknowns.

Computation Scheme

One option of the computer algorithm developed in the research is the search for the regions of miscibility and partial miscibility. One routine is included in the computer

program to search the temperature region at specified pressure to locate where homogeneous regions and where phase splitting occurs. To use the computer program for the searching work, one has to specify the pressure of the system, the molecular weight of the polymer, the pure component parameters, the adjustable parameters (z or k) and the temperature range for searching. The pure component parameters are specified in the input data files and other quantities are entered from the screen.

When phase separation occurs at a certain temperature and pressure, the two components are distributed into two phases differing in concentration. Our objective is to search for the compositions in the two phases so that the component chemical potentials are equal. Figure 9 illustrates the computing scheme. In this figure curves of μ_1 and μ_2 are constructed as functions of the composition of the solvent. The interval (b,c) is thermodynamically unstable because $\partial\mu_1/\partial x_1$ and $\partial\mu_2/\partial x_2$ are both negative. The rectangular construction (uvxy) represents the solution of the concentrations of component 1 in the two equilibrating phases. Component 1 is distributed in such way that its chemical potentials in the two phases are equal. A locus of the two composition points (x_1' , x_1'') at different temperatures forms the binodal curve.

It is noted that the points where $(\partial\mu_1/\partial x_1)$ and $(\partial\mu_2/\partial x_1)$ are zero at exactly the same values of concentrations. According to Gibbs-Duhem equation, in a binary mixture, the following equation should be satisfied:

$$x_1(\partial\mu_1/\partial x_1) + x_2(\partial\mu_2/\partial x_1) = 0 \quad (116)$$

It is obvious that when $(\partial\mu_1/\partial x_1)$ is zero, $(\partial\mu_2/\partial x_1)$ also goes to zero. An adequate theory should satisfy this condition.

A nonlinear equation solver routine called "DNEQNF" in the IMSL Math/Lib was used to solve the Equations (112) and (113). The "DNEQNF" routine is based on a modification of Levenberg-Marquardt method. As can be seen in the Figure 9, a,b,c,d are defined by the values of extrema in μ_1 or μ_2 . x_1' must be in (a,b) and x_1'' in (c,d). In order

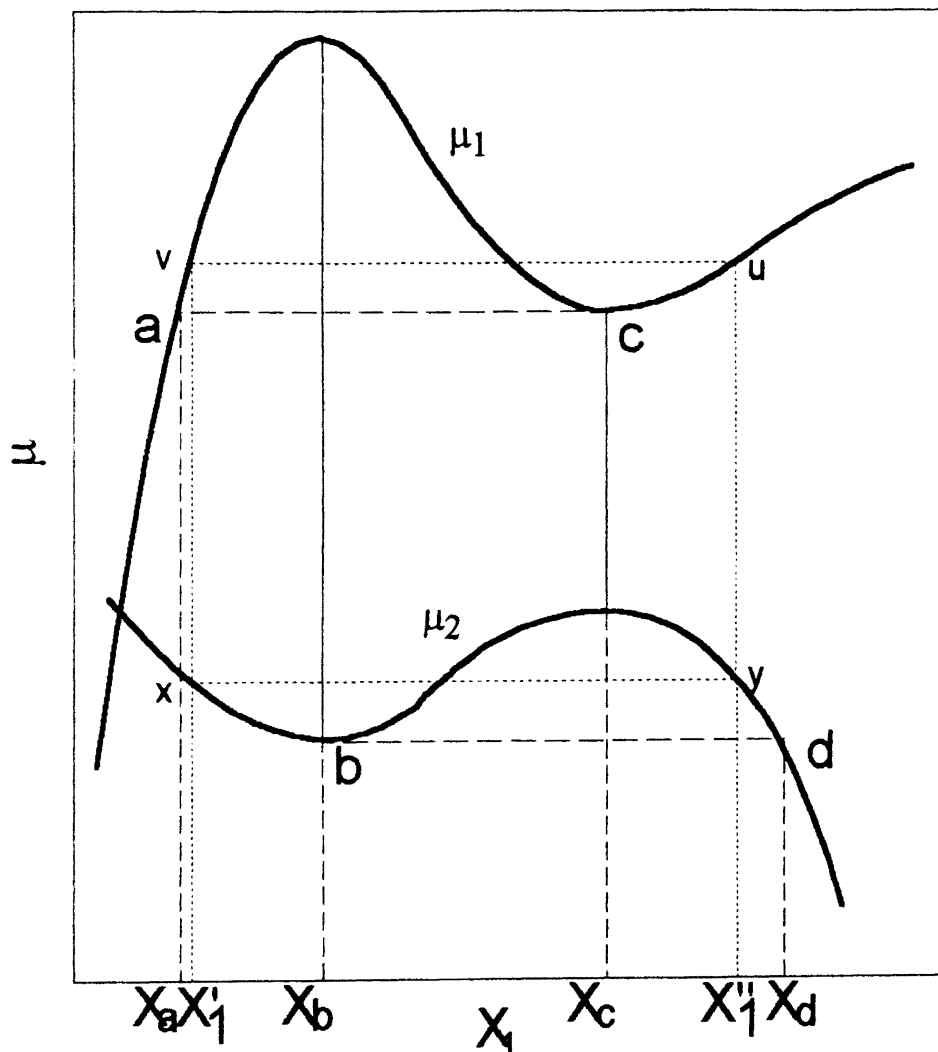


Figure 9. Chemical Potentials (μ_1 and μ_2) As Functions of Composition x_1 In a Binary System Undergoing Phase Splitting. The Rectangular Construction (uvxy) Represent the Solution of the Concentrations of Component 1 In the Coexisting Phases. (Modified from Sanchez and Lacombe, 1976b)

to avoid the trivial solution, this constraint is employed in the calculation. Values of x_a and x_d are used as initial guess for component 1 in the computing scheme.

It is observed that the magnitude of chemical potential of the polymer is significantly larger than that of the solvent. Scaling is introduced to make chemical potentials for the solvent and polymer have the same magnitude. The chemical potential for each segment, as suggested by Hsu and Prausnitz (1970), is used throughout the calculation. The chemical potentials in Equations (112) and (113) are divided by the length of the molecules (r_1 and r_2) before calling the IMSL routines to solve the nonlinear equations.

The calculation of the spinodal curve is much easier. The stability conditions, (97) and (102), can be rearranged leading to the following functions:

$$f_{sl} = -\tilde{\rho} \left\{ 2 \frac{\phi_1 \phi_2}{\phi_1^o \phi_2^o} \left[\frac{\phi_1 \phi_2}{\phi_1^o \phi_2^o} \chi - \left(\frac{\phi_1}{\phi_1^o} - \frac{\phi_2}{\phi_2^o} \right) \lambda_{12} \right] + \tilde{T} \psi^2 P^* \beta \right\} \\ + \left(\frac{\phi_2}{\phi_2^o} \right)^2 \left(\frac{1}{r_1^o \phi_1^o} \right) + \left(\frac{\phi_1}{\phi_1^o} \right)^2 \left(\frac{1}{r_2^o \phi_2^o} \right) \quad (117)$$

$$f_{scf} = \frac{zq_1 q_2^2}{2q^2 \Gamma_{22}} \left[\frac{\Gamma_{12} - 1}{\theta_2^2} - \frac{\bar{\theta}_1}{\theta_2} \left(\frac{\partial \Gamma_{12}}{\partial \theta_2} \right) \right] + \frac{v_1^*}{x_2 v^*} - \frac{1}{v} \frac{\partial v}{\partial x_2} \\ - \frac{q_2}{\tilde{v}(\tilde{v} - 1)} \left(\frac{\partial \tilde{v}}{\partial x_2} \right) - q_2 \left(\frac{1}{\tilde{T}_2} + \frac{1}{\tilde{T}} \right) \frac{\partial \theta}{\partial x_2} - \frac{zq_2 \theta}{2RT} \frac{\partial \epsilon^*}{\partial x_2} \quad (118)$$

The functions above are the derivatives of chemical potentials. The curves of the functions are convex downward. In the two-phase region, each function will have a minimum that is less than zero and there are two concentrations that lead the functions to be zero. Our aim is to find the solutions of the two concentrations that form the spinodal curves. The bisection method is used in the computer program.

Recall that the definition of the critical point is that the densities in coexisting phases becomes identical at certain temperature and pressure. Thermodynamically, the second

and third derivatives of Gibbs energy is zero at the critical point, the spinodal curve and binodal curve coincide at the critical point. Calculation of the second and third derivatives of Gibbs energy requires significant computer time. An alternative way can be used which finds the temperature that leads to the equality of the concentrations obtained in the spinodal calculation. The searching of the critical temperature starts from the two-phase region. The program takes a small temperature step (0.01 K) to approach the critical temperature, and it calculates the concentrations of spinodal points at each temperature step. If the difference between the two concentrations is less than some convergence criterion ($|x_1' - x_1''| < 0.0001$), the program determines that the temperature is the critical temperature, otherwise the calculation continues by taking one more temperature step in the direction approaching the critical temperature. If one temperature step causes the change from two-phase region to one-phase region, the average of the temperatures of the last two iterations is taken as the critical temperature.

The binary interaction energies were determined by minimizing the deviations between the calculated and experimental critical solution temperatures. For the systems with only a LCST or a UCST, the adjustable parameters were determined by the experimental critical temperature. The optimization of the parameters was done via the golden section method. The objective function can be expressed as:

$$f(\zeta) = (T_{\text{exp}} - T_{\text{cal}})^2 \quad (119)$$

where ζ refers to the adjustable parameters, z or k .

For the system where both a LCST and a UCST exist, the adjustable parameters were determined by forcing the deviations of the LCST and UCST to be minimum.

Though the tabulated parameters were given only in three or four significant digits, all calculations were carried out with double precision. Care should be taken with the convergence criteria in the intermediate computation. It is safe to set the convergence criteria in the intermediate calculation to be 10^{-12} .

The computer programs were verified by reproducing the phase diagrams in the previous works. The computer program using the Sanchez-Lacombe model was used to reproduce the temperature-composition phase diagrams in Sanchez and Lacombe's paper (Lacombe and Sanchez, 1976b), which included a vapor-liquid phase diagram (n-butane/n-heptane system) and two liquid-liquid phase diagrams (aniline/cyclohexane and propane/stearic acid systems). The computer program for the GCLF model was verified by reproducing the diagrams of solvent activity coefficients versus composition in the polystyrene\cyclohexane and poly(ethylene glycol)\water systems in vapor-liquid equilibrium (High, 1990).

Some Observation from the Application of Sanchez-Lacombe EOS

The Sanchez-Lacombe equation of state is a simple model. The Sanchez-Lacombe model has some problems representing the binodal curve because of some thermodynamic discrepancies in the expression of chemical potential and the stability condition.

Note that in Figure 9, the points where $(\partial\mu_1/\partial x_1)$ and $(\partial\mu_2/\partial x_1)$ are zero are exactly at the same values of concentrations according to the Gibbs-Duhem equation. In the application of Sanchez-Lacombe EOS, the concentrations satisfying the conditions that $(\partial\mu_1/\partial x_1)$ and $(\partial\mu_2/\partial x_1)$ equal zero are not equal. The equation of state can represent the binodal curves in low molecular weight systems, but the discrepancy causes problems in finding binodal curves near the critical region. The convergence criterion has to be set larger in order to find a solution.

The Sanchez-Lacombe model usually fails to represent binodal curves in polymer-solvent systems with high molecular weight polymers. In a polymer-solvent system, the chain length of a polymer is much larger than that of a solvent ($r_2 > r_1$), the temperature-composition phase diagram becomes very distorted. When r_2 becomes very large the miscibility and the critical point occurs when the solution is very dilute in polymer ($\phi_2 \cong 0$

) (Sanchez and Lacombe, 1978). In the case of a mixture with very high molecular weight polymer, a diagram of chemical potentials versus composition like Figure 9 cannot always be obtained. Figure 10 is an example of the PIB/n-pentane system, where chemical potentials are plotted against concentration. As the molecular weight of PIB increases, the maximum of the curve of polymer chemical potential goes to the dilute polymer region, and the minimum of the curve of solvent chemical potential disappears. A rectangle like that in Figure 9 cannot be constructed; therefore, equal chemical potentials in the two phases cannot be found and thus the binodal curve cannot be obtained.

Low Molecular Weight Systems

Figure 11 is a comparison of the predictions for the liquid-liquid equilibrium of methanol/cyclohexane system using the Sanchez-Lacombe EOS (abbreviated as S-L EOS in all diagrams) and the GCLF EOS. The binary interaction energies used in the two models are determined by matching the theoretical UCST to the experimental UCST of 319 K. All the binary interaction energies used in low molecular weight systems are determined by fitting the theoretical critical temperatures to the experimental ones. The Sanchez-Lacombe EOS predicts a much narrower binodal curve than the experimental curve. The GCLF EOS predicts a broader UCST curve and tends to predict a higher concentration of methanol than the experiments. Figure 12 compares the UCST binodal curves of methanol/n-heptane system. It shows the Sanchez-Lacombe EOS predicts a much narrower binodal curve and the curve shifts to a lower concentration of methanol. The GCLF equation of state gives a poor representation in the n-heptane-rich phase. There are substantial discrepancies between the theoretical curves predicted with the two models and the experimental data.

Figure 13 and 14 are comparisons for the systems of acetic acid/decane and acetic acid/dodecane, respectively. The Sanchez-Lacombe model predicts much narrower binodal curves in these systems, and the theoretical binodal curve shifts to the side of

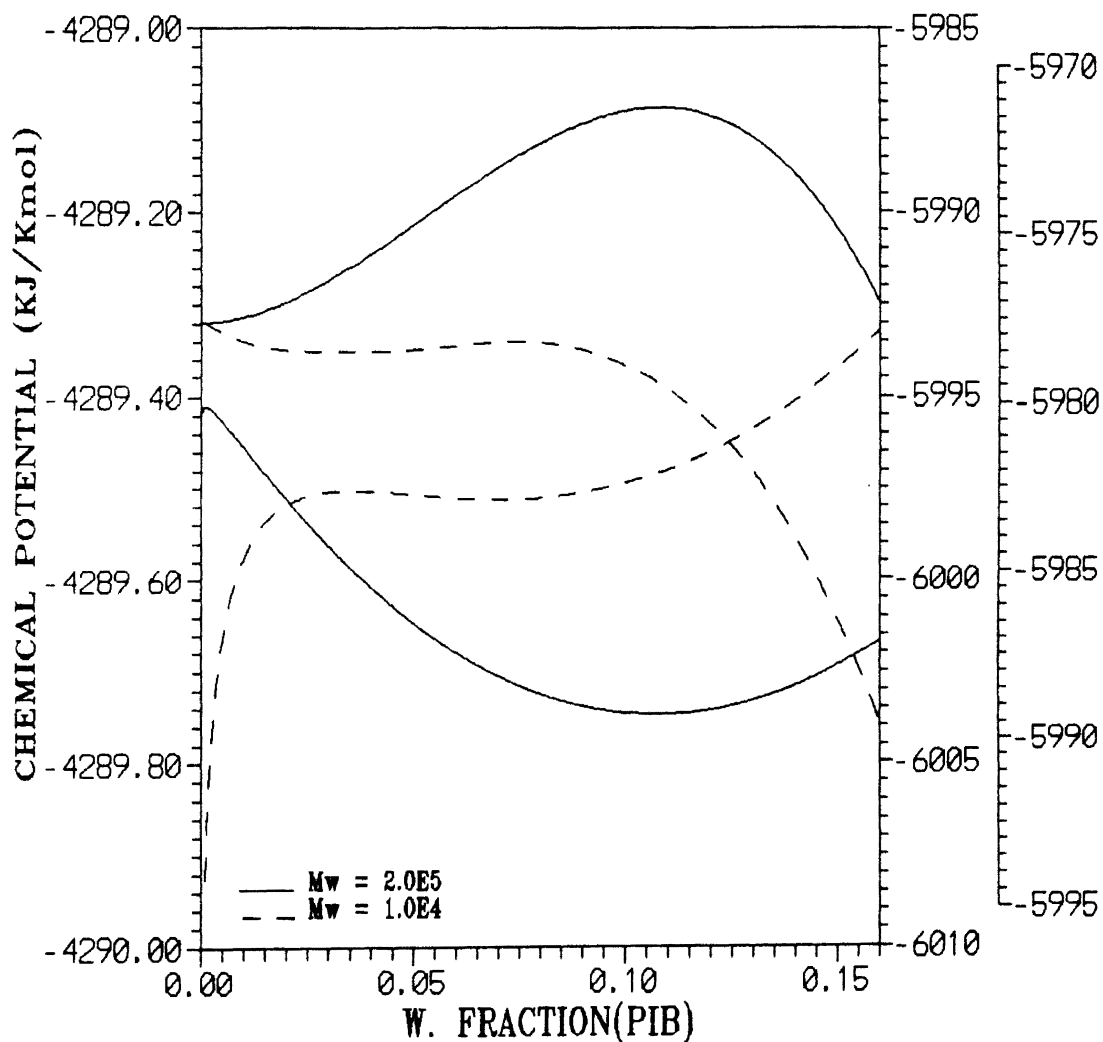


Figure 10. Diagram of Chemical Potential Versus Concentration in the PIB/
n-Pentane System. In the Mixture with PIB of M_w of $1.0E4$, A
Rectangle like that in Figure 9 can be constructed. As the M_w
of PIB increases, the Minimum of the Curve of Solvent Chemical
Potential Vanishes, There is No Solution for the Compositions
in the Coexisting Phases.

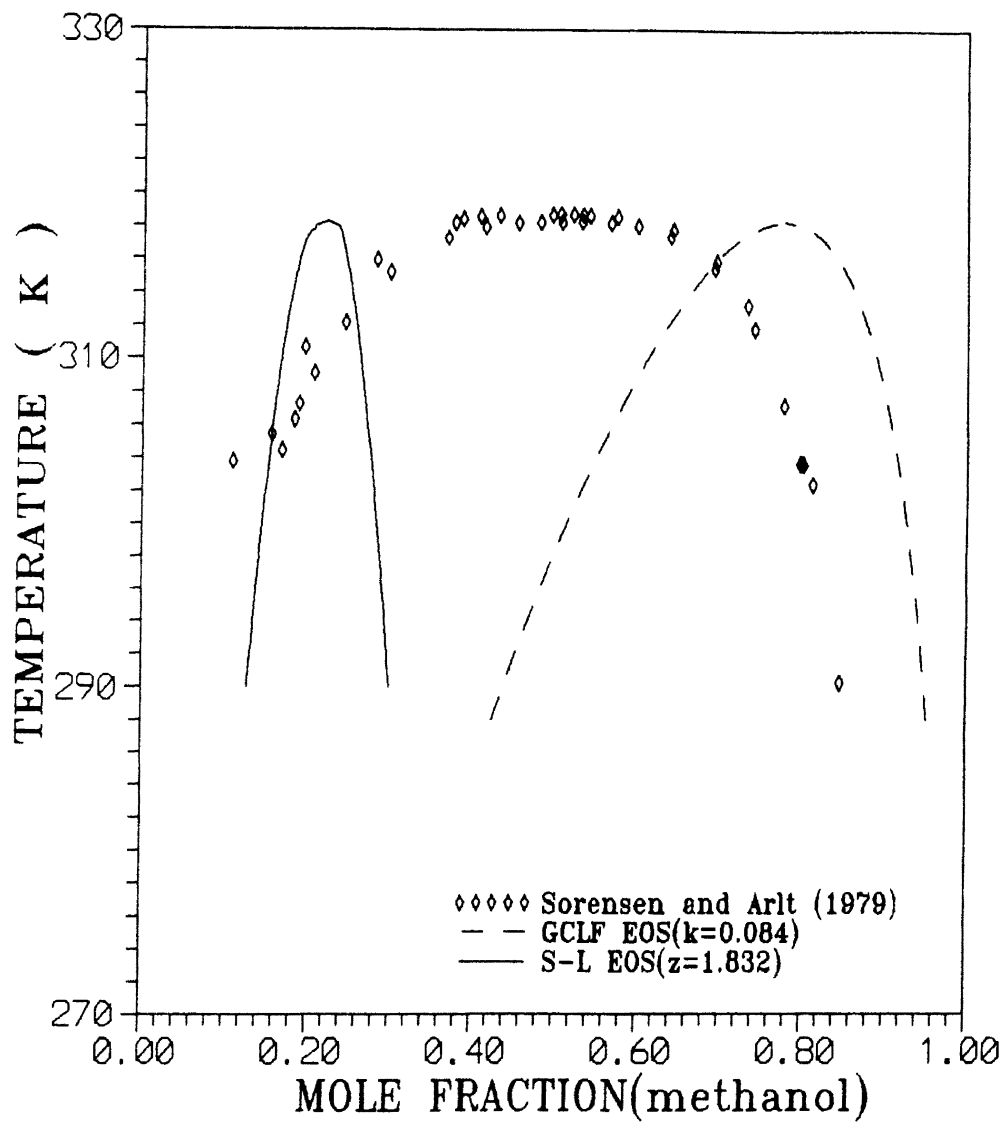


Figure 11. Comparison of Theoretical Binodal Curves in the Methanol\Cyclohexane System with Experimental Data.

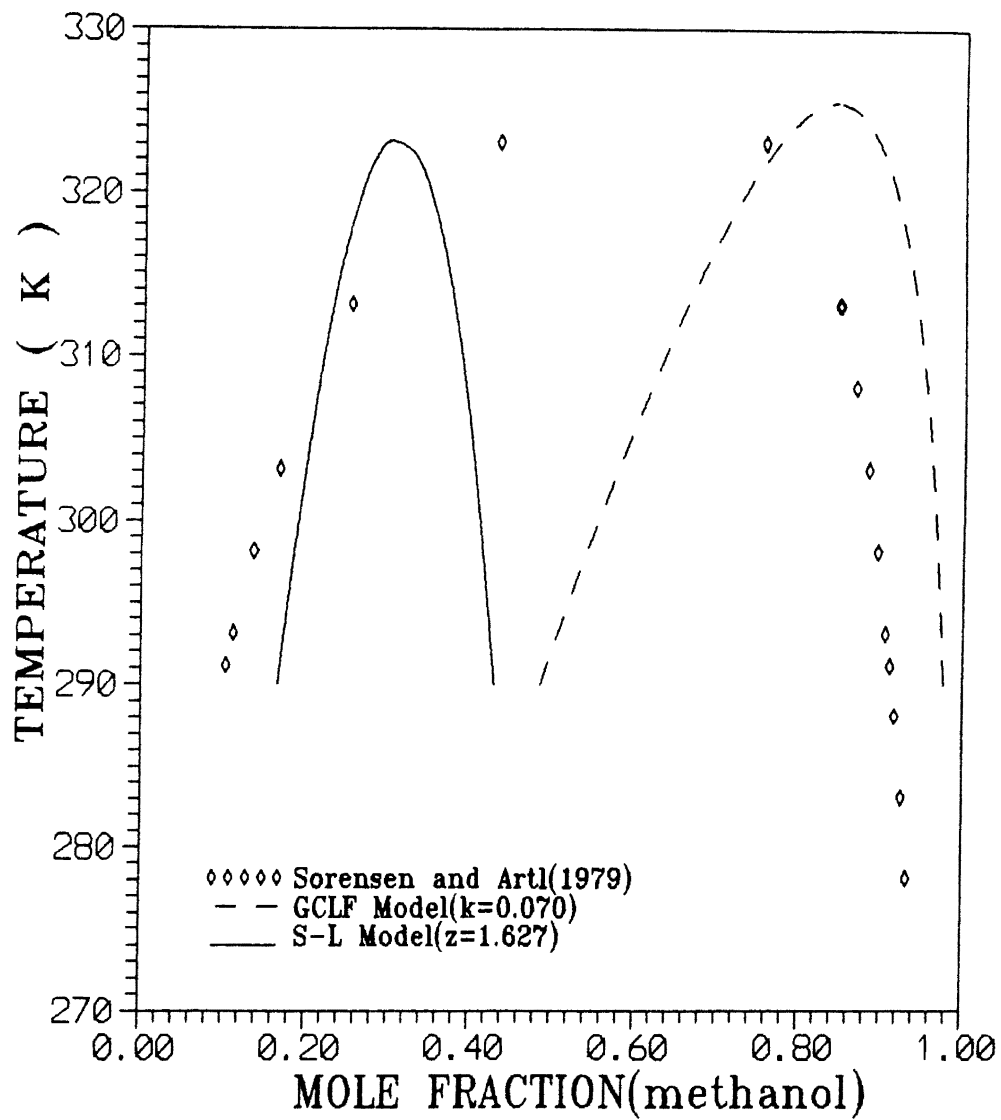


Figure 12. Comparison of Theoretical Binodal Curves in the Methanol/n-Heptane System with Experimental Data.

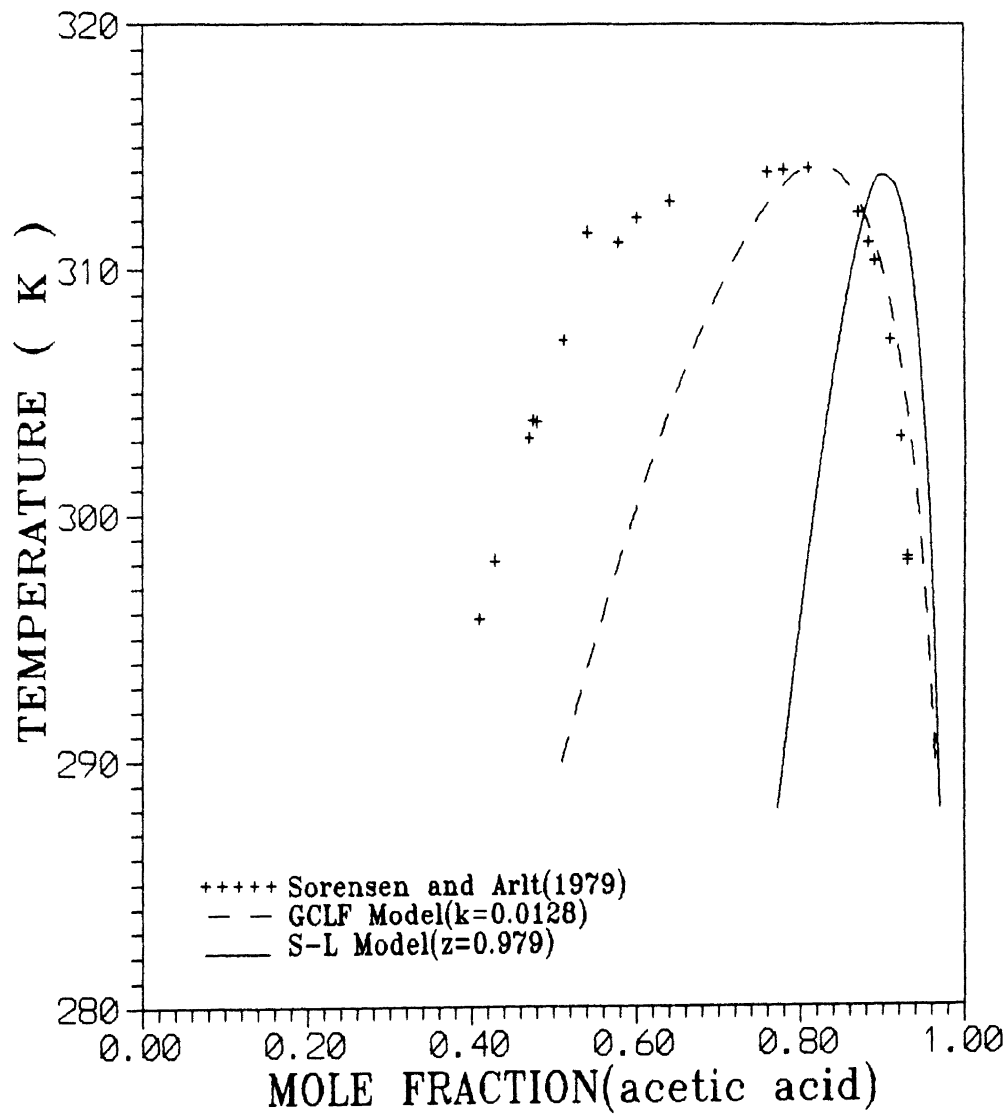


Figure 13. Comparison of Theoretical Binodal Curve in the Acetic acid/Decane System with Experimental Data.

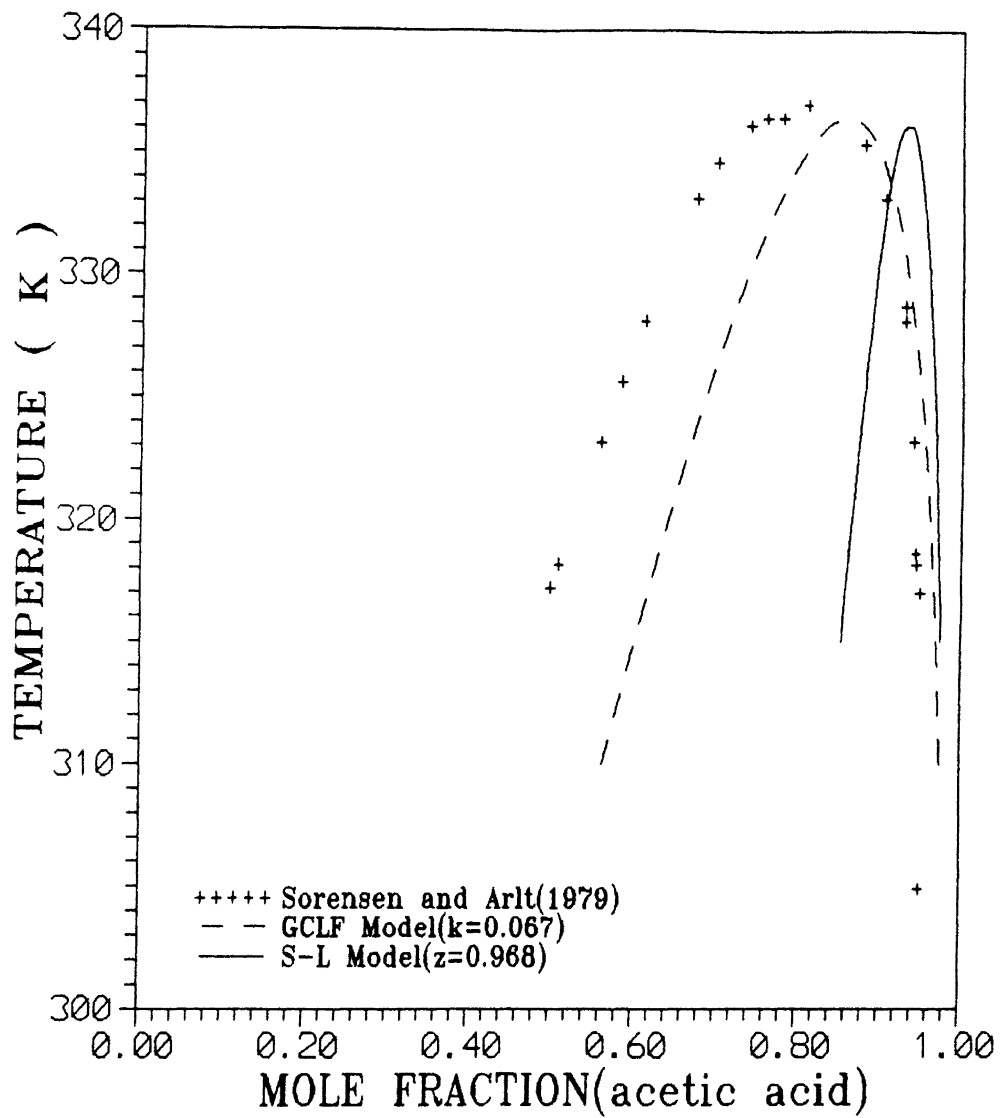


Figure 14. Comparison of Theoretical Binodal Curves in the Acetic acid/Dodecane System with Experimental Data.

higher concentration of acetic acid. The Sanchez-Lacombe EOS only gives qualitatively representation for these two systems. The GCLF model gives good representations of concentrations of acetic acid in the acetic acid-rich phases in these two systems but gives a higher prediction in the decane-rich phase and dodecane-rich phase.

Figure 15 shows the comparison in the stearic acid/propane system, where LCST is observed. The LCST behavior is relatively uncommon in the systems in which both components have low molecular weights. The predictions of LCSTs are based on binary interaction energies determined by the experimental LCST ($z = 0.0959$, $k=0.083$). The binodal curve predicted with the Sanchez-Lacombe EOS shifts to the low concentration side of stearic acid. The Sanchez-Lacombe does not give an accurate prediction of the compositions in the coexisting phases. The GCLF EOS gives a much better representation of composition at critical point and in the stearic acid-rich phase, but the prediction of the composition in propane-rich phase is not accurate.

In the studies of liquid-liquid equilibria in the low molecular weight systems, the interaction energies between the unlike molecules are determined by the critical solution temperatures. The geometric mean formula for the binary interaction energy term is not sufficient to give an adequate representation for the phase behavior. Neither of the models is able to achieved an accurate description of the experimental data. The theoretical binodal curves predicted with Sanchez-Lacombe model is much narrower than the experimental binodal curves. The GCLF EOS gives a marginally better representation of composition than Sanchez-Lacombe EOS in the investigated systems.

Polymer-Solvent Systems

The Sanchez-Lacombe EOS is usually incapable of predicting a binodal curve in polymer-solvent systems with polymers of high molecular weight. The predicted binodal curves using GCLF were compared with the experimental cloud point data. A spinodal curve is very close to the corresponding binodal curve and is located inside the binodal

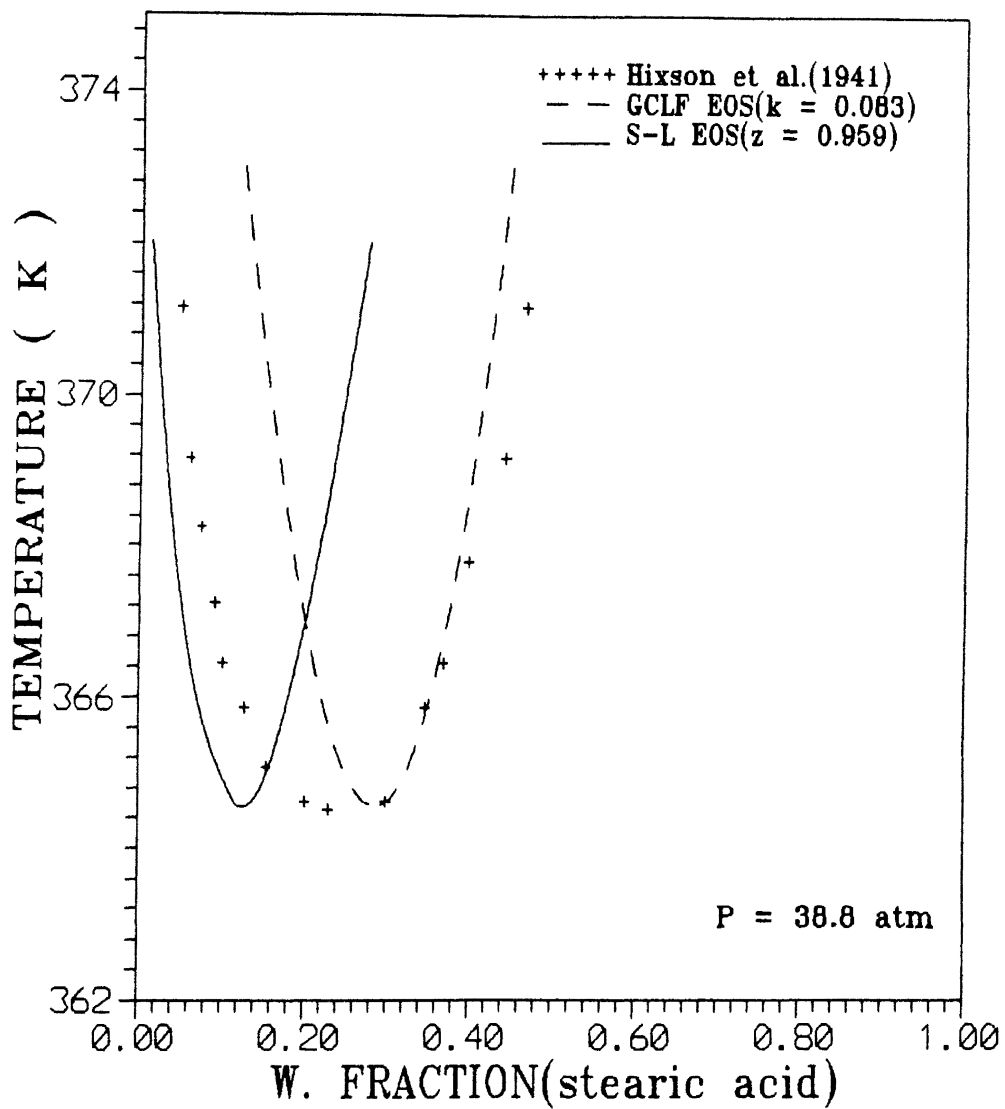


Figure 15. Comparison of Theoretical Binodal Curves in the Stearic acid/Propane System with Experimental Data.

curve. They coincide at the critical point. It is usually difficult to distinguish the spinodal and binodal in the experimental measurements. Therefore, all spinodal curves predicted using the Sanchez-Lacombe EOS are shown in the diagrams together with binodal curves predicted using the GCLF EOS. The effects of molecular weight of the polymer and pressure on critical solution temperatures are discussed.

Polyisobutylene-Solvent Systems

Figure 16, 17, 18 illustrate the predictions of LCST's in polyisobutylene-solvent systems. The cross interaction energy terms in both models are determined by matching the experimental LCST. Figure 16 illustrates the behavior of the two equations of state in the PIB/n-pentane system. The Sanchez-Lacombe equation of state fails to represent binodal curve in this system with PIB of high molecular weight ($M_w = 6.22 \times 10^4$), but gives a satisfactory prediction of the composition at the critical point. The results predicted with GCLF EOS are in good agreement with the experimental data in the critical temperature region, but deviate from the experimental data in the higher temperatures. Figure 17, 18 illustrate the predictions of the LCST behavior in PIB/isopentane and PIB/n-hexane systems, respectively. The GCLF EOS gives semiquantitative representations of the compositions in these systems. The Sanchez-Lacombe EOS always predicts narrow spinodal curves in the low concentration of polyisobutylene region.

HDPE-Solvent Systems

Three examples of the HDPE-solvent liquid-liquid equilibria are given. Figure 19 and 20 illustrate the predictions of LCST in HDPE/n-pentane and HDPE/n-hexane systems, respectively. Only four data points are available in Figure 19, so a comparison over a large temperature range is not available; however, a good representation is achieved with GCLF EOS in the vicinity of critical point. The GCLF EOS predicts a broader binodal curve than the experimental data in HDPE/n-hexane system. In these two

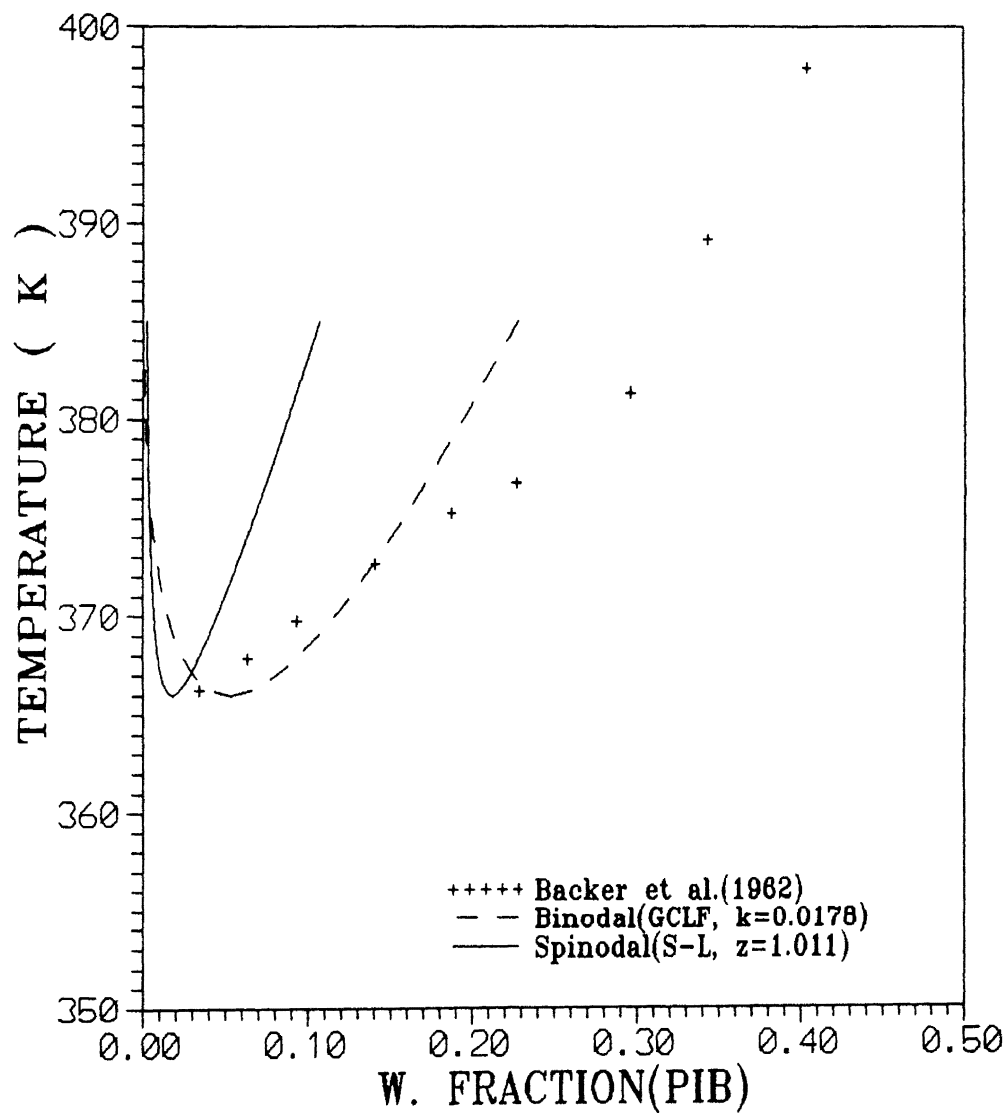


Figure 16. Theoretical Binodal Curve of the PIB/n-Pentane System Compared with Experimental Data. The M_w of PIB is 6.22×10^4 .

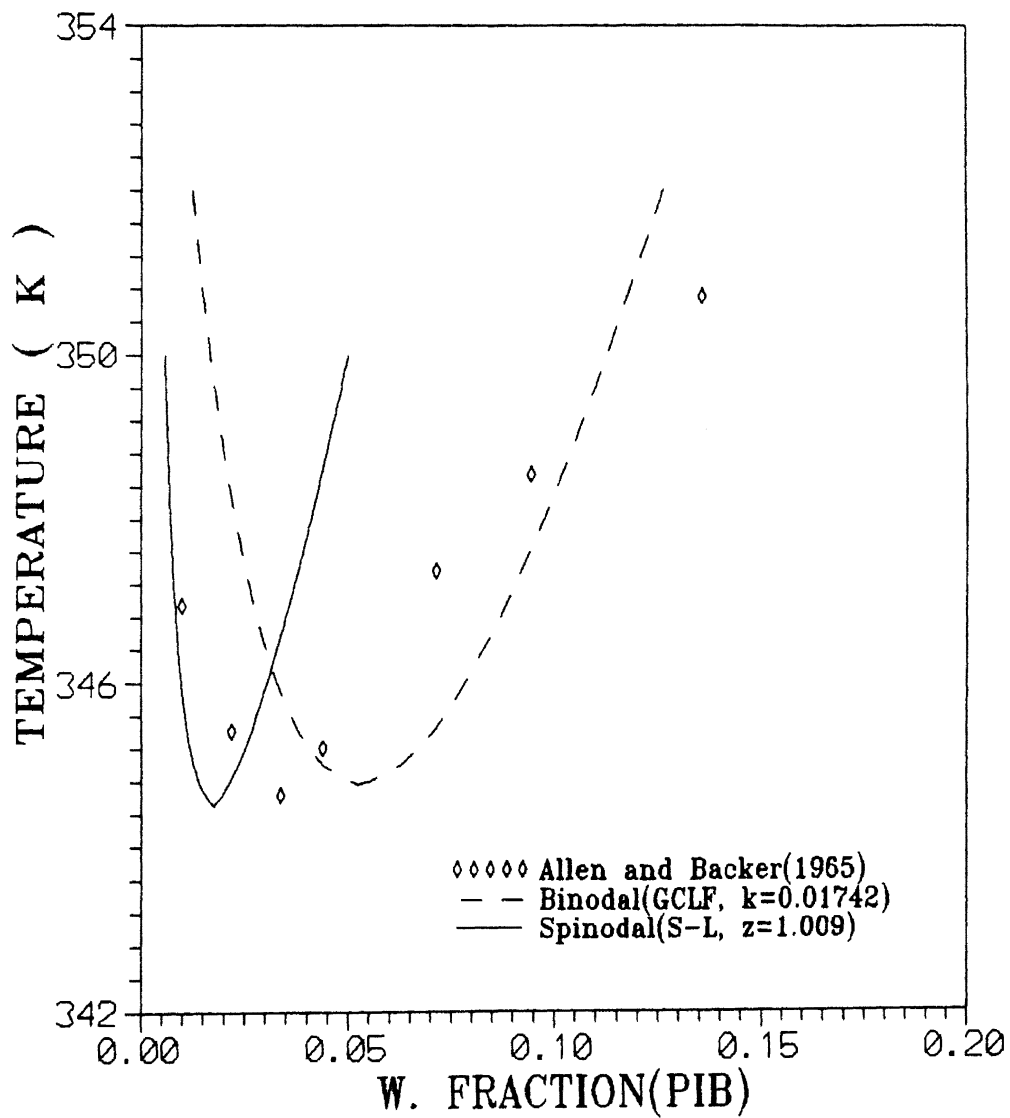


Figure 17. Theoretical Binodal Curve of the PIB/Isopentane System Compared with Experimental Data. The M_w of PIB is 6.20×10^4 .

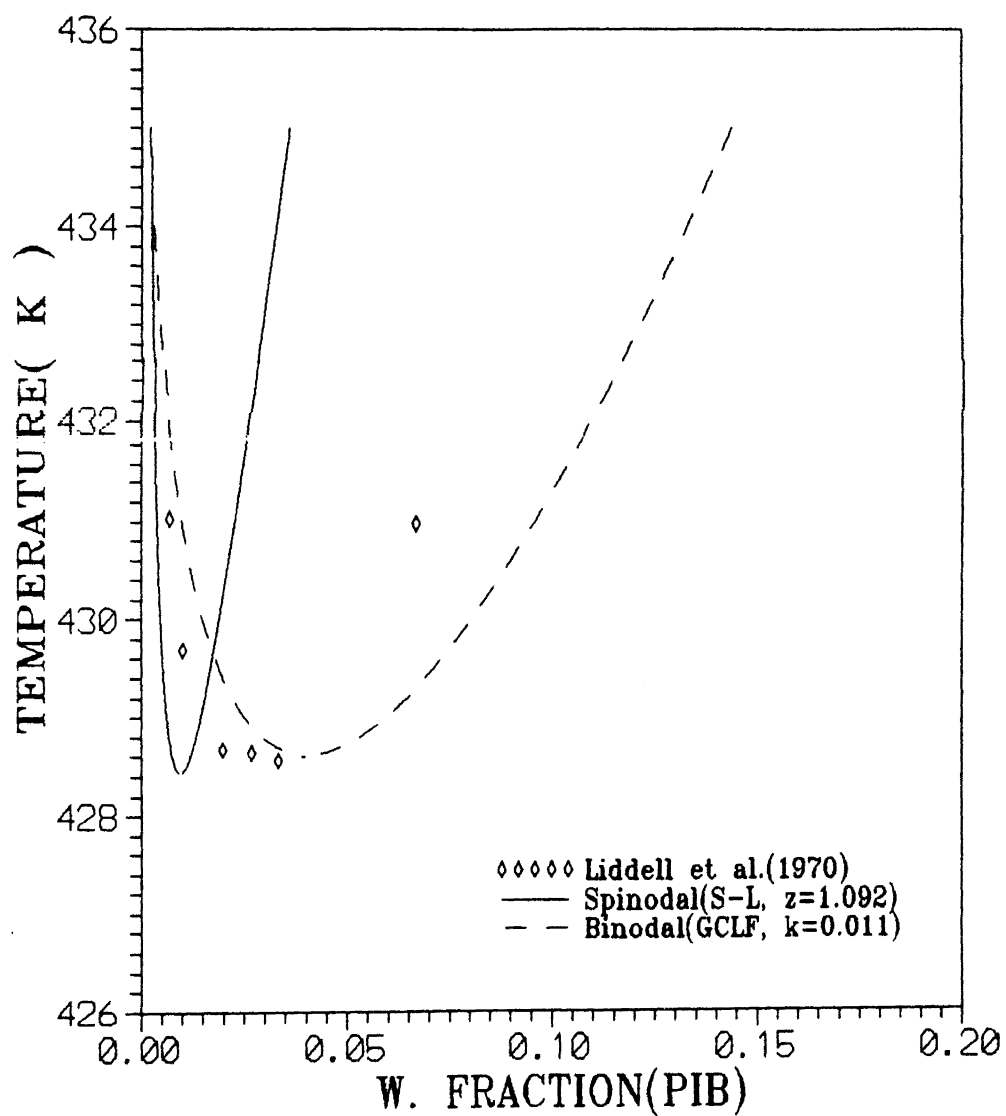


Figure 18. Theoretical Binodal Curve of the PIB/n-Hexane System Compared with Experimental Data. The M_w of PIB is 7.20×10^4 .

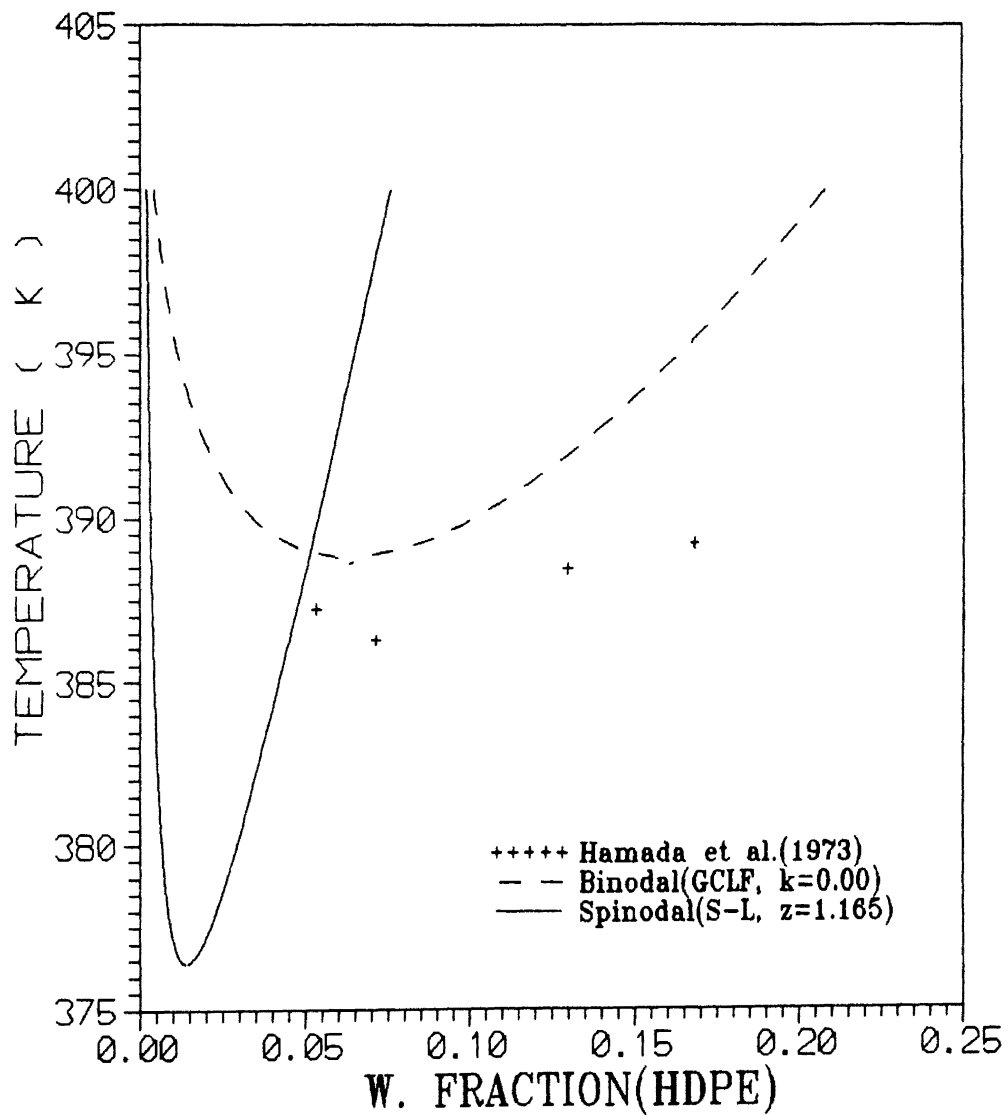


Figure 19. Theoretical Binodal Curve of the HDPE/n-Pentane System Compared with Experimental Data. The M_w of Polyethylene is 1.25×10^4 .

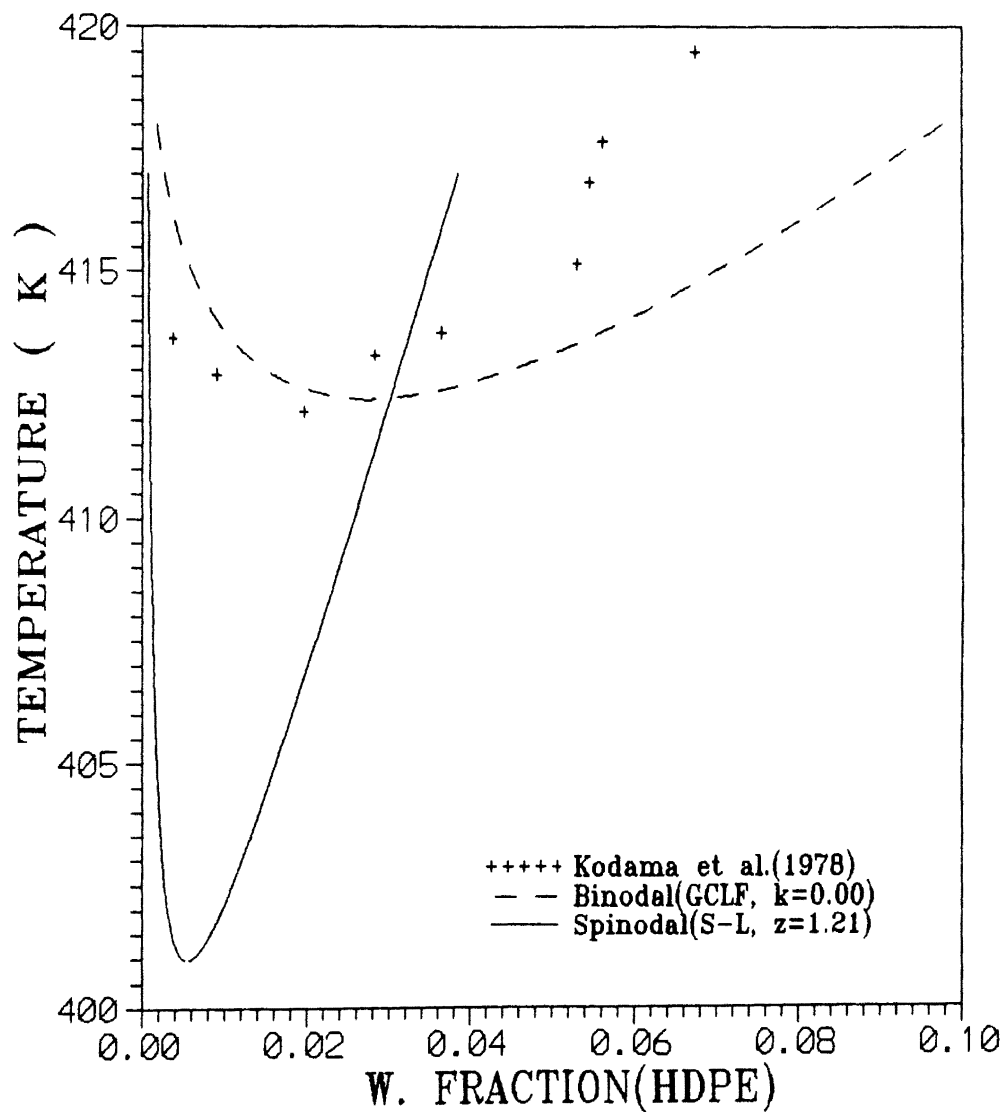


Figure 20. Theoretical Binodal Curve of the HDPE/n-Hexane System Compared with Experimental Data. The M_w of Polyethylene is 8.26×10^4 .

cases, the Sanchez-Lacombe EOS is unable to obtain the same LCST's as the experimental data even by adjusting the cross interaction term, because the parameters used for HDPE are beyond the applicable temperature region. It predicts 10 K lower than experimental LCST in PIB/n-Pentane system with a z of 1.165 and predicts 11 K lower than experimental LCST in PIB/n-Hexane system.

Both LCST and UCST exist in the HDPE/n-butyl acetate system, as shown in Figure 21. The miscibility region predicted with the Sanchez-Lacombe EOS is far lower than the experimental data, the theoretical LCST spinodal curve is even 100 K lower than the experimental UCST. The most likely interpretation is that the parameters used cannot represent the properties of the polymer, inaccurate parameters lead to poor representation of the phase behavior in the mixtures. The GCLF gives a satisfactory prediction of LCST binodal curve but the UCST curve is more than 100 K lower than the experimental data.

In the systems with only LCST in the phase diagram, the Sanchez-Lacombe z and the GCLF k can be adjusted to give satisfactory results by fitting the lower critical solution temperature. However, in systems showing both a LCST and a UCST, the determination of the adjustable parameters took into account the deviations of theoretical curves from both the experimental LCST and UCST.

Polystyrene-Solvent Systems

Figure 22 and 23 show the prediction in PS/toluene and PS/benzene systems, respectively. Both equations of state predict a much lower LCST than experimental data. The theoretical LCST curves move up as the z value increases and the k value decrease. The highest theoretical LCST's are obtained at the values of z and k as indicated in Figure 22 and 23. As the z value increases and the k value decreases further, the theoretical LCST begin to decrease.

Figure 24 illustrates the results of the PS/cyclohexane system. The miscibility region predicted with the two equations of state are both much lower than the experimental data.

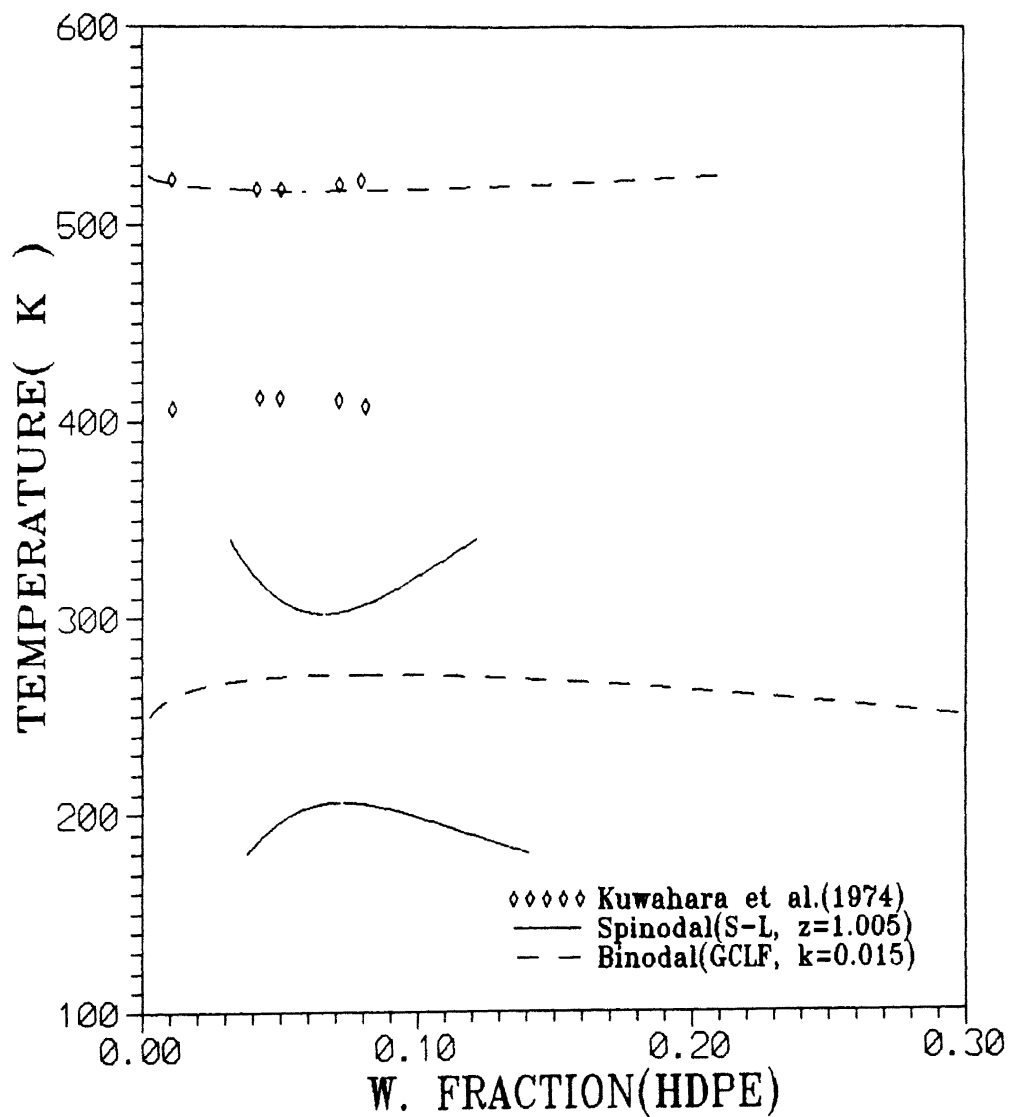


Figure 21. Theoretical Binodal Curve of the HDPE/n-Butyl Acetate System Compared with Experimental Data. The Mw of HDPE is 1.36×10^6 .

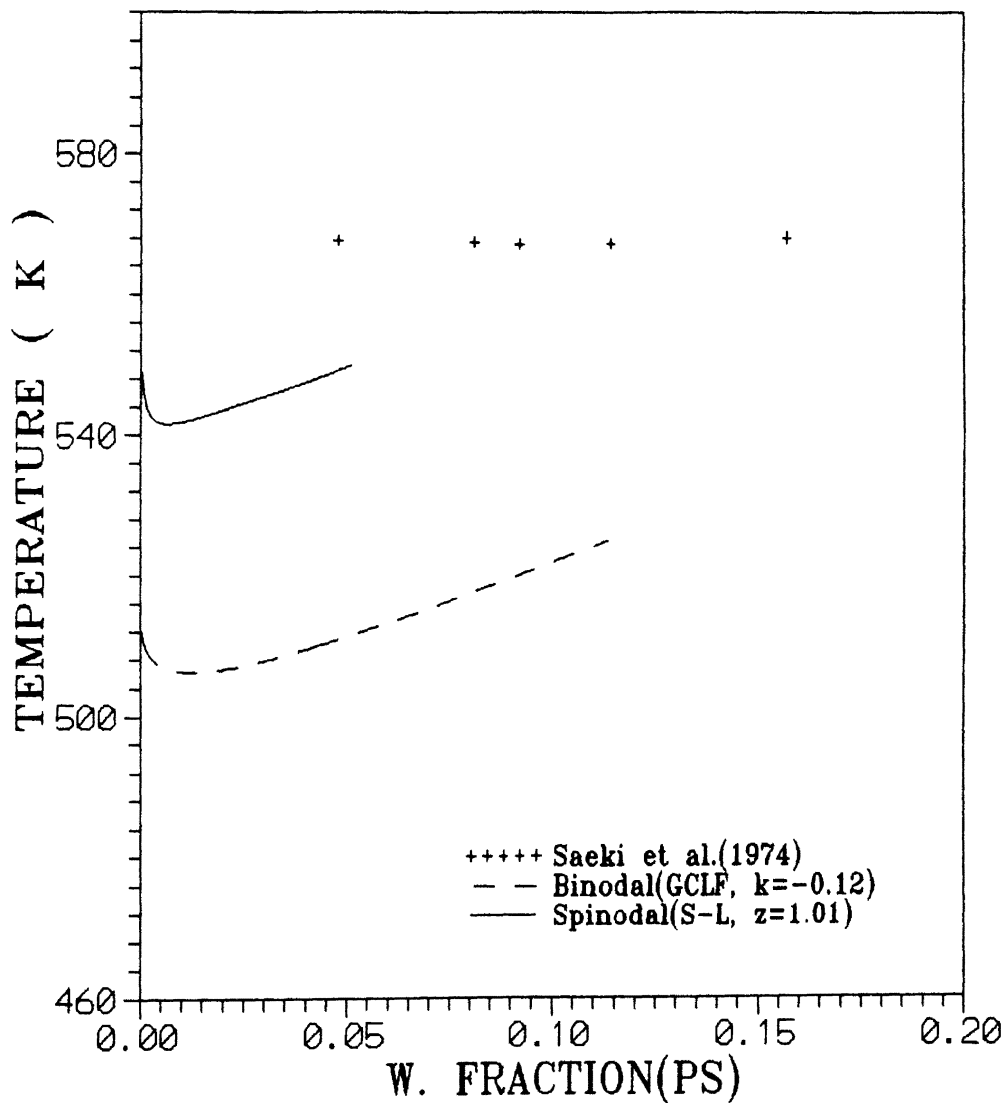


Figure 22. Theoretical Binodal Curve of the PS/Toluene System Compared with Experimental Data. The Mw of Polystyrene is 3.7×10^4 .

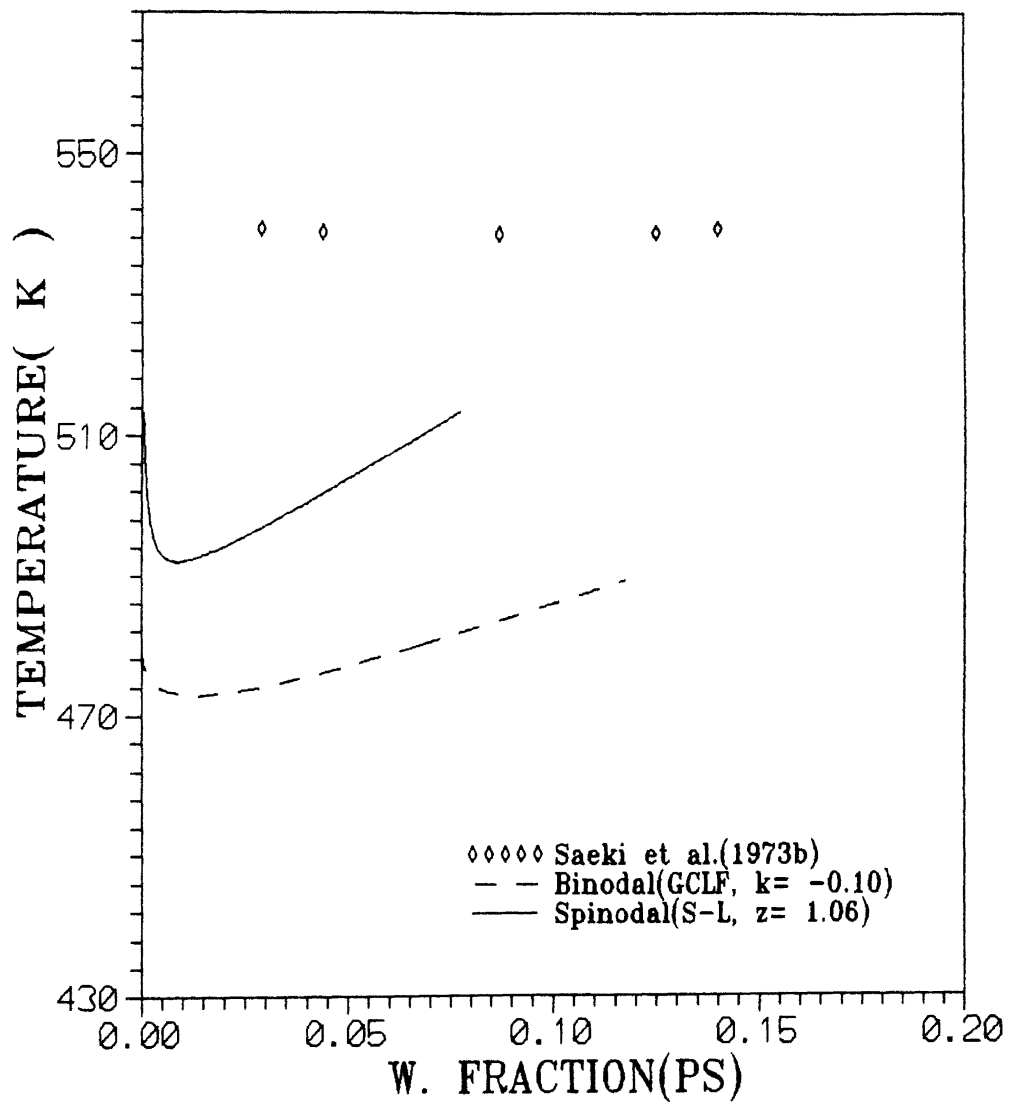


Figure 23. Theoretical Binodal Curve of the PS/Benzene System Compared with Experimental Data. The M_w of Polystyrene is 3.7×10^4 .

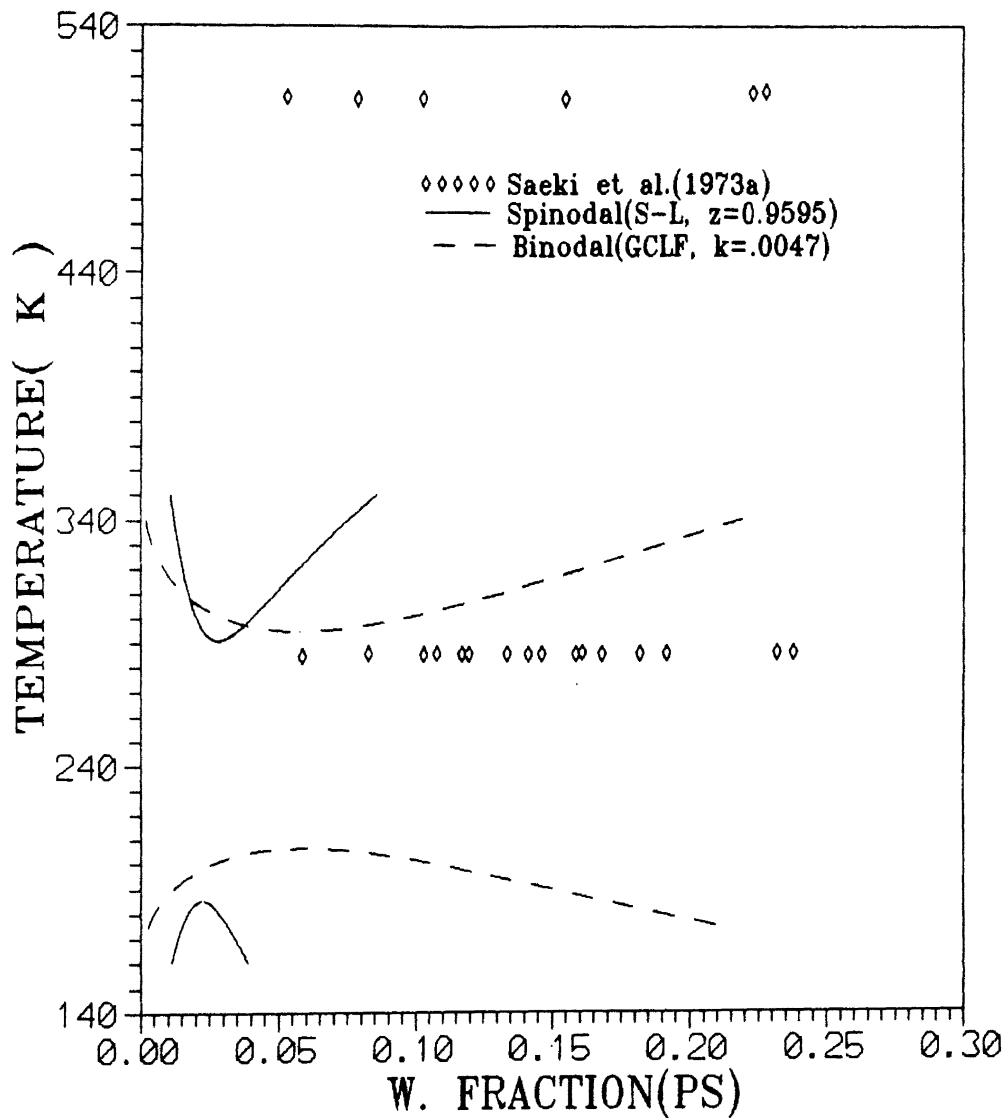


Figure 24. Theoretical Binodal Curves of the PS/Cyclohexane System Compared with Experimental Data. The M_w of Polystyrene is 3.7×10^4 .

The theoretical LCST's are near the experimental UCST curve. In the PS/acetone system both LCST and UCST are present, as shown in Figure 25. The GCLF EOS predicts the LCST and UCST at a lower value than the experimental data. The Sanchez-Lacombe EOS predicts a much lower UCST than the experimental one and predicts a much narrower spinodal curves. The substantial discrepancies between the theoretical curves and the experimental data in these systems are due to the inaccuracy of the parameters for pure components.

Poly(ethylene glycol)-Solvent Systems

Figure 26 shows the poly(ethylene glycol)/water system which demonstrates a closed-loop phase diagram. Because no molecular parameters can be found for the Sanchez-Lacombe EOS for poly(ethylene glycol), the comparison is made between the theoretical binodal curve from the GCLF EOS and the experimental data. A closed-loop curve is observed for low molecular weight PEG. This diagram shows that the GCLF EOS is unable to predict this closed-loop phase diagram and it only gives a qualitative representation of lower critical solution temperatures in this system.

Molecular Weight Dependence of Critical Solution Temperatures

Figure 27 and 28 show the molecular weight dependence of LCST's. Both the Sanchez-Lacombe and GCLF equations of state predict that the LCSTs decreases as the molecular weight of polymers increase. In the liquid-liquid equilibrium of PIB/n-pentane, the predictions are based on the same adjustable parameters determined in the system with the polyisobutylene of molecular weight of 6.22×10^4 (see Fig. 16). It shows that the Sanchez-Lacombe EOS predicts the molecular weight dependence of the LCST. The GCLF EOS predicts a higher LCST with a binodal curve with similar shape to the

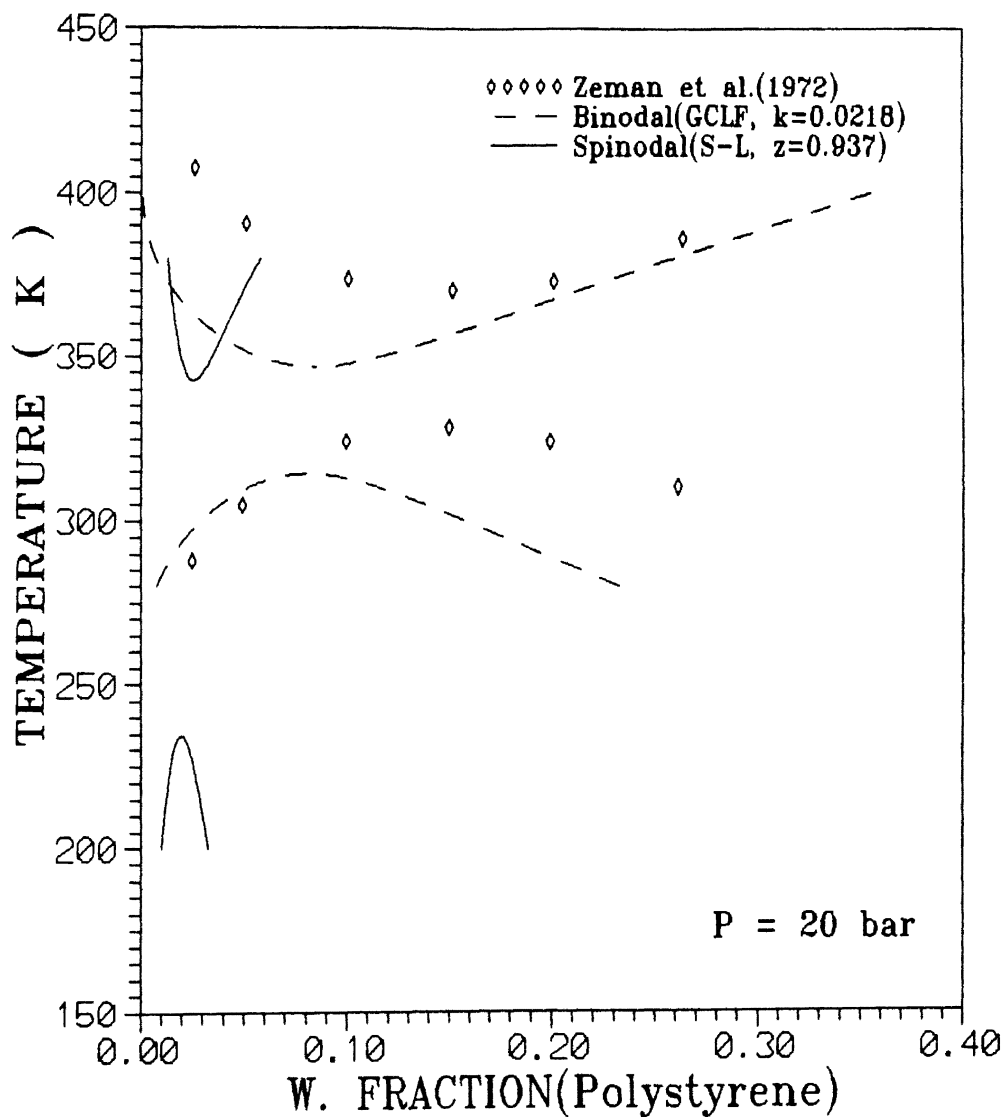


Figure 25. Theoretical Binodal Curves of the PS/Acetone System Compared with Experimental Data. The M_w of Polystyrene is 2.04×10^6 .

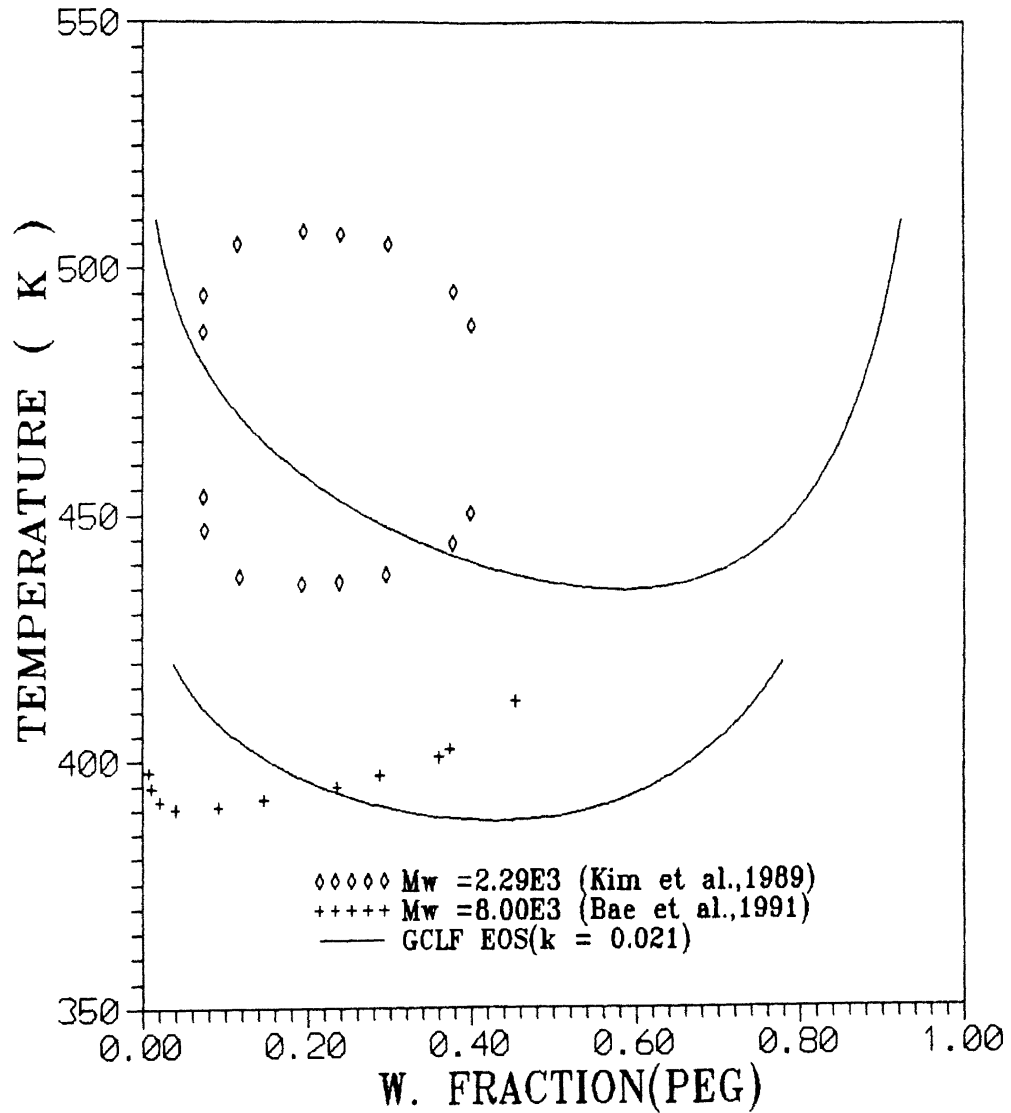


Figure 26. Comparison of Theoretical Binodal Curves of the PEG/Water System with Experimental Data.

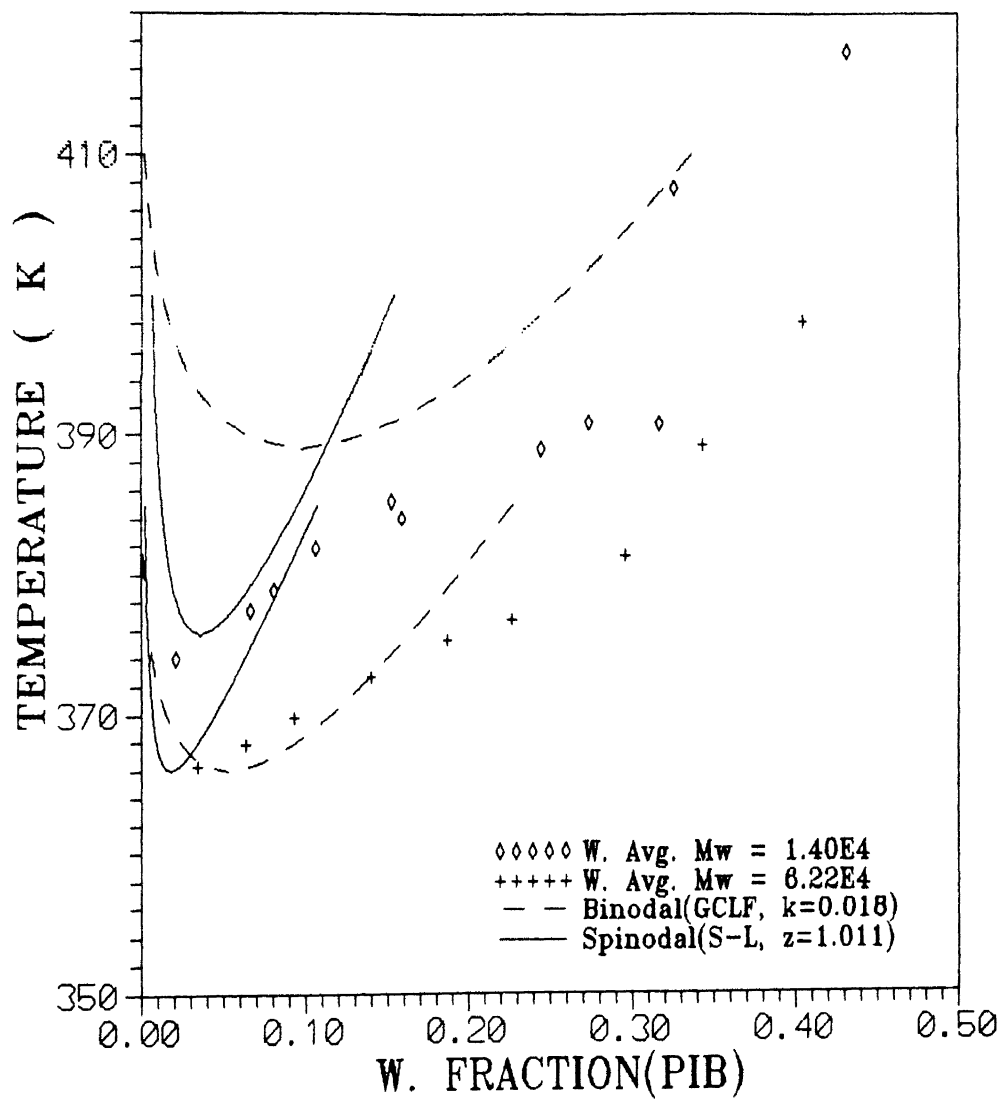


Figure 27. Effect of the Molecular Weight of Polybutylene on LCST's in the PIB/n-Pentane System. Theoretical curves are compared with experimental data of Backer et al.(1962).

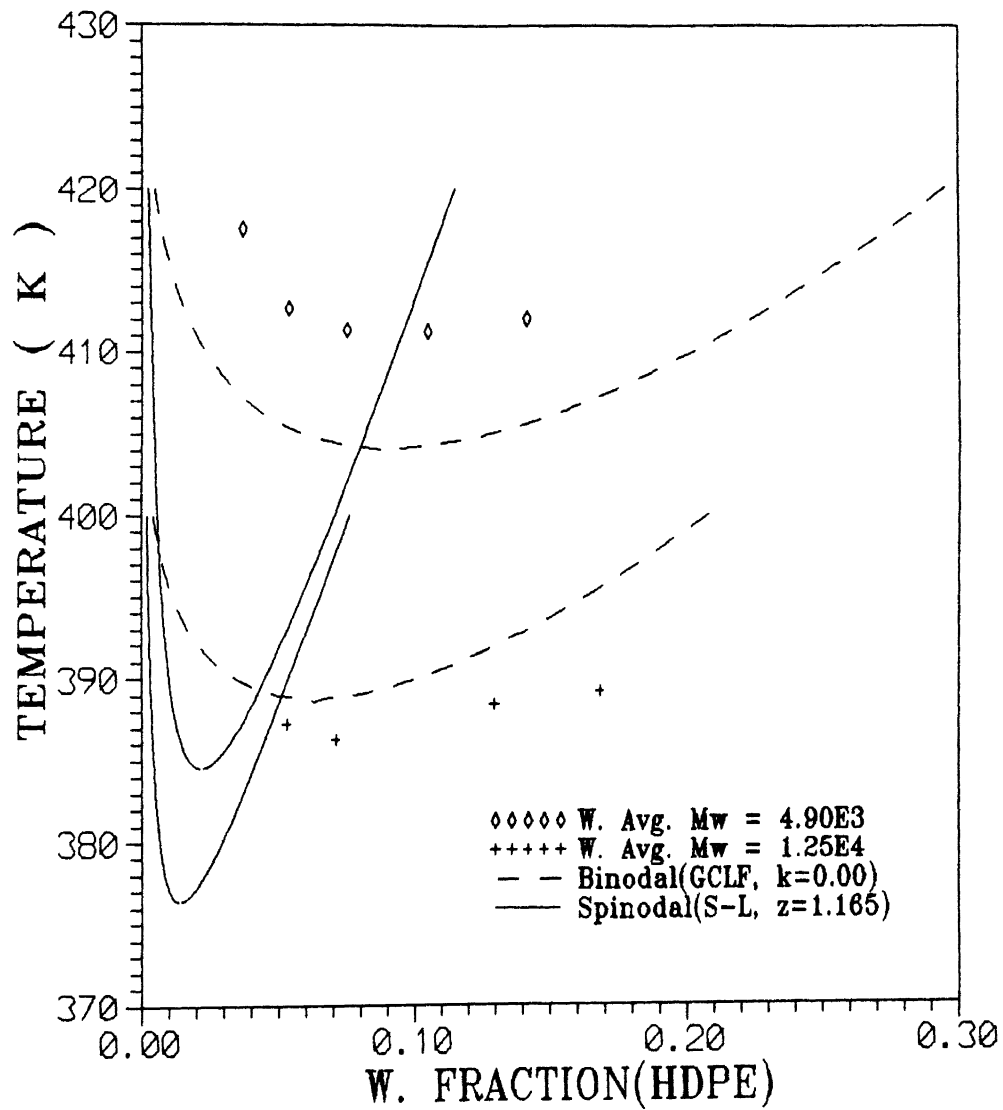


Figure 28. Effect of the Molecular Weight of HDPE on LCST's in the HDPE/n-Pentane System. The Experimental Data are from Hamada et al.(1973).

experimental data. Figure 28 is an example of HDPE/n-pentane system. Both equations of state show the LCST increases as the molecular weight of the polymer increases.

Pressure Dependence of Critical Solution Temperatures

It is well known that as the pressure of the system increases, the UCST decreases and LCST increases. Figure 29 and 30 show the effect of pressure on the critical solution temperatures in PS/acetone and PIB/isopentane system. In the liquid-liquid equilibrium of Polystyrene/acetone system, both equations of state show inadequate pressure dependence of critical solution temperatures. The UCST predicted with S-L EOS does not change as the pressure of the system varies. It shows that the adjustable parameters can be a function of pressure. Figure 30 show that both equations of state predict adequate pressure dependence of LCST in PIB/Isopentane system.

Polymer-Polymer Miscibility

The GCLF equation of state can be easily extended to the application to polymer-polymer miscibility. The only difference is that the degree of polymerization is taken into account for both components in the calculation of the molecular parameters. Only one polymer pair was studied in this research because of lack of group contributions data and experimental data. The GCLF model is able to qualitatively predict the miscibility of the Polystyrene\Poly(vinyl methyl ether) (PVME) system, as shown in Figure 31. The binary interaction energy is determined by matching the calculated LCST and the experimental data. The GCLF equation of state tends to predict a lower concentration than the measured composition. No molecular parameters of PVME for the Sanchez-Lacombe model is available, the comparison is made only between the prediction using the GCLF model and the experimental data. It is necessary to investigate more systems so as to reach a generalized conclusion about the abilities of the models in representing polymer-polymer miscibility.

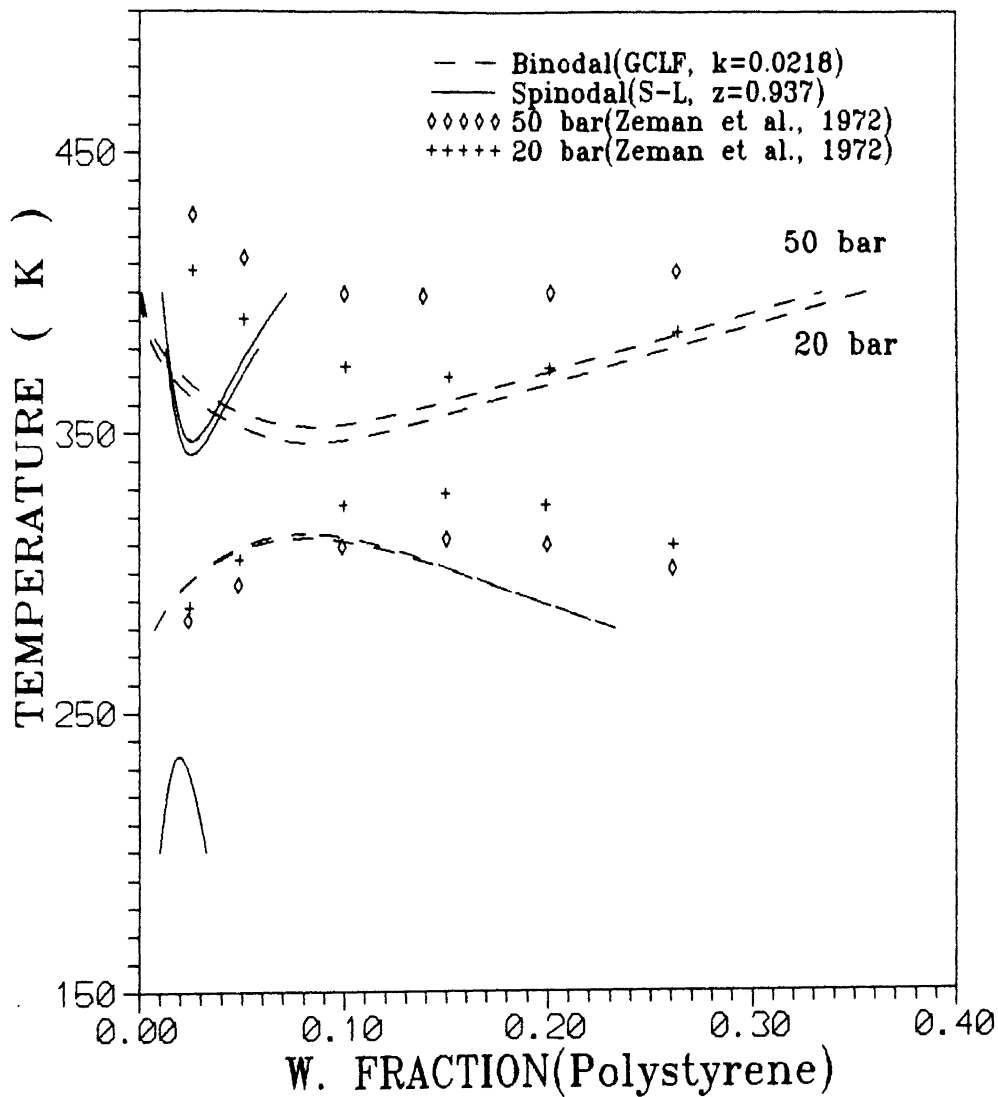


Figure 29. Effect of Pressure on Critical Solution Temperatures in the PS/Acetone system. The M_w of Polystyrene is 2.04×10^4 .

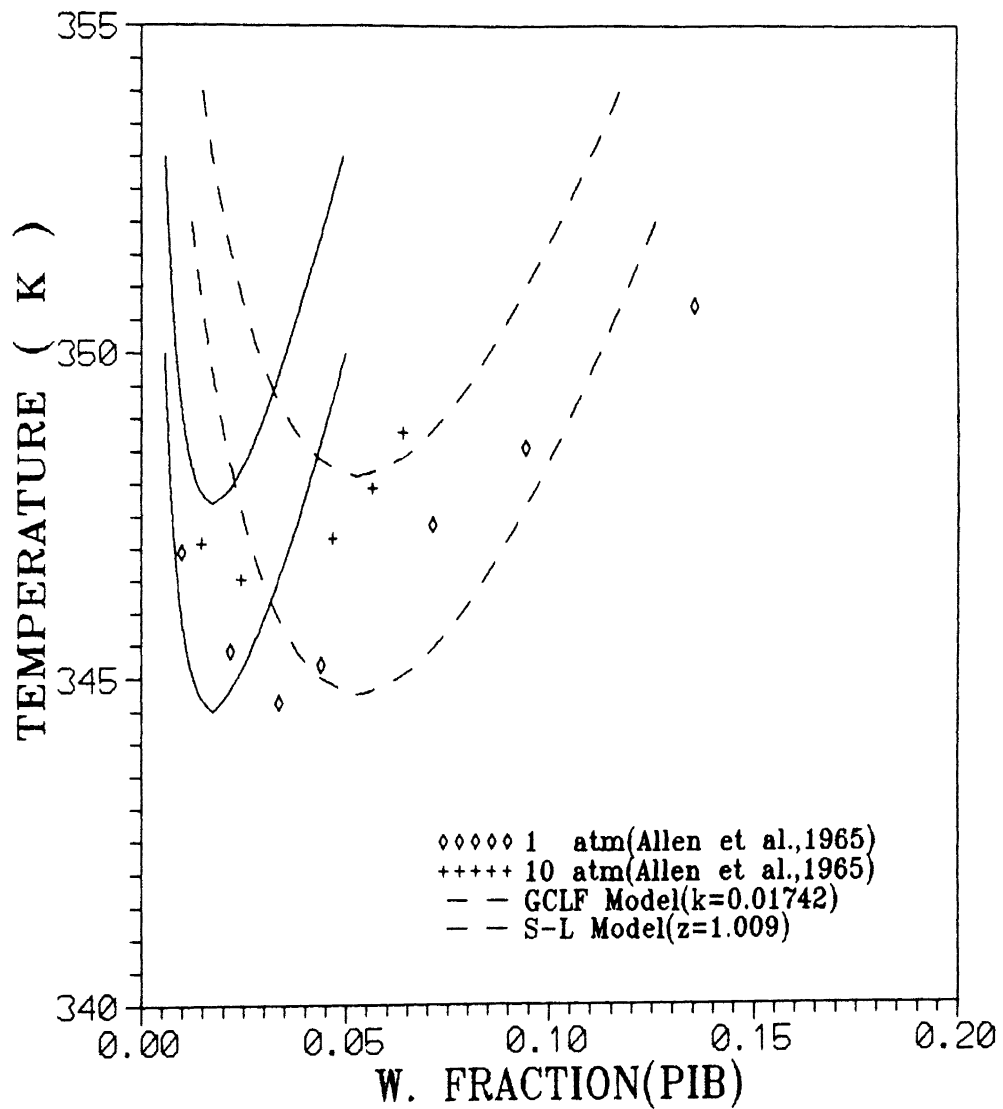


Figure 30. Effect of Pressure on LCST's in the PIB/Isopentane System.

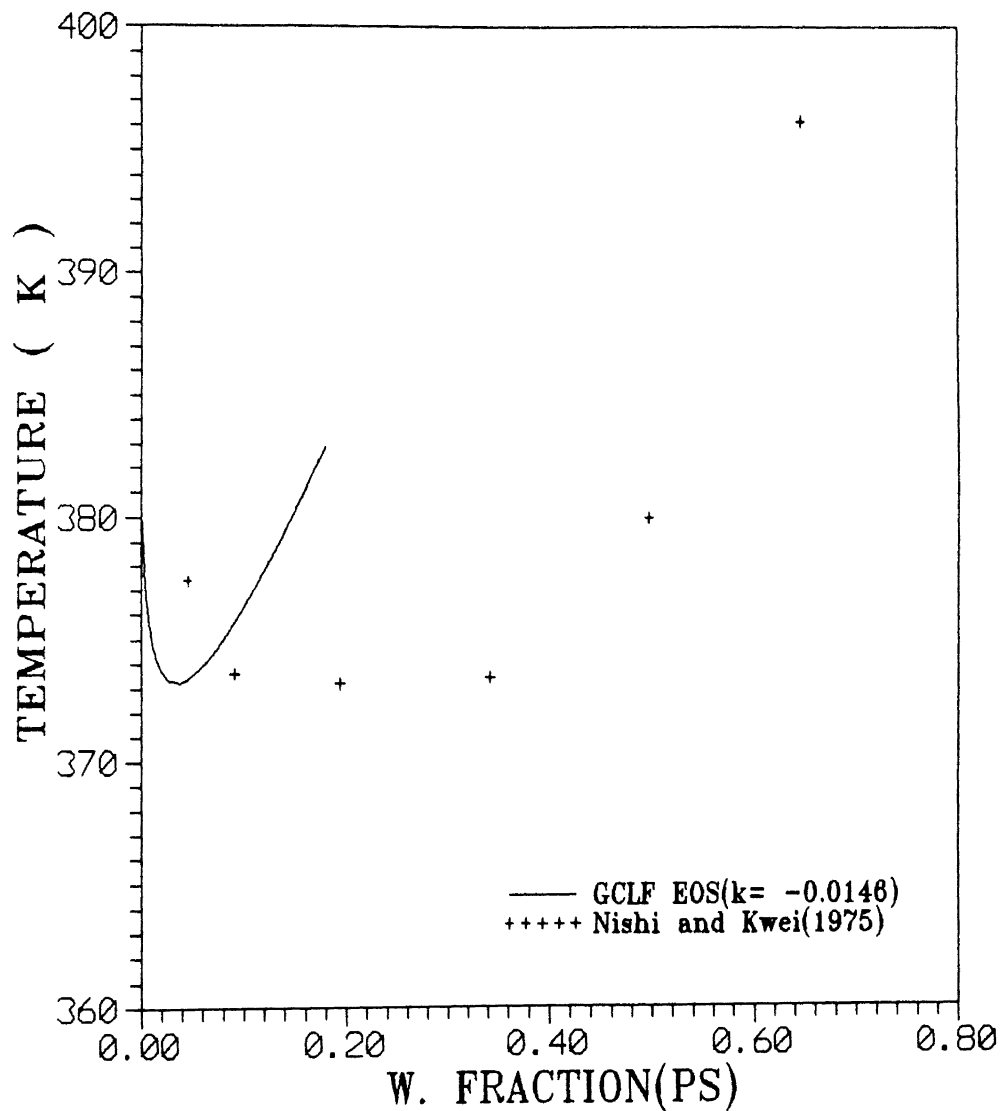


Figure 31. Comparison of Theoretical Binodal Curve of a PS/PVME Blend with Experimental Data. The M_w of PS and PVME is 200000 and 51500, Respectively.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this chapter is to summarize the findings in the present work. The recommendations for future work are also given.

Conclusions

1. For liquid-liquid equilibria of low molecular weight systems, the GCLF model is superior to the Sanchez-Lacombe model. The Sanchez-Lacombe EOS always predicts too narrow of a binodal curve compared to the experimental data.

2. For polymer-solvent systems, the GCLF model gives a better representation of liquid-liquid equilibrium than Sanchez-Lacombe EOS. The GCLF EOS gives a good representation of critical solution temperatures for the systems where only LCST exist. The Sanchez-Lacombe EOS fails to represent binodal curves in many polymer-solvent liquid-liquid systems.

3. Both equations of state only qualitatively predict LCST and UCST phenomena. They fail to give a quantitative representation of coexisting curves in these systems. The GCLF EOS failed to predict closed-loop phase diagram in the poly(ethylene glycol)/water system.

4. The geometric mean mixing rule used for estimating the binary interaction energies is of limited usefulness. In the present research work, adjustable parameters are used to adjust the binary interaction energies, a small change in the adjustable parameters (z and k) dramatically change the phase behavior prediction. Increasing the interaction

energies between unlike molecules leads to the change from a phase diagram where only LCST exist to a diagram with the hourglass shape.

5. Phase stability analysis is a convenient way to study the liquid-liquid equilibria. The investigation of liquid-liquid phase equilibria can usually be reduced to a stability analysis study.

6. It shows that the adjustable parameters for interaction energies between unlike molecules are molecular weight dependent and pressure dependent.

Recommendations

As a predictive method, the GCLF equation of state has been proven to be a good method for vapor-liquid equilibrium. The representation of liquid-liquid equilibrium requires very precise molecular parameters, thus greatly reducing the predictivity of the model in liquid-liquid equilibrium. There are a number of ways for improving the model's performance in liquid-liquid equilibrium.

1. Better predictions of pure component properties should lead to better description for the mixtures. Further improvement of the model's performance in liquid-liquid equilibrium stem from better estimates of the molecular parameters for pure components, especially the interaction energy. A more accurate temperature dependence of the interaction energy and reference volume could improve the ability of the model to represent liquid-liquid equilibrium.

2. The GCLF equation of state tends to underpredict the solvent activity coefficients. Small changes in the predicted activity coefficients usually produce large qualitative changes in the shapes of binodal and spinodal curves. It is necessary to make suitable corrections to the theory for the dilute polymer regions. The nonrandom hole GCLF equation of state (High, 1990) could be used to account for the effect of non-uniform distribution of holes in the polymer solutions, thus improving the predictive capability of the model in liquid-liquid equilibrium.

3. The binary interaction energy could be assumed to a function of molecular weight and pressure to improve the prediction of molecular weight and pressure dependence of critical solution temperatures. A more accurate pressure dependence of the interaction energies could improve the ability to represent the liquid-liquid equilibrium.

4. Further investigation in the group contribution technique can be made to improve the precision of the calculated molecular parameters. As already pointed out by High (1990), developing group contributions for polymers based on polymer repeat units instead of the small functional groups defined in the previous and present work could improve the results in the equilibrium calculation.

5. Further the study of the present model into the area of polymer-polymer miscibility. An example of the system of PS/poly(vinyl methyl ether) (PVME) is shown in Figure 31.

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APPENDIX A

**COMPUTER PROGRAM FOR CALCULATING
BINODAL CURVE USING THE GCLF EOS**

```

C *****
C PROGRAM NAME      GCLF.FOR
C
C WEI WANG          APRIL 16 1993
C
C PURPOSE           - THIS PROGRAM IS WRITTEN FOR FINDING THE
C                   PHASE SPLITTING REGION AND CALCULATING WEIGHT
C                   CONCENTRATIONS OF THE POLYMER IN TWO PHASES IN
C                   A POLYMER-SOLVENT BINARY SYSTEM.
C -----
C USAGE             - THE DATA FILE NAMED GPDATA IS READ IN.  THE
C                   DATA CAN BE MODIFIED BY CHANGING THE NUMBER OF
C                   FUNCTION GROUPS FOR DIFFERENT COMPOUNDS.
C                   - THERE ARE TWO OPTIONS IN THE COMPUTER PROGRAM:
C                     * 1. FIND THE TEMPERATURE REGION FOR MISCIBILITY
C                       AT GIVEN PRESSURE.
C                     * 2. FIND THE BINODAL CURVE.  THE CALCULATION IS
C                       PERFORMED FROM SPECIFIED TEMPERATURE IN TWO
C                       PHASE REGION TO THE CRITICAL TEMPERATURE.
C                   - THE PRESSURE OF THE SYSTEM, MOLECULAR WEIGHT OF
C                   THE POLYMER AND THE PRAUSNITZ'S K IS ENTERED
C                   FROM SCREEN.
C
C LIMITATIONS       - THE EQUATION OF STATE IS LIMITED FOR BINARY
C                   MIXTURE.
C
C NOMENCLATURE
C   T      ---    TEMPERATURE OF THE SYSTEM (KELVINS)
C   P      ---    PRESSURE OF THE SYSTEM (PASCALS)
C   NGROUP ---    NUMBER OF FUNCTION GROUP IN ONE COMPONENT
C   PK     ---    PRAUSNITZ'S K FOR CROSS INTERACTION ENERGY TERM
C   X(1)   ---    MOLE FRACTION OF SOLVENT IN ONE PHASE
C   X(2)   ---    MOLE FRACTION OF POLYMER IN ONE PHASE
C   WF(1)  ---    WEIGHT FRACTION OF SOLVENT IN ONE PHASE
C   WF(2)  ---    WEIGHT FRACTION OF POLYMER IN ONE PHASE
C   WM(1)  ---    MOLECULAR WEIGHT OF SOLVENT
C   WM(2)  ---    MOLECULAR WEIGHT OF POLYMER
C   UM(1)  ---    RELATIVE CHEM. POTENTIAL OF SOLVENT IN ONE PHASE
C   UM(2)  ---    RELATIVE CHEM. POTENTIAL OF POLYMER IN ONE PHASE
C   WGUSS(i) --- INITIAL GUESS OF SOLVENT COMPOSITION IN THE C
C                   ITH PHASE
C
C WARNINGS
C   IER = 101  PRESSURE IS LESS THAN OR EQUAL TO ZERO.
C   IER = 102  TEMPERATURE IS LESS THAN OR EQUAL TO ZERO.
C   IER = 105  NUMBER OF FUNCTION GROUP IS LESS THAN ZERO.
C   IER = 501  THE EQUATION OF STATE HAS NO LIQUID DENSITY ROOT
C             FOR ONE COMPONENT.  THE COMPONENT IS VAPORIZED AT
C             THIS TEMPERATURE & PRESSURE.
C   IER = 502  THE EQUATION OF STATE HAS NO ROOTS.
C   IER = 801  THE CALCULATION IS PERFORMING IN THE RANGE OF
C             MISCIBILITY AREA, NO PHASE SPLITTING SHOWN.
C   IER = 802  THE CHEMICAL POTENTIAL CURVE HAS MORE THAN 2
C             EXTREME VALUES.  CHECK THE PARAMETERS.
C   IER = 803  THE CHEMICAL POTENTIAL CURVE HAS ONLY 1 EXTREME
C             VALUE.
C *****

```

```

C MAIN ROUTINE
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
  COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
  COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+      GDOT,VREF(2),EII(2),UM(2)
  COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4

  OPEN (UNIT=7, FILE='COMPONT.DAT', STATUS='UNKNOWN')
  OPEN (UNIT=8, FILE='LLE.DAT', STATUS='UNKNOWN')

C
C THIS PROGRAM WRITTEN ONLY FOR SOLVING COMPOSITIONS IN EQUILIBRIUM
C PHASES IN BINARY SYSTEM.  THUS, 'NCOMP' IS SET TO BE 2.
C
  NCOMP = 2

C
  WRITE (*,*) 'ENTER YOUR OPTION'
  WRITE (*,*) 'OPTION 1 --- SEARCH THE 2-PHASE AND 1-PHASE REGION'
  WRITE (*,*) '          SEPECIFIED PRESSURE.'
  WRITE (*,*) 'OPTION 2 --- CALCULATE THE COMPOSITIONS AT SPECIFIED'
  WRITE (*,*) '          PRESSURE & TEMPERATURE.'
  READ (*,*) IOPT

C
C SPECIFY THE CONDITIONS OF THE SYSTEM
C
  WRITE (*,*) 'SPECIFY THE PRESSURE OF THE SYSTEM ( Pa ) '
  READ (*,*) P
  WRITE (8,25) P
  P = P/1000.D00
  IF (P.LE.0.D00) THEN
    IER = 101
    WRITE (*,*) 'PRESSURE IS LESS THAN OR EQUAL TO ZERO. '
    GO TO 1000
  ENDIF

C
C READ DATA FILE TO GET THE NUMBER OF DIFFERENT FUNCTION GROUPS IN
C THE MIXTURE AND PARAMETERS OF THE EOS.
C
  CALL GCDATA(NCOMP,NGROUP,PK,WM,IER)
  IF (IER.NE.0) THEN
    GO TO 1000
  ENDIF

C
  IF (IOPT.EQ.1) THEN
    CALL SEARCH
  ENDIF

C
  WRITE (*,*) 'CALCULATE UCST CURVE(1) OR LCST CURVE(2) '
  READ (*,*) IST
  WRITE (*,*) 'TEMPERATURE TO START CALCULATION TILL CRITICAL'
  WRITE (*,*) 'TEMPERATURE.( K )(FIND THE BINODAL CURVE)'
  READ (*,*) T
  WRITE (8,90) T
  IF (T.LE.0.D00) THEN
    IER = 101
    WRITE (*,*) 'TEMPERATURE IS LESS THAN OR EQUAL TO ZERO. '
    GO TO 1000
  ENDIF

```

```

C
C   CALL CONSTR TO CHECK IF THE CALCULATION IS PERFORMED IN THE TWO
C   PHASE REGION.  FIND THE CONSTRAIN OF THE SOLUTION RANGE AND
C   INITIAL GUESS FOR THE COMPOSITIONS FOR THE SOLVENT.
C
C   CALL CONSTR
C   IF (IER.NE.0) THEN
C     GO TO 1000
C   ENDIF
C
C   CALL BINODAL TO SOLVE THE CONCENTRATIONS OF THE POLYMER IN TWO
C   PHASES AT EEQUILIBRIUM.  THE SUBROUTINE BINODAL CALLS IMSL ROUTINE
C   TO SOLVE THE NONLINEAR EQUATIONS.
C
C   CALL BINODAL
C
1000  CONTINUE
C
25   FORMAT (5X,'PRESSURE(KPa) IS:',F11.5)
90   FORMAT (2X,'TEMPERATURE OF THE SYSTEM',3X,F11.5)
C
C   STOP
C   END
C
C *****
C   SUBROUTINE SEARCH
C   -----
C   USAGE          -   SEARCH FROM 200K TO 550K TO CHECK IF THE PHASE
C                     SEPARATION OCCURS AT THE SPECIFIED PRESSURE.
C *****
C   IMPLICIT REAL*8 (A-H,O-Z)
C   COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
C   COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
C   COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
C   +      GDOT,VREF(2),EII(2),UM(2)
C   COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4
C
C   WRITE (*,*) 'THE TEMPERATURE RANGE WANTED TO SEARCH(T1,T2) (T1<T2) '
C   READ (*,*) TT1,TT2
C   NT = INT((TT2-TT1)/10.D00)
C
C   DO 200 I=1,NT+1
C     IER = 0
C     T = TT1 + (I-1)*10.D00
C     CALL CONSTR
C     IF (IER.EQ.0) THEN
C       WRITE (*,500) T,X2,X3
500   FORMAT(F10.4,5X,'TWO-PHASE REGION',2X,'(',F8.5,',',F8.5,')')
C     ELSE IF (IER.EQ.801) THEN
C       WRITE (*,600) T
600   FORMAT(F10.4,5X,'ONE-PHASE REGION')
C     ENDIF
C     PAUSE
200   CONTINUE
C
C   STOP
C   END

```

```

C *****
C SUBROUTINE CONSTR
C -----
C USAGE          - CALL DIFF1 TO CHECK IF THE PHASE SEPARATION
C                 OCCURS. IF IT HAPPENS, FIND THE SPINODAL
C                 POINTS.
C                 - CALL BISECT TO FIND THE SOLUTION RANGE OF
C                 CONCENTRATIONS OF SOLVENT IN DIFFERENT PHASES.
C *****
C   IMPLICIT REAL*8 (A-H,O-Z)
C   COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
C   COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
C   COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+   GDOT,VREF(2),EII(2),UM(2)
C   COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4
C   DIMENSION WX(5),UX(5),F(1100),DF1(1100)

C   W1 = 1.D-12
C   W2 = 1.D00-1.D-12
C   NLIMIT = 1000
C   DELTAW = (W2-W1)/NLIMIT

C   CALCULATE THE CHEMICAL POTENTIAL OF THE POLYMER

C   CALL PARAME(NCOMP,NGROUP,T,WM,WMG,VREF,EII)
C   CALL PURE
C   IF (IER.NE.0) THEN
C     RETURN
C   ENDIF

C   DO 100 I = 1,NLIMIT+1
C     WF(1) = W1+(I-1)*DELTAW

C   CALL MIXTURE
C   IF (IER.NE.0) THEN
C     RETURN
C   ENDIF

C   CALL MIXPTL
C   F(I) = UM(2)
100 CONTINUE

C   CALL DIFF1 TO CHECK IF THE MINIMA(WLEFT) AND MAXIMA(WRIGHT) OF THE
C   CURVE OF CHEMICAL POTENTIAL OF THE POLYMER EXIST. IF THEY EXIST,
C   FIND THEIR VALUES.
C *****
C   WX(I) --- WEIGHT FRACTIONS OF SOLVENT AT THE EXTREME POINTS OF
C             THE CURVE OF CHEMICAL POTENTIAL OF THE POLYMER.
C   UX(I) --- VALUE OF CHEMICAL POTENTIAL AT THE EXTREME POINTS.

C   CALL DIFF1(F,W1,DELTAW,DF1,NLIMIT,IER,WX,UX)
C   IF (IER.NE.0) THEN
C     RETURN
C   ENDIF

C   X2 = WX(1)
C   X3 = WX(2)
C   IF (IOPT.EQ.1) THEN

```



```

      RETURN
    ENDIF

C     CALL BISECT TO FIND THE SOLUTION RANGE FOR THE CONCENTRATIONS OF
C     SOLVENT IN TWO PHASES: (X1,X2) AND (X3,X4).
C
    AA = 1.D-12
    BB = X2
    CALL BISECT(AA, BB, UX(2), WA)
    WRITE (*,*) '(A,B) =', WA, X2
    X1 = WA

    AA = X3
    BB = 1.D00 - 1.D-12
    CALL BISECT(AA, BB, UX(1), WA)
    WRITE (*,*) '(C,D) =', X3, WA
    X4 = WA
    PAUSE

    RETURN
  END

C     *****
C     SUBROUTINE BISECT(AA, BB, REFER, WA)
C     *****
    IMPLICIT REAL*8 (A-H, O-Z)
    COMMON /A1/NCOMP, NGROUP(2, 23), P, T, PK, IOPT, IST, IER
    COMMON /B2/VRED, PRED, TRED, EPSLON, VHARD, RR, Q
    COMMON /C3/TRD(2), VRD(2), CTA(2), RI(2), QI(2), THEBAR(2), SUMTH,
+      GDOT, VREF(2), EII(2), UM(2)
    COMMON /D4/X(2), WF(2), WM(2), X1, X2, X3, X4
    DIMENSION FUNC(3)

300  ERR = ABS(BB-AA)

    IF (ERR.LT.1.E-5) THEN
      WA = (AA + BB)/2.D00
      GO TO 350
    END IF

C
    DO 330 I=1, 3
    IF (I.EQ.1) THEN
      WF(1) = AA
    END IF
    IF (I.EQ.2) THEN
      WF(1) = BB
    END IF
    IF (I.EQ.3) THEN
      CC = AA + ERR/2.D00
      WF(1) = CC
    END IF

    CALL MIXTURE
    CALL MIXPTL
    FUNC(I) = UM(2) - REFER
330  CONTINUE

    IF ((FUNC(1)*FUNC(3)).LT.0.0) THEN

```

```

        BB = CC
    ELSE
        AA = CC
    END IF
    GO TO 300

350  CONTINUE
    RETURN
    END

C *****
  SUBROUTINE DIFF1(F,W1,DELTAW,DF1,NLIMIT,IER,WX,UX)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION WX(5),UX(5),F(1100),DF1(1100)

  NP=0

C
  DO 100 I=2,NLIMIT
    DF1(I)=(F(I+1)-F(I-1))/(2.D00*DELTAW)
    IF (I.GT.2) THEN
      ADJUST = DF1(I-1)*DF1(I)
      IF(ADJUST.LT.0.0) THEN
        NP = NP+1
        WX(NP) = W1 + DELTAW*(I-1.5D00)
        UX(NP) = (F(I-1)+F(I))/2.D00
      END IF
    END IF
  END IF

C
100  CONTINUE

  IF (NP.EQ.0) THEN
    IER = 801
    RETURN
  ELSE IF (NP.GT.2) THEN
    IER = 802
    WRITE (*,*) 'THE CHEMICAL POTENTIAL CURVE HAS MORE THAN 2'
    WRITE (*,*) 'EXTREME VALUES. CHECK THE PARAMETERS.'
    RETURN
  ELSE IF (NP.EQ.1) THEN
    IER = 803
    WRITE (*,*) 'THE CHEMICAL POTENTIAL CURVE HAS ONLY 1 EXTREME'
    WRITE (*,*) 'VALUE.'
    RETURN
  ENDIF

  RETURN
  END

C *****
  SUBROUTINE GCDATA(NCOMP,NGROUP,PK,WM,IER)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION NGROUP(2,23),WM(2)

```

```

DO 20 I=1,8
20  READ(7,74) ANTT
    DO 50 N =1, NCOMP
      READ(7,71) (NGROUP(N,I), I=1,23)
      WRITE(8,71) (NGROUP(N,I), I=1,23)
      DO 50 I=1,23
        IF (NGROUP(N,I).LT.0) THEN
          IER = 105
          RETURN
        ENDIF
      CONTINUE
50  CONTINUE
C
C  INPUT PARAMETERS FOR EQUATION OF STATE AND MOLECULAR WEIGHT OF
C  POLYMER
C
      WRITE (*,*) 'MOLECULAR WEIGHT OF POLYMER =?'
      READ (*,*) WM(2)
      WRITE (8,*) 'MOLECULAR WEIGHT OF POLYMER IS:', WM(2)
      WRITE (*,*) 'PRAUSNITZ"S K'
      READ (*,*) PK
      WRITE (8,*) 'PRAUSNITZ"S K = ', PK

74  FORMAT(A72)
71  FORMAT(23I3)

      RETURN
      END

C *****
C  SUBROUTINE BINODAL
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /A1/NCOMP, NGROUP(2,23), P, T, PK, IOPT, IST, IER
      COMMON /B2/VRED, PRED, TRED, EPSLON, VHARD, RR, Q
      COMMON /C3/TRD(2), VRD(2), CTA(2), RI(2), QI(2), THEBAR(2), SUMTH,
+          GDOT, VREF(2), EII(2), UM(2)
      COMMON /D4/X(2), WF(2), WM(2), X1, X2, X3, X4
      DIMENSION WGUSS(2), WP(2)
      EXTERNAL FCN, DNEQNF

      WGUSS(1) = X1
      WGUSS(2) = X4
      WRITE (*,1212) WGUSS(1), WGUSS(2)
      WRITE (8,105)
1212  FORMAT(2X, 'INITIAL GUESS FOR SOLVENT IN TWO PHASES FOUND:', /,
+          2X, 2(F10.6, 3X))
      WRITE (*,*) 'TEMPERATURE STEP? '
      READ (*,*) DIFT
105   FORMAT('=====', /,
+          '=====', /, 3X, 'TEMP. (K)', T15, 'PHASE 1(SOLVENT)'
+          , T35, 'PHASE 2(SOLVENT)', T55, 'RESIFDUAL')

      IT = 0
100  IT = IT + 1
C
C  SET THE SOLUTIONS OF EQUATION OF STATE AS THE INITIAL GUESS FOR
C  THE NEXT TEMPERATURE STEP

```

```

C
  IF (IT.GT.1) THEN
  IF (IST.EQ.1) THEN
    T = T + DIFT
  ELSE IF(IST.EQ.2) THEN
    T = T - DIFT
  ENDIF
  WGUESS(1) = WP(1)
  WGUESS(2) = WP(2)
  END IF

  CALL PARAME(NCOMP,NGROUP,T,WM,WMG,VREF,EII)
  CALL PURE
  IF (IER.NE.0) THEN
    RETURN
  ENDIF

C
C  CALL IMSL ROUTINES TO SOLVE THE NONLINEAR EQUATIONS
C

  N = 2
  ERRREL = 1.d-6
  ITMAX = 100

  CALL DNEQNF(FCN, ERRREL, N, ITMAX, WGUESS, WP, FNORM)

  WW1 = 1.D00-WP(2)
  WW2 = 1.D00-WP(1)
  WRITE (8,110) T,WW1,WW2, FNORM
110  FORMAT (2X,F8.2,T17,F12.8,T37,F12.8,T52,F12.8)
  IF (ABS(WP(1)-WP(2)).LT.1.E-6) THEN
  STOP
  ENDIF

  IF (IT.LT.500) GO TO 100

  RETURN
  END
C *****
C  SUBROUTINE FCN(WP,FOBJ,N)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
  COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
  COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+   GDOT,VREF(2),EII(2),UM(2)
  COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4
  DIMENSION WP(2),US(2),UP(2),FOBJ(2)

C
C   WP(1) --- W. FRACTION OF SOLVENT IN PHASE 1
C   WP(2) --- W. FRACTION OF SOLVENT IN PHASE 2
C   WF(1) --- W. FRACTION OF SOLVENT IN ANY PHASE
C   WF(2) --- W. FRACTION OF POLYMER IN ANY PHASE
C   NPH --- THE ITH PHASE
C

  DO 120 NPH=1,2
  IF (NPH.EQ.1) THEN
    WF(1) = WP(1)
  ELSE

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```

      WF(1) = WP(2)
      END IF

      DO 115 I=1,2
      IF (ABS(WF(I)-0.D00).LT.1.E-7) THEN
      WF(I) = 1.D-7
      END IF
115  CONTINUE

      CALL MIXTURE
      IF (IER.NE.0) THEN
      RETURN
      ENDIF
      CALL MIXPTL

      DO 118 I=1,2
      IF (ABS(WF(I)).LT.3.0E-7) THEN
      WF(I) = 0.D00
      END IF
118  CONTINUE

      US(NPH) = UM(1)
      UP(NPH) = UM(2)
120  CONTINUE

      FOBJ(1) = (US(1)-US(2))
      FOBJ(2) = (UP(1)-UP(2))

      RETURN
      END

C *****
C  SUBROUTINE PURE
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
      COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
      COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+          GDOT,VREF(2),EII(2),UM(2)
      DATA VH/9.75D-3/,Z/10.D00/

C
C  SOLVE THE PURE COMPONENT EQUATION OF STATE FOR COMPONENT 1 & 2
C  RESPECTIVELY.  N=1 REPRESENTS SOLVENT AND N=2 POLYMER.
C
      DO 51 N=1,2
      VHARD = VREF(N)
      EPSLON = EII(N)
      RR = VREF(N)/VH
      Q = ((Z-2.D00)*RR+2.D00)/Z

      CALL INITIAL(N,P,T,VHARD,EPSLON,RR,Q,VRED,IER)
      IF (IER.NE.0) THEN
      RETURN
      ENDIF
C
      CALL EOS

```

```

VRD(N) = VRED
CTA(N) = SUMTH
TRD(N) = TRED
51  CONTINUE

      RETURN
      END

C *****
C   SUBROUTINE INITIAL(NCP,P,T,VHAD,EPSON,RR1,QQ1,VRED,IER)
C   -----
C   THE FUNCTION OF THIS SUBROUTINE IS NOT ONLY TO FIND
C   REASONABLE INITIAL GUESS OF REDUCED VOLUME FOR EQUATION OF
C   STATE, BUT ALSO TO LIMITATION OF THE STATE AT THE SPECIFIC
C   PRESSURE AND TEMPERATURE
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION ROT(5),RHO(500),F(500)
      DATA RGAS/8.31439D00/, Z/10.D00/, VH/9.75D-3/

      NP = 100
      RHO1 = 1.D-5
      RHO2 = 1.D00-1.D-5
500  NROOT = 0
      DELRHO = (RHO2-RHO1)/NP

1000 DO 1200 I=1,NP+1
      RHO(I) = RHO1 + (I-1)*DELRHO
      THTA = QQ1/((VHAD/(VH*RHO(I))-RR1)+QQ1)
      F(I) = DLOG(1.D00/(1.D00-RHO(I)))+(Z/2.D00)*DLOG(1.D00+(QQ1/RR1)
+          *RHO(I)-RHO(I))-THTA**2*(Z*EPSON)/(2.D00*RGAS*T)
+          -(P*VH)/(RGAS*T)
      IF (I.NE.1) THEN
      ADJUST = F(I-1)*F(I)
      IF (ADJUST.LT.0.0) THEN
      NROOT = NROOT +1
      ROT(NROOT) = (RHO(I-1)+RHO(I))/2.D00
      IF (NROOT.GT.3) THEN
      WRITE (*,*) 'THE EOS HAS MORE THAN 3 ROOTS'
      STOP
      END IF
      END IF
      END IF
      END IF

1200 CONTINUE

      IF (NROOT.EQ.3) THEN
      VREDV = 1.D00/ROT(1)
      VREDL = 1.D00/ROT(3)
      ELSE IF (NROOT.EQ.1) THEN
      IF (ROT(1).LT.0.2) THEN
      VREDV = 1.D00/ROT(1)
      WRITE (*,*) 'THE EQUATION OF STATE HAS NO LIQUID ROOT FOR'
      WRITE (*,*) 'COMPONENT',NCP,', THE COMPONENT IS VAPORIZED'
      WRITE (*,*) 'AT THIS TEMPERATURE & PRESSURE.'
      IER = 501
      RETURN
      ELSE

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          VREDL = 1.D00/ROT(1)
        END IF
      ELSE IF (NROOT.EQ.2) THEN
        WRITE (*,*) 'THE EOS HAS 2 ROOTS'
        RHO1 = 1.D-5
        RHO2 = (1.D00-1.D-5)
        NP = 400
        GO TO 500
      ELSE
        IER = 502
        WRITE (*,*) 'THE EQUATION OF STATE HAS NO ROOTS '
        WRITE (*,*) 'CHECK THE EQUATION PARAMETERS'
        RETURN
      END IF

      VRED = VREDL

      RETURN
    END

C *****
C   SUBROUTINE MIXTURE
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
      COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
      COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+          GDOT,VREF(2),EII(2),UM(2)
      COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4
      DATA TOL/1.e-12/
      WF(2) = 1.D00 - WF(1)

C
C   CONVERT W. FRACTION INTO MOLE FRACTION
C
      TOTALW = 0.0
      DO 110 I=1,NCOMP
110  TOTALW = TOTALW + WF(I)/WM(I)
      DO 112 I=1,NCOMP
112  X(I) = (WF(I)/WM(I))/TOTALW
      CONTINUE

      CALL MIXING
      CALL INITIAL(3,P,T,VHARD,EPSLON,RR,Q,VRED,IER)
      IF (IER.NE.0) THEN
        RETURN
      ENDIF

C
      DELV = VRED*0.005D00

      DO 220 I=1,150
      VREDX = VRED
      CALL MIXING
      F = EQN(VRED,PRED,TRED,SUMTH,RR,Q)
      IF (ABS(F).LT.TOL) GO TO 95

      VRED1 = VREDX + DELV
      VRED = VRED1
      CALL MIXING

```

```

F1 =EQN (VRED, PRED, TRED, SUMTH, RR, Q)

VRED2 = VREDX - DELV
VRED = VRED2
CALL MIXING
F2 =EQN (VRED, PRED, TRED, SUMTH, RR, Q)

DFDV = (F1-F2)/(VRED1-VRED2)
V = VREDX - F/DFDV

220 VRED = V

WRITE (8,*) 'NO CONVERGENCE', I
WRITE (8,*) 'CANNOT FIND A ROOT FOR VRED'

95 VRED = V

CALL MIXING

500 FORMAT (5X, 'MIXTURE', /, 3X, 'F, F1, VRED, V =', /, 3X, 4 (E12.6, 2X))
600 FORMAT (5X, 'RED. V FOR MIX.', E15.10)

RETURN
END

C *****
C SUBROUTINE MIXING
C *****
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 NH, NQ
COMMON /A1/NCOMP, NGROUP (2, 23), P, T, PK, IOPT, IST, IER
COMMON /B2/VRED, PRED, TRED, EPSLON, VHARD, RR, Q
COMMON /C3/TRD (2), VRD (2), CTA (2), RI (2), QI (2), THEBAR (2), SUMTH,
+ GDOT, VREF (2), EII (2), UM (2)
COMMON /D4/X (2), WF (2), WM (2), X1, X2, X3, X4
DIMENSION TH (2)
DATA VH/9.75D-3/, RGAS/8.314D00/, Z/10.D00/

Q = 0.0
RR = 0.0
VHARD= 0.0

DO 100 I=1,2
C
C CALCULATE THE REFERENCE VOLUME OF MIXTURE
C
VHARD = VHARD + VREF (I)*X (I)
C CALCULATE THE NUMBER OF SITES OCCUPIED BY COMPONENT i & THE
C SURFACE AREA OF COMPONENT i.
C
RI (I) = VREF (I)/VH
QI (I) = ((Z-2.D00)*RI (I)+2.D00)/Z
RR = RR + RI (I)*X (I)
Q = Q + X (I)*QI (I)

100 CONTINUE
C
C CALCULATE THE NUMBER OF HOLES IN THE LATTICES & THE NUMBER OF

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C     SEGMENTAL INTERACTIONS
C
      NH = (VRED*VHARD)/VH-RR
      NQ = NH + Q

      SUMTH = 0.0
      SUME = 0.0

      DO 120 N=1,NCOMP
C
C     CALCULATE THE SURFACE AREA FRACTION ON A HOLE FREE BASIS FOR
C     COMPONENT i & THE SURFACE AREA FRACTION INCLUDING HOLES FOR
C     COMPONENT i
C
      THEBAR(N)=QI(N)*X(N)/Q
      TH(N) = QI(N)*X(N)/NQ
      SUMTH = SUMTH +TH(N)
C
C     CALCULATE THE SUM OF THE INTERACTION ENERGIES NORMALIZED BY THE
C     SURFACE AREA FRACTIONS
C
      SUME = SUME + THEBAR(N)*EII(N)
120  CONTINUE

      E12=DSQRT(EII(1)*EII(2))*(1.D00- PK)
      DELEP=EII(1)+EII(2)-2.D00*E12

      GDOT=DEXP(SUMTH*DELEP/(RGAS*T))
      THTT=THEBAR(1)*THEBAR(2)
      GAMMA=2.D00/(1.D00+DSQRT(1.D00-4.D00*THTT*(1.D00-GDOT)))

      EPSLON = -THEBAR(1)*THEBAR(2)*GAMMA*DELEP
      EPSLON = SUME + EPSLON

      TRED=2.*RGAS*T/(Z*EPSLON)
      PRED=2.*VH*P/(Z*EPSLON)

      RETURN
      END

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      FUNCTION EQN(VRED, PRED, TRED, SUMTH, RR, Q)
      IMPLICIT REAL*8 (A-H, O-Z)
      DATA Z/10.D00/

      FV = DLOG(VRED/(VRED-1.D00))
      FV = FV+(Z/2.0)*DLOG((VRED+(Q/RR)-1.D00)/VRED)
      EQN = FV-SUMTH**2/TRED -PRED/TRED

      RETURN
      END

C *****
C     SUBROUTINE PARAME(NCOMP,NGROUP,T,WM,WMG,VREF,EII)
C     -----
C           THIS SUBROUTINE IS TO CALCULATE MOLECULAR INTERACTION
C           ENERGY (EPSLON) AND CHARACTERISTIC MOLECULAR VOLUME (VHARD)
C           FROM GROUP INTERACTION ENERGY (EK), REFERENCE VOLUME PARAME-

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C          TER (RK) AND SURFACE AREA PARAMETER (QK)
C *****
C          IMPLICIT REAL*8 (A-H,O-Z)
C          DIMENSION NGROUP(2,23),WMOL(23),EII300(23),EII400(23),RK300(23),
C          +          RK400(23),QK(23),RKT(23),EKT(23),THETA(23),WM(2),
C          +          WMG(2),VREF(2),EII(2)
C          DATA VREF300/0.021231D00/, VREF400/0.022373D00/
C
C          INITIALIZE MOLECULAR WEIGHTS FOR GROUPS
C
C          DATA WMOL/15.03482, 14.02688, 13.01894, 12.01100, 14.02688,
C          *          13.01894, 12.01100, 13.01894, 27.04582, 26.03788,
C          *          25.02994, 12.01100, 15.99940, 18.01534, 41.02967,
C          *          42.03764, 48.47212, 26.03800, 44.01000, 17.00700,
C          *          29.04200, 44.08500, 30.02100/
C
C          INITIALIZE GROUP VOLUME PARAMETERS AT 300 K
C
C          DATA RK300/0.015956, 0.015220, 0.013018, 0.008539, 0.012595,
C          *          0.012552, 0.012415, 0.010536, 0.024649, 0.023513, 0.027334,
C          *          0.006227, 0.006703, 0.076110, 0.031174, 0.029685, 0.029016,
C          *          0.024117, 0.022357, 0.006851, 0.024904, 0.033756, 0.021052/
C
C          INITIALIZE GROUP VOLUME PARAMETERS AT 400 K
C
C          DATA RK400/0.016278, 0.015180, 0.013017, 0.007624, 0.012561,
C          *          0.011990, 0.011262, 0.010353, 0.024562, 0.023023, 0.024632,
C          *          0.006797, 0.006060, 0.075440, 0.032545, 0.030389, 0.026365,
C          *          0.023902, 0.023270, 0.007518, 0.024432, 0.032850, 0.022632/
C
C          INITIALIZE GROUP INTERACTION PARAMETERS
C
C          DATA EII300/640.870, 943.332, 2209.375, 5378.382, 895.440,
C          *          1727.561, 4069.493, 975.380, 994.410, 1471.588,
C          *          2780.928, 5546.980, 868.470, 949.122, 1237.100,
C          *          1542.000, 1364.400, 1054.480, 1341.670, 1867.920,
C          *          1280.830, 1064.430, 2181.980/
C
C          DATA EII400/640.793, 987.667, 2708.659, 7731.244, 911.401,
C          *          2043.284, 5993.668, 971.622, 1022.675, 1581.805,
C          *          3281.526, 5661.260, 679.560, 1154.306, 1171.500,
C          *          1509.500, 1387.300, 1110.630, 1308.800, 1466.870,
C          *          1215.760, 1343.840, 2275.410/
C
C          INITIALIZE GROUP AREA PARAMETERS.
C
C          DATA QK/0.848, 0.540, 0.228, 0.150, 0.540, 0.228, 0.150,
C          *          0.400, 0.968, 0.660, 0.348, 0.120, 0.240, 1.400, 1.488,
C          *          1.180, 0.952, 0.867, 1.200, 1.200, 0.936, 0.4657, 0.76/
C
C          DO 500 L=1,NCOMP
C          DO 25 I= 1,23
25          WMG(L) = 0.0
C          DO 30 I= 1,23
C          WMG(L) = WMG(L) + NGROUP(L,I)*WMOL(I)
30          CONTINUE
C
C          FIND DEGREE OF POLYMERIZATION OF THE POLYMER

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C
  IF (L.EQ.1) THEN
    WM(L) = WMG(L)
    DP = 1.0
  ELSE
    DP = WM(L)/WMG(L)
  END IF

C *****
C   EVALUATE THE MOLECULAR REFERENCE VOLUME OF THE POLYMER AND
C   SOLVENT AT THE TEMPERATURE OF THE SYSTEM
C
  VHARD = 0.0
  VREF(L) = ((VREF400-VREF300)/100.)*(T-300.)+VREF300
  DO 60 I=1,23
60   RKT(I) = ((RK400(I)-RK300(I))/100.)*(T-300.)+RK300(I)

  DO 70 I=1,23
  VREF(L) = VREF(L) + DP*NGROUP(L,I)*RKT(I)
70   CONTINUE

C *****
C   CALCULATE THE MOLECULAR INTERACTION ENERGY OF THE POLYMER AND
C   SOLVENT
C
  SUMQK=0.0
  DO 120 I=1,23
120  SUMQK=SUMQK+DP*NGROUP(L,I)*QK(I)
  DO 130 I=1,23
  THETA(I)=DP*NGROUP(L,I)*QK(I)/SUMQK
130  continue
  DO 140 I=1,23
140  EKT(I) = ((EII400(I)-EII300(I))/100.)*(T-300.)+EII300(I)
  EII(L) = 0.0

  DO 155 I=1,23
  DO 155 J=1,23
  EII(L) = EII(L) + THETA(I)*THETA(J)*DSQRT(EKT(I)*EKT(J))
155  CONTINUE

500  CONTINUE

  RETURN
  END
C *****
  SUBROUTINE EOS
C -----
C   THIS IS THE GCLF EQUATION OF STATE. THIS SUBROUTINE
C   USES NEWTON'S METHOD TO CALCULATE THE REDUCED VOLUME. A
C   REASONABLE REDUCED VOLUME FOR VAPOR OR LIQUID SHOULD BE
C   GIVEN AS INITIAL GUESS.
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  REAL*8 NH
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
  COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
  COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+      GDOT,VREF(2),EII(2),UM(2)

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DATA VH/9.75D-3/,RGAS/8.314D00/,Z/10.D00/,TOL/1.E-12/

PRED = 2.D00*P*VH/(Z*EPSLON)
TRED = 2.D00*RGAS*T/(Z*EPSLON)
RR = VHARD/VH
Q = ((Z-2.D00)*RR+2.D00)/Z

DO 20 I=1,50
NH = VRED*(VHARD/VH)-RR
SUMTH = Q/(NH+Q)
FV = DLOG(VRED/(VRED-1.D00))
FV = FV+(Z/2.D00)*DLOG((VRED+(Q/RR)-1.D00)/VRED)
FV = FV-SUMTH**2/TRED-PRED/TRED
C
C      DERIVATIVE OF F=F(VRED) WITH RESPECT TO VRED
C
DFV=(1.D00/VRED)-(1.D00/(VRED-1.D00))
DFV=DFV+(Z/2.D00)*(1.D00/(VRED+(Q/RR)-1.D00)-1./VRED)
DFV=DFV+(2.D00*SUMTH/TRED)*(Q/(NH+Q)**2)*(VHARD/VH)

V=VRED-FV/DFV
IF(ABS(FV).LT.TOL) GO TO 30

VRED=V
IF (VRED.LT.1.0) THEN
  VRED = 1.001
END IF
20  CONTINUE

WRITE(8,200)
GO TO 50
30  VRED=V

200  FORMAT(5X,'NO CONVERGENCE,CANNOT FIND VRED')

50  RETURN
END

C *****
C      SUBROUTINE MIXPTL
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IOPT,IST,IER
      COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
      COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+      GDOT,VREF(2),EII(2),UM(2)
      COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4

      DIMENSION TII(2)
      DATA Z/10.D00/ RGAS/8.31439D00/

      T12 = 2.D00/(1.D00+DSQRT(1.D00-4.D00*THEBAR(1)*THEBAR(2)*
+      (1.D00 - GDOT)))
      TII(1) = (1.D00-THEBAR(2)*T12)/THEBAR(1)
      TII(2) = (1.d00-thebar(1)*t12)/thebar(2)

      SUMV = 0.0
      DO 51 I=1,2

```

```
51      SUMV = SUMV + VREF(I)*X(I)
      CONTINUE

      DO 50 N=1,2
      UM(N) = DLOG(X(N)*VREF(N)/SUMV) + DLOG(VRD(N)/VRED)
      UM(N) = UM(N) + QI(N)*DLOG(VRED*(VRD(N)-1.D00)/
+      ((VRED-1.D00)*VRD(N)))
      UM(N) = UM(N) + QI(N)*((2.D00*CTA(N)-SUMTH)/TRD(N) - SUMTH/
+      TRED)
      UM(N) = UM(N) + (Z*QI(N)/2.D00)*DLOG(TII(N))
      UM(N) = UM(N)*RGAS*T
      UM(2) = UM(2)/RI(2)
50      CONTINUE

      RETURN
      END
```

APPENDIX B

**COMPUTER PROGRAM FOR CALCULATING
BINODAL CURVE USING THE
SANCHEZ-LACOMBE EOS**

```

C *****
C SUBROUTINE BINODAL
C -----
C PURPOSE - THIS SUBROUTINE IS WRITTEN FOR CALCULATE WEIGHT
C CONCENTRATIONS OF THE POLYMER IN TWO PHASES IN
C A POLYMER-SOLVENT BINARY SYSTEM. SANCHEZ-LACOMBE
C EQUATION OF STATE IS USED.
C *****
C IMPLICIT REAL*8 (A-H,O-Z)
C COMMON /A1/NCOMP,P,T,ZETA,RI0(2),RHOI(2),VREFI(2),TREFI(2),
+ PREFI(2),EII(2),WM(2),IOPT,IST,IER
C COMMON /B2/BK,AVG,THM(2),THM0(2),RI(2),CHI,PRED,TRED,R,X(2),RHO,
+ WF(2),UM(2),STAB,GR(2),DGDV(2)
C COMMON /C3/X1,X2,X3,X4
C DIMENSION WGUESS(2),WP(2)
C EXTERNAL FCN,DNEQNF

C WGUESS(1) = X1
C WGUESS(2) = X4
C WRITE (*,*) 'INITIAL GUESS ',WGUESS(1),WGUESS(2)

C WRITE (8,105)
105 FORMAT ('=====',
+ '=====', /,3X,'TEMP.(K)',T15,'PHASE 1(SOLVENT)'
+ ',T35,'PHASE 2(SOLVENT)',T55,'RESIFDUAL')

C IT = 0
100 IT = IT + 1
C
C SET THE SOLUTIONS OF EQUATION OF STATE AS THE INITIAL GUESS FOR
C THE NEXT TEMPERATURE STEP
C
C IF (IT.GT.1) THEN
C IF (IST.EQ.1) THEN
C T = T + DIFT
C ELSE IF (IST.EQ.2) THEN
C T = T - DIFT
C ENDIF
C IF (ABS(WP(1)-WP(2)).LT.0.1) THEN
C DIFT = 0.02D00
C ENDIF
C WGUESS(1) = WP(1)
C WGUESS(2) = WP(2)
C ENDIF

C CALL IMSL ROUTINES TO SOLVE THE NONLINEAR EQUATIONS
C
C N = 2
C ERRREL = 1.d-6
C ITMAX = 100

C CALL DNEQNF(FCN, ERRREL, N, ITMAX, WGUESS, WP, FNORM)

C WW1 = 1.D00-WP(2)
C WW2 = 1.D00-WP(1)
C WRITE (8,110) T,WW1,WW2, FNORM
110 FORMAT (2X,F8.2,T17,F12.8,T37,F12.8,T52,F12.8)
C IF (ABS(WP(1)-WP(2)).LT.1.E-6) THEN

```

```

      STOP
      ENDIF
      IF (IT.LT.500) GO TO 100

      RETURN
      END
C *****
C SUBROUTINE FCN(WP,FOBJ,N)
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /A1/NCOMP,P,T,ZETA,RI0(2),RHOI(2),VREFI(2),TREFI(2),
+          PREFI(2),EII(2),WM(2),IOPT,IST,IER
      COMMON /B2/BK,AVG,THM(2),THM0(2),RI(2),CHI,PRED,TRED,R,X(2),RHO,
+          WF(2),UM(2),STAB,GR(2),DGDV(2)
      COMMON /C3/X1,X2,X3,X4
      DIMENSION WP(2),US(2),UP(2),FOBJ(2)
C
C      WP(1) --- W. FRACTION OF SOLVENT IN PHASE 1
C      WP(2) --- W. FRACTION OF SOLVENT IN PHASE 2
C      WF(1) --- W. FRACTION OF SOLVENT IN ANY PHASE
C      WF(2) --- W. FRACTION OF POLYMER IN ANY PHASE
C      NPH --- THE ITH PHASE
C
      DO 120 NPH=1,2
      IF (NPH.EQ.1) THEN
          WF(1) = WP(1)
      ELSE
          WF(1) = WP(2)
      END IF

      DO 115 I=1,2
      IF (ABS(WF(I)-0.D00).LT.1.E-10) THEN
          WF(I) = 1.D-10
      END IF
115 CONTINUE

      CALL MIXING
      CALL EOS
      CALL CHEMPL

      DO 118 I=1,2
      IF (ABS(WF(I)).LT.3.0E-10) THEN
          WF(I) = 0.D00
      END IF
118 CONTINUE
      US(NPH) = UM(1)
      UP(NPH) = UM(2)
120 CONTINUE
C
      FOBJ(1) = (US(1)-US(2))
      FOBJ(2) = (UP(1)-UP(2))

      RETURN
      END
C *****
C SUBROUTINE SLDATA
C *****

```



```

      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON /A1/NCOMP,P,T,ZETA,RI0(2),RHOI(2),VREFI(2),TREFI(2),
+          PREFI(2),EII(2),WM(2),IOPT,IST,IER

C      N = 1 REPRESENTS SOLVENT & 2 REPRESENTS POLYMER
C
      DO 20 I=1,8
20     READ (7,70) ANTT
        READ (7,80) TREFI(1),TREFI(2)
        READ (7,80) PREFI(1),PREFI(2)
        READ (7,80) VREFI(1),VREFI(2)
        READ (7,80) RHOI(1),RHOI(2)
        READ (7,80) EII(1),EII(2)
        READ (7,90) RI0(1)
        READ (7,90) WM(1)

C
      WRITE (*,*) 'MOLECULAR WEIGHT OF POLYMER?'
      READ (*,*) WM(2)
      RI0(2) = WM(2)/(RHOI(2)*VREFI(2))

      WRITE (*,*) 'ZETA =?'
      READ (*,*) ZETA
      WRITE (8,*) ' ZETA  =',ZETA

C
70     FORMAT(A72)
80     FORMAT(30X,2D20.9)
90     FORMAT(30X,D20.9)

      RETURN
      END

C *****
C      SUBROUTINE MIXING
C *****
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 MI(2)
      COMMON /A1/NCOMP,P,T,ZETA,RI0(2),RHOI(2),VREFI(2),TREFI(2),
+          PREFI(2),EII(2),WM(2),IOPT,IST,IER
      COMMON /B2/BK,AVG,THM(2),THM0(2),RI(2),CHI,PRED,TRED,R,X(2),RHO,
+          WF(2),UM(2),STAB,GR(2),DGDV(2)
      COMMON /C3/X1,X2,X3,X4

      WF(2) = 1.D00 - WF(1)
      TOTALW = 0.0
      DO 1300 L=1,NCOMP
1300    TOTALW = TOTALW + WF(L)/WM(L)
        DO 1350 L=1,NCOMP
1350    X(L) = (WF(L)/WM(L))/TOTALW
        CONTINUE

C      CALCULATE PURE COMPONENT PARAMETERS
C
      SUMM = 0.0
      SUMT = 0.0
      SUMO = 0.0

      DO 100 N=1,NCOMP
100    SUMM = SUMM + X(N)*WM(N)

```

```

DO 110 N=1, NCOMP
MI(N) = X(N)*WM(N)/SUMM
110 CONTINUE

DO 200 N=1, NCOMP
SUM0 = SUM0 + RI0(N)*X(N)
200 SUMT = SUMT + MI(N)/RHOI(N)

DO 210 N=1, NCOMP
THM0(N) = RI0(N)*X(N)/SUM0
THM(N) = MI(N)/RHOI(N)/SUMT
210 CONTINUE
C
C CALCULATE MIXTURE PARAMETERS BY COMBINING RULES
C
VREF = 0.0
R = 0.0
RATIO = VREFI(1)/VREFI(2)
DO 400 N=1, NCOMP
400 VREF = VREF + THM0(N)*VREFI(N)

DO 450 N=1, NCOMP
RI(N) = RI0(N)*VREFI(N)/VREF
R = R + X(N)*RI0(N)
450 CONTINUE

E12 = ZETA*DSQRT(EII(1)*EII(2))
CHI = (EII(1)+EII(2)-2.D00*E12)/(AVG*BK*T)
EPSLON = THM(1)*EII(1)+THM(2)*EII(2)
*      - (BK*AVG)*T*THM(1)*THM(2)*CHI
C
TREF = EPSLON/(AVG*BK)
TRED = T/TREF
PREF = EPSLON/VREF
PRED = P/PREF

RETURN
END

C *****
C SUBROUTINE INITIAL(PRED, TRED, R, RHOV, RHOL, IER)
C -----
C THE FUNCTION OF THIS SUBROUTINE IS NOT ONLY TO FIND
C REASONABLE INITIAL GUESS OF REDUCED VOLUME FOR EQUATION OF
C STATE, BUT ALSO TO LIMITATION OF THE STATE AT THE SPECIFIC
C PRESSURE AND TEMPERATURE
C *****
C IMPLICIT REAL*8 (A-H, O-Z)
C DIMENSION ROT(5), RHORED(500), F(500)

NP = 100
RHO1 = 1.D-5
RHO2 = 1.D00-1.D-5
500 NROOT = 0
DEL RHO = (RHO2-RHO1)/NP

1000 DO 1200 I=1, NP+1

```

```

RHORED(I) = RHO1 + (I-1)*DELRHO
F(I) = EQN(RHORED(I), PRED, TRED, R)
IF (I.NE.1) THEN
ADJUST = F(I-1)*F(I)
  IF (ADJUST.LT.0.0) THEN
    NROOT = NROOT +1
    ROT(NROOT) = (RHORED(I-1)+RHORED(I))/2.D00
    IF (NROOT.GT.3) THEN
      WRITE (*,*) 'THE EOS HAS MORE THAN 3 ROOTS'
      STOP
    END IF
  END IF
END IF
1200 CONTINUE

IF (NROOT.EQ.3) THEN
  RHOV = ROT(1)
  RHOL = ROT(3)
ELSE IF (NROOT.EQ.1) THEN
  IF (ROT(1).LT.0.2) THEN
    RHOV = ROT(1)
    IER = 501
    RETURN
  ELSE
    RHOL = ROT(1)
  END IF
ELSE IF (NROOT.EQ.2) THEN
  WRITE (*,*) 'THE EOS HAS 2 ROOTS'
  PAUSE
  RHO1 = 1.D-6
  RHO2 = (1.D00-1.D-6)
  NP = 400
  GO TO 500
ELSE
  IER = 501
  RETURN
END IF

RETURN
END

C *****
FUNCTION EQN(RHO, PRED, TRED, R)
IMPLICIT REAL*8 (A-H, O-Z)

EQN = RHO**2+PRED+TRED*(DLOG(1.D00-RHO)+(1.D00-1.D00/R)*RHO)

RETURN
END

C *****
SUBROUTINE EOS
C *****
IMPLICIT REAL*8 (A-H, O-Z)
COMMON /A1/NCOMP, P, T, ZETA, RI0(2), RHOI(2), VREFI(2), TREFI(2),
+      PREFI(2), EII(2), WM(2), IOPT, IST, IER
COMMON /B2/BK, AVG, THM(2), THM0(2), RI(2), CHI, PRED, TRED, R, X(2), RHO,

```

```

+          WF(2),UM(2),STAB,GR(2),DGDV(2)
COMMON /C3/X1,X2,X3,X4
DATA TOL/1.E-14/

CALL INITIAL(PRED,TRED,R,RHOV,RHOL,IER)
RHO = RHOL
DELD = RHO*0.002D00

DO 220 I=1,100
RHOX = RHO
F = EQN(RHOX,PRED,TRED,R)
IF (ABS(F).LT.TOL) GO TO 95

RHO1 = RHOX + DELD
F1 = EQN(RHO1,PRED,TRED,R)
RHO2 = RHOX - DELD
F2 = EQN(RHO2,PRED,TRED,R)
C
DFDRHO = (F1-F2)/(RHO1-RHO2)
RO = RHOX - F/DFDRHO
220 RHO = RO

WRITE (8,*) 'NO CONVERGENCE',I
WRITE (8,*) 'CANNOT FIND A ROOT FOR RHO'

95  RHO = RO

500  FORMAT (5X,'MIXTURE',/,3X,'F,F1,RHO,RO =',/,3X,4(E12.6,2X))
600  FORMAT (5X,'RED. RHO FOR MIX.',E15.10)

RETURN
END

C *****
SUBROUTINE CHEMPL
C *****
IMPLICIT REAL*8 (A-H,O-Z)
COMMON /A1/NCOMP,P,T,ZETA,RI0(2),RHOI(2),VREFI(2),TREFI(2),
+       PREFI(2),EII(2),WM(2),IOPT,IST,IER
COMMON /B2/BK,AVG,THM(2),THM0(2),RI(2),CHI,PRED,TRED,R,X(2),RHO,
+       WF(2),UM(2),STAB,GR(2),DGDV(2)
COMMON /C3/X1,X2,X3,X4
DIMENSION TREDI(2),PREDI(2),RUMDA(2)

DO 200 N=1,NCOMP
TREDI(N) = T/TREFI(N)
PREDI(N) = P/PREFI(N)
200 CONTINUE
VRED = 1.D00/RHO

RUMDA(1) = 1.D00/TREDI(1) - 1.D00/TREDI(2) + (THM(1)-THM(2))*CHI
RUMDA(2) = -RUMDA(1)
C
SI = RHO*(THM(1)*THM(2)/(THM0(1)*THM0(2)))*RUMDA(1)
*   - (1.D00/RI0(1)-1.D00/RI0(2))
SI = SI + (P*VRED/(BK*AVG*T))*(VREFI(1)-VREFI(2))
PBETA = VRED**2/(TRED*VRED*(1.D00/(VRED-1.D00)+1.D00/R)-2.D00)
XLEFT = (THM(1)*THM(2)/(THM0(1)*THM0(2)))*CHI-(THM(1)/THM0(1)

```

```

*      -THM(2)/THM0(2))*RUMDA(1)
XLEFT = RHO*(2.D00*(THM(1)*THM(2)/(THM0(1)*THM0(2)))*XLEFT
*      + TRED*SI**2*PBETA)
RIGHT = (THM(2)/THM0(2))**2/(RI0(1)*THM0(1))
*      + (THM(1)/THM0(1))**2/(RI0(2)*THM0(2))
STAB = RIGHT - XLEFT
C
DO 1000 N=1,NCOMP
GR(N) = TREDI(N)*((VRED - 1.D00)*DLOG(1.D00 - RHO)
*      + (1.D00/RI0(N))*DLOG(RHO))
GR(N) = RI0(N)*EII(N)*(GR(N) - RHO + PREDI(N)*VRED)
DGDV(N) = (BK*AVG)*T*(DLOG(THM(N))+(1.D00-RI(N)/RI(3-N))
*      *THM(3-N) + RI0(N)*RHO*(CHI + (1.D00-VREFI(N)
*      /VREFI(3-N))*RUMDA(N))*THM(3-N)**2)
UM(N) = GR(N) + DGDV(N)
1000 CONTINUE

RETURN
END

```

APPENDIX C

**COMPUTER PROGRAM FOR CALCULATING
SBINODAL CURVE USING THE
SANCHEZ-LACOMBE EOS**

```

C *****
C SUBROUTINE SPINODAL
C -----
C PURPOSE - THIS SUBROUTINE IS WRITTEN FOR FIND THE SPINODAL
C CURVE IN THE TEMPERATURE-COMPOSITION DIAGRAM.
C THE SANCHEZ-LACOMBE EOS IS USED.
C *****
C IMPLICIT REAL*8 (A-H,O-Z)
C COMMON /A1/NCOMP,P,T,ZETA,RI0(2),RHOI(2),VREFI(2),TREFI(2),
+ PREFI(2),EII(2),WM(2),IOPT,IST,IER
C COMMON /B2/BK,AVG,THM(2),THMO(2),RI(2),CHI,PRED,TRED,R,X(2),RHO,
+ WF(2),UM(2),STAB,GR(2),DGDV(2)
C COMMON /C3/X1,X2,X3,X4
C DIMENSION WGS(2),WSP(2)

WGS(1) = X2 - 5.D-4
WGS(2) = X3 + 5.D-4
1100 CONTINUE
IT = 0
1800 IT = IT + 1
IF (IT.GT.2) THEN
WGS(1) = WSP(1)
WGS(2) = WSP(2)
ENDIF
DIM = (WGS(1) + WGS(2))/2.D00
WF(1) = DIM
CALL MIXING
CALL EOS
CALL CHEMPL
FD = STAB
IF (FD.GT.0.0) THEN
STOP
ENDIF
C
DO 2000 NUM = 1,2
IF (NUM.EQ.1) THEN
AA = WGS(1)
BB = DIM
CALL BISECT(AA,BB,WA)
WSP(1) = WA
ELSE
AA = DIM
BB = WGS(2)
CALL BISECT(AA,BB,WA)
WSP(2) = WA
ENDIF
2000 CONTINUE
C
WS1 = 1.D00 - WSP(2)
WS2 = 1.D00 - WSP(1)
WRITE (8,1401) T,WS1,WS2
1401 format (2x,3(F15.8,2X))
C
IF (ABS(WSP(1)-WSP(2)).LT.1.D-5) THEN
STOP
ENDIF
C
IF (IT.LT.800) THEN

```

```
IF (ABS(WSP(1)-WSP(2)).LT.0.01) THEN
  IF (IST.EQ.1) THEN
    T = T + 0.02D00
  ELSE IF(IST.EQ.2) THEN
    T = T - 0.01D00
  ENDIF
ELSE
  IF (IST.EQ.1) THEN
    T = T + 0.5D00
  ELSE
    T = T - 0.5D00
  ENDIF
ENDIF
GO TO 1800
ENDIF

RETURN
END
```


APPENDIX D

COMPUTER PROGRAM FOR OPTIMIZING THE
BINARY INTERACTION PARAMETERS

```

C *****
C   PURPOSE           - THIS PROGRAM IS WRITTEN TO OPTIMIZE THE BINARY
C                     ADJUSTABLE PARAMETER BY MINIMIZING THE
C                     DEVIATIONS BETWEEN THE CALCULATED AND
C                     EXPERIMENTAL CRITICAL SOLUTION TEMPERATURES.
C                     THE GOLDEN SECTION METHOD IS USED.
C *****
C MAIN ROUTINE
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IER
  COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
  COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+      GDOT,VREF(2),EII(2),UM(2)
  COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4

  OPEN (UNIT=7, FILE='COMPONT.DAT', STATUS='UNKNOWN')
  OPEN (UNIT=8, FILE='LLE.DAT', STATUS='UNKNOWN')

C THIS PROGRAM WRITTEN ONLY FOR SOLVING COMPOSITIONS IN EQUILIBRIUM
C PHASES IN BINARY SYSTEM.  THUS, 'NCOMP' IS SET TO BE 2.
C
  NCOMP = 2

  WRITE (*,18)
  READ (*,*) P
  WRITE (8,25) P
  P = P/1000.D00

  WRITE (*,*) 'EXPERIMENTAL CRITICAL TEMPERATURE'
  READ (*,*) TEXP
  WRITE (*,*) 'TEMPERATURE TO START SEARCHING THE CRITICAL TEMP.'
  WRITE (*,*) 'ASSUME A TEMPERATURE LOWER THAN THE EXPERIMENTAL'
  WRITE (*,*) 'UCST OR HIGHER THAN THE EXPERIMENTAL LCST'
  READ (*,*) TS

C
  CALL GCDATA
C
  CALCULATE THE CRITICAL TEMPERATURE
C
  CALL OPTIM(TS,TEXP,OK)

  WRITE (*,*) 'OPTIMIZED PRAUSNITZ"S K',PK

18  FORMAT (1X,'PRESSURE(Pa) OF THE SYSTEM =')
25  FORMAT (5X,'PRESSURE(Pa) OF THE SYSTEM IS:',F15.5)

  STOP
  END

C *****
C   SUBROUTINE OPTIM(TS,TEXP,OK)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IER
  COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
  COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+      GDOT,VREF(2),EII(2),UM(2)
  COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4

```

```

C INPUT THE BOUNDARY OF THE K VALUE
  WRITE (*,*) 'INPUT THE BOUNDARY OF THE K VALUE'
  READ (*,*) XLB,XRB
  ERR = 1.E-4
  IMAX = 200
C
C EVALUATEY AT THE BOUNDARIES
  YLB=FOBJ (TEXP,TS,XLB)
  YRB=FOBJ (TEXP,TS,XRB)
C INITIATE THE MODIFIED FIBONACCI SEARCH
  WL=XRB-XLB
  X1=XLB+.382*WL
  Y1=FOBJ (TEXP,TS,X1)
  X2=XRB-.382*WL
  Y2=FOBJ (TEXP,TS,X2)
1 IF (Y2.LT.Y1)GO TO 2
C DISCARD THE RIGHT SIDE OF THE REGION OF UNCERTAINTY
  XRB=X2
  YRB=Y2
  X2=X1
  Y2=Y1
  WL=XRB-XLB
  IF (WL.LT.ERR) GO TO 1000
  X1=XLB+.382*WL
  Y1=FOBJ (TEXP,TS,X1)
  GO TO 1
C DISCARD THE LEFT SIDE OF THE REGION OF UNCERTAINTY
2 XLB=X1
  YLB=Y1
  X1=X2
  Y1=Y2
  WL=XRB-XLB
  IF (WL.LT.ERR)GO TO 1000
  X2=XRB-.382*WL
  Y2=FOBJ (TEXP,TS,X2)
  GO TO 1

1000 CONTINUE
  OK = (XLB+XRB)/2.D00

  RETURN
  END

C *****
  FUNCTION FOBJ (TEXP,TS,XK)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)

  CALL CTEMP (TS,XK,TC)
  FOBJ = (TEXP-TC)**2
  RETURN
  END

C *****
  SUBROUTINE CTEMP (TS,XK,TC)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IER

```

```

COMMON /B2/VRED, PRED, TRED, EPSLON, VHARD, RR, Q
COMMON /C3/TRD(2), VRD(2), CTA(2), RI(2), QI(2), THEBAR(2), SUMTH,
+      GDOT, VREF(2), EII(2), UM(2)
COMMON /D4/X(2), WF(2), WM(2), X1, X2, X3, X4
DIMENSION F(1000), DF1(1000)

WW1 = 1.0D-4
WW2 = 1.0D00-1.0D-4
C
DEL = 1.D-3
DELT = 0.02D00
ERR = 4.*1.D-3
T =TS
PK = XK
W1 = WW1
W2 = WW2
WRITE (*,*) ' TS', TS

1000 CONTINUE
WRITE (*,*) 'T =', T
NLIMIT = INT((W2-W1)/DEL)
WRITE (8,*) NLIMIT
DO 10 I = 1, NLIMIT

DELW=(W2-W1)/NLIMIT
W = W1+(I-1)*DELW
WF(1) = W
CALL GCLF
F(I) = UM(2)
C
10 CONTINUE
C
C      FIND WLEFT AND WRIGHT
C
INDEX = 0
CALL DIFF1(F, W1, DELW, DF1, NLIMIT, INDEX, WLEFT, WRIGHT)

IF (ABS(WRIGHT-WLEFT).LT.ERR) THEN
  TC = T
  WRITE (8,99) WLEFT, WRIGHT
99  FORMAT (3X, '(WL,WR) =', 2F11.7)
  RETURN
END IF

IF (INDEX.EQ.2) THEN
  TC = T + DELT/2.D00
  WRITE (8,*) 'TC =', TC
  RETURN
ELSE
  T = T - DELT
  W1 = WLEFT - 0.01
  W2 = WRIGHT + 0.01
END IF
GO TO 1000

RETURN
END

```

```

C *****
C SUBROUTINE DIFF1(F,W1,DELW,DF1,NLIMIT,INDEX,WLEFT,WRIGHT)
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION NW(2),F(1000),DF1(1000)
  DATA NW/0,0/

  NP=0

  DO 100 I=2,NLIMIT-1
  C   WRITE (8,*) F(I-1),F(I),F(I+1)
  DF1(I)=(F(I+1)-F(I-1))/(2.*DELW)
  C   WRITE (8,*) 'DF1 ',DF1(I)
    IF (I.GT.2) THEN
      ADJUST = DF1(I-1)*DF1(I)
      IF(ADJUST.LT.0.0) THEN
        NP = NP+1
        NW(NP)=I
        WRITE (8,*) NW(NP)
      END IF
    END IF

    IF (NW(2).NE.0) THEN
      INDEX=1
    ENDIF
  C
  100 CONTINUE

  IF (NP.EQ.0) THEN
    INDEX = 2
    RETURN
  END IF

  IF(INDEX.EQ.1) THEN
    WLEFT=W1+DELW*(NW(1)-1)
    WRIGHT=W1+DELW*(NW(2)-1)
    WRITE (*,199) WLEFT,WRIGHT
  199   FORMAT (3X,'(WLEFT,WRIGHT) ',2E15.9)
    INDEX=0
  END IF
  C

  RETURN
  END

C *****
C SUBROUTINE GCLF
C *****
  IMPLICIT REAL*8 (A-H,O-Z)
  COMMON /A1/NCOMP,NGROUP(2,23),P,T,PK,IER
  COMMON /B2/VRED,PRED,TRED,EPSLON,VHARD,RR,Q
  COMMON /C3/TRD(2),VRD(2),CTA(2),RI(2),QI(2),THEBAR(2),SUMTH,
+   GDOT,VREF(2),EII(2),UM(2)
  COMMON /D4/X(2),WF(2),WM(2),X1,X2,X3,X4

  C CALCULATE THE MOLECULAR PARAMETERS (MOLECULAR REFERENCE VOLUMES &
  C MOLECULAR INTERACTION ENERGIES) FOR PURE COMPONENTS.

```

```
C
CALL PARAME(NCOMP,NGROUP,T,WM,WVG,VREF,EII)
C
C  CALCULATE RED. VOLUMES, RED. TEMPERATURE & SURFACE AREA FRACTIONS
C  OF EACH COMPONENT.
C
CALL PURE
C
C  CALCULATE THE PARAMETERS BY MIXING RULE.  SOLVE THE EQUATION OF
C  STATE FOR MIXTURE.  THEN CHEMICAL POTENTIAL FOR EACH COMPONENT IS
C  COMPUTED.
C
CALL MIXTURE
CALL MIXPTL

RETURN
END
```

APPENDIX E

**INPUT INFORMATION FOR CALCULATIONS USING
THE SANCHEZ-LACOMBE AND GCLF
EQUATIONS OF STATE**

```

C *****
C   FILE NAME       - SLDATA.DAT
C   PURPOSE        - THIS DATA FILE IS TO PROVIDE THE MOLECULAR
C                   PARAMETERS FOR THE EQUILIBRIUM CALCULATION
C                   USING SANCHEZ-LACOMBE EQUATION OF STATE.
C *****
C   SYSTEM:  HDPE/n-PENTANE          SOLVENT (1)          POLYMER(2)
C -----
TREFI(i)  ( KELVIN )                441.D00              649.D00
PREFI(i)  (   Pa   )                310.0545D6           425.0D6
VREFI(i)  (M**3/MOL)                11.82D-6              12.7D-6
RHOI(i)   (GRAM/M**3)               0.755D6               904.0D3
EII(i)    (J/MOL)                   3667.6368D00          5397.5D00
RIO(i)    (DIMENSIONLESS)           8.09D00
WM(i)     (KG/MOL)                   72.15028D0

```



```
C *****
C FILE NAME      - GPDATA.DAT
C
C PURPOSE        - THID DATA FILE IS TO ACCOUNT THE NUMBER OF
C                  FUNCTION GROUPS AVAILABLE IN THE COMPOUNDS IN
C                  THE BINARY SYSTEMS.
C *****
C SYSTEM: PEG/H20
0 0 0 0 0 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0
0 2 0 0 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0
```

APPENDIX F

**EXPRESSION FOR STABILITY CONDITIONS USING
THE GCLF EQUATION OF STATE**

It is well known that the stability of a homogeneous phase in a binary mixture must simultaneously satisfy the following conditions:

$$\frac{\partial \mu_1}{\partial x_1} > 0 \quad \text{and} \quad \frac{\partial \mu_2}{\partial x_2} > 0 \quad (\text{F.1})$$

It is necessary to calculate the derivative of the relative chemical potential of the polymer with respect to mole fraction of polymer.

$$\begin{aligned} \frac{\partial}{\partial x_2} \left(\frac{\Delta \mu_2}{RT} \right) &= \frac{\partial}{\partial x_2} \left(\ln \frac{x_2 v_2^*}{v^*} \right) + \frac{\partial}{\partial x_2} \left(\ln \frac{\bar{v}_2}{\bar{v}} \right) + q_2 \frac{\partial}{\partial x_2} \left(\frac{\bar{v} - \bar{v}_2 - 1}{\bar{v} - 1} \right) \\ &+ q_2 \frac{\partial}{\partial x_2} \left(\frac{2\theta_{2,p} - \theta}{\bar{T}_2} - \frac{\theta}{\bar{T}} \right) + \frac{zq_2}{2} \frac{\partial}{\partial x_2} (\ln \dot{\Gamma}_{22}) \end{aligned} \quad (\text{F.2})$$

$$\begin{aligned} &= \frac{v_1^*}{x_2 v^*} - \frac{1}{\bar{v}} \left(\frac{\partial \bar{v}}{\partial x_2} \right) - \frac{q_2}{\bar{v}(\bar{v} - 1)} \left(\frac{\partial \bar{v}}{\partial x_2} \right) - q_2 \left(\frac{1}{\bar{T}_2} - \frac{1}{\bar{T}} \right) \frac{\partial \theta}{\partial x_2} \\ &- \frac{zq_2 \theta}{2RT} \left(\frac{\partial \varepsilon^*}{\partial x_2} \right) + \frac{zq_2}{2\dot{\Gamma}_{12}} \left(\frac{\partial \dot{\Gamma}_{12}}{\partial x_2} \right) \end{aligned} \quad (\text{F.3})$$

where $(\partial \dot{\Gamma}_{22} / \partial x_2)$ can be calculated from equation (85),

$$\begin{aligned} \frac{\partial \dot{\Gamma}_{22}}{\partial x_2} &= \frac{\partial}{\partial x_2} \left(\frac{1 - \bar{\theta}_1 \dot{\Gamma}_{12}}{\theta_2} \right) = \frac{\partial}{\partial \theta_2} \left(\frac{1 - \bar{\theta}_1 \dot{\Gamma}_{12}}{\theta_2} \right) \frac{\partial \bar{\theta}_2}{\partial x_2} \\ &= \frac{q_1 q_2}{q^2} \left[\frac{\dot{\Gamma}_{12} - 1}{\theta_2^2} - \frac{\bar{\theta}_1}{\theta_2} \left(\frac{\partial \dot{\Gamma}_{12}}{\partial \theta_2} \right) \right] \end{aligned} \quad (\text{F.4})$$

The derivatives of \bar{v} , ε^* and θ with respect to x_2 and $(\partial \dot{\Gamma}_{12} / \partial x_2)$ can be obtained from equation of state for mixture. The equation of state can be rearranged:

$$f = \ln \frac{\bar{v}}{\bar{v} - 1} + \frac{z}{2} \ln \left(\frac{\bar{v} + q/r - 1}{\bar{v}} \right) - \frac{\theta^2}{\bar{T}} - \frac{Pv_h}{RT} = 0 \quad (\text{F.5})$$

$$\frac{\partial f}{\partial x_2} = -\frac{1}{\bar{v}(\bar{v} - 1)} \frac{\partial \bar{v}}{\partial x_2} + \frac{z}{2} \frac{\partial}{\partial x_2} \left(\ln \frac{\bar{v} + q/r - 1}{\bar{v}} \right) - \frac{\partial}{\partial x_2} \left(\frac{\theta^2}{\bar{T}} \right) = 0 \quad (\text{F.6})$$

where,

$$\frac{\partial}{\partial x_2} \left(\ln \frac{\bar{v} + q/r - 1}{\bar{v}} \right) = -\frac{q/r - 1}{\bar{v}(\bar{v} + q/r - 1)} \frac{\partial \bar{v}}{\partial x_2} + \zeta \quad (\text{F.7})$$

$$\zeta = \frac{(q_2 - q_1)r - (r_2 - r_1)q}{(\bar{v} + q/r - 1)r^2}$$

$$\frac{\partial}{\partial x_2} \left(\frac{\theta^2}{\bar{T}} \right) = \frac{\partial}{\partial x_2} \left(\frac{z\varepsilon^*\theta^2}{2RT} \right) = \frac{z}{2RT} \left(\theta^2 \frac{\partial \varepsilon^*}{\partial x_2} + 2\theta\varepsilon^* \frac{\partial \theta}{\partial x_2} \right) \quad (\text{F.8})$$

All the derivatives can be expressed as functions of $(\partial \bar{v} / \partial x_2)$.

$$\begin{aligned} \frac{\partial \theta}{\partial x_2} &= -\frac{\partial \theta_h}{\partial x_2} = -\frac{(\partial N_h / \partial x_2)N_q - (\partial N_h / \partial x_2 - q_1 + q_2)N_h}{N_q^2} \\ &= -\frac{v^*q}{v_h N_q^2} \left(\frac{\partial \bar{v}}{\partial x_2} \right) - \frac{(v_2^* - v_1^*)\bar{v}q / v_h + (r_1 - r_2)q + (q_1 - q_2)N_h}{N_q^2} \end{aligned} \quad (\text{F.9})$$

$$\chi = \frac{(v_2^* - v_1^*)\bar{v}q / v_h + (r_1 - r_2)q + (q_1 - q_2)N_h}{N_q^2} \quad (\text{F.10})$$

Thus,

$$\frac{\partial \theta}{\partial x_2} = -\frac{v^*q}{v_h N_q^2} \left(\frac{\partial \bar{v}}{\partial x_2} \right) - \chi \quad (\text{F.11})$$

$$\begin{aligned} \frac{\partial \varepsilon^*}{\partial x_2} &= \frac{\partial}{\partial \theta_2} (\bar{\theta}_1 \varepsilon_{11} + \bar{\theta}_2 \varepsilon_{22} - \bar{\theta}_1 \bar{\theta}_2 \dot{\Gamma}_{12} \Delta \varepsilon_{12}) \frac{\partial \bar{\theta}_2}{\partial x_2} \\ &= \frac{\partial \bar{\theta}_2}{\partial x_2} \left[-\varepsilon_{11} + \varepsilon_{22} + (\bar{\theta}_2 - \bar{\theta}_1) \dot{\Gamma}_{12} \Delta \varepsilon_{12} - \bar{\theta}_1 \bar{\theta}_2 \Delta \varepsilon_{12} \frac{\partial \dot{\Gamma}_{12}}{\partial \bar{\theta}_2} \right] \end{aligned} \quad (\text{F.12})$$

$$\frac{\partial \dot{\Gamma}_{12}}{\partial \bar{\theta}_2} = \frac{\dot{\Gamma}_{12}^2 \left[(1 - \dot{G})(\bar{\theta}_1 - \bar{\theta}_2) - \bar{\theta}_1 \bar{\theta}_2 \left(\frac{\partial \dot{G}}{\partial \bar{\theta}_2} \right) \right]}{\sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}} \quad (\text{F.13})$$

where,

$$\frac{\partial \dot{G}}{\partial \bar{\theta}_2} = \frac{q^2}{q_1 q_2} \frac{\dot{G} \Delta \varepsilon_{12}}{RT} \left(\frac{\partial \theta}{\partial x_2} \right) \quad (\text{F.14})$$

Assuming:

$$\beta = \frac{\dot{\Gamma}_{12}^2 (1 - \dot{G})(\bar{\theta}_1 - \bar{\theta}_2)}{\sqrt{1 - 4\bar{\theta}_1\bar{\theta}_2(1 - \dot{G})}} \quad (\text{F.15})$$

$$\psi = -\varepsilon_{11} + \varepsilon_{22} + \dot{\Gamma}_{12}\Delta\varepsilon_{12}(\bar{\theta}_2 - \bar{\theta}_1) - \bar{\theta}_1\bar{\theta}_2\Delta\varepsilon_{12}\beta \quad (\text{F.16})$$

Combining all equations from (F.12) to (F.16), yield:

$$\frac{\partial \varepsilon^*}{\partial x_2} = \frac{q_1 q_2}{q^2} \psi + \frac{\bar{\theta}_1^2 \bar{\theta}_2^2 \Delta \varepsilon_{12}^2 \dot{\Gamma}_{12}^2 \dot{G}}{RT \sqrt{1 - 4\bar{\theta}_1\bar{\theta}_2(1 - \dot{G})}} \left(\frac{\partial \theta}{\partial x_2} \right) \quad (\text{F.17})$$

assuming:

$$\alpha = \frac{\bar{\theta}_1^2 \bar{\theta}_2^2 \Delta \varepsilon_{12}^2 \dot{\Gamma}_{12}^2 \dot{G}}{RT \sqrt{1 - 4\bar{\theta}_1\bar{\theta}_2(1 - \dot{G})}} \quad (\text{F.18})$$

therefore equation (F.17) can be simplified as:

$$\frac{\partial \varepsilon^*}{\partial x_2} = \frac{q_1 q_2}{q^2} \psi + \alpha \frac{\partial \theta}{\partial x_2} \quad (\text{F.19})$$

Substituting equations (F.7), (F.8), (F.11) and (F.19) into equation (F.6), the derivative of \tilde{v} with respect to x_2 can be obtained:

$$\begin{aligned} \frac{\partial \tilde{v}}{\partial x_2} = & \left[\frac{z}{2} \zeta - \frac{z q_1 q_2 \theta^2}{2 R T q^2} \psi + \frac{z \theta}{2 R T} (\alpha \theta + 2 \varepsilon^*) \chi \right] / \left[\frac{1}{\tilde{v}(\tilde{v} - 1)} \right. \\ & \left. + \frac{z(q/r - 1)}{\tilde{v}(\tilde{v} + q/r - 1)} - \frac{z \theta}{2 R T} (\alpha \theta + 2 \varepsilon^*) \frac{v^* q}{v_h N_q^2} \right] \quad (\text{F.20}) \end{aligned}$$

The stability conditions can be satisfied if the equation (F.3) is positive. Equation (F.3) can be rewritten by rearrangement:

$$\begin{aligned} -\frac{z q_1 q_2^2}{2 q^2 \dot{\Gamma}_{22}} \left[\frac{\dot{\Gamma}_{12} - 1}{\theta_2^2} - \frac{\bar{\theta}_1}{\theta_2} \left(\frac{\partial \dot{\Gamma}_{12}}{\partial \theta_2} \right) \right] < \frac{v_1^*}{x_2 v^*} - \frac{1}{\tilde{v}} \frac{\partial \tilde{v}}{\partial x_2} \\ -\frac{q_2}{\tilde{v}(\tilde{v} - 1)} \left(\frac{\partial \tilde{v}}{\partial x_2} \right) - q_2 \left(\frac{1}{\tilde{T}_2} + \frac{1}{\tilde{T}} \right) \frac{\partial \theta}{\partial x_2} - \frac{z q_2 \theta}{2 R T} \frac{\partial \varepsilon^*}{\partial x_2} \quad (\text{F.21}) \end{aligned}$$

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