## THE UNIVERSITY OF CALGARY

## SOME COMPUTATIONAL AND EXPERIMENTAL ASPECTS OF POLYMER SOLUTION PHASE BEHAVIOUR

by

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#### ABSTRACT

Experimental cloud point data are reported for the polystyrene + methylcyclohexane system in the vicinity of UCST. Two samples of polystyrene were used. One is nearly monodisperse with  $M_W=31,600$  and  $M_N=29,100$ . The other has  $M_W=250,000$  and  $M_N=64,000$ . The influence of CO<sub>2</sub> as an additional component on the phase behaviour of the monodisperse polystyrene + methylcyclohexane system is investigated for two approximately constant polymer mass fractions. Normally CO<sub>2</sub> adversely affects the solubility of the polymer. However, it was found that under certain conditions of pressure, temperature and compositions, the mixed solvent can be a better solvent for polystyrene than either methylcyclohexane or CO<sub>2</sub> alone.

The computational part of this work involved phase equilibrium computations with three models applicable to polymer solutions namely, (i) the Sanchez-Lacombe EOS, (ii) the Kleintjens-Koningsveld EOS and, (iii) the PHSC EOS. Computational difficulties were encountered with the conventional successive-substitution flash calculation procedure. It is shown that these can be eliminated with a simple modification to the iterative procedure. A scheme is presented for performing phase boundary calculations when the polymer is polydisperse. Multiphase equilibrium calculations were also performed with the models by modifying an existing multiphase successive substitution algorithm.

The models used in this work gave a satisfactory representation of pure component vapor pressure data for compounds n-hexane,  $CO_2$  and methylcyclohexane. The results are also satisfactory for the system  $CO_2$  + methylcyclohexane. The models were applied to

describe the phase behaviour of two polymer-solvent systems. The first was a polydisperse sample of polyethylene in n-hexane where the experimental data showed LCST type behaviour. The models gave a satisfactory representation of the data including vaporliquid-liquid equilibria. The second system was a monodisperse sample of polystyrene in methylcyclohexane and the data were measured in the vicinity of the UCST. In this case, only qualitative representation of the data could be obtained by an empirical modification to the models. This may be a consequence of the polymer parameters employed to perform calculations.

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## CHAPTER 1

#### Introduction

## 1.0 General

Understanding of the phase behavior of polymer solutions is of great importance. For instance, in a polymerization reactor, it is important to know under what conditions of temperature, pressure, composition and polymer molar mass the reaction mixture will be homogeneous or heterogeneous. In solution polymerization, in order to obtain a product with good properties and for kinetic reasons, it is important that the reaction mixture be in one phase (de Loos et al., 1996). In some instances it is desirable to carry out the reaction in a two-phase region (Folie and Radosz, 1995). Low density polyethylene (LDPE) produced in a two-phase system has superior film properties owing to a narrow molar mass distribution. Sometimes the polymer may precipitate from the reaction mixture and cause fouling in the reactor. The production of polyethylene by the high pressure polyethylene process (HPPE) is usually carried out in a single phase (Folie and Radosz, 1995). The reaction is exothermic and a single-phase is more desirable from a heat removal point of view. Also, a polyethylene rich phase is viscous and can form hot spots in the reactor. This can degrade the polymer and cause undesirable reactions in the reactor.

The product stream coming out of a polymerization reactor is usually a mixture of polymer molecules of varying chain lengths, unreacted monomer(s), residual initiator and

catalyst molecules, solvent etc. (Kiran, 1994). Depending on the ultimate use, further purification is required. Knowledge of the polymer solution phase behavior is important to carry out these steps economically and to develop newer and more economical methods. One of the most important technique for separating the polymer from the solvent is by steam stripping (McHugh and Guckes, 1985). However, this is a very energy intensive process as the solvent may comprise up to 95 wt % of the solution. Separation in a polymer solution can also be achieved by a lower critical solution temperature (LCST) phase split (Seckner et al., 1988). This type of phase separation occurs when the temperature of the polymer solution is raised, usually in the vicinity of the solvent critical temperature. This type of phase behavior is discussed in detail in a later Chapter. The higher temperatures in this case also imply a higher energy consumption. However, the LCST temperature can be lowered by the addition of a supercritical gas as reported by among others, McHugh and Guckes (1985), Seckner et al. (1988) and Kennis et al. (1990). The density of a gas is strongly dependent on pressure. The solubility of the polymer in the solvent mixture is a function of density and hence pressure can be employed to cause homogeneity or heterogeneity in the system.

Affecting the solubility of a polymer mixture by addition of a non-solvent, such as a supercritical gas, has applications in areas such as particle formation and crystallization (Kiran, 1994). Another important application is the fractionation of a widely polydisperse polymer into fractions with narrower molar mass distributions using the supercritical antisolvent (SAS) process (Chen et al., 1994). In this process, the polymer solubility is controlled by adjusting the temperature, pressure and the composition of the mixed solvent consisting of a solvent and an anti-solvent.

A substantial amount of work has been done to understand the phase behavior of polymer mixtures both from experimental and theoretical points of view. Experiments, in addition to providing important data, enable evaluation of equation of state models for correlation and/or prediction of phase behavior. An adequate model on the other hand can significantly reduce the amount of experimental effort and guide the experimentalist in the right direction.

The subsequent two sections cover some theoretical and experimental developments of importance to this work. The final section of this Chapter gives an overview of the Chapters to follow.

## 1.1 Equations of state

The most well known and widely used theory for polymer solutions is the Flory-Huggins theory (Flory, 1953). This theory uses an incompressible lattice to model the mixture of solvent and polymer molecules. The solvent molecules and the segments of the polymer molecules occupy the sites on the lattice. The number of configurations available to the molecules comprising the mixture gives the combinatorial entropy of mixing. A van Laar like enthalpy of mixing term accounting for the interactions between polymer segments solvent molecules is added to the combinatorial entropy of mixing to get the Gibbs free energy of mixing. This theory and its variations have been successful at

correlating and/or predicting upper critical solution temperature (UCST) behavior and closed loop phase behavior. The variations include making the interaction parameter in the enthalpy of mixing term composition and/or temperature dependent. Some important work along these lines has been done by Nies et al. (1985), Cheluget et al. (1993) and Bae et al. (1993). UCST behavior, typified by the transition from a two-phase system to a one-phase system, occurs because of energetic effects. Closed loop phase behavior normally happens when specific interactions such as hydrogen bonding are present. The compressibility of the polymer solution is not a key issue and thus can be modeled by a theory based on an incompressible lattice. However, as mentioned before, polymer solutions also exhibit LCST behavior which occurs as a consequence of different volume expansions of the polymer and solvent molecules. For such systems a theory that accounts for compressibility effects is required. Significant work has been done to extend the Flory-Huggins theory to such systems by the inclusion of vacancies or holes on the lattice, the number of which varies, to allow for a compressible lattice. Of note are the equation of state models developed by Sanchez and Lacombe (1976), Kleintjens and Koningveld (1980), and, Panayiotou and Vera (1982).

In the Sanchez and Lacombe (1976) treatment, a pure component is treated as a binary mixture of filled and vacant sites (holes) on a lattice. The combinatorial entropy term is then obtained from a Flory-Huggins type expression for the number of configurations. The Helmholtz free energy equation is then obtained by adding an energy term to the entropy term. From this fundamental equation the rest of the thermodynamic

equations can be derived. This equation of state has three pure component parameters accounting for the volume of a lattice site, the energy of interactions and the chain length of the molecule. A component dependent lattice site volume requires adoption of some mixing rule for this quantity in case of mixtures. The parameters of the model are usually obtained from saturation pressures and densities and in case of polymers from liquid densities of the polymers. The model has been shown to be successful at correlating pure component saturation data (Sanchez and Lacombe, 1976), polymer densities (Sanchez and Lacombe, 1978) and binary VLE and LLE data for some systems (Lacombe and Sanchez, 1976). Lacombe and Sanchez (1976) have also shown that this model. depending on the values of parameters used, is capable of exhibiting both LCST and UCST type phase behaviors. McHugh and coworkers (McHugh and Krukonis, 1994) have shown that the model is capable of describing high pressure polymer-solvent behavior with temperature dependent interaction parameters. This model will be discussed in detail in a later Chapter as it was one of the models used in this work.

The Kleintjens and Koningsveld (1980) treatment is along similar lines to that of Sanchez and Lacombe (1976). A pure component is considered to be a mixture of filled and empty sites. The combinatorial entropy of mixing term is that used by Flory and Huggins. They, however, add an empirical entropy correction term to the combinatorial entropy of mixing. They state that this is necessary to get a better quantitative description of experimental data. The Helmholtz free energy of mixing is obtained by adding an energy of mixing term to the two terms mentioned above. The Kleintjens-Koningsveld energy term accounts for the contact surface areas available to segments. Unlike the Sanchez-Lacombe equation of state, the volume of a lattice site is fixed a priori and is substance independent. The model can have five parameters or more for a pure component as some parameters are temperature dependent. The model has been shown to be successful at describing both pure component and multi-component phase behavior (Kleintjens and Koningsveld, 1980; Beckman et al., 1987; Kennis et al., 1990). This model was also used in this work and is covered in more detail in a later Chapter.

The equation of state model of Panayiotou and Vera (1982) is another variation of the lattice fluid approach. As is the case for the two lattice based models mentioned above, the compressibility effects are introduced by having holes on the lattice. The partition function used by Panayiotou and Vera is a product of three terms. The first term is a Flory-Huggins type random combinatorial part. The second term in the partition function accounts for the non-randomness of molecules on the lattice and the third factor accounts for interaction between segments. The non-random factor does not have a significant effect on the properties of pure components as shown by Panayiotou and Vera (1982). For mixtures, the non-random approximation gives better results for one of the systems investigated by them. As is the case for Kleintjens-Koningsveld model, the volume of a lattice site is fixed a priori. The interaction energy parameter is given a linear temperature dependence and, along with the chain length of a molecule, this results in three parameters for a pure component. The model gives a satisfactory representation of pure polymer properties. Recently Wang et al. (1996) and Lee and Danner (1996) have shown that this model is capable of exhibiting both LCST and UCST behavior.

One of the earlier theoretical equations of state for polymeric systems is that of Flory et al. (1964). These researchers derived a partition function that was a product of three factors. One accounted for the free volume or, in other words, for the difference between the actual volume and the hard core volume of the molecules. The second factor was a van der Waals like energy term. The third factor was a volume and temperature independent combinatorial term. The equation of state was obtained from this partition function. However, their equation of state does not reduce to the ideal gas law at low densities and is only applicable to the liquid state.

Beret and Prausnitz (1975) have developed an equation of state applicable to small as well as large molecules. The starting point for this model is the generalized van der Waals partition function that takes into account the free volume effect, contributions from rotational and vibrational degrees of freedom and the energy of interaction between molecules. The free volume factor is obtained from the work of Carnahan and Starling (1972). For the intermolecular interactions the molecular dynamic results of Alder et al. (1972) are used. The factor in the partition function that accounts for the rotational and vibrational effects is postulated so as to satisfy the ideal gas limit, the close packed limit, Prigogine's results for large molecules at liquid like densities and the fact that for simple fluids (no rotational and vibrational degrees of freedom) this factor has a value of unity. A pure component is characterized by three adjustable parameters reflecting the molecular size, molecular potential energy and the number of degrees of freedom, in addition to universal temperature functions in the model fitted to experimental data on methane. Parameters are given for three polymers, however, no results are shown. The model is quite complicated and may be difficult to use for multi-component mixtures.

The Chain-of-Rotators equation of state developed by Chien et al. (1983) is another attempt to describe the fluid state for small and large molecules. The starting point for this model is a partition function which is a product of three factors - (i) the translational partition function, (ii) the partition function of an elementary rotator and, (iii) an attractive factor which accounts for intermolecular interactions. For the translational part, the partition function is obtained from Carnahan-Starling's equation of state (Carnahan and Starling, 1972). The rotational partition function is obtained from the work of Boublik and Nezbeda (1977). The perturbation attractive term is based on the work of Alder et al. (1972). The model has three pure component parameters related to the hard core volume of a molecule, intermolecular attractions and flexibility of the molecular chains. The model is tested for small molecule systems only and no polymeric systems are investigated.

A recent model for describing polymer solution phase behavior is the SAFT (Statistical Associating Fluid Theory) equation of state (Chapman et al., 1990; Huang and Radosz, 1990, 1991). A pure SAFT fluid is a collection of hard-spherical segments in a mean-field of dispersion forces that (i) can be covalently bonded to form chains, and, (ii) can be weakly bonded to form clusters such as due to hydrogen bonding. The residual

Helmholtz energy for this model is given as the sum of a reference part and a perturbation part. The reference part of the model has hard-sphere, covalently bonded chains and association contributions. The perturbation part is a power series in density and temperature which was obtained by Alder et al. (1972) from molecular dynamics data. A non-associating pure component is characterized by three adjustable parameters reflecting the energetic interactions, chain length and the volume of a segment. Chen et al. (1992) have shown that the model is capable of showing both LCST and UCST behavior. Hasch and McHugh (1995) have also used this equation of state to model high pressure polymer solvent behavior.

The final model covered in this section is the Perturbed Hard Sphere-Chain (PHSC) equation of state of Song et al. [1994, (a)]. This model was chosen as one of the models used in this work and is discussed in detail in a later Chapter. The PHSC equation of state has two parts - (i) a reference part, and, (ii) a van der Waals like attractive or perturbation term. The reference part is based on the work of Chiew (1990) who obtained an equation of state for hard sphere chains and mixtures. This model has three parameters for a pure component that account for the chain length, the hard sphere diameter of segments and an interaction energy parameter. The model has been shown by Song et al. [1994, (a)] to give a better description of polymer densities than either SAFT or the Sanchez-Lacombe equations of state. Song et al. [1994 (b)] have shown that the model is capable of describing various liquid-liquid phase diagrams for hypothetical systems.

#### **1.2 Experiments**

For the purposes of this work, the cloud point (phase boundary) data on polymersolvent mixtures has been classified into two types. First are the measurements that only report temperature-composition information without any reference to pressure, or it is tacitly assumed that the pressure is the vapor pressure of the solvent. Second are the measurements that include the information on pressure also. A comprehensive collection of the data of the first type is available in the data compilation of Danner and High (1993). In this section only the papers dealing with polystyrene-methylcyclohexane system are covered as this system was investigated in the vicinity of UCST type behavior in this work. The review paper by Imre and van Hook (1996) is an excellent source of low pressure liquid-liquid demixing data of polystyrene solutions.

Saeki et al. (1973) measured UCST and LCST type cloud points curves for solutions of polystyrene in methylcyclohexane. The polymer samples used had a very small polydispersivity index and had molar masses 37000, 97200, 200000, 400000, 670000 and 2700000. The samples were flame sealed under dry nitrogen in cylindrical cells and the cloud point was taken as the temperature at which a dramatic change was observed in the pattern of a He-Ne laser beam. Nose et al. (1976) measured coexistence curves in the vicinity of the UCST for a polystyrene sample ( $M_w = 37000$ ) in methylcyclohexane. Dobashi et al. (1980) measured coexistence curves in the vicinity of the UCST for polystyrene samples having molar masses 10200, 16100, 17300, 20200, 34900, 46400, 109000, 181000 and 719000. Concentrations of the phases were measured

by differential refractometry techniques. Shinozaki et al. (1982) have measured coexistence curves in the neighborhood of the UCST for polystyrene samples with molar masses 9000, 17500, 37000, 110000, 233000 and 1260000. Coexistence curves for polystyrenes with molar masses 17200 and 719000 have been measured by Dobashi et al. (1984) using differential refractometry techniques in the vicinity of upper critical solution temperatures. Shen et al. (1991) report upper critical solution temperatures for polystyrene samples with molar masses 13000, 23000 and 29000. The critical temperatures were measured by the phase volume method, which is based on the fact that at the critical point the volumes of the coexisting phases are equal. Solutions of methylcyclohexane and polystyrene samples having molar masses 17500, 42500, 86300 and 175000 have been investigated by Heinrich and Wolf (1992). The phase diagrams in this case were obtained by visual observation.

A considerable amount of work has been done to generate pressure-temperaturecomposition cloud point data for polymer solutions. Some important work is covered below. First the investigations for binary or pseudo-binary systems (since the polymer almost always has a molar mass distribution) are covered. This is followed by a review of the studies that investigated the effect of an additional component. The list is by no means comprehensive. The reader is referred to the book by McHugh and Krukonis (1994) and the article by Kiran (1994) for more references.

Zeman et al. (1972) report cloud point measurements (pressure-temperature isopleths) for the systems polyisobutylene and polydimethylsiloxane in lower alkanes for

LCST type phase behavior. The alkanes include ethane, propane, butane, 2-methylbutane and pentane. The temperature range is from 0-200 °C. The maximum pressures are in the vicinity of 350 bars. The measurements were made in a steel optical cell with glass windows. The transition from clear to a cloudy solution was observed over a pressure interval of one bar. The temperature had an accuracy of  $\pm 0.25$  °C. Zeman et al. report that on increasing the pressure the LCST boundaries are moved to higher temperatures.

Zeman and Patterson (1972) investigated the pressure effects in polymer-solvent systems showing both UCST and LCST phase behavior. The systems investigated were solutions of polystyrene in methyl acetate and acetone and polypropylene oxide in propane. The data are reported in the form of liquid-liquid isopleths. The apparatus and procedure were the same as that of Zeman et al. (1972). The results of Zeman and Patterson indicate that while pressure always increases the LCST, the UCST may either be decreased or increased. This is related to the sign of the volume of mixing. The authors also show that, in the case of polystyrene in acetone and polypropylene oxide in propane, the LCST and UCST curves merge together as the molar mass of the polymer is increased.

Saeki et al. (1975) investigated the pressure dependence of upper critical solution temperatures in the polystyrene-cyclohexane system. Saeki et al. report an accuracy of  $\pm 0.005$  °C in cloud point temperatures by the aid of the scattering pattern of a He-Ne laser beam. The solution was housed in a pressure cell with two glass windows for the passage

of the He-Ne laser beam. Saeki et al. report that the sign of  $(dT/dP)_{Critical}$  is positive for the 37000 g/mol and becomes negative as the molar mass of the polymer is increased.

Saeki et al. (1976) report the pressure dependence of upper and lower critical solution temperatures in solutions of polystyrene in *tert*-butyl acetate and diethyl ether over a pressure range of  $1 \sim 50$  atm. The experimental procedure was the same as that of Saeki et al. (1975). The results of Saeki et al. (1976) show that the UCST type phase behavior has a smaller pressure dependence than that of LCST type phase behavior. This is the expected result as LCST type phase behavior is caused by disparity in volume expansions of the solute and the solvent.

de Loos et al. (1983) investigated the fluid phase equilibria in the system polyethylene-ethylene at very high pressures. The temperature range was 380-445 K and the pressures ranged from 900 to 2000 bar. The measurements were carried out in an optical high pressure cell. de Loos et al. (1983) report that the temperature in the high pressure autoclave could be maintained constant to within 0.03 K and the pressure in the cell was constant to within 0.1 bar. The reproducibility of the measured cloud point pressures was within 1 bar in most cases. Their results indicate that an increase in the molar mass of the polymer raises the cloud point pressures or in other words, the polymer solubility decreases with molar masses as may be expected.

Meilchen et al. (1991) report high pressure phase behavior and fractionation data for polyethylene, poly(methyl acrylate) and two copolymers poly (ethylene-co-methyl acrylate) in propane and chlorodifluoromethane. The copolymers had different

concentrations of ethylene and methyl acrylate. The fractionation was carried out using a dynamic flow technique. In this technique, the polymer is charged in an extraction column and a solvent flows through the column at different pressures. Since the solubility of polymers is a function of molar mass, different fractions are obtained at different pressures. Meilchen et al. obtained fractions with polydispersivity indices smaller than or equal to 2.2 for poly (methyl acrylate). The polydispersivity indices of the fractions for the two copolymers were less than or equal to 2.4 in one case and 1.4 for the other. The polyethylene fractions had polydispersivity indices less than or equal to 2.3. The cloud point measurements were made in a variable-volume view cell. The equipment is capable of an accuracy in pressure of  $\pm 2.8$  bar at pressure greater than 1000 bar and  $\pm 1.4$  bar for pressure less than 1000 bar. The temperature was measured with an accuracy of  $\pm 0.2$  °C. The cloud point measurements of Meilchen et al. (1991) show that, as the acrylate content in the backbone of the copolymer increases, the polar solvent chlorodifluoromethane dissolves the copolymer better.

Wells et al. (1993) investigated the phase behavior of the system polystyrene  $(M_w=22000 \text{ g/mol})$  in methylcyclohexane using the pressure pulse induced critical scattering technique. This technique enables evaluation of both binodal and spinodal pressures and temperatures. Their results for some isopleths indicate that, at pressures less than 400 bar, increasing pressure decreases both binodal and spinodal temperatures. However, for pressures greater than 500 bar the opposite trend is observed.

de Loos et al. (1995) report cloud point curves in fluid systems of ethylene and branched polyethylene. The measurements were made in an optical high pressure cell. The temperature range is 380-445 K and pressures range from 90 to 200 MPa. de Loos et al. show that branching of the polymer significantly lowers the cloud point curves as compared to those for system with a linear polyethylene with a comparable molar mass distribution.

Recently de Loos et al. (1996) investigated the liquid-liquid phase separation in Linear Low Density Polyethylene (LLDPE) - solvent systems. LLDPE is a copolymer of ethylene and a comonomer like octene, hexene, propene etc.. The solvents used were nhexane, n-heptane, n-octane, isohexane and cyclohexane. Lower solution temperatures were measured in the temperature range of 400-600 K and at pressures up to 13 MPa. The observations were carried out in an optical cell using the Cailletet apparatus. They conclude that for the systems investigated the solvent type is the key to phase behavior and factors such as polymer density and the type of comonomer are not so significant.

Kiran and co-workers (Kiran, 1994) have made high pressure phase equilibrium measurements on systems consisting of polyethylene and n-alkanes. Their results show that demixing pressures for a polymer solvent mixture increase as the polymer molar mass increases. For a particular molar mass polymer, the demixing pressures decrease as the carbon number of alkane is increased.

McHugh and Guckes (1985) have investigated the effect of a supercritical additive on the phase behavior of poly(ethylene-co-propylene) - mixed solvent system. The mixed solvent consisted of 3-methylpentane, n-hexane and methylcyclopentane. The supercritical additives used were ethylene, propylene, carbon dioxide and methane. The observations were made in a variable volume view pressure cell. McHugh and Guckes report that, with the addition of a supercritical additive at an approximately constant mass fraction of the polymer, the cloud point curves are shifted to lower temperatures. The effect is greatest for methane followed by  $CO_2$ , ethylene and propylene. In some cases the LCST type cloud point curve is shifted by more than 100 °C to lower temperatures. They also show that, at sufficiently high concentrations of methane and ethylene, the UCST and LCST type cloud point curves merge.

Seckner et al. (1988) have investigated the high pressure phase behavior of the system polystyrene-toluene-ethane. The observations were made in a variable volume optical cell. The measurements of Seckner et al. show that, with the addition of ethane, the LCST type cloud point curves can be shifted to temperatures lower by 231 °C. At even higher concentrations of ethane, the LCST and UCST type curves merge to give a region of immiscibility below the isopleths.

Kennis et al. (1990) have studied the effect of the addition of nitrogen on the phase behavior of linear high density polyethylene (HDPE) + n-hexane system. The observations were made in the Cailletet apparatus. Experimental temperatures range from 393-453 K with pressures up to 7.5 MPa. Their results show that small amounts of nitrogen cause a shift of the LCST type phase boundary to much lower temperatures at constant pressure. The lowering of temperature is of the order of 22 K per mass percent of nitrogen.

## 1.3 Overview of this work.

This Chapter is concluded with a brief overview of this work. In Chapter 2 the general patterns of fluid phase behavior are covered. The thermodynamic nature of UCST and LCST phase behaviors is discussed along with the effect of the polydispersivity of the polymer on the phase behavior of polymer-solvent systems. Chapter 3 deals with the various types of computations such as vapor pressure, phase boundary, two-phase and multi-phase flash computations with equation of state models. In Chapter 4 the experimental method used in this work is described and the experimental results are presented. Chapter 5 introduces the model equations employed in this work. In Chapter 6 the model performance is compared with the experimental data on some systems followed by the conclusions of this work in Chapter 7. Then a list of literature quoted in this work is presented. Finally, the tables of data are presented in the appendices along with a brief discussion of phase equilibrium and stability pertinent to this work.

#### **CHAPTER 2**

#### Patterns of fluid phase behavior

## **2.0 Introduction**

The Chapter begins with a discussion of the phase rule of Gibbs (1961) which is essential to the understanding of phase behavior. The following section deals with some aspects of critical behavior and azeotropy in binary mixtures. The reader is referred to the book by Prigogine and Defay (1954) for a comprehensive coverage of this topic. In the following section of this Chapter some features of binary phase diagrams are highlighted. Then some typical phase diagrams for polymer solutions are shown and the thermodynamic nature of UCST and LCST phase behaviors is discussed. van Konynenburg and Scott (1980) have classified the patterns of fluid phase behavior in binary mixtures into six classes. Their classification scheme is briefly covered with emphasis on phase diagrams for polymeric systems. The Chapter is concluded with a brief discussion regarding the effect of the polydispersivity of the polymer on polymer solution phase behavior.

### 2.1 Phase rule

The phase rule of Gibbs gives the number of degrees of freedom F for a system in equilibrium. This is the number of variables whose values are chosen freely before conducting an experiment (Denbigh, 1981). The derivation of the phase rule follows.

Consider an equilibrium of  $\pi$  phases in a n component system. The equilibrium conditions are

$$T_1 = T_2 = \dots = T_n$$
 (2.1)

$$P_1 = P_2 = \dots = P_n$$
 (2.2)

$$\mu_i^1 = \mu_i^2 = \dots = \mu_i^x, \quad i = 1, 2, \dots, n$$
 (2.3)

These are  $(\pi-1)(n+2)$  equations. Each phase is characterized by pressure, temperature and independent composition variables, e.g. (n-1) mole fractions. Hence, the number of variables for  $\pi$  phases is  $\pi(n+1)$ . The difference between the number of variables and equations connecting these variables is F and is given by

$$\mathbf{F} = \mathbf{n} - \boldsymbol{\pi} + 2 - \boldsymbol{\phi} \tag{2.4}$$

In special cases one has to account for extra conditions and the number of these conditions is given by  $\phi$ . For instance, for a binary azeotrope the vapor and liquid compositions are identical and  $\phi$  is one.  $\pi$  critical phases can be counted as  $\pi$  phases with  $\phi$  equal to  $\pi$ -1. This can be seen from the following development that is extracted from the paper by Zernicke (1949).

A result from analytical geometry states that: k spaces each of dimension m situated in a space of dimension n have in common a space of dimension n-k(n-m). Now consider two coexisting phases with n components each. This equilibrium has n degrees of freedom. Therefore each phase exists in a space of n dimensions situated in a space of n+1 dimensions (P, T, n-1 independent concentration variables). The two n dimensional spaces containing these phases intersect in a space of dimensions n-1 as obtained from the
result above(k=2, n=n+1, m=n). Now consider the case where  $\pi$  phases are becoming critical with each other. Before the critical point is reached there are  $\pi$ -1 two phase equilibria. The  $\pi$  phases become critically identical in a space common to  $\pi$ -1 spaces each of dimension n-1. The dimension of this space is given by

$$n+1-(\pi-1)[n+1-(n-1)] = n-2\pi+3$$
(2.5)

The degrees of freedom for a  $\pi$  phase equilibrium is  $n-\pi + 2$  from the phase rule. So the case where  $\pi$  phases become critical with each other can be considered as a virtual  $\pi$  phase equilibria with a degree of freedom given by

$$n - 2\pi + 3 = n + 2 - \pi$$
 (2.6)

This gives

$$\pi' = 2\pi - 1 = \pi + (\pi - 1) \tag{2.7}$$

Comparing this equation with equation (2.4) we get for the case where  $\pi$  actual phases are becoming critical with each other, a value of  $\phi$  given by

$$\phi = \pi - 1 \tag{2.8}$$

A one component system can be represented in a pressure-temperature plane. The number of degrees of freedom is given by

$$\mathbf{F} = \mathbf{3} - \boldsymbol{\pi} - \boldsymbol{\phi} \tag{2.9}$$

A one phase system in this case has two degrees of freedom and is a region in the P-T plane. A two phase equilibrium has one degree of freedom and is a curve in the P-T plane. A three phase equilibrium or a critical point has zero degrees of freedom and is a point in the P-T plane.

In order to represent a binary system three dimensions are needed, e.g. pressure, temperature and an independent composition variable such as a mole fraction. F in this case is given by

$$\mathbf{F} = \mathbf{4} - \boldsymbol{\pi} - \boldsymbol{\phi} \tag{2.10}$$

A one phase system has F=3 and is a region in the P-T-x space. A two-phase equilibrium has two degrees of freedom and is represented by two surfaces  $x^{\alpha}(P,T)$  and  $x^{\beta}(P,T)$ . A three phase equilibrium has F=1 and is represented by three curves  $x^{\alpha}[P(T)]$ ,  $x^{\beta}[P(T)]$  and  $x^{\gamma}[P(T)]$ . A critical curve with F=1 is given by  $x^{c}[P(T)]$  and a critical endpoint which has zero degrees of freedom requires two points at one P and T in order to be represented. A critical endpoint is defined as the condition for which two phases of a three-phase equilibrium become identical.

# 2.2 Displacement along an equilibrium line (The Gibbs-Konovalow Theorems)

In this section some important conditions are derived for azeotropy and critical points in binary systems. The development is due to Progogine and Defay (1954). Consider a binary system at P and T with equilibrium mole fractions in the two phases (I and II) to be  $x_2^{I}$  and  $x_2^{II}$ . The equilibrium conditions are the equality of chemical potential  $(\mu_i)$  of each component in the two phase I and II as given by

$$\mu_1^{\rm I} = \mu_1^{\rm II} \tag{2.11}$$

and

$$\mu_2^{I} = \mu_2^{II} \tag{2.12}$$

Now consider a neighboring equilibrium state at (P+dP), (T+dT),  $(x_2^{I} + dx_2^{I})$ ,  $(x_2^{II} + dx_2^{II})$ . We have

$$\mu_{1}^{t} + d\mu_{1}^{t} = \mu_{1}^{II} + d\mu_{1}^{II}$$
(2.13)

and

$$\mu_2^i + d\mu_2^i = \mu_2^{ii} + d\mu_2^{iii}$$
(2.14)

Since the neighbouring phase is an equilibrium phase as well the following conditions hold.

$$\mathbf{d}\boldsymbol{\mu}_{1}^{\mathrm{f}} = \mathbf{d}\boldsymbol{\mu}_{1}^{\mathrm{ff}} \tag{2.15}$$

and

$$d\mu_2^I = d\mu_2^{II}$$
 (2.16)

Now the total derivative of  $\mu_1^{I}$  is given by

$$d\mu_{I}^{t} = \left(\frac{\partial \mu_{I}}{\partial \Gamma}\right)_{P,x}^{t} dT + \left(\frac{\partial \mu_{I}}{\partial P}\right)_{T,x}^{t} dP + \left(\frac{\partial \mu_{I}}{\partial x_{2}}\right)_{T,P}^{t} dx_{2}^{t}$$
(2.17)

The derivatives of the chemical potential with respect to pressure and temperature are given by the following relations

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T} = v_i$$
, and,  $\left(\frac{\partial \mu_i}{\partial T}\right)_{P} = -s_i$  (2.18)

where  $v_i$  and  $s_i$  are partial molar volume and partial molar entropy respectively of component i.

Also the molar Gibbs free energy of the system is given by

$$g = (1 - x_2)\mu_1 + x_2\mu_2 \tag{2.19}$$

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Hence,

$$\frac{\partial g}{\partial x_2} = \mu_2 - \mu_1 \tag{2.20}$$

since the summation involving the derivatives of the chemical potential is zero from the Gibbs-Duhem equation.

Further differentiation gives

$$\frac{\partial^2 g}{\partial x_2^2} = \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} - \left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P}$$
(2.21)

From the Gibbs-Duhem equation

$$\mathbf{x}_{1} \left( \frac{\partial \mu_{1}}{\partial \mathbf{x}_{2}} \right)_{\mathrm{T,P}} + \mathbf{x}_{2} \left( \frac{\partial \mu_{2}}{\partial \mathbf{x}_{2}} \right)_{\mathrm{T,P}} = 0$$
(2.22)

This gives

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = -\frac{x_2}{1-x_2} \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}$$
(2.23)

Substituting in equation (2.21) the following relation is obtained.

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = (1 - x_2) \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}$$
(2.24)

and,

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = -x_2 \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}$$
(2.25)

Substituting the expressions for the derivatives of the chemical potential in (2.17) the following equation is obtained.

$$d\mu_{1}^{I} = -s_{1}^{I}dT + v_{1}^{I}dP - x_{2}^{I}\left(\frac{\partial^{2}g}{\partial x_{2}^{2}}\right)_{T,P}^{I}dx_{2}^{I}$$
(2.26)

Similarly the following equation can be derived for phase II.

$$d\mu_1^{II} = -s_1^{II} dT + v_1^{II} dP - x_2^{II} \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{II} dx_2^{II}$$
(2.27)

Substitution in equilibrium relation (2.15) gives for component 1,

$$-\Delta s_1 dT + \Delta v_1 dP - x_2^{ff} \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{ff} dx_2^{ff} + x_2^{ff} \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{f} dx_2^{ff} = 0$$
(2.28)

where,  $\Delta s_1 = s_1^{\pi} - s_1^{\tau}$  and so on. In a similar manner we get the following equation for component 2.

$$-\Delta s_2 dT + \Delta v_2 dP + (1 - x_2^{\mathfrak{q}}) \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{\mathsf{T},\mathsf{P}}^{\mathfrak{q}} dx_2^{\mathfrak{q}} - (1 - x_2^{\mathfrak{l}}) \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{\mathsf{T},\mathsf{P}}^{\mathfrak{l}} dx_2^{\mathfrak{l}} = 0 \qquad (2.29)$$

At equilibrium  $\Delta \mu_1 = \Delta h_1 - T\Delta s_1 = 0$  which implies  $\Delta s_1 = \Delta h_1 / T$ . The above two equation can be written as

$$-\frac{\Delta h_1}{T}dT + \Delta v_1 dP - x_2^{II} \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{II} dx_2^{II} + x_2^{II} \left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{I} dx_2^{II} = 0$$
(2.30)

and

$$-\frac{\Delta h_2}{T}dT + \Delta v_2 dP + (1 - x_2^{II})\left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{II} dx_2^{II} - (1 - x_2^{I})\left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{II} dx_2^{II} = 0 \qquad (2.31)$$

These are two equations in terms of variations dP, dT and  $dx_2$  along an equilibrium line. Deductions regarding azeotropy and critical behavior in binary mixtures can be made from these equations and these deductions are collectively known as Gibbs-Konovalow theorems [Rowlinson and Swinton (1982), Prigogine and Defay (1954)].

At constant pressure (dP=0) the following partial derivatives for the two phases are obtained.

$$\left(\frac{\partial T}{\partial \mathbf{x}_2}\right)_{\mathbf{p}}^{\mathbf{I}} = \frac{T(\mathbf{x}_2^{\mathbf{I}} - \mathbf{x}_2^{\mathbf{I}})\left(\frac{\partial^2 \mathbf{g}}{\partial \mathbf{x}_2^2}\right)^{\mathbf{I}}}{-[\mathbf{x}_2^{\mathbf{I}} \Delta \mathbf{h}_2 + (1 - \mathbf{x}_2^{\mathbf{I}}) \Delta \mathbf{h}_1]}$$
(2.32)

and

$$\left(\frac{\partial T}{\partial x_2}\right)_{\mathbf{p}}^{\mathbf{I}} = \frac{T(\mathbf{x}_2^{\mathbf{I}} - \mathbf{x}_2^{\mathbf{I}})\left(\frac{\partial^2 \mathbf{g}}{\partial \mathbf{x}_2^2}\right)^{\mathbf{I}}}{-[\mathbf{x}_2^{\mathbf{I}}\Delta \mathbf{h}_2 + (1 - \mathbf{x}_2^{\mathbf{I}})\Delta \mathbf{h}_1]}$$
(2.33)

At constant temperature (dT=0) we get the following pressure derivatives.

$$\left(\frac{\partial P}{\partial x_2}\right)_{T}^{I} = \frac{(x_2^{II} - x_2^{I})\left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^{I}}{x_2^{II}\Delta v_2 + (1 - x_2^{II})\Delta v_1}$$
(2.34)

and

$$\left(\frac{\partial \mathbf{P}}{\partial \mathbf{x}_2}\right)_{\mathrm{T}}^{\mathrm{II}} = \frac{(\mathbf{x}_2^{\mathrm{II}} - \mathbf{x}_2^{\mathrm{I}}) \left(\frac{\partial^2 \mathbf{g}}{\partial \mathbf{x}_2^2}\right)_{\mathrm{T,P}}^{\mathrm{I}}}{\mathbf{x}_2^{\mathrm{I}} \Delta \mathbf{v}_2 + (1 - \mathbf{x}_2^{\mathrm{I}}) \Delta \mathbf{v}_1}$$
(2.35)

For an azeotrope  $x_2^{II} = x_2^{I}$ . Therefore,

$$\left(\frac{\partial P}{\partial x}\right)_{T} = 0$$
,  $\left(\frac{\partial T}{\partial x}\right)_{P} = 0$  (2.36)

These equations are also valid at a critical point. However, unlike an azeotropic point, the derivation of these conditions is not so obvious as  $\Delta h_1$ ,  $\Delta v_1$  etc. are zero for identical phases in addition to the compositions being equal. The condition at constant pressure, i.e.  $\partial T/\partial x = 0$ , can be obtained as follows from equation (2.32).

At constant pressure consider an equilibrium between two phases in the vicinity of the critical point  $[T=T+dT, x_2^{II}=x_2^{c}+dx_2^{II}, x_2^{I}=x_2^{c}+dx_2^{I}]$ . Expanding  $h_1^{I}$  and  $h_1^{II}$  in a Taylor series around the critical point as given by

$$\mathbf{h}_{1}^{I} = (\mathbf{h}_{1})_{c} + \left(\frac{\partial \mathbf{h}_{1}}{\partial \mathbf{x}_{2}}\right)_{c} \mathbf{d}\mathbf{x}_{2}^{I} + \left(\frac{\partial \mathbf{h}_{1}}{\partial T}\right)_{c} \mathbf{d}T$$
(2.37)

$$\mathbf{h}_{1}^{\mathbf{II}} = (\mathbf{h}_{1})_{c} + \left(\frac{\partial \mathbf{h}_{1}}{\partial \mathbf{x}_{2}}\right)_{c} \mathbf{d}\mathbf{x}_{2}^{\mathbf{II}} + \left(\frac{\partial \mathbf{h}_{1}}{\partial T}\right)_{c} \mathbf{d}T$$
(2.38)

We obtain for component 1

$$\Delta \mathbf{h}_{1} = \mathbf{h}_{1}^{\mathfrak{l}} - \mathbf{h}_{1}^{\mathfrak{l}} = \left(\frac{\partial \mathbf{h}_{1}}{\partial \mathbf{x}_{2}}\right)_{c} (\mathbf{d}\mathbf{x}_{2}^{\mathfrak{l}} - \mathbf{d}\mathbf{x}_{2}^{\mathfrak{l}})$$
(2.39)

Similarly for component 2 we get

$$\Delta h_2 = h_2^{II} - h_2^{I} = \left(\frac{\partial h_2}{\partial x_2}\right)_c (dx_2^{II} - dx_2^{I})$$
(2.40)

Using equations (2.39) and (2.40) the denominator in equation (2.32) can be written as

$$-[(x_{2}^{c} + dx_{2}^{II})\Delta h_{2} + (1 - x_{2}^{c} - dx_{2}^{II})\Delta h_{1}]$$
  
=  $-dx_{2}^{II}(dx_{2}^{II} - dx_{2}^{I})[(\partial h_{2} / \partial x_{2})_{c} - (\partial h_{1} / \partial x_{2})_{c}]$  (2.41)

Now,

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$$\left(\frac{\partial \mathbf{h}}{\partial \mathbf{x}_2}\right) = \mathbf{h}_2 - \mathbf{h}_i \tag{2.42}$$

and

$$\left(\frac{\partial^2 \mathbf{h}}{\partial \mathbf{x}_2^2}\right) = \left(\frac{\partial \mathbf{h}_2}{\partial \mathbf{x}_2}\right) - \left(\frac{\partial \mathbf{h}_1}{\partial \mathbf{x}_2}\right)$$
(2.43)

Therefore we have for the denominator in equation (2.32)

$$-dx_{2}^{II}(dx_{2}^{II}-dx_{2}^{I})\left(\frac{\partial^{2}h}{\partial x_{2}^{2}}\right)_{c}$$
(2.44)

The variations  $dx_2^{II}$  and  $dx_2^{I}$  are arbitrary. Hence, at the critical point  $(\partial T/\partial x)_P$  is equal to zero. Similarly the condition  $(\partial P/\partial x)_T = 0$  can be derived.

# 2.3 Some features of binary phase diagrams

In binary systems for critical and azeotropic points the following conditions have to be satisfied

$$\left(\frac{\partial \mathbf{P}}{\partial \mathbf{x}}\right)_{\mathrm{T}} = 0$$
 ,  $\left(\frac{\partial \mathbf{T}}{\partial \mathbf{x}}\right)_{\mathrm{P}} = 0$  (2.36)

The implication of these conditions is that critical and azeotropic points are points of extrema in binary P-x and T-x sections as shown in Figure (2.1).

Figures (2.2) and (2.3) show the possible location of 1- and 2- phase equilibria around a three phase equilibrium in binary P-x and T-x sections (de Loos, 1994). The occurrence of these arrangements can be qualitatively understood by an analysis of the



Figure 2.1. Examples of critical and azeotropic points in a binary system. P-x sections at constant temperature.



Figure 2.2. Location of 1- and 2- phase equilibria around a 3-phase equilibrium in a binary system. T-x sections at constant pressure.



Figure 2.3. Location of 1- and 2- phase equilibria around a 3-phase equilibrium in a binary system. P-x sections at constant temperature.

Gibbs free energy vs composition diagrams. On such diagrams, coexisting phases are located at points on the free energy curves with common tangent lines (de Loos, 1994).

Figure (2.4) shows a three phase equilibrium, the phases being I, II and III with compositions given by  $x_i < x_{II} < x_{III}$ . The equilibrium phases have a common tangent plane. Now let us say that the conditions of equilibrium are perturbed, for example, by addition or extraction of heat. After the perturbation, the possible arrangements of the Gibbs free energy curves is given in Figures (2.5 a,b). If a positive perturbation results in the arrangement given by Figure (2.5 a), then a negative perturbation would give the arrangement in Figure (2.5 b), and, vice-versa. In the case of Figure (2.5 a), a I-II-III equilibrium is transformed to a I-III equilibrium. For the case shown in Figure (2.5 b) there are three options depending on the location of the feed composition  $x_F$ . If  $x_I < x_F < x_{II}$ , then a I-II-III equilibrium is changed to a I-II equilibrium. If  $x_{II} < x_F < x_{III}$ , then a I-II-III equilibrium is changed to a II-III equilibrium. However, if  $x_F = x_{II}$ , then a I-II-III equilibrium reverts to a single phase (phase II). The net result of this analysis is the arrangements shown in the Figures (2.2) and (2.3).

### 2.4 Some phase diagrams for polymer systems (liquid phases)

Figure (2.6) shows some typical temperature-composition (constant pressure) phase diagrams for polymer systems. Upper critical solution temperature (UCST) behavior is shown in Figure (2.6 a). In this case the system goes from a two phase region to a one phase region on increasing temperature. Figure (2.6 b) contains lower critical solution temperature (LCST) behavior. Systems conforming to LCST phase behavior go



Figure 2.4. Three phase equilibrium line in a binary system in a g-x diagram at constant temperature and pressure.



Figure 2.5. Phase transitions around a three-phase line in a g-x diagram.



Figure 2.6. Some T-x phase diagrams at constant pressure for polymer systems. (a) UCST. (b) LCST. (c) UCST + LCST. (d) Closed loop. (e) Hour glass.

from a homogeneous region to a region of immiscibility on increasing temperature. A system can show simultaneous occurrence of UCST and LCST behavior and this type of phase behavior is shown in Figure (2.6 c). In some systems showing this kind of phase behavior, LCST and UCST curves merge together to open up a region of immiscibility in the middle and this is shown in Figure (2.6 e). It is also possible to have closed loop phase behavior, in which the loop contains a region of immiscibility, as shown in Figure (2.6 d).

# 2.5 UCST and LCST behavior

At a critical point in a binary mixture

$$\left(\frac{\partial \mathbf{T}}{\partial \mathbf{x}_2}\right)_{\mathbf{p}}^{\mathbf{r}} = \left(\frac{\partial \mathbf{T}}{\partial \mathbf{x}_2}\right)_{\mathbf{p}}^{\mathbf{r}} = 0$$
(2.45)

Also, the equilibrium phases have identical properties; i.e.,

$$(\mathbf{x}_{2}^{I})_{c} = (\mathbf{x}_{2}^{II})_{c}$$
 (2.46)

$$(\Delta \mathbf{h}_1)_{\mathbf{c}} = (\Delta \mathbf{h}_2)_{\mathbf{c}} = 0 \tag{2.47}$$

And the criteria for a critical point must be satisfied; i.e.,

$$\left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P}^c = \left(\frac{\partial^3 g}{\partial x_2^3}\right)_{T,P}^c = 0$$
(2.48)

with, for a locally stable critical point,

$$\left(\frac{\partial^4 \mathbf{g}}{\partial \mathbf{x}_2^4}\right)_{\mathbf{T},\mathbf{P}}^{\mathbf{c}} > 0 \tag{2.49}$$

Binary UCST and LCST behaviors are shown in the Figures (2.7 a,b). According to the figures the convention followed is  $(x_2^{II}-x_2^{I})>0$ . For UCST behavior  $\left(\frac{\partial T}{\partial x}\right)_p > 0$  in the vicinity of C (the critical point) on the AC side and vice-versa for LCST behavior. The sign of the slope is determined by the sign of the denominator (2.44) in the expression (2.32), since for a stable phase

$$\left(\frac{\partial^2 \mathbf{g}}{\partial \mathbf{x}_2^2}\right)^{\mathrm{T}} > 0 \tag{2.50}$$

Also,

$$\mathrm{d}\mathbf{x}_2^{\mathrm{fl}} = -\mathrm{d}\mathbf{x}_2^{\mathrm{fl}} \tag{2.51}$$

This can be seen by expanding T (for a two-phase equilibrium) in a Taylor series around the critical point in terms if  $x_2^{I}$  and  $x_2^{II}$  as given by

$$T = T_{c} + (dx_{2}^{i})^{2} \left(\frac{\partial^{2}T}{\partial x_{2}^{2}}\right)_{c}$$
(2.52)

and

$$T = T_{c} + (dx_{2}^{II})^{2} \left(\frac{\partial^{2}T}{\partial x_{2}^{2}}\right)_{c}$$
(2.53)

The higher order terms are neglected and the first derivatives are zero at the critical point. Therefore we get  $dx_2^{II} = -dx_2^{I}$ , since  $x_2^{II} (= x_C + dx_2^{II}) > x_2^{II} (= x_C + dx_2^{II})$ .

The sign convention followed here is  $(x_2^{11}-x_2^{1})>0$ , which gives  $dx_2^{11} > dx_2^{1}$ . Now we have for denominator in equation (2.32):



Figure 2.7. (a) Constant pressure T-x section for UCST behavior in a binary system. (b) Constant pressure T-x section for LCST behavior in a binary system.



Figure 2.8. Molar enthalpy as a function of composition at constant T and P in a binary system.

deno min ator = 
$$-2(dx_2^{II})^2 \left(\frac{\partial^2 h}{\partial x_2^2}\right)_c$$
 (2.54)

For UCST  $[\partial T/\partial x > 0$  on the AC side in Figure (2.7 a)]

$$\left(\frac{\partial^2 \mathbf{h}}{\partial \mathbf{x}_2^2}\right)_{\mathbf{c}} < 0 \tag{2.55}$$

and, for LCST  $[\partial T/\partial x < 0$  on the AC side in Figure (2.7 b)]

$$\left(\frac{\partial^2 \mathbf{h}}{\partial \mathbf{x}_2^2}\right)_c > 0 \tag{2.56}$$

Hence, near the critical point, the molar enthalpy (h) is convex upwards for UCST, and, convex downwards for LCST behavior.. With these deductions in mind, we consider Figure (2.8). Assuming, as is generally the case (Prigogine and Defay, 1954), that the curvature of the relation between h and composition does not change sign, the formation of a UCST type mixture [curve 1 in Figure (2.8)] is endothermic and the LCST type mixing (curve 2) is exothermic.

Inequalities (2.55) and (2.56) can be expressed in terms of the mixture molar entropy, s.

$$g = h - Ts \tag{2.57}$$

and

$$\left(\frac{\partial^2 \mathbf{g}}{\partial \mathbf{x}_2^2}\right)_{\mathrm{T,P}} = \left(\frac{\partial^2 \mathbf{h}}{\partial \mathbf{x}_2^2}\right)_{\mathrm{T,P}} - T\left(\frac{\partial^2 \mathbf{s}}{\partial \mathbf{x}_2^2}\right)_{\mathrm{T,P}}$$
(2.58)

At the critical point  $\left(\frac{\partial^2 g}{\partial x_2^2}\right)_{T,P} = 0$ , and we get in terms of s,

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$$\left(\frac{\partial^2 \mathbf{s}}{\partial \mathbf{x}_2^2}\right)_{\mathbf{c}} < 0; \quad \text{UCST}$$
 (2.59)

and,

$$\left(\frac{\partial^2 \mathbf{s}}{\partial \mathbf{x}_2^2}\right)_c > 0; \quad \text{LCST}$$
 (2.60)

The molar entropy of mixing  $\Delta s_M$  has the same sign as the molar enthalpy of mixing. Now,

$$\Delta g_{M} = \Delta h_{M} - T \Delta s_{M} \tag{2.61}$$

Some insight into the nature of UCST and LCST phase behavior can be gained by a consideration of the signs and magnitudes of the two competing effects  $\Delta h_M$  and  $-T \Delta s_M$ . For UCST phase behavior, it is the interactions between the components giving a positive enthalpy of mixing that cause immisciblity. The molar entropy of mixing makes a favorable contribution to the molar Gibbs free energy of mixing. On the other hand, for LCST type phase behavior, the molar enthalpy of mixing is favorable for a condition of homogeneity. A negative molar entropy of mixing is responsible for phase separation as temperature is raised. On increasing the temperature, the solvent molecules take a more expanded state and it is the difference in the densities of the two components that leads to demixing (Folie and Radosz, 1995).

This section is concluded by derivation of the slope of the critical pressuretemperature curve in terms of curvature properties of molar volume v and molar entropy s (Rowlinson and Swinton, 1982). At the critical point the second and third derivatives of molar Gibbs free energy with respect to composition are zero. In the P-T-x space consider a small displacement (dP, dT and dx) along the critical curve given by the Taylor series expansion

$$d\left(\frac{\partial^2 g}{\partial x^2}\right)^c = \left(\frac{\partial^3 g}{\partial P \partial x^2}\right)^c dP + \left(\frac{\partial^3 g}{\partial T \partial x^2}\right)^c dT + \left(\frac{\partial^3 g}{\partial x^3}\right)^c dx = 0$$
(2.62)

The third term is zero. Therefore, we get for the slope

$$\left(\frac{\partial T}{\partial P}\right)^{c} = -\left(\frac{\partial^{3}g}{\partial P\partial x^{2}}\right)^{c} / \left(\frac{\partial^{3}g}{\partial T\partial x^{2}}\right)^{c} = \left(\frac{\partial^{2}v}{\partial x^{2}}\right)^{c} / \left(\frac{\partial^{2}s}{\partial x^{2}}\right)^{c}$$
(2.63)

#### 2.6 Classification scheme of van Konynenburg and Scott

Although the polymer-solution phase behavior patterns discussed so far are most commonly observed, the picture can be more complicated even for binary systems. The more complex phenomena along with the ones shown above are covered below with reference to the classification scheme of van Konynenburg and Scott (1980). It is assumed that the polymer has a well defined molar mass. The effect of polydispersivity of the polymer will be discussed in a later section.

van Konynenburg and Scott have classified binary fluid phase behavior into six main types using pressure-temperature projections. The projections employ non-variant equilibria (such as the critical point of a pure component and the critical endpoint in a binary system) and monovariant equilibria (such as the critical and three phase curves in a binary system) to mark regions of different types of phase behavior. With the exception of Type VI phase behavior all these types are predicted by a simple equation of state such as the van der Waals equation. Azeotropy leads to further subdivisions of these six main types but it is not covered here. All experimentally measured systems to date conform to this classification with the exception of some systems involving water (de Loos, 1994).

### 2.6.1 Type I phase behavior

The usual conditions for a binary mixture to exhibit Type I phase behavior are that the two substances be of similar chemical types and/or their critical properties be of comparable magnitude. The P-T and T-x projections of Type I phase behavior are shown in Figure (2.9 a). This type of phase behavior is characterized by a continuous gas-liquid critical curve and the absence of liquid-liquid immiscibility. Some examples are mixtures of methane with n-alkanes upto n-pentane. Two representative P-x sections are shown in Figure (2.9 b).

#### 2.6.2 Type II phase behavior

Type II phase behavior has a continuous gas-liquid critical curve with a liquidliquid critical line at lower temperatures. The liquid-liquid critical line terminates at a lower pressure in an upper critical end point where the two critical liquid phases are in equilibrium with a vapor phase. A three phase (liquid-liquid-vapor) curve extends to lower temperatures from the upper critical end point. The P-T and T-x projections of type II phase behavior are shown in Figure (2.10 a). Some examples of this type of phase behavior are binary systems of carbon dioxide + n-alkanes for carbon number n 6 < n < 12.



Χ

Figure 2.9. (a) Type I phase behavior P-T and T-x projections. (b) Two constant temperature P-x sections for Type I phase behavior.





Figure2.10. (a) Type II phase behavior P-T and T-x projections.
(b) Two constant pressure T-x sections for Type II phase behavior showing UCST behavior.

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Also, this type of phase behavior is seen in some polymer solutions although the norm for polymer solution phase behavior is Type IV phase behavior discussed below.

Two representative T-x sections are shown in Figure (2.10 b). As can be seen from this figure the T-x curves are of UCST type where on increasing the temperature at constant pressure a transition from a region of liquid-liquid immiscibility to a region of one liquid takes place.

# 2.6.3 Type VI phase behavior

In Type VI phase behavior, there is a continuous liquid-vapor critical line connecting the critical points of the two pure components with a liquid-liquid immiscibility at lower temperatures. This type of phase behavior differs from Type II because of the presence of a lower critical end-point in addition to an upper critical end point. The three phase (vapor-liquid-liquid) curve terminates at lower temperatures in a LCEP where again the two liquid phases become critical in the presence of a vapor phase. A liquid-liquid critical line emerges from this point. The P-T and T-x projections of Type VI phase behavior are shown in Figure (2.11 a). This type of phase behavior is observed in systems comprising chemically complex substances where components may self associate or there may be inter molecular associations due to hydrogen bonding (e.g., polyethylene glycol + water).

A representative T-x section for a Type VI system is shown in Figure (2.11 b). The loop encloses the region of liquid-liquid immiscibility.





Х

Figure 2.11. (a) Type VI phase behavior P-T and T-x projections.

(b) Constant pressure T-x section for Type VI phase behavior showing closed phase behavior.

### 2.6.4 Type V phase behavior

Type V phase behavior does not have a continuous gas-liquid critical curve as shown in the P-T and T-x projections in Figure (2.12). The gas-liquid critical line emerging from the critical point of the more volatile component terminates in an upper critical end point where the vapor phase is critical with a liquid phase in the presence of another liquid phase. A vapor-liquid-liquid curves extends from the upper critical end point and terminates in a lower critical end point at lower temperatures. At the lower critical end point two liquid phases are critical with each other in the presence of a vapor phase. A liquid-liquid critical curve emerges from the lower critical end point and finally terminates in the critical point of the less volatile component. This type of phase behavior or, type IV discussed below, can be observed in binary hydrocarbon mixtures once the two components differ sufficiently in their critical properties. An example is the binary mixture of methane and n-hexane.

Figures (2.13 a,b) contain two T-x sections for Type V phase behavior. The section contained in Figure (2.13 a) is typical of LCST type phase behavior where a transition from a region of two liquids to that of one liquid occurs on decreasing temperature at constant pressure. However, depending on the pressure of the system the phase behavior can be more complicated as shown in Figure (2.13 b). In this case there is a region characteristic of LCST behavior. There is also a three phase line (vapor-liquid-liquid) bounded by the LCST region, two vapor-liquid regions and one vapor and one



Figure 2.12. Type V phase behavior P-T and T-x projections.



Х



Figure 2.13. Two constant pressure T-x sections for Type V phase behavior. (a) LCST phase behavior. (b) LCST phase behavior in the vicinity of a three-phase equilibria.

liquid regions. This type of phase diagrams have been observed for a sample of polyethylene in n-hexane (Kennis et al., 1990).

### 2.6.5 Type IV phase behavior

Type IV phase behavior is a combination of Type II and Type V phase behaviors as shown in the P-T and T-x projections in Figure (2.14). Depending on the pressure of the system different type of T-x sections can be observed as shown in Figures (2.15 a) and (2.15 b). Figure (2.15 a) shows simultaneous occurrence of LCST and UCST behaviors with a one liquid region in the middle. Figure (2.15 b) shows a little more complex phase diagram. In addition to the LCST and UCST regions there is a three phase line bounded by vapor-liquid, one vapor and one liquid regions as shown.

### 2.6.6 Type III phase behavior

In Type III phase behavior the LCST and UCST branches of the Type IV phase behavior merge as shown in the P-T and T-x projections in Figure (2.16 a). This happens when the mutual immiscibilities if the two components become sufficiently great. For instance, in a polymer-solvent system exhibiting type IV phase behavior, if the polymer chain length is increased, a transition from Type IV to Type III can occur. In Type III phase behavior, as in TypeV and Type IV, the gas-liquid critical curve is not continuous.

Figure (2.16 b) shows a T-x section for Type III phase behavior for the case where the system pressure is slightly below the pressure minimum on the liquid-liquid critical



Figure 2.14. Type IV phase behavior P-T and T-x projections.





Figure 2.15. Two constant pressure T-x sections for Type IV phase behavior.

- (a) Simultaneous UCST and LCST phase behaviors.
- (b) LCST phase behavior in the vicinity of a three-phase equilibria and UCST phase behavior at lower temperatures.





X

Figure 2.16. (a) Type III phase behavior P-T and T-x projections.
(b) Constant pressure T-x section for Type III phase behavior showing hour glass phase behavior.

curve. The phase diagram observed is of hour glass type with a region of immiscibility in the middle.

# 2.7 Cloud point curves for solutions of a polydisperse polymer

The effect of the polydispersivity of the polymer is discussed with reference to a polymer with two homologs with differing chain lengths, following the treatment of Koningsveld (1968). Let the solvent and the polymer be denoted by S and P respectively with  $P_1$  and  $P_2$  representing the two homologs of the polymer. The solution can be represented on a ternary phase diagram at constant pressure as shown in Figure (2.17). The temperature axis is perpendicular to the plane of the paper. The solid curves labeled T<sub>1</sub>, T<sub>2</sub> etc. are binodals at different temperatures. The binodals represent coexisting phase compositions located at the ends of tie-lines. The dashed curves are the spinodals (limit of stability). The points labeled C1, C2 etc. are plait or critical points depending on the terminology used. At these points the length of tie-lines is zero and the two phases become identical. SP is the composition axis for the solutions of P in S with a constant ratio of  $P_1$  and  $P_2$ . This ratio is determined by the molar mass or chain-length distribution of the pure polymer. The line SP corresponds to adding solvent to a polymer with a distribution of  $P_1$  and  $P_2$  given by point P. The cloud point for a known composition polymer solution is defined as the temperature and pressure condition at which a second phase just appears, i.e., one is at the phase boundary. In Figure (2.18) the temperature axis is explicitly shown and contains the binodal surface of a ternary polymer solution.



Figure 2.17. Binodals and spinodals in a ternary polymer solution. Modified from Koningsveld (1968).



Figure 2.18. Constant pressure Temperature-composition space for a ternary polymer solution. Modified from Koningsveld (1968).

The plane TPS corresponds to a quasibinary section for which the ratio of  $P_1$  to  $P_2$  is determined by point P.

Let us assume that the pressure and temperature are fixed at p and T<sub>1</sub> respectively and we add solvent S to the polymer P. As more solvent is added we ultimately reach the phase boundary at A as shown in Figure (2.18). If we add more solvent we would reach the point B. Both A and B are points on the binodal but usually do not represent the compositions of the coexisting phases. The compositions of the coexisting phases are given by the ends of the tie-lines starting at A and B. The quasibinary T-x section separating the two-phase region from the one-phase region, where x is the cumulative concentration of the polymer corresponding to the polymer distribution P, is shown in Figure (2.19). The important point here is that the peak of the quasibinary T-x section is no longer the critical temperature which is the case for a binary solution. Rather it lies on the right-hand branch of the T-x section. The maximum of the quasi-binary T-x section has been called the precipitation threshold temperature by Tompa (1956). These considerations are also valid for a polymer of more than two components. The binodal curve and the spinodal curve (limit of stability) have a common tangent at the critical point.





Figure 2.19. Constant pressure T-x diagram for a solution of polydisperse polymer showing the location of the critical point on the right hand branch.

### **CHAPTER 3**

# **Computations**

## 3.0 Introduction

This Chapter deals with the aspects of phase equilibrium calculations. The first section outlines a strategy for a volume solver for an equation of state that cannot be solved analytically for volume roots. A volume solver is the cornerstone of any phase equilibrium calculation with an equation of state. The second section contains a method for performing pure component vapor pressure calculations. This is followed by a discussion of two-phase equilibrium calculations. The method of successive substitution for performing two-phase constant temperature and pressure calculations is covered and a scheme for doing two-phase boundary calculations is presented. The last but one section of the Chapter deals with multiphase constant temperature and pressure equilibrium calculations. Finally, a scheme is presented for discretizing a polydisperse polymer into pseudocomponents, based on the knowledge of mass average and weight average molar masses. Almost always a polymer, instead of having a well defined molar mass, consists of homologus molecules of varying chain lengths. Often the only information one may have regarding the polydispersivity of a polymer are its average molar masses. Hence, it is convenient to have a scheme which uses the values of the experimental average molar masses to give some information regarding the distribution of molar masses in the polymer.
### 3.1 Strategy for a volume solver for an equation of state

As mentioned above, in this section a strategy is outlined for solving for volume roots of equations of state that cannot be solved analytically. The requirement is that the model isotherms have the form shown in Figure (3.1 b). The strategy employs Newton technique for solving for the volumes.

Consider Figures (3.1 a) and (3.1 c). These figures show experimental pressurevolume isotherms for a pure compound and for a mixture of fixed composition respectively. At the critical point of a pure compound [Figure (3.1a)] the following equations have to be satisfied

$$\left(\frac{\partial \mathbf{P}}{\partial \mathbf{V}}\right)_{\mathrm{T}} = 0 \tag{3.1}$$

$$\left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{V}^2}\right)_{\mathrm{T}} = 0 \tag{3.2}$$

The critical point of a mixture need not satisfy equations (3.1) and (3.2), rather the point corresponding to equations (3.1) and (3.2) occurs inside the two-phase region (Mills et al.,1980). In both cases, the left hand side is the liquid region and the right hand side is the vapor region. Also, since normally the mixture bubble point pressures are higher than dew point pressures they are no longer connected by horizontal lines which is the case for a pure compound.

The models are designed to mimic experimental data and hence show similar behavior. However, the models connect the two-phase regions by sigmoidal sections as



Figure 3.1. (a) Experimental isotherms for a pure compound. (b) Model isotherms for a pure compound. (c) Experimental isotherms for a mixture of constant composition. (d) Model isotherms for a mixture of constant composition.

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shown in Figures (3.1 b,d). The points in Figure (3.1 b,d) where the first derivative of pressure with respect to volume (constant temperature) is zero give the limit of mechanical stability from the model. The isotherm for the mixture which contains the point corresponding to equations (3.1) and (3.2) can be called a quasicritical isotherm

At temperatures above the quasicritical temperature the sigmoidal sections are missing from the isotherms. This has implications on solving for volumes at a given pressure. If  $T>T_C$  (critical or quasicritical temperature) there is only one volume root and if  $T<T_C$  there are potentially three volumes root for a given pressure. The Figures (3. 1b,d) are intended to show the similarities between the pure component and mixture P-V behavior for the purpose of solving for the volumes at a given pressure and temperature.

Based on the nature of isotherms shown in Figures (3.1 b,d) the following strategy for a volume solver can be developed. The first step is to determine whether the given temperature is above or below the critical temperature or the quasicritical temperature (depending on whether one is dealing with a pure compound or a mixture). This can be conveniently done by checking the sign of  $\partial P/\partial V$  for a range of volumes. The equations normally involve terms of the type (v-b) so that b/v ranges from one to zero and gives a convenient interval. If  $\partial P/\partial V$  is always less than zero it corresponds to the case where the temperature is greater than the critical or quasicritical temperature and there is only one root. However, if the mixture temperature is less than the critical temperature or the quasicritical temperature (some  $\partial P/\partial V>0$ ) there are potentially three roots. The limit of mechanical stability is given by the maximum pressure on an isotherm Pmax and the minimum pressure on an isotherm Pmin. If the given pressure is above Pmax then there is only one liquid like root and if it is less than Pmin then there is only one vapor like root. However, if the pressure falls between Pmax and Pmin then, three volume roots can be found. The middle root corresponding to  $\partial P/\partial V>0$  is to be rejected as it corresponds to a physically impossible situation. Then one is left with a liquid like root and a vapor like root one of which can be chosen depending on whether one is looking at a liquid phase or a vapor phase. Now, at a specified temperature and pressure (and composition if necessary) one can solve the following equation with Newton's method

$$f(\mathbf{v}) = P(\mathbf{v}) - P(\text{specified}) = 0$$
(3.3)

updating v as given by

$$\mathbf{v}^{k+1} = \mathbf{v}^{k} - \frac{\mathbf{f}(\mathbf{v})}{(\partial \mathbf{f} / \partial \mathbf{v})}$$
(3.4)

where k is the iteration count. When solving for a vapor-like root, a reasonable starting guess is factor\*RT/P where the factor is less than unity. For the case where a liquid-like root is required a reasonable guess would be factor\*b where the factor is greater than unity. The strategy explained in this section was employed for obtaining volume roots for the equations of state used in this work.

#### 3.2 Pure component vapor pressure calculation

At an equilibrium between the vapor and liquid phases of a pure component the equality of chemical potentials has to be satisfied as given by

$$g = \mu^{v} - \mu^{l} = 0 \tag{3.5}$$

where superscripts v and l correspond to the vapor and liquid phases respectively. At a given temperature g can be taken as a function of pressure and then the vapor pressure can be obtained by solving the above equation using the Newton method as shown below.

$$P^{k+l} = P^{k} - \frac{g(P)}{\frac{\partial g}{\partial P}}$$
(3.6)

 $\partial g / \partial P$  can be obtained from the Gibbs-Duhem equation which for a molar amount of a pure compound is given by

$$-\mathbf{sdt} + \mathbf{vdp} - \mathbf{d\mu} = 0 \tag{3.7}$$

At constant temperature

$$\left(\frac{\partial \mu}{\partial P}\right)_{T} = v \tag{3.8}$$

Hence,

$$\left(\frac{\partial g}{\partial P}\right)_{T} = \left(\frac{\partial \mu^{v}}{\partial P}\right)_{T} - \left(\frac{\partial \mu^{l}}{\partial P}\right)_{T} = v^{v} - v^{l}$$
(3.9)

Equation (3.6) can then be written as

$$P^{k+l} = P^{k} - \frac{\mu^{v} - \mu^{l}}{v^{v} - v^{l}}$$
(3.10)

# 3.3 Two-phase equilibrium calculations

At a two-phase equilibrium in a nc component system the temperatures and pressures in the two phases are equal and the equality of the chemical potentials have to be satisfied as given by

$$g(i) = \mu_i^{II} - \mu_i^{I} = 0; \quad i = 1,...,nc$$
 (3.11)

In terms of fugacities  $f_i$ , equation (3.11) can be written as

$$g(i) / RT = \ln f_i^{II} - \ln f_i^{I}$$
 (3.12)

The equations are solved through the constraint that the mole fractions of the components in the two phases sum to unity. This can be expressed as

$$\sum_{i=1}^{nc} (y_i - x_i) = 0$$
 (3.13)

 $y_i$ s and  $x_i$ s correspond to the mole fractions in phases I and II respectively. Equation (3.13) can be expressed in a different form by mass balance considerations. The mole balance on component i gives

$$z_i = \beta y_i + (1 - \beta) x_i \qquad (3.14)$$

where  $z_i$ s are the feed mole fractions and  $\beta$  is the fraction of phase I.

The equal chemical potential equation is rearranged in the form

$$\mathbf{y}_{\mathbf{i}} = \mathbf{K}_{\mathbf{i}} \mathbf{x}_{\mathbf{i}} \tag{3.15}$$

where  $K_i$  is the distribution coefficient of component I.  $K_i$  in general depends on temperature, pressure and compositions in the two phases.

Substituting  $y_i = K_i x_i$  in equation (3.14) and rearranging it we get

$$x_{i} = \frac{z_{i}}{\beta K_{i} + (1 - \beta)}; y_{i} = \frac{K_{i} z_{i}}{\beta K_{i} + (1 - \beta)}$$
(3.16)

Now substituting from equations (3.15) and (3.16) into equation (3.13) we get

$$f(\beta) = \sum_{i=1}^{nc} \frac{z_i(K_i - 1)}{1 + \beta(K_i - 1)} = 0$$
(3.17)

This is the Rachford-Rice formulation of the equilibrium problem (Walas, 1985).

Equation (3.17) and the nc equations for the equalities of chemical potentials of a component in the two-phases give (nc+1) equations which can be solved for (nc+1) variables. If a constant temperature-pressure two-phase equilibrium is required then  $K_{is}$  and  $\beta$  can be solved to give the equilibrium set of  $x_{is}$  and  $y_{is}$ . Another situation of interest is the case when  $\beta$  is zero. This corresponds to a phase boundary calculation (bubble point, dew point, cloud point etc.). In this case equation (3.13) is

$$\sum_{i=1}^{nc} z_i (K_i - 1) = \sum_{i=1}^{nc} y_i - 1 = 0$$
(3.18)

This equation with the set of nc equilibrium relations involving chemical potentials can be solved for  $K_is$  and T or P for a given feed ( $z_is$ ) and P or T to give the composition of the incipient phase ( $y_is$ ).

### 3.3.1 Constant temperature and pressure two-phase equilibrium calculations

In this work, the two-phase equilibrium calculations were carried out employing the conventional successive substitution method (Walas, 1985). The methodology was to decouple the solution of the mass balance equation (3.17), which solves for  $\beta$ , from the solution of equations for equality of chemical potentials. A set of  $K_i$ s was chosen as an initial guess and the mass balance was solved for assuming the distribution coefficients to be composition independent to give the phase fraction  $\beta$ . This is the Rachford-Rice procedure (Walas, 1985). This value of phase fraction was then used to calculate the set of  $x_i$ s and  $y_i$ s from equations (3.16) and (3.17), respectively. The chemical potentials for the two phases were evaluated using this set of  $x_i$ s and  $y_i$ s. If the criterion for equilibrium expressed in the set of equations (3.11) or (3.12) was satisfied to the specified tolerance the computations were stopped. Otherwise a new set of  $K_i$ s was obtained from

$$\ln K_{i}^{k+1} = \ln K_{i}^{k} - m^{*} \ln (f_{i}^{II} / f_{i}^{I})^{k}$$
(3.19)

k is the iteration count variable. The process was then repeated with the new set of  $K_i$ s. Coefficient m is a damping or acceleration factor in these computations and its significance is discussed below. The following tolerance criterion was normally used to terminate the phase equilibrium calculations

$$\sum_{i=1}^{n_{c}} \{ \ln f_{i}^{II} - \ln f_{i}^{I} \}^{2} \le 10^{-12}$$
(3.20)

Equation (3.19) can be obtained as follows. At equilibrium we have for component i

$$\mathbf{f}_i^{II} = \mathbf{f}_i^1 \tag{3.21}$$

In terms of fugacity coefficients  $\phi_i$ s this relation can be expressed as

$$\mathbf{x}_{i}\boldsymbol{\phi}_{i}^{II}\mathbf{P} = \mathbf{y}_{i}\boldsymbol{\phi}_{i}^{I}\mathbf{P} \tag{3.22}$$

$$\phi_i$$
 is defined as  $\frac{(\text{fugacity of } i)}{(\text{mole fraction of } i)(\text{pressure})}$ . Equation (3.22) gives

$$K_{i}^{k+1} = \left(\frac{\phi_{i}^{II}}{\phi_{i}^{I}}\right)^{k} = \left(\frac{y_{i}}{x_{i}}\right)^{k} \left(\frac{f_{i}^{II}}{f_{i}^{I}}\right)^{k} = K_{i}^{k} \left(\frac{f_{i}^{II}}{f_{i}^{I}}\right)^{k}$$
(3.23)

Taking the natural logarithm of this equation we get equation (3.19).

The mass balance function is a monotonically decreasing function of  $\beta$  as can be seen from its first derivative with respect to the phase fraction.

$$f'(\beta) = -\sum z_i (K_i - 1)^2 / [\beta + (K_i - 1)\beta]^2$$
(3.24)

Hence, for a root  $(0 < \beta < 1)$  to exist the following inequalities have to be satisfied. These are obtained by substituting  $\beta=0$  and  $\beta=1$  in equation (3.17).

$$\sum_{i=1}^{n_{c}} K_{i} z_{i} > 1 \tag{3.25}$$

$$\sum_{i=1}^{nc} z_i / K_i > 1$$
 (3.26)

# 3.3.1.1 Convergence of successive substitution

The process of solving equilibrium equations simultaneously by successive substitution can be represented in vector notation (overbars) as

$$\overline{\mathbf{y}}^{k+1} = \overline{\mathbf{f}}(\overline{\mathbf{y}}^k) \tag{3.27}$$

which is presumed to have a solution  $\overline{y}$  that satisfies

$$\overline{\mathbf{y}} = \overline{\mathbf{f}}(\overline{\mathbf{y}})$$
(3.28)

Heidemann and Michelsen (1995) point out that a necessary condition for convergence to  $\overline{y}$  is that the eigenvalues of the matrix given by

$$\overline{\overline{E}} = \{\partial f_i / \partial y_j\}_{\overline{y}}.$$
(3.29)

be less than unity in absolute value. This can be seen as follows.

In the vicinity of the solution, let us assume at the  $(k+1)^{th}$  iterate, the error vector is given by

$$\overline{\mathbf{y}}^{\mathbf{k}} - \overline{\mathbf{y}}^{\mathbf{*}} = \overline{\mathbf{f}}(\overline{\mathbf{y}}^{\mathbf{k}}) - \overline{\mathbf{f}}(\overline{\mathbf{y}}^{\mathbf{*}})$$
(3.30)

or

$$\overline{e}^{k+1} = \overline{E} \overline{e}^{k}$$
(3.31)

This equation is obtained by expanding  $\overline{f(y)}^k$  in a first order Taylor series expansion around the solution vector. Let the eigenvectors of  $\overline{E}$  be  $\overline{u_i}$  and the corresponding eigenvalues be  $\lambda_i$ . Expanding  $\overline{e_k}$  on the set of eigenvectors we get

$$\bar{e}^{k} = \sum c_{j} \bar{u}_{j}$$
(3.32)

The error vector at the  $(k+1)^{th}$  iterate is given by

$$\bar{\mathbf{e}}^{k+1} = \sum \bar{\mathbf{c}}_{j} \bar{\mathbf{u}}_{j} \lambda_{j}$$
(3.33)

and at the (k+m)<sup>th</sup> iterate by

$$\bar{\mathbf{e}}^{\mathbf{k}+\mathbf{m}} = \sum \mathbf{c}_{j} \bar{\mathbf{u}}_{j} \lambda_{j}^{\mathbf{m}}$$
(3.34)

It is evident from equation (3.34) that the absolute magnitude of the eigenvalues of  $\overline{E}$  has to be less than unity for the convergence of the iterative process. It has been shown by Heidemann and Michelsen (1995) that this is not always the case for the solution of equilibrium equations by successive substitution. They propose the use of a factor m in updating K<sub>i</sub>s to overcome this difficulty. The relation between the eigenvalues of an undamped process (m=1) and a damped process (m<1) can be easily established.

Consider the undamped process given by

$$\ln K_{i}^{k+1} = \ln K_{i}^{k} - \ln (f_{i}^{II} / f_{i}^{I})^{k}$$
(3.35)

The behaviour of the process is governed by the eigenvalues of the matrix  $\overline{N}$  with elements

$$N_{ij} = (\partial \ln K_i / \partial \ln K_j)_{\overline{K}^*} - \left[\frac{\partial \ln(f_i^{II} / f_i^{I})}{\partial \ln K_j}\right]_{\overline{K}^*}$$
(3.36)

or,

$$N_{ij} = \delta_{ij} - \left[\frac{\partial \ln(f_i^{il} / f_i^{l})}{\partial \ln K_j}\right]_{\overline{K}^*}$$
(3.37)

The damped process is represented by

$$\ln K_{i}^{k+1} = \ln K_{i}^{k} - m^{*} \ln (f_{i}^{II} / f_{i}^{I})^{k}$$
(3.38)

and the convergence depends on the eigenvalues of the matrix  $\overline{\mathbf{M}}$  with elements

$$M_{ij} = \delta_{ij} - m^* \left[ \frac{\partial \ln(f_i^{II} / f_i^{I})}{\partial \ln K_j} \right]_{\overline{K}^*}$$
(3.39)

Let,

$$\vec{N} = \vec{I} - \vec{N}$$
(3.40)

and

$$\overline{\overline{M}} = \overline{\overline{I}} - m^* \overline{\overline{N}}$$
(3.41)

Also assume,

$$\overline{\widetilde{N}x} = \lambda \overline{x}$$
(3.42)

which implies,

$$\overline{\overline{\mathbf{N}}}' \,\overline{\mathbf{x}} = (1 - \lambda) \overline{\mathbf{x}} \tag{3.43}$$

In terms of  $\overline{M}$  we get

$$\overline{\mathbf{M}}\overline{\mathbf{x}} = [1 - \mathbf{m}(1 - \lambda)]\overline{\mathbf{x}}$$
(3.44)

which gives the relation between the eigenvalues of the damped and undamped processes

$$\lambda_{\rm m} = 1 - {\rm m}(1 - \lambda) \tag{3.45}$$

The effect of damping is to reduce the magnitude of the eigenvalues of the undamped process to make the modified process convergent. However, a consequence of this is a slower convergence as the eigenvalues of the modified process are pushed towards unity for very small damping factors. In some cases the iterative process can be accelerated by using values of m > 1 (Mehra et al., 1982).

Michelsen (1982 a,b) has shown that the direct substitution process converges to at least a local minimum. This is shown below following the treatment of Michelsen (1982 a,b).

Consider at given P and T one mole of a mixture of composition  $(z_1, z_2, ..., z_{nc})$ . This splits into two phases with mole numbers  $(l_1, l_2, ..., l_{nc})$  and  $(v_1, v_2, ..., v_{nc})$  corresponding to phases I and II respectively. Conservation of mass requires  $l_i + v_i = z_i$ . We choose  $l_i$ s as the independent variables.

The phase split represents a stationary point in Gibbs energy if

$$\frac{\partial G / RT}{\partial l_i} = \frac{\partial (G_L + G_V) / RT}{\partial l_i} = (\mu_i^I - \mu_i^I) / RT = 0; i = 1, nc$$
(3.46)

is satisfied, which is the case for an equilibrium calculation.

The stationary point is a local minimum if the Hessian matrix is positive definite. The elements of the Hessian matrix  $\overline{\overline{B}}$  are given by

$$B_{ij} = \frac{1}{RT} \frac{\partial^2 G}{\partial l_i \partial l_j} = -\frac{\partial \ln(f_i^{II} / f_i^{I})}{\partial l_j}$$
(3.47)

The elements of matrix  $\overline{\overline{N}}$  can be expressed as

$$N_{ij} = \delta_{ij} - \sum_{m=1}^{nc} \frac{\partial \ln(f_i^{II} / f_i^{I})}{\partial l_m} \frac{\partial l_m}{\partial \ln K_j}$$
(3.48)

Now,

$$\ln K_{j} = \ln(z_{j} - l_{j}) / l_{j} + \ln L / V$$
(3.49)

where,  $L = \sum_{i} l_i$  and  $V = \sum_{i} v_i$ .

Also,

$$\frac{\partial \ln K_j}{\partial l_m} = -\frac{\delta_{mj}}{v_j} - \frac{\delta_{mj}}{l_j} + \frac{1}{V} + \frac{1}{L}$$
(3.50)

 $N_{ij}$  can be expressed in terms of the elements of  $\overline{\overline{B}}\,$  as

$$N_{ij} = \delta_{ij} - \sum_{m} B_{im} \left( -\frac{\partial l_m}{\partial \ln K_j} \right)$$
(3.51)

and the matrix  $\overline{\overline{N}}$  in terms of matrices  $\overline{\overline{B}}$  and  $\overline{\overline{D}}$  as

$$\overline{\overline{N}} = \overline{\overline{I}} - \overline{\overline{BD}}$$
(3.52)

where the elements of  $\overline{\overline{D}}$  are given by

$$D_{mj} = \frac{1}{\frac{\delta_{mj}}{v_j} + \frac{\delta_{mj}}{l_j} - \frac{1}{V} - \frac{1}{L}}$$
(3.53)

Let,

$$\overline{Nx} = \lambda \overline{x}$$
(3.54)

Therefore,

$$(\overline{I} - \overline{BD})\overline{x} = \lambda \overline{x}$$
 (3.55)

Now,  $\overline{D} = \overline{Q}^{-1}$  where  $\overline{Q}$  is a symmetric and positive definite matrix. Therefore using Cholesky decomposition (Broyden, 1975) it can be expressed as

$$\overline{\overline{Q}} = \overline{\overline{E}}\overline{\overline{E}}^{T}$$
(3.56)

and,

$$\overline{\overline{Q}}^{-1} = \overline{\overline{E}}^{-T} \overline{\overline{E}}^{-1}$$
(3.57)

From equation(3.55) after suitable premultiplication we get

$$\overline{\overline{E}}^{-1}(\overline{\overline{I}} - \overline{\overline{B}}\overline{\overline{E}}^{-T}\overline{\overline{E}}^{-1})\overline{x} = \lambda \overline{\overline{E}}^{-1}\overline{x}$$
(3.58)

$$\overline{\overline{E}}^{-1}\overline{\overline{B}}\overline{\overline{E}}^{-T}\overline{v} = (1-\lambda)\overline{v}$$
(3.59)

At the converged solution  $|\lambda| < 1$  and so  $(1-\lambda)$  is greater than zero. This implies that the matrix  $\overline{\overline{E}}^{-1} \overline{\overline{BE}}^{-T}$  is positive definite. As a consequence the Hessian matrix  $\overline{\overline{B}}$  is positive definite. This can be seen as follows.

Positive definiteness of  $\vec{E} \cdot \vec{B} \vec{E}$  implies that for any vector  $\vec{x}$ 

$$\overline{x} \stackrel{\tau}{E} \stackrel{\tau}{BE} \stackrel{\tau}{x} > 0$$
 (3.60)

Let,

$$\bar{\bar{E}}^{-T}\bar{\bar{x}} = \lambda_{\bar{E}}\bar{\bar{x}}$$
(3.61)

Therefore,

$$\bar{\mathbf{x}}^{\mathsf{T}} \bar{\mathbf{E}}^{-1} = \lambda_{\mathsf{E}} \bar{\mathbf{x}}^{\mathsf{T}}$$
(3.62)

Substituting in expression (3.60) we get

$$\lambda_{\rm E}^2 \bar{\mathbf{x}}^{\rm T} \overline{\mathbf{B}} \bar{\mathbf{x}} > 0 \tag{3.63}$$

This shows that  $\overline{B}$  is positive definite. Hence, the converged solution of a phase equilibrium calculation using successive substitution is at least a local minimum.

## 3.3.2 Two-phase boundary calculations

The equations to be solved for a two-phase boundary calculation are

$$g_i = \left(\frac{\mu_i}{RT}\right)^{ii} - \left(\frac{\mu_i}{RT}\right)^{i} = 0$$
;  $i = l, 2, ..., nc$  (3.64)

i.e., equality of chemical potentials of each component in the two phases, and,

$$g_{nc+1} = \sum_{i=1}^{nc} Y_i - 1 = \sum_{i=1}^{nc} z_i K_i - 1 = 0$$
(3.65)

 $Y_i$  would be the mole fraction  $y_i$  of component i in the phase I or the incipient phase, when the conditions of equilibrium are satisfied.  $z_i$  is the composition of the feed phase or phase II.

Equations represented by (3.64) to (3.65) are (nc+1) equations in (nc+1) variables. Following the approach of Michelsen (1980) these equations can be solved for using a Newton scheme. The most obvious choice of (nc+1) variables is the set of K<sub>i</sub>'s and either T or P. In this work, for this case, the temperature and K<sub>i</sub>'s were solved for keeping the pressure and the feed composition ( $z_i$ 's constant). The variable set is given by the vector  $\alpha^T = (\ln K_1, \ln K_2, ..., \ln K_{nc}, \ln T)$ . As suggested by Michelsen  $\ln K_i$ 's and  $\ln T$  were used instead of simply K<sub>i</sub>'s and T for scaling the variables as a K<sub>i</sub> may range from very large to very small numbers. The Newton procedure for solution is shown in vector notation by the following equation

$$\overline{g}^{k} + \overline{J}^{k} \overline{\Delta \alpha}^{k+1} = 0$$
(3.66)

k is the iteration count.  $\overline{J}$  is the Jacobian given by

$$\bar{\bar{J}} = \begin{pmatrix} \frac{\partial g_i}{\partial \ln K_j} \\ \frac{\partial g_{nc+1}}{\partial \ln T} \\ \frac{\partial g$$

In  $\overline{J}$ , i is the row count and has range 1 through nc and j is the column count and has range 1 through nc.  $\overline{\Delta \alpha}$  is the correction vector.

The expressions for the derivatives involved in the calculation of the Jacobian are presented below. The top left hand corner ( $nc \times nc$ ) minor has elements given by

$$\left(\frac{\partial g_i}{\partial \ln K_j}\right)_{T,P} = -y_j n_T \left[\frac{\partial \mu_i / RT}{\partial n_j}\right]_{T,P}^I \quad ; \quad i = 1, 2, ..., nc \quad ; \quad j = 1, 2, ..., nc \quad (3.68)$$

where,

$$\left[\frac{\partial \mu_{i} / RT}{\partial n_{j}}\right]_{T,P} = \frac{1}{RT} \frac{\left(\frac{\partial P}{\partial n_{i}}\right)_{T,V} \left(\frac{\partial P}{\partial n_{j}}\right)_{T,V}}{\left(\frac{\partial P}{\partial V}\right)_{T,n}} + \left(\frac{\partial \mu_{i} / RT}{\partial n_{j}}\right)_{T,V}$$
(3.69)

 $n_T$  is the total number of moles of phase I i.e.,  $n_T = \Sigma Y_{i.}$ 

The other derivatives involved in the computation are

$$\left(\frac{\partial g_{i}}{\partial \ln T}\right)_{K,P} = T \left[ \left(\frac{\partial \mu_{i} / RT}{\partial T}\right)_{K,P}^{II} - \left(\frac{\partial \mu_{i} / RT}{\partial T}\right)_{K,P}^{I} \right] ; \quad i = 1, 2, ..., nc \quad (3.70)$$
$$\left(\frac{\partial g_{nc+1}}{\partial \ln K_{j}}\right)_{T,P} = Y_{j} ; \quad j = 1, nc \quad (3.71)$$

$$\left(\frac{\partial g_{nc+1}}{\partial \ln T}\right)_{K,P} = 0 \tag{3.72}$$

So the bottom row of the Jacobian is given by  $(Y_1, Y_2, ..., Y_{nc}, 0)$ .

In order to initiate computations, one requires fairly accurate initial estimates of the temperature and the  $K_i$ 's for one or two points on the phase boundary. Sometimes, a point on each side of the critical point is required. This is so because a trivial solution,  $(y_i=z_i \text{ and } K_i=1)$ , may be obtained if one is very close to the critical point. Rough estimates of initial guesses can be obtained from a two-phase flash routine. Unfortunately, to our knowledge, unlike hydrocarbons there are no good correlations available for  $K_i$ 's for the polymer which may be used as initial guesses. Once a point on the phase boundary is found, the rest of the phase boundary can be generated by taking small steps along the phase boundary.

Since one may be dealing with pseudocomponents having extremely large molar masses, numerical problems may arise due to extremely small mole fractions and distribution coefficients. If such a problem is encountered, that particular  $K_i$  can be dropped from the variable set.

### 3.3.2.1 Variable polymer mass fraction

A variation of the phase boundary calculation problem is the case where the mass of the polymer in the mixture is treated as a variable. Then some other variable, say a  $K_i$ , could be fixed and substituted for by the mass of the polymer and the resulting set of equations solved for. The mass of the polymer can be included in the variable set as follows.

Consider phase II or the fixed phase. Let exp(v) be the mass of the polymer in the mixture per unit mass of the solvent. The mass fraction of the solvent, taken as component 1, is

$$w_1 = \frac{1}{1 + e^v}$$
(3.73)

Let  $wt_i$  be the mass fractions of the pseudocomponents of the solvent-free polymer, based on some appropriate molar mass distribution. The number of moles of the polymer species i present are

$$\mathbf{n}_{i}^{\mathrm{ff}} = \mathbf{e}^{\mathrm{v}} \frac{\mathbf{w}\mathbf{t}_{i}}{\mathbf{M}\mathbf{W}_{i}}; \quad \mathbf{i} = 2, \mathrm{nc}$$
(3.74)

where  $MW_i$  is the molar mass of the pseudocomponent i. Obviously the number of moles of the solvent is  $n_1^{II} = 1/MW_I$ . The total number of moles is given by

$$\mathbf{n}_{\mathrm{T}}^{\mathrm{II}} = \sum_{i=1}^{\mathrm{nc}} \mathbf{n}_{i} = \frac{1}{\mathrm{MW}_{1}} + \sum_{i=2}^{\mathrm{nc}} \frac{\mathbf{e}^{\mathrm{v}} \mathbf{w} \mathbf{t}_{i}}{\mathrm{MW}_{i}}$$
(3.75)

and the composition of phase II by

$$z_i = \frac{n_i}{n_T^{II}} \tag{3.76}$$

Now for phase I we have

$$\mathbf{Y}_{i} = \mathbf{K}_{i} \mathbf{z}_{i} \tag{3.77}$$

and the composition is given by

$$y_i = \frac{K_i z_i}{\sum_{i=1}^{nc} K_i z_i}$$
(3.78)

The mass of various components  $w_i$  (i = 2,nc) per unit mass of solvent is given by

$$\mathbf{w}_{i} = \frac{\mathbf{K}_{i} \mathbf{z}_{i} \mathbf{M} \mathbf{W}_{i}}{\mathbf{K}_{1} \mathbf{z}_{1} \mathbf{M} \mathbf{W}_{1}}$$
(3.79)

The moles of solvent in phase I are  $n_1^{I} = 1/MW_1$ . The moles of the polymer species are

$$n_{i}^{I} = \frac{K_{i} z_{i}}{K_{1} z_{1} M W_{1}} = \frac{K_{i} (e^{v} w t_{i} / M W_{i})}{K_{1}}$$
(3.80)

Now the derivatives of equilibrium relations  $g_i$  with respect to the variable v can be determined.

$$\frac{\partial g_{nc+1}}{\partial v} = z_1 (1 - K_1) \tag{3.81}$$

And for i=1,nc

$$\frac{\partial \mathbf{g}_{i}}{\partial \mathbf{v}} = \frac{\partial}{\partial \mathbf{v}} \left( \frac{\Delta \boldsymbol{\mu}_{i}^{\mathrm{II}}}{\mathrm{RT}} - \frac{\Delta \boldsymbol{\mu}_{i}^{\mathrm{I}}}{\mathrm{RT}} \right)$$
(3.82)

This can be expressed in a different form using chain rule

$$\frac{\partial \mathbf{g}_{i}}{\partial \mathbf{v}} = \left(\sum_{k=1}^{nc} \left(\frac{\partial}{\partial \mathbf{n}_{k}^{II}} \frac{\Delta \boldsymbol{\mu}_{i}^{II}}{RT}\right) \frac{\partial \mathbf{n}_{k}^{II}}{\partial \mathbf{v}}\right) - \left(\sum_{k=1}^{nc} \left(\frac{\partial}{\partial \mathbf{n}_{k}^{I}} \frac{\Delta \boldsymbol{\mu}_{i}^{I}}{RT}\right) \frac{\partial \mathbf{n}_{k}^{I}}{\partial \mathbf{v}}\right)$$
(3.83)

where,

$$\frac{\partial \mathbf{n}_{1}^{\mathrm{I}}}{\partial \mathrm{v}} = \frac{\partial \mathbf{n}_{1}^{\mathrm{II}}}{\partial \mathrm{v}} = 0 \tag{3.84}$$

and for k=2,nc

$$\frac{\partial \mathbf{n}_{k}^{\mathrm{II}}}{\partial \mathbf{v}} = \frac{\mathbf{e}^{\mathrm{v}} \mathbf{w}_{k}}{\mathbf{M} \mathbf{W}_{k}} = \mathbf{n}_{k}^{\mathrm{II}}$$
(3.85)

and

$$\frac{\partial \mathbf{n}_{k}^{\mathrm{I}}}{\partial \mathbf{v}} = \frac{\mathbf{K}_{k}}{\mathbf{K}_{1}} \frac{\mathbf{e}^{\mathrm{v}} \mathbf{w}_{k}}{\mathbf{M} \mathbf{W}_{k}} = \mathbf{n}_{k}^{\mathrm{I}}$$
(3.86)

Therefore equation (3.83) can be written

$$\frac{\partial \mathbf{g}_{i}}{\partial \mathbf{v}} = \sum_{k=2}^{nc} \frac{\partial \Delta \mu_{i}^{II} / RT}{\partial \mathbf{n}_{k}^{II}} \mathbf{n}_{k}^{II} - \sum_{k=2}^{nc} \frac{\partial \Delta \mu_{i}^{II} / RT}{\partial \mathbf{n}_{k}^{II}} \mathbf{n}_{k}^{II}$$
(3.87)

This can be simplified further by using Gibbs-Duhem equation and by noting that

$$\frac{\partial \Delta \mu_i / RT}{\partial n_k} = \frac{\partial \Delta \mu_k / RT}{\partial n_i}$$
(3.88)

to

$$\frac{\partial \mathbf{g}_{i}}{\partial \mathbf{v}} = -\mathbf{n}_{1}^{\mathrm{II}} \frac{\partial \Delta \boldsymbol{\mu}_{i}^{\mathrm{II}} / \mathbf{RT}}{\partial \mathbf{n}_{1}^{\mathrm{II}}} + \mathbf{n}_{1}^{\mathrm{I}} \frac{\partial \Delta \boldsymbol{\mu}_{i}^{\mathrm{I}} / \mathbf{RT}}{\partial \mathbf{n}_{1}^{\mathrm{I}}}$$
(3.89)

Also,  $n_1^{II} = z_1 n_T^{II}$  and  $n_1^{I} = y_1 n_T^{I}$ . Therefore for i = 1, no the partial derivative of  $g_i$  with respect to v can be written

$$\frac{\partial \mathbf{g}_{i}}{\partial \mathbf{v}} = -\mathbf{z}_{1} \mathbf{n}_{T}^{\Pi} \frac{\partial \Delta \boldsymbol{\mu}_{i}^{\Pi} / \mathbf{R}T}{\partial \mathbf{n}_{1}^{\Pi}} + \mathbf{y}_{1} \mathbf{n}_{T}^{I} \frac{\partial \Delta \boldsymbol{\mu}_{i}^{I} / \mathbf{R}T}{\partial \mathbf{n}_{1}^{I}}$$
(3.90)

As shown by Michelsen (1980) a better way of doing these calculations would be to solve equations (3.64) to (3.65) along with the following equation

$$g_{nc+2} = \alpha_j - S = 0 \tag{3.91}$$

S is a specification variable which could be used to fix the values of one of the variables, say the mass of the polymer or one of the  $K_i$ s. This gives nc+2 equations in nc+2 variables. Once a particular point on the phase boundary is found we have for that point

$$g_i = 0; \quad i = l, nc + 2$$
 (3.92)

and,

$$dg_{i} = \sum \frac{\partial g_{i}}{\partial \alpha_{j}} d\alpha_{j} + \frac{\partial g_{i}}{\partial S} dS = 0; \quad i = 1, nc$$
(3.93)

which gives the set of equations

$$\overline{\overline{J}}\frac{\overline{d\alpha}}{dS} + \frac{\overline{\partial g}}{\partial S} = \overline{0}$$
(3.94)

This gives us the set of estimates in the direction of a particular change in S since  $d\alpha/dS$  is the derivative of the vector of the variables with respect to the specified variable along a line where all the equations are specified.

## 3.4 Constant temperature and pressure multiphase calculations

These calculations were carried out using the multiphase successive substitution method of Abdel-Ghani et al. (1994). The method of Abdel-Ghani et al. combines the calculation of equilibrium phases with the tangent plane distance (TPD) stability criterion developed by Michelsen (1982 a). For an equilibrium to be stable at a given temperature and pressure the tangent plane distance has to be greater than or equal to zero at the stationary points of the TPD function. The TPD inequality is given by

$$D = \sum_{i=1}^{n_{c}} n_{ik} \left( \mu_{ik} - \hat{\mu}_{i} \right) \ge 0$$
 (3.95)

where  $\hat{\mu}_i$  is the chemical potential of the component i in the apparent equilibrium or the equilibrium being tested for stability with respect to the addition of the k<sup>th</sup> phase. The stationary points of D satisfy the condition

$$\mu_{ik} = \hat{\mu}_i + \theta_k RT \tag{3.96}$$

or in terms of fugacities

$$\ln f_{ik} = \ln \hat{f}_i + \theta_k \tag{3.97}$$

If a phase is present at equilibrium,  $\theta_k=0$ , and, for the equilibrium to be stable with respect to the addition of phase k,  $\theta_k>0$ . Therefore, the criterion for a stable equilibrium with some phases not present can be expressed as

$$g_{ik} = \ln f_{ik} - \ln \hat{f}_i - \theta_k = 0$$
 (3.98)

Abdel-Ghani et al. use this criterion as the basis of their equilibrium calculations. The initiation of the calculations is done by assuming the existence of the maximum number of phases as given by the phase rule. In the process of solving for equilibrium phases, if two phases become identical with respect to the distribution coefficients of the components and the densities of the phases, the number of phases is reduced by one by combining phases. Their procedure does not require employing one of the existing phases as the reference phase. Rather an average fugacity is defined by

$$\ln \hat{\mathbf{f}}_{i} = \sum_{j=1}^{\pi} \beta_{j} \ln \mathbf{f}_{ij}$$
(3.99)

where  $\beta_j$  is the fraction of phase j. As a consequence, at equilibrium

$$\hat{\mathbf{f}}_{i} = \mathbf{f}_{ij}; \quad j = 1,...,\pi$$
 (3.100)

which is what is desired.

Now equation (3.97) gives

$$f_{ij} = \hat{f}_i \exp(\theta_j) = \hat{x}_i \hat{\phi}_i \exp(\theta_j) P \qquad (3.101)$$

The mole fraction of the component i in the phase j is given by

$$\mathbf{x}_{ij} = \hat{\mathbf{x}}_i \mathbf{K}_{ij} \exp(\boldsymbol{\theta}_j) \tag{3.102}$$

with

$$\mathbf{K}_{ij} = \hat{\boldsymbol{\phi}}_i / \boldsymbol{\phi}_{ij} \tag{3.103}$$

The mole fractions in a phase have to sum to unity which gives

$$\sum_{i=1}^{nc} x_{ij} = \exp(\theta_j) \sum_{i=1}^{nc} K_{ij} \hat{x}_i = 1$$
(3.104)

or in a different form

$$\sum_{i=1}^{nc} K_{ij} \hat{\mathbf{x}}_i = \exp(-\Theta_j)$$
(3.105)

If  $\theta_j = 0$ , implying the presence of a phase at equilibrium

$$\sum_{i=1}^{nc} K_{ij} \hat{\mathbf{x}}_i = 1$$
 (3.106)

For a missing phase  $\theta_i > 0$ 

$$\sum_{i=1}^{nc} \mathbf{K}_{ij} \mathbf{\hat{x}}_i < 1 \tag{3.107}$$

A mass balance on component i requires

$$\sum_{j=1}^{\pi} \beta_j x_{ij} = z_i$$
 (3.108)

where  $z_i$  is the feed fraction. Substituting for  $x_{ij}$  in the above equation we get

$$\hat{x}_{i} = \frac{z_{i}}{\sum_{j=1}^{\pi} \beta_{j} K_{ij} \exp(\theta_{j})} = \frac{z_{i}}{\sum_{j=1}^{\pi} \beta_{j} K_{ij}} = \frac{z_{i}}{E_{i}}$$
(3.109)

Note that  $exp(\theta_j)\beta_j=\beta_j$ , as  $\theta_j=0$  for  $\beta_j>0$ .

x<sub>ij</sub> can be written as

$$\mathbf{x}_{ij} = \exp(\boldsymbol{\theta}_j) \mathbf{K}_{ij} \mathbf{z}_i / \mathbf{E}_i$$
(3.110)

Finally the mole fractions in a phase have to sum to unity and we get

$$1 + \sum_{i=1}^{n_{c}} x_{ij} = 1 - \exp(\theta_{j}) \sum_{i=1}^{n_{c}} K_{ij} z_{i} / E_{i} = 0; j = 1, \pi$$
(3.111)

These are  $\pi$  non-linear equations to be solved for mass balance. The solution of these equations is equivalent to solving for

$$h_{j} = 1 - \sum_{i=1}^{n_{c}} X_{ij} = 0, \beta_{j} > 0$$
(3.112)

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$$h_{j} = 1 - \sum_{i=1}^{n_{c}} X_{ij} > 0, \beta_{j} = 0$$
(3.113)

where  $X_{ij}=K_{ij}z_i/E_i$ . When  $\beta_j$  is positive,  $X_{ij}$  is equal to the mole fraction  $x_{ij}$ , otherwise

$$x_{ij} = X_{ij} / \sum_{i=1}^{nc} X_{ij}$$
 (3.114)

The mass balance equations are solved for using a damped Newton iteration process as given by

$$\bar{\beta}^{k+1} = \bar{\beta}^k - \lambda \bar{A}^{-1} \bar{h}^k$$
(3.115)

where  $\lambda$  is a damping factor.  $\overline{\overline{A}}$  matrix has elements given by

$$\mathbf{a}_{ij} = \frac{\partial \mathbf{h}_i}{\partial \beta_j} = -\sum_{k=i}^{nc} \mathbf{X}_{ki} \mathbf{X}_{kj} / \mathbf{z}_i$$
(3.116)

The distribution coefficients  $\boldsymbol{K}_{ij}$  are updated using

$$\ln K_{ij}^{k+1} = \ln \hat{\phi}_i^k - \ln \phi_{ij}^k$$
(3.117)

which in terms of fugacities is

$$\ln K_{ij}^{k+1} = \ln(x_{ij}^{k} / \hat{x}_{i}^{k}) - (\ln f_{ij}^{k} - \ln \hat{f}_{i}^{k})$$
(3.118)

Now,

$$\ln(\mathbf{x}_{ij}^{k} / \hat{\mathbf{x}}_{i}^{k}) = \ln \mathbf{K}_{ij}^{k} + \boldsymbol{\theta}_{j}^{k}$$
(3.119)

which gives the updating formula in terms of g<sub>ij</sub>

$$\ln K_{ij}^{k+1} = \ln K_{ij}^{k} - g_{ij}^{k}$$
(3.120)

The convergence criterion normally used to terminate the equilibrium calculations

was

$$\sum_{j=1}^{\pi} \sum_{i=1}^{n_{c}} g_{ij}^{2} / \pi N_{c} \le 10^{-12}$$
(3.121)

# Michelsen (1994) has shown that the function

$$Q(\beta) = \sum_{j=1}^{\pi} \beta_j - \sum_{i=1}^{nc} z_i \ln E_i$$
 (3.122)

has derivatives

$$\frac{\partial Q}{\partial \beta_{j}} = \mathbf{h}_{j} = 1 - \sum_{i=1}^{nc} \mathbf{X}_{ij}$$
(3.123)

Michelsen states that  $Q(\beta)$  is at least positive semi-definite in the region of positive phase amounts. Thus the phase split problem is equivalent to a constrained minimization problem with a unique solution.

### 3.5 Discretization of a polydisperse polymer

In this section a method is described for obtaining molar mass distribution data from experimental information on average molecular weights. The methodology is based on the recipe proposed by Kang and Sandler (1988). This is useful because in many instances the experimental average molar masses are reported instead of the complete experimental molar mass distribution.

We begin with some terminology used in this section. For a continuous molar mass distribution a frequency function or differential distribution function D(M) is defined as the amount of material per unit change of molar mass M. The amount could be a mass fraction or a mole fraction. A plot of frequency function versus the molar mass gives a differential distribution curve of the type shown in Figure (3.2 a). The fractional amount of material having molar masses between  $M_1$  and  $M_2$  is given by the shaded area. The total area under the curve is unity. We can also plot the cumulative fractional amount versus the molar mass to give the integral distribution curve as shown in the Figure (3.2 b). Cumulative mass fraction corresponding to molar mass M is the fraction of material



Figure 3.2. (a) Differential distribution curve. (b) Integral distribution curve.

having molar mass smaller than or equal to M. The relation between D(M) and the integral distribution function I(M) is given by

$$\Delta I(M) = D(M)\Delta M, \text{ or, } dI(M) = D(M)dM \qquad (3.124)$$

which gives

$$I(M) = \int_{0}^{\infty} D(M) dM \qquad (3.125)$$

Also, the relation between N(M), the number distribution function, and, W(M), the mass distribution function, is

$$N(M) = \frac{W(M)}{M} / \int_0^\infty \frac{W(M)}{M} dM$$
(3.126)

or,

$$W(M) = N(M)M / \int_{0}^{\infty} N(M)MdM \qquad (3.127)$$

The number average molar mass  $M_N$  for the continuous case is given by

$$M_{N} = \int_{0}^{\infty} N(M) M dM \qquad (3.128)$$

The mass average molar mass  $M_W$  for the continuous case is given by

$$M_{W} = \int_{0}^{\infty} W(M) M dM \qquad (3.129)$$

And the z-average molar mass  $M_Z$  is

$$M_{Z} = \int_{0}^{\infty} W(M) M^{2} dM / \int_{0}^{\infty} W(M) M dM$$
 (3.130)

The ratios  $M_W/M_N$ ,  $M_Z/M_W$  etc. give an indication of the spread of the molar masses of the polymer or the polydispersivity of the polymer. Following the usual convention  $M_W/M_N$  is taken as the polydispersivity index of the polymer.

The average molar masses are defined for the discrete case as follows. The number average molar mass is

$$M_{N} = \sum x_{i}M_{i} = \frac{1}{\sum w_{i}/M_{i}}$$
 (3.131)

where  $x_i$  and  $w_i$  are the mole fraction and the weight fraction of component with molar mass  $M_i$ . The mass average molar mass is

$$\mathbf{M}_{\mathbf{W}} = \sum \mathbf{w}_{i} \mathbf{M}_{i} = \frac{\sum x_{i} \mathbf{M}_{i}^{2}}{\sum x_{i} \mathbf{M}_{i}}$$
(3.132)

Using an appropriate distribution function, we can construct discrete analogs of a polydisperse polymer as shown below for the Log-Normal distribution (Lansing and Kraemer, 1935) and Schulz distribution (1939). Both these distributions have two adjustable parameters and yield discrete pseudocomponents of a polydisperse polymer in a fairly straightforward manner by the application of Gaussian Quadrature.

## 3.5.1 Log-Normal distribution

Lansing and Kraemer (1935) pointed out the utility of the log-normal distribution for quantifying the non-uniformity of polymers. Subsequently, it was used by Granath (1958) and Koningsveld and Staverman (1968) among others. There are additional references in the Granath paper. In recent years Kang and Sandler (1988) have employed the log-normal distribution to account for the polydispersivity of dextran in phase equilibrium calculations.

In the log-normal distribution, the normalized number distribution function is given by F/M, where the function F is,

$$F = \frac{1}{\beta \sqrt{\pi}} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{M}{M_o}\right)$$
(3.133)

 $M_0$  and  $\beta$  are the parameters of the distribution. Then,

$$\int_{M=0}^{M=\infty} \frac{F}{M} dM = 1$$
 (3.134)

The number-average molar mass is given by

$$M_{N} = \int_{M=0}^{M=\infty} M(F/M) dM = M_{0} e^{\beta^{2}/4}$$
(3.135)

and the weight-average molar mass is given by

$$M_{w} = (1/M_{N}) \int_{M=0}^{M=\infty} M^{2} (F/M) dM = M_{0} e^{3\beta^{2}/4}$$
(3.136)

The polydispersivity index is

$$b = M_w / M_N = e^{\beta^2/2}$$
(3.137)

Given the experimental values of  $M_w$  and  $M_N$ ,  $M_o$  and  $\beta$ , the parameters of the distribution, can be determined from equations (3.135) or (3.136) and (3.137). These values can then be used to construct a discrete analog of the polydisperse polymer

through Hermitian quadrature. Hermitian quadrature permits approximation of certain integrals through function evaluations at a few points. The quadrature formula is

$$M = \int_{-\infty}^{\infty} \exp(-x^2) G(x) dx \equiv \sum_{k=1}^{n} (H_k / \sqrt{\pi}) G(x_k) \sqrt{\pi}$$
(3.138)

Values of  $H_k$  and  $x_k$  for various number of quadrature points, n, can be obtained from mathematical tables. In this work these values were obtained from Abramowitz and Stegun(1972). ( $H_k/\sqrt{\pi}$ ) can be interpreted as the fraction of polymer with molar mass ( $G(x_k)\sqrt{\pi}$ ). Note that equation (3.135) can be rearranged in the same form as equation (3.138) by a simple transformation as given by

$$M_{N} = \int_{-\infty}^{\infty} \exp(-x^{2}) \left( \frac{M_{o}}{\sqrt{\pi}} \exp(\beta x) \right) dx \qquad (3.139)$$

where x is

$$x = \frac{1}{\beta} \ln \frac{M}{M_o}$$
(3.140)

In this form the quadrature formula can be applied to the equation for  $M_N$ .

For the discrete case the molar mass of the k<sup>th</sup> component is

$$M_{k} = M_{o} \exp(\beta x_{k})$$
(3.141)

and  $(H_k / \sqrt{\pi})$  is its mole fraction. Figure (3.3) shows the error in calculated b as a function of number of the pseudocomponents. From this plot some idea can be obtained about the number of pseudocomponents required to represent a particular polydisperse polymer.



Figure 3.3. Effect of the number of pseudocomponents on the error in the calculated polydispersivity index.

The Schulz distribution function has the mass frequency function given by

$$W(M) = \frac{(-\ln\alpha)^{\beta+2}}{\Gamma(\beta+2)} M^{\beta+1} \alpha^{M}$$
(3.142)

 $\beta$  and  $\alpha$  are the parameters of the distribution.

$$\Gamma(\beta+2) = \int_{0}^{\infty} x^{[(\beta+2)-1]} \exp(-x) dx \qquad (3.143)$$

This is convergent for  $(\beta+2)>0$ .

The mass average molar mass is

$$M_{W} = \int_{0}^{\infty} M \frac{(-\ln \alpha)^{\beta+2}}{\Gamma(\beta+2)} M^{\beta+1} \alpha^{M} dM \cong \sum w_{i} M_{i}$$
(3.144)

where  $w_i$  is the mass fraction of the i<sup>th</sup> pseudocomponent and  $M_i$  is its molar mass.

Let,

$$\alpha^{M} = \exp(-y) \tag{3.145}$$

which gives

$$dM = dy / (-\ln \alpha) \tag{3.146}$$

Changing the variable of integration in equation (3.144)

$$M_{W} = \int_{0}^{\infty} \frac{(y)^{\beta+2}}{\Gamma(\beta+2)} \frac{\exp(-y)}{-\ln\alpha} dy \cong \sum H_{k} f(y_{k})$$
(3.147)

where  $y_k$ s are the zeroes of Laguerre-Gauss quadrature and

$$f(y_k) = \frac{y_k^{\beta+2}}{\Gamma(\beta+2)(-\ln\alpha)}$$
(3.148)

Now,

$$\mathbf{M}_{\mathbf{W}} = \sum \mathbf{h}_{i} \mathbf{f}(\mathbf{y}_{i}) (\sum \mathbf{H}_{j})$$
(3.149)

This gives the mass fraction and the molar mass of the i<sup>th</sup> pseudocomponent

.

$$w_i = h_i = H_i / \sum H_j$$
 (3.150)

and

$$\mathbf{M}_{i} = \mathbf{f}(\mathbf{y}_{i})(\sum \mathbf{H}_{j}) \tag{3.151}$$

## **CHAPTER 4**

### Experiments

### 4.0 Introduction

The two most important techniques for measurement of phase equilibria at high pressures are the analytical and the synthetic methods (Schneider, 1994). In the analytical method, the components are filled into an autoclave and the system is brought to the conditions of temperature and pressure in a heterogeneous region, such as, conditions of a vapor-liquid equilibrium. The compositions of the equilibrium phases are determined mostly by sampling and analysis, by chromatography for example.

In the synthetic method, first a mixture of known composition is prepared. The pressure and temperature are then adjusted such that the mixture is in the homogeneous region. The pressure and/or temperature is then so varied that the phase boundary is reached, as detected by the appearance of a second phase as in a bubble point, a dew point or a cloud point determination. The phase boundary between the two-phase and one-phase region is obtained as a pressure-temperature curve for a fixed composition, i.e. an isopleth. This is done for a number of compositions of interest. After having gathered this information, the P-x and T-x sections can be prepared by interpolation. The disadvantage of this method is that tie-lines connecting equilibrium compositions in systems with more than two components cannot be obtained.
In this work the synthetic method was employed for making phase equilibrium measurements on polystyrene/methylcyclohexane/CO<sub>2</sub> systems. The experiments were performed at The Technical University of Delft in the Laboratory of Applied Thermodynamics and Phase Equilibria under the direction of Dr. Th. W. de Loos. An extensive infrastructure was in place in this laboratory to assist with performing the essential measurements.

There are two parts to the procedure:

(i) Preparing a mixture of known composition.

(ii) Making phase equilibrium measurements on the sample.

In the first section of this Chapter, the procedure for making a filling of known composition is described. This is followed by a brief description of the Cailletet apparatus used for making phase equilibrium measurements in this work. The subsequent section provides information about the materials used. Then the methodology employed for making the measurements is discussed briefly. Finally, the results of the measurements are presented.

## 4.1 Procedure for making a filling

The fillings are made in a capillary Pyrex glass tube sealed at one end. The tube is first weighed and then a known amount of solvent is added to it by weighing. The accuracy of the weight balance for this part was  $\pm 0.01$  mg. Typically 100-150 mg of the solvent was weighed in. Subsequently a known amount of the polymer is added to the solvent for the measurements where the polymer is required as one of the components. The polymer was weighed in with an accuracy of  $\pm 0.001$  mg. The mass of polymer sample added typically ranged from 5-35 mg. A small permanent magnet is added in the glass tube for stirring the sample. The capillary tube is then attached to a piece of equipment called the gas rack. The gas rack is shown schematically in Figure (4.1). The purpose of the gas rack is two-fold. First the solvent is degassed by repeated freezing and melting with liquid nitrogen under a vacuum. Then a known amount of a gas is added by opening the connection to the gas storage. When carbon dioxide was included as one of the components it was added via the gas rack.

In order to add a known amount of carbon dioxide to the sample, the tube connection half of the gas rack is filled with the gas to approximately the desired pressure. In this work the pressures typically ranged from 40-370 mbar. The pressure was measured with a tranducer having a range 0-0.1 MPa with an accuracy of 0.01 %. The gas is then displaced by mercury and part of it is confined to a bulb of known volume as shown in Figure (4.1). The point to note here is that when mercury just touches the tip of the bulb the pressure in the bulb is same as the system pressure. From a knowledge of the pressure and the room temperature, the amount of gas can be calculated. As a final step, the gas is frozen with the rest of the sample and sealed with mercury. The tube with the frozen sample is then removed from the gas rack and placed in the apparatus for making the phase equilibrium measurements. The sample is pressurized in the apparatus before



Figure 4.1. Schematic of the gas rack. Modified from Stamoulis (1994).

melting. In this work mixtures were prepared with an accuracy in the weight fraction on the order of 0.0002 to 0.0005.

## 4.2 Apparatus for phase equilibrium measurements

Phase equilibria were measured in the glass tube Cailletet apparatus described by de Loos et al. (1986). In this apparatus, visual observations are made of phase transitions in a mixture of fixed composition by fixing temperature and varying pressure or vice-versa. The sample is confined over mercury in the sealed end of a capillary glass tube. The open end of the glass tube is immersed in the mercury in the autoclave. The pressure is applied hydraulically with a screw pump with mercury acting as the intermediary. The glass tube is kept at the desired temperature by a thermostat with circulating fluid. The sample is agitated by a small iron magnet stirrer immersed in the sample. The stirrer is moved by a pair of button magnets on the outside, which move up and down. The temperature can be measured with an accuracy of  $\pm 0.01$  K by a platinum resistance thermometer. The temperature of the bath can be regulated to within  $\pm 0.02$  K. The pressure is measured with a dead-weight pressure gauge, which has an accuracy of 0.05 bar.

#### 4.3 Materials

In this study, two samples of polystyrene were used for cloud point measurements. One was an Aldrich standard (Lot number: 01302 KN) with  $M_w=31,600$  g/mol and  $M_N=29,100$  g/mol as determined from gel permeation chromatography. The manufacturer also reports for the same sample  $M_W$ =29,300 g/mol from light scattering measurements and  $M_N$ =28,900 g/mol from membrane osmometry. The other sample was supplied by Novacor Technology and Research Corporation (Lot number: 9-1-4823-1) and had a  $M_N$ =64,000 g/mol and  $M_W$ =250,000 g/mol as determined from gel permeation chromatography. Methylcyclohexane was purchased from MERCK-Schuchardt with a guaranteed purity of 99%. Chromatographic analysis of methylcyclohexane gave a purity of 99.5%. It was degassed before use by repeated freezing and melting with liquid nitrogen. The carbon dioxide was obtained from Air products with a purity of 99.95 wt%.

# 4.4 Experimental method

The Gibbs phase rule when applied to a two-phase equilibrium involving n components yields for the degrees of freedom F the following equation.

$$\mathbf{F} = \mathbf{n} \tag{4.1}$$

For bubble point, dew point and cloud point measurements the phase boundary is traced. Therefore, in principle, the composition of the sample is fixed. In other words the (n-1) independent composition variables are fixed. Now if the temperature is fixed then there is a unique pressure for the occurrence of a phase boundary and vice-versa. In this work mainly two-phase boundaries were measured.

The cloud point measurements on the polystyrene(29100) + methylcyclohexane system were made by fixing pressure and varying temperature in intervals of 0.04~0.05 K. The cloud point was taken as the lower temperature of the temperature interval over which a

turbid phase appeared and disappeared starting from a homogeneous liquid phase. When a cloud point was detected, it was confirmed by the disappearance of turbidity at an elevated pressure while keeping the temperature constant. For cloud point measurements with the polydisperse polystyrene sample and when CO<sub>2</sub> was present the temperature was fixed and the pressure was varied. The cloud point was defined as the mid-point of the pressure interval over which a turbid dispersed phase appeared and disappeared over the whole system, starting from a homogeneous liquid phase. The maximum uncertainty in pressure for cloud point measurements when the temperature was held constant was 0.1 MPa. In all cases the cloud point was checked by moving back and forth across the phase boundary. The bubble points were measured with an accuracy of 0.01 MPa. The methodology followed was similar to that for cloud point measurements when the temperature was fixed and the pressure varied.

# 4.5 Results and discussion

#### 4.5.1 Carbon dioxide vapour pressures

Figure (4.2) shows a comparison of a few measured vapour pressures with the values from the Dortmund Data Bank. The vapour pressures were measured with an accuracy of 0.01 MPa. From the figure it is obvious that the agreement between the measurements in this work and the values from the literature is excellent.



Figure 4.2. Carbon dioxide vapor pressures. (+) Measured. ( $\Delta$ ) All property data bank.

## 4.5.2 Carbon dioxide + methylcyclohexane system

Figure (4.3) shows a few pressure-temperature bubble point isopleths for the system carbon dioxide + methylcyclohexane. An isopleth is a pressure-temperature curve of constant composition separating the two-phase region from the one-phase region. For this figure, the region above the isopleths is the one liquid region and the region below the isopleths is the vapour-liquid region. The isopleths represent the vapour-liquid phase boundary. The bubble points were measured with an accuracy of 0.01 MPa.

Figure (4.4) contains two pressure-composition sections at constant temperature. These were obtained by interpolating pressure values from the P-T isopleths for various compositions at a fixed temperature. The region above the P-x curves is one liquid and the region below the P-x curves is the vapour-liquid region.

# 4.5.3 Połystyrene(29100) + methylcyclohexane system

Figure (4.5) contains liquid-liquid pressure temperature isopleths for the system polystyrene(29100) + methylcyclohexane. These were measured by fixing pressure and varying the temperature in intervals of 0.04~0.05 K. The region to the right of the curves is the one liquid region and the region to the left of the curves is the liquid-liquid region. The isopleths are the locus of cloud points or the points where phase separation just occurs. Figure (4.6) contains a few temperature-composition sections at constant pressure. These curves were obtained from the data shown in Figure (4.5) by fixing the pressure and



Figure 4.3. Bubble point P-T isopleths for the system Carbon dioxide/Methylcyclohexane. CO<sub>2</sub> mass percent: (+) 4.83, (+) 7.09, (Δ) 9.75, (▲) 11.19, (Ο) 15.19.





Figure 4.5. P-T isopleths for the system Polystyrene(29100)/Methylcyclohexane.
Polymer mass percent: (♠) 3.23, (△) 4.94, (O) 7.26, (♣) 8.82, (∇) 10.97,
(▲) 12.81, (●) 15.19, (□) 18.21, (◊) 20.6, (■) 22.51, (▼) 26.34.



interpolating the temperature for various isopleths. The region above the curves is the onephase region and the region below the curves is the two-liquids region.

The T-x curves shown in Figure (4.6) represent typical upper critical solution temperature behaviour. This is classified as Type II behaviour in the scheme of van Konynenburg and Scott. However, there is reason to believe that this system actually is of Type IV. Saeki et al. (1973) report low pressure measurements on a number of polystyrene + methylcyclohexane systems (differing in the molar mass of polystyrene) which show UCST behaviour at low temperatures and as the temperature is raised there is an occurrence of lower critical solution temperature or LCST behaviour. In this work measurements were made in the vicinity of the upper critical solution temperature.

The polystyrene used for the measurement shown in Figures (4.5) and (4.6) had a polydispersivity index very close to unity in value. Hence, this system can be treated as a binary system and in that case the maximum temperature on a particular T-x curve is the upper critical solution temperature. The system polystyrene + methylcyclohexane has been investigated extensively by a number of research groups for a range of molar mass of polystyrene. These researchers also report the measured UCSTs. This enables a comparison between the extrapolated value (P=1bar) of the critical temperature from this work with the measurements reported in the literature. The comparison is in Figure (4.7). The comparison is made by plotting the inverse of the critical temperature in K against the inverse of the square root of the molar mass of the polymer. It can be seen that the measurements made in this work fall along with the measurements reported in the literature. The comparison is the inverse of plotting the inverse of the polymer. It can be seen that the measurements made in



Figure 4.7. Comparison of upper critical solution temperatures for systems Polystyrene/Methylcyclohexane. (+) Literature, ( $\Delta$ ) Measured.

is based on the work of Flory (1953) who has shown theoretically that a plot of the inverse of the critical temperature versus the inverse of the square root of the molar mass should exhibit a linear trend. The literature references for Figure (4.7) are listed in Table (4.1). The list of references was supplied by Dr. S. Enders (1996).

This sub-section is concluded with a remark regarding the sign of volume change of mixing for this system in the vicinity of UCST. Consider the following equation derived previously.

$$\left(\frac{\partial T}{\partial P}\right)_{C} = \frac{\left(\frac{\partial^{2} v}{\partial x^{2}}\right)_{C}}{\left(\frac{\partial^{2} s}{\partial x^{2}}\right)_{C}}$$
(4.2)

The left hand side is negative in this case. Also, for UCST type behaviour the second partial derivative of molar entropy with respect to composition is less than zero. Therefore, the volume derivative has to be positive. Following an argument similar to that employed to obtain the sign of the enthalpy change of mixing in section (2.5) it can be deduced that the volume change of mixing has a negative sign.

#### 4.5.4 Polystyrene(64000) + methylcyclohexane system

Figures (4.8) contains the liquid-liquid Pressure-Temperature isopleth data for the system polystyrene(64000) + methylcyclohexane. Figure (4.9) contains a few Temperature-composition curves. These measurements were made by fixing the temperature and varying the pressure. The cloud points are accurate to within 0.1 MPa.

# Table 4.1 List of literature references for Figure (4.8)

- 1. Wells P.A., de Loos Th.W. and Kleintjens L.A., Fluid Phase Equil., 83, 383, 1990.
- 2. Nose T.and van Tan T., Polymer Letters Ed. 14, 705, 1976.
- 3. Dobashi T., Nakata M. and Kaneko M., J. Chem Phys., 80, 948, 1984.
- 4. Chu B., Linlium P. Xie K., Ying Q., Wang Z. and Shook J.W., Rev. Sci. Instrum., 62, 2252, 1991.
- 4. Dobashi T., Nakata M. and Kaneko M., J. Chem. Phys., 72, 6685, 1980.
- 6. Saeki S., Kuwahara N., Konno S. and Kaneko M., Macromolecules, 6, 246, 1973.
- 7. Shen W., Smith G.R., Knobler C.M. and Scott R.L., J. Phys. Chem., 95, 3376, 1991.
- 8. Shinozaki K., Tan T., Saito Y. and Nose T., Polymer, 23, 7280, 1982.
- 9. Heinrich M. and Wolf B.A., Polymer, 33, 1926, 1992.



Figure 4.8. P-T isopleths for the system Polystyrene(64000)/Methylcyclohexane. Polymer mass percent: (O) 2.11, ( $\bigtriangledown$ ) 3.3, ( $\bigstar$ ) 5.11, (+) 6.48, ( $\bigtriangleup$ ) 9.71, (O) 13.6.





This system also shows UCST behaviour. However, the polystyrene sample used for these measurements had a mass average molar mass of 250,000 g/mol and a number average molar mass of 64,000 g/mol. As a consequence of the polydispersivity of the polymer the maximum temperature on the T-x curves is in all probability not the upper critical solution temperature. Rather, it would be expected to lie on the right hand branch of the T-x curve as discussed in section (2.7).

#### 4.5.5 Polystyrene(29100) + methylcyclohexane + carbon dioxide system

The objective of these measurements was to study the effect of  $CO_2$  on the phase behaviour of the system polystyrene(29100) + methylcyclohexane. The investigation was carried out by keeping the polymer concentration approximately constant and replacing part of the solvent with carbon dioxide. This was done for two approximate polymer concentrations of 0.05 and 0.11 mass fraction.

The expected phase behaviour of the systems such as polystyrene(29100) + methylcyclohexane + carbon dioxide is shown schematically in Figure (4.10) for relatively lower concentrations of carbon dioxide (McHugh and Krukonis, 1994). At higher pressures and lower temperatures (in the vicinity of polymer-solvent UCST) there is a liquid-liquid isopleth that separates the one-liquid region from the two-liquid region. However, as the pressure is lowered there is a transition from a liquid-liquid region to a three phase liquidliquid-vapour region. Further lowering of temperature gives a vapour-liquid region. At lower pressures and higher temperatures there is a vapour-liquid isopleth that separates the



Figure 4.10. P-T schematic for a polymer-solvent-solvent mixture of constant composition.

one-liquid region from the vapour-liquid region. As temperature is raised further (in the vicinity of polymer solvent LCST), the phase behavior is an image of that for lower temperatures. The lower temperature branch (in the vicinity of polymer-solvent UCST) is shown for an approximate polymer mass fraction of 0.05 and CO<sub>2</sub> mass fraction of 0.11 in Figure (4.11). The point of intersection (VLLE point) of the liquid-liquid and vapour-liquid isopleths is unique for a particular composition as a consequence of the phase rule. However, for higher concentrations of CO<sub>2</sub> the LCST and UCST type behaviours can merge to give liquid-liquid isopleths of the form shown in Figure (4.12) for carbon dioxide mass fractions of 0.209 and 0.211. For these isopleths the region above the curves one liquid and the region below the curves is a region of liquid-liquid immiscibility.

Figure (4.12) contains the liquid-liquid isopleth data for the system polystyrene(29100) + methylcyclohexane + carbon dioxide for an approximate polymer mass fraction of 0.05. Except for the two  $CO_2$  concentrations mentioned in the previous paragraph the one liquid region lies to the right of the curves and the two-liquid region is on the left of the curves.

Figure (4.13) contains a few temperature-composition sections prepared from the data shown in Figure (4.12). The sections are for pressures greater than the VLLE point pressures. The region of immiscibility is below the T-x curves. Figure (4.13) shows that addition of  $CO_2$  initially increases the solubility of the polymer a little which is followed by a sharp decline in solubility as the carbon dioxide concentration is raised. The improved solubility of the polymer in the mixed solvent at lower concentrations of carbon dioxide is



Figure 4.11. P-T isopleths for the system Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>. Polymer mass percent ~ 5.0. CO<sub>2</sub> mass percent ~ 11.2. (+) LLE; (Δ) VLE; (Ο) VLLE.



Figure 4.12. P-T isopleths for the system Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>. Polymer mass percent ~ 5.0. CO<sub>2</sub> mass percent: ( $\Delta$ ) 0, ( $\Delta$ ) 3.77, ( $\bigcirc$ ) 7.75, ( $\Box$ ) 11.22, (O) 12.21, (+) 14.79, ( $\nabla$ ) 18.12, (+) 20.95, ( $\Diamond$ ) 21.14.



Figure 4.13. Isobars for the system Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>. Polymer mass percent ~ 5.0. Pressure (MPa): (+) 4, ( $\Delta$ ) 6, (O) 8, (+) 10.

probably related to the density behaviour of systems containing carbon dioxide as found by Kordikowski et al. (1995). These researchers report that the liquid density as a function of carbon dioxide concentration in certain  $CO_2$  + organic solvents shows a maximum. They point out that, as a consequence of this kind of density behaviour carbon dioxide at certain conditions may act as a solvent.

Similar behaviour is observed for the case where the polymer mass fraction is kept constant at approximately 0.11. The liquid-liquid isopleths for this case are shown in Figure (4.14). Figure (4.15) contains a few T-x sections at pressures greater than VLLE point pressures.

The VLLE points determined by the intersection of the LLE and VLE curves are plotted for all the isopleths showing the behaviour in Figure (4.16). The points shown in Figure (4.16) are the temperatures and pressures where a homogeneous phase of the indicated composition is in equilibrium with two new phases: (i) a liquid phase and, (ii) a vapour phase rich in  $CO_2$ .

Shown in Figure (4.17) are constant temperature bubble points for the binary methylcyclohexane/ $CO_2$  system and polystyrene(29100)/methylcyclohexane/ $CO_2$  systems at a temperature of 313.15 K. At the same carbon dioxide mass percent, the bubble point pressure is increased by replacing part of the methylcyclohexane with the polymer.



Figure 4.14. P-T isopleths for the system Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>. Polymer mass percent ~ 11.0. CO<sub>2</sub> mass percent: (▲) 2.42, (+) 4.28, (O) 5.08, (+) 7.42, (●) 10.37, (△) 11.67, (∇) 14.57, (□) 16.57.



Figure 4.15. Isobars for the system Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>. Polymer mass percent ~ 11.0. Pressure (MPa): ( $\pm$ ) 4, (O) 6, ( $\Delta$ ) 8, (+) 10.



Figure 4.16. VLLE points for the system Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>. (+) ~ 5 mass percent polymer; ( $\Delta$ ) ~ 11 mass percent polymer.



Figure 4.17. Pressure-composition sections (bubble points, T=313.15 K) for the systems Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub> (+) and Methylcyclohexane/CO<sub>2</sub> (O). Polymer mass percent ~ 5.0.

#### **CHAPTER 5**

#### Models

# **5.0 Introduction**

In this Chapter the three equation of state models employed in this work are presented.

The equation of state modeling of polymer-solvent systems has followed two main approaches:

(i) Lattice-based models.

(ii) Models based on perturbation theory.

The lattice-based models conceptualize a mixture on a lattice. The fundamental equation in terms of Helmholtz free energy is obtained by adding a configurational entropy term (i.e., a term accounting for the number of configurations available to molecules on the lattice) to an energetic term accounting for the interaction between segments. The perturbation theory approach employs a reference fluid, such as a mixture of chains of hard spheres as in the model used in this work. The equation of state for the real fluid is obtained by adding a perturbation term to the reference fluid term.

The following models were chosen for this work:

(i) The Sanchez-Lacombe equation of state.

(ii) The Kleintjens-Koningsveld version of the Mean Field Lattice Gas Model.

(iii) The Perturbed Hard Sphere Chain (PHSC) equation of state.

The first two are lattice based models and, as the name suggests the third is a model derived from perturbation theory. The versions of model equations used in this work employ mole number or mole fraction as the principal composition variables instead of the traditional choice of site fraction as the principal composition variable. Although the choice is subjective, in the author's opinion the versions presented in this Chapter are easier to use from a computational point of view.

## 5.1 Sanchez-Lacombe equation of state

Conceptually, the lattice based equation of state of Sanchez and Lacombe (1976, 1978) is very similar to the lattice theory of Flory and Huggins (1953) for polymer solutions. The Flory-Huggins theory employs a rigid lattice and, as a consequence, in principle cannot model behavior caused by changes in compressibility, for example, LCST behavior. The Sanchez-Lacombe equation of state circumvents this shortcoming by allowing for a variable number of vacant sites on the lattice. In the Sanchez-Lacombe formulation, as in the treatment of Kleintjens and Koningsveld (1980) discussed in a later section, a pure component is treated as a binary mixture of vacant and occupied lattice sites.

The number of configurations available on the lattice  $\Omega$ , are calculated from the expression developed by Guggenheim (1952) in the limit of a large coordination number z. This is the Flory approximation. The expression for  $\Omega$  for a nc component mixture is

$$\lim_{z \to \infty} \Omega = \left(\frac{1}{f_o}\right)^{n_o} \left(\frac{\omega_1}{f_1}\right)^{n_1} \left(\frac{\omega_2}{f_2}\right)^{n_2} \dots \left(\frac{\omega_{nc}}{f_{nc}}\right)^{nc}$$
(5.1)

where,

$$\omega_{i} = \frac{\delta_{i} d_{i}}{\sigma_{i} e^{d_{i} - 1}}$$
(5.2)

and,

$$f_{o} = \frac{n_{o}}{n_{o} + \sum n_{j}d_{j}} = \frac{n_{o}}{n_{d}} ; \quad f_{i} = \frac{n_{i}d_{i}}{n_{d}}$$
(5.3)

 $d_i$  is the number of segments occupied on the lattice by component i.  $n_i$  is the number of molecules of component i.  $n_o$  is the number of empty lattice sites.  $\sigma_i$  is a symmetry number and  $\delta_i$  is a flexibility parameter.  $f_i$  is the fraction of sites occupied by the component i in the mixture and  $f_o$  is the fraction of empty sites. From equation (5.1) and the following equation from statistical mechanics (Hill, 1986)

$$\mathbf{S} = \mathbf{R} \ln \Omega \tag{5.4}$$

the configurational entropy of the mixture can be calculated as

$$S = -R n_{o} \ln f_{o} - R \sum_{i=1}^{n_{c}} n_{i} \ln f_{i} + R \sum_{i=1}^{n_{c}} n_{i} \ln \omega_{i}$$
 (5.5)

R is the gas constant. The last summation in this equation will be neglected from here on as it does not affect phase equilibrium computations of interest in this work.

Sanchez and Lacombe obtain the configurational energy E for their model from the following equation (McQuarrie, 1976)

$$E = 2\pi (\sum d_i n_i) \rho \sum \sum \phi_i \phi_j \int_0^{\infty} \varepsilon_{ij} g_{ij} r^2 dr$$
(5.6)

where  $\phi_i$  is a site fraction, given by

$$\phi_i = \frac{\mathbf{d}_i \mathbf{n}_i}{\sum \mathbf{d}_j \mathbf{n}_j} \tag{5.7}$$

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 $g_{ij}$  is the pair distribution function, and  $\varepsilon_{ij}$  is related to the depth of the potential well.  $\rho$  is the number density of all segments in the mixture. r is the distance between two segments. Sanchez and Lacombe assume that mers have hard cores and interact attractively with each other at a distance r via an inverse power law.

$$\varepsilon_{ij}(\mathbf{r}) = \infty \quad ; \quad \mathbf{r} < \sigma_{ij}$$

$$\varepsilon_{ij}(\mathbf{r}) = -\varepsilon_{ij}^{o} \left(\frac{\sigma_{ij}}{\mathbf{r}}\right)^{n} \quad ; \quad \mathbf{r} > \sigma_{ij} \qquad (5.8)$$

 $\sigma_{ij}$  is the distance of closest approach.

In the mean field approximation  $g_{ij}$  is given by

$$g_{ij}(r) = 0$$
;  $r < \sigma_{ij}$   
 $g_{ij}(r) = 1$ ;  $r > \sigma_{ij}$  (5.9)

Substitution of equations (5.8) and (5.9) into equation (5.6) yields for E the following van der Waal's like expression.

$$\mathbf{E} = -(\sum \mathbf{d}_{j}\mathbf{n}_{j})\bar{\boldsymbol{\rho}} \,\boldsymbol{\varepsilon}^{*} \tag{5.10}$$

where the mixture interaction energy parameter  $\varepsilon^{\bullet}$  is given by

$$\boldsymbol{\varepsilon}^{*} = \frac{1}{\mathbf{v}^{*}} \sum \sum \boldsymbol{\phi}_{i} \boldsymbol{\phi}_{j} \boldsymbol{\varepsilon}_{ij}^{*} \mathbf{v}_{ij}^{*}$$
(5.11)

 $\bar{\rho}$  is the reduced density of the mixture and is given by

$$\overline{\rho} = \frac{\sum d_j n_j}{n_o + \sum d_j n_j} \frac{\mathbf{v}^*}{\mathbf{v}^*} = \frac{\mathbf{V}^*}{\mathbf{V}}$$
(5.12)

 $v^*$  is the mixture lattice site volume and V is the total volume. It is assumed that  $v_{ij}^* = \sigma_{ij}^3$ .

The ij energy of interaction,  $\varepsilon_{ij}$ , is given as

$$\varepsilon_{ij}^* = 2\pi\varepsilon_{ij}^\circ / (n-3) \tag{5.13}$$

The mixture lattice volume v' is calculated using the following mixing rule.

$$\mathbf{v}^* = \sum \sum \phi_i \phi_j \mathbf{v}_{ij}^* \tag{5.14}$$

The model has three parameters for a pure component, namely  $\varepsilon_{ii}$ ,  $v_{ii}$  and  $d_i$ . For a mixture, the cross parameters can be obtained as

$$\boldsymbol{\varepsilon}_{ij}^{*} = (1 - k_{ij}) \sqrt{\boldsymbol{\varepsilon}_{ii}^{*} \boldsymbol{\varepsilon}_{jj}^{*}}$$
(5.15)

where  $\mathbf{k}_{ij}$  is a binary interaction parameter, and,

$$\mathbf{v}_{ij}^{*} = \frac{\mathbf{v}_{ii}^{*} + \mathbf{v}_{jj}^{*}}{2}$$
(5.16)

As a consequence of the mixing rule for the mixture lattice volume  $v^*$  and equation (5.16) the hard core volumes of the pure-components are preserved.

Now the expression for the Helmholtz free energy can be calculated from

$$\mathbf{A} = \mathbf{E} - \mathbf{T} \mathbf{S} \tag{5.17}$$

From the fundamental equation for A all the thermodynamic properties of the mixture can be obtained.

Sanchez and Lacombe (1976, 1978) expressed the model equations with the site fraction as the principal composition variable. Although the choice of variables to work with depends on the user, in the author's opinion, the version of model equations with mole number or mole fraction as the principal composition variable is easier to work with. The model equations in terms of the mole numbers/mole fractions are derived now.

In order to restructure the Sanchez-Lacombe expression for A let,

$$\mathbf{b}_{ij} = \mathbf{d}_i \mathbf{d}_j \mathbf{v}_{ij}^* \tag{5.18}$$

$$n^{2}b = \sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}b_{ij}$$
 (5.19)

$$\mathbf{a}_{ij} = \mathbf{d}_i \mathbf{d}_j \boldsymbol{\epsilon}_{ij}^* \mathbf{v}_{ij}^* \tag{5.20}$$

$$n^{2}a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}a_{ij}$$
(5.21)

$$\mathbf{nd} = \sum_{i=1}^{n_c} \mathbf{n}_i \mathbf{d}_i \tag{5.22}$$

Therefore in terms of  $n^2a$ ,  $n^2b$  and nd (a, b and d are these quantities in terms of mole fractions) we have,

$$\mathbf{v}^* = \frac{\mathbf{b}}{\mathbf{d}^2} \tag{5.23}$$

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and,

$$\varepsilon^* = \frac{a}{b} \tag{5.24}$$

The reduced density  $\bar{\rho}$ ,  $f_i$ ,  $f_o$  and  $n_o$  can now be expressed as

$$\bar{\rho} = \frac{\dot{V}}{V} = \frac{1}{V} \frac{n^2 b}{nd}$$
(5.25)

$$f_i = \frac{n_i d_i}{V} \frac{b}{d^2}$$
(5.26)

$$f_o = 1 - \sum_{i=1}^{nc} f_i = \frac{V - n^2 b / nd}{V}$$
 (5.27)

$$n_o = \frac{d^2}{b} (V - n^2 b / nd)$$
 (5.28)

After substitution we get for A,

$$A = -\frac{n^2 a}{V} + RT \frac{d^2}{b} (V - n^2 b / nd) \ln(1 - \frac{n^2 b / nd}{V}) + RT \sum_{i=1}^{n_c} n_i \ln(\frac{n_i}{V} \frac{d_i b}{d^2})$$
(5.29)

Pressure is related to A by

$$\mathbf{P} = -(\partial \mathbf{A} / \partial \mathbf{V})_{\mathsf{T},\mathsf{n}} \tag{5.30}$$

and, for the Sanchez-Lacombe equation of state, it is given by

$$P = -\frac{n^2 a}{V^2} - \frac{RTnd}{V} - RT\frac{d^2}{b}\ln(1 - \frac{n^2 b/nd}{V}) + nRT/V$$
(5.31)

The chemical potential of component k can be found from A by differentiation as given by the following expression

$$\mu_{k} = (\partial A / \partial n_{k})_{T,V}$$
(5.32)

For the Sanchez-Lacombe equation of state it is given by
$$\mu_{k} = -\frac{2}{V} \sum_{i=1}^{n} n_{i} a_{ik}$$

$$+RT(V - n^{2}b / nd) \ln(1 - \frac{n^{2}b / nd}{V}) [\frac{2d_{k}nd}{n^{2}b} - \frac{2(nd)^{2}}{(n^{2}b)^{2}} (\sum_{i=1}^{n} n_{i} b_{ik})]$$

$$+RT \frac{d^{2}}{b} (d_{k} \frac{b}{d^{2}} - \frac{2}{nd} \sum_{i=1}^{n} n_{i} b_{ik}) [1 + \ln(1 - \frac{n^{2}b / nd}{V})]$$

$$+RT[1 + \ln d_{k} + \ln(n_{k} / V)]$$

$$+RT[\ln(b / d^{2}) + \frac{2n}{n^{2}b} \sum_{i=1}^{n} n_{i} b_{ik} - \frac{2d_{k}}{d}]$$
(5.33)

#### 5.2 Kleintjens-Koningsveld Mean Field Lattice Gas equation of state

As mentioned before, in the Mean Field Lattice Gas model, a pure substance is conceived as a binary mixture of occupied and vacant sites (holes) distributed randomly (the mean field approximation). Changing the number of holes gives a lattice of variable volume and allows for the representation of both gas-like and liquid-like states. After obtaining the energy of mixing  $\Delta E$ , the Helmholtz free energy of mixing is obtained by adding the following terms to  $\Delta E$  (Kleintjens, 1985):

(i) A Flory-Huggins combinatorial entropy of mixing term (Flory, 1953).

(ii) An empirical entropy of mixing correction term of the form: constant  $\mathbf{*} \phi_i \phi_i$ .

The Helmholtz free energy of mixing for the Mean Field Lattice Gas model of Kleintjens and Koningsveld for a multicomponent system is given by (Kennis et al., 1990),

$$\frac{\Delta A}{N_{\phi}RT} = \phi_o \ln \phi_o + \sum_{i=1}^{nc} \frac{\phi_i}{m_i} \ln \phi_i + \sum_{i=1}^{nc} g_{oi} \phi_o \phi_i + \sum_{i=1}^{nc-1} \sum_{j=l+1}^{nc} \chi_{ij} \phi_i \phi_j$$
(5.34)

where, o refers to holes and nc is the number of components.  $m_i$  is the number of lattice sites occupied by component i.  $N_{\phi}$  is the total number of lattice sites  $(N_{\phi}=N_o+\sum_i N_i m_i)$ .  $\phi_i$ is the principal composition variable and is a measure of the fraction of sites occupied by the component i.

 $\mathbf{g}_{oi}$  is a temperature dependent pure component parameter given by

$$g_{oi} = \alpha p_i + g p_i / Q \tag{5.35}$$

where,  $\alpha p_i$  is related to an empirical entropy correction term.  $gp_i$  is temperature dependent with the temperature dependence given by

$$gp_i = \beta_{oii} + \beta_{1ii} / T + \dots$$
 (5.36)

The cross interactions are represented through  $\chi_{ii}$  and are expressed as

$$\chi_{ij} = \alpha_{ij} + g_{ij}(1 - \gamma_j) / Q$$
 (5.37)

where,

$$Q = 1 - \sum_{i=1}^{nc} \gamma_i \phi_i$$
 (5.38)

 $\gamma$  is a parameter related to the surface area of contact.  $g_{ij}$  is given by

$$g_{ij} = \beta_{0ij} + \beta_{1ij} / T + ...$$
 (5.39)

The principal composition variable  $\phi_i$  is given by

$$\phi_i = n_i m_i v_o / V \tag{5.40}$$

The total volume V is calculated from  $N_{\phi}$  and  $v_o$  as

$$\mathbf{V} = \mathbf{N}_{\bullet} \mathbf{v}_{\circ} \tag{5.41}$$

where  $v_0$  is the constant volume of a lattice site.

The volume fractions of holes is

$$\phi_{o} = 1 - \sum_{i=1}^{nc} \phi_{i}$$
(5.42)

For a pure component, the parameters required are  $m_i$ ,  $\alpha p_i$ ,  $\gamma_i$ ,  $\beta_{0ii}$ ,  $\beta_{1ii}$  if only two terms are included in the expression for  $gp_i$ . For a mixture  $\alpha_{ij}$ ,  $\beta_{0ij}$ ,  $\beta_{1ij}$  etc. are also required.

The equations so far briefly describe the Kleintjens-Koningsveld model. The objective now is to reorganize the model equations so that the equations are expressed in terms of total volume and individual mole numbers. This is to facilitate the evaluation of derivatives and computations with the model.

Define,

$$\mathbf{nb} = \sum_{i=1}^{n_c} \mathbf{n}_i \mathbf{m}_i \mathbf{v}_o \tag{5.43}$$

and,

$$nd = \sum_{i=1}^{nc} (-\gamma_i) n_i m_i v_o \qquad (5.44)$$

Therefore,

$$\phi_{o} = \frac{V - nb}{V} \tag{5.45}$$

and,

$$Q = \frac{V + nd}{V}$$
(5.46)

Let,

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$$na = \sum_{i=1}^{nc} \alpha p_i n_i m_i v_o$$
 (5.47)

and,

 $ng = \sum_{i=1}^{nc} gp_i n_i m_i v_o$ (5.48)

Therefore,

$$\sum_{i=1}^{nc} g_{oi}\phi_o\phi_i = (V-nb)\left[\frac{na}{V^2} + \frac{ng}{V(V+nd)}\right]$$
(5.49)

$$\sum_{i=1}^{nc-1} \sum_{j=i+1}^{nc} \chi_{ij} \phi_i \phi_j = \sum_{i=1}^{nc-1} \sum_{j=i+1}^{nc} \alpha_{ij} \phi_i \phi_j + \sum_{i=1}^{nc-1} \sum_{j=i+1}^{nc} \frac{g_{ij}(1-\gamma_j)}{Q} \phi_i \phi_j$$
(5.50)

$$f_{ij} = \alpha_{ij} / 2$$
;  $f_{ii} = 0$  (5.51)

with

$$f_{ji} = f_{ij}$$
;  $f_{ji} \neq \alpha_{ji} / 2$  (5.52)

and,

$$n^{2}f = \sum_{i=1}^{nc} \sum_{j=i}^{nc} f_{ij}n_{i}n_{j}m_{i}m_{j}v_{o}^{2}$$
(5.53)

 $S_1$  can now be expressed as

$$S_1 = \frac{n^2 f}{V^2}$$
 (5.54)

Define,

Now,

Let,

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$$h_{ij} = \frac{g_{ij}(1-\gamma_j)}{2}$$
;  $h_{ii} = 0$  (5.55)

with

$$h_{ji} = h_{ij}$$
;  $h_{ji} \neq g_{ji}(1-\gamma_i)/2$  (5.56)

and,

$$n^{2}h = \sum_{i=1}^{nc} \sum_{j=1}^{nc} h_{ij}n_{i}n_{j}m_{i}m_{j}v_{o}^{2}$$
(5.57)

 $S_2$  can now be expressed as

 $S_2 = \frac{n^2 h}{V(V + nd)}$ (5.58)

With these new definitions the Helmholtz energy of mixing is,

$$\frac{\Delta A v_{o}}{RT} = (V - nb) \ln \frac{V - nb}{V} + \sum_{i=1}^{nc} n_{i} v_{o} \ln \frac{n_{i} m_{i} v_{o}}{V} + na + ng + \frac{n^{2} f - (na)(nb)}{V} + \frac{n^{2} h - (ng)(nb) - (ng)(nd)}{(V + nd)}$$
(5.59)

In order to simplify this equation define,

$$n^{2}\alpha = n^{2}f - (na)(nb)$$
  
=  $\sum_{i=1}^{nc} \sum_{j=1}^{nc} [f_{ij} - \frac{(\alpha p_{i} + \alpha p_{j})}{2}]n_{i}n_{j}m_{i}m_{j}v_{o}^{2}$  (5.60)

and,

$$n^{2}g\gamma = n^{2}h - (ng)(nb) - (ng)(nd)$$
  
=  $\sum_{i=1}^{nc} \sum_{j=1}^{nc} [h_{ij} + \frac{1}{2} \{gp_{i}(\gamma_{j} - 1) + gp_{j}(\gamma_{i} - 1)\}]n_{i}n_{j}m_{i}m_{j}v_{o}^{2}$  (5.61)

The final expression for Helmholtz free energy of mixing is

$$\frac{\Delta A v_o}{RT} = (V - nb) \ln \frac{V - nb}{V} + \sum_{i=1}^{nc} n_i v_o \ln \frac{n_i m_i v_o}{V} + na + ng + \frac{n^2 \alpha}{V} + \frac{n^2 g \gamma}{(V + nd)}$$
(5.62)

The pressure is given by the equation

$$\frac{-Pv_{o}}{RT} = \ln\frac{V - nb}{V} + \frac{nb}{V} - \sum_{i=1}^{nc} n_{i}v_{o} / V - \frac{n^{2}\alpha}{V^{2}} - \frac{n^{2}g\gamma}{(V + nd)^{2}}$$
(5.63)

The chemical potential of component j is given by the following equation

$$\frac{\Delta \mu_{j}}{RT} = \frac{1}{RT} (\partial \Delta A / \partial V)_{n_{i}'x_{j} \neq j}$$

$$= 1 - m_{j} + \alpha p_{j}m_{j} + gp_{j}m_{j}$$

$$-m_{j} \ln \frac{V - nb}{V} + \ln \frac{n_{j}m_{j}v_{o}}{V}$$

$$+ \frac{2}{V} \sum_{i=1}^{nc} [f_{ij} - \frac{\alpha p_{i} + \alpha p_{j}}{2}]n_{i}m_{i}m_{j}v_{o}$$

$$+ \frac{2}{V + nd} \sum_{i=1}^{nc} [h_{ij} + \frac{1}{2} \{gp_{i}(\gamma_{j} - 1) + gp_{j}(\gamma_{i} - 1)\}]n_{i}m_{i}m_{j}v_{o}$$

$$+ \frac{\gamma_{j}m_{j}(n^{2}g\gamma)}{(V + nd)^{2}}$$

(5.64)

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# 5.3 PHSC equation of state

The PHSC equation of state of Song et al.(1994 a,b; 1996) is based on the work of Chiew (1990). Chiew developed an expression for pressure for mixtures of hard-sphere chains modeled by a series of freely jointed tangent spheres. Chiew's pressure equation has the form

$$P = P_{hs} + P_{bond}$$
(5.65)

 $P_{hs}$  is the hard sphere part and  $P_{bond}$  accounts for chain connectivity. Each sphere in a chain interacts with every other sphere through the hard-sphere potential. Song et al. (1994 a,b; 1996) added a van der Waals like attractive term to equation (5.65) to get the equation for the pressure of a real fluid.

The perturbed hard-sphere-chain (PHSC) equation of state (Song et al., 1994) is

$$P = \rho k_{b} T + \rho^{2} k_{b} T \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_{i} x_{j} r_{i} r_{j} b_{ij} g_{ij}$$
  
-  $\rho k_{b} T \sum_{i=1}^{nc} x_{i} (r_{i} - 1) [g_{ii} - 1] - \rho^{2} \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_{i} x_{j} r_{i} r_{j} a_{ij}$  (5.66)

where, P is the pressure, T is the temperature, and,  $k_b$  is Boltzmann constant.  $\rho$  is the number density (number of molecules/total volume),  $x_i$  is the number fraction of molecules and  $r_i$  is the number of hard spheres comprising component i.  $g_{ij}$  is the pair radial distribution function of hard-spheres.  $b_{ij}$  is the second cross virial coefficient of hard-sphere mixtures and is related to temperature dependent hard-sphere diameters.  $a_{ij}$  is a parameter that reflects the attractive force between two segments. In a later paper (Song et al., 1996) the temperature dependence of  $b_{ij}$  and  $a_{ij}$  was altered. This does not affect the equations that follow. Only the corresponding parameters have to be used.

b<sub>ii</sub> is obtained from the following expression

$$b_{ij}(T) = \frac{2\pi}{3} d_{ij}^3(T) = \frac{2\pi}{3} \sigma_{ij}^3 F_b(k_B T / \epsilon_{ij})$$
(5.67)

a<sub>ii</sub> is obtained from

$$a_{ij}(T) = \frac{2\pi}{3} \sigma_{ij}^3 \varepsilon_{ij} F_a(k_B T / \varepsilon_{ij})$$
(5.68)

 $\varepsilon_{ij}$  is related to the depth of the minimum of the pair potential and  $\sigma_{ij}$  is the separation distance at this minimum. The model has three pure component parameters namely  $\varepsilon_{ii}$ ,  $\sigma_{ii}$  and  $r_i$ . The cross parameters  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are obtained from the following equations.

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$
(5.69)

$$\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj})$$
(5.70)

 $k_{ij}$  is a binary interaction parameter.  $F_b$  and  $F_a$  in equations (5.67) and (5.68) are universal functions determined from the thermodynamic properties of fluid argon and methane over large ranges of temperature and density. In the later version of the PHSC equation of state (Song et al., 1996) these are given by

$$F_{s}(k_{B}T/\epsilon) = 1.8681 \exp[-0.0619(k_{B}T/\epsilon)] + 0.6715 \exp[-1.7317(k_{B}T/\epsilon)^{3/2}]$$
(5.71)
$$F_{b}(k_{B}T/\epsilon) = 0.7303 \exp[-0.1649(k_{B}T/\epsilon)^{1/2}] + 0.2697 \exp[-2.3973(k_{B}T/\epsilon)^{3/2}]$$

The latter version of PHSC equation of state is the more important for this work as it was the one used for most of the calculations.

Song et al. (1994 a,b; 1996) approximate  $g_{ij}$  with the expression from the BMCS equation (Boublik, 1970; Mansoori et al., 1971) that is given by

$$\mathbf{g}_{ij} = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1-\eta)^3}$$
(5.73)

where  $\eta$  is the packing fraction of hard-sphere mixtures given by

(5.72)

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$$\eta = \frac{\rho}{4} \sum x_i r_i b_{ii} \tag{5.74}$$

 $\xi_{ij}$  is given by the expression

$$\xi_{ij} = \frac{\rho}{4} \left( \frac{b_{ii} b_{jj}}{b_{ij}} \right)^{1/3} \sum x_i r_i b_{ii}^{2/3}$$
(5.75)

In terms of the total volume V the pressure equation is

$$P = \frac{n}{V}RT + \frac{RT}{V^{2}}\sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}r_{i}r_{j}b_{ij}g_{ij}$$
  
-  $\frac{RT}{V}\sum_{i=1}^{nc} n_{i}(r_{i}-l)[g_{ii}-l] - \frac{1}{V^{2}}\sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}r_{i}r_{j}a_{ij}$  (5.76)

where now,

$$b_{ij} = N_{AV}b_{ij}$$
;  $a_{ij} = N_{AV}^2a_{ij}$  (5.77)

R is the gas constant and  $n_i$  is the number of moles of component i. V is the total volume. The equation of state is now in terms of molar quantities. The density now would be the molar density and  $x_i$  would be the mole fraction and so on.

Before proceeding with the restructuring we need to introduce some definitions. Define,

$$nb = \sum_{i=1}^{n} n_i r_i (b_i / 4)$$
 (5.78)

$$nd = \sum_{k=1}^{n} n_k r_k b_k^{2/3} / 4$$
 (5.79)

and,

$$bc_{ij} = (b_i b_j / b_{ij})^{1/3}$$
(5.80)

Therefore the original variables  $\eta$  and  $\xi_{ij}$  in  $g_{ij}$  can be expressed as

$$\eta = \frac{nb}{V} \tag{5.81}$$

and

$$\xi_{ij} = \frac{(bc_{ij})(nd)}{V}$$
(5.82)

# The radial distribution function $g_{ij}$ , after restructuring, in terms of volume is

$$g_{ij} = \frac{V}{V - nb} + \frac{3}{2} \frac{bc_{ij}(nd)V}{(V - nb)^2} + \frac{1}{2} \frac{(bc_{ij})^2 (nd)^2 V}{(V - nb)^3}$$
(5.83)

A few more definitions follow. Let,

$$n^{2}a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}r_{i}r_{j}a_{ij}$$
(5.84)

$$nr = \sum_{i=1}^{nc} n_i (r_i - 1)$$
 (5.85)

$$n^{2}db = \sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}r_{i}r_{j}b_{ij}$$
(5.86)

$$n^{2}db_{1} = \sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}r_{i}r_{j}b_{ij}(\frac{3}{2}bc_{ij})$$
(5.87)

$$n^{2}db_{2} = \sum_{i=1}^{nc} \sum_{j=1}^{nc} n_{i}n_{j}r_{i}r_{j}b_{ij}(\frac{1}{2}bc_{ij}^{2})$$
(5.88)

Now the equation for pressure can be written in terms of these definition as

$$\frac{P}{RT} = \frac{1}{v} + \frac{(db)}{v(v-b)} + \frac{(d)(db_1)}{v(v-b)^2} + \frac{(d)^2(db_2)}{v(v-b)^3} - r\left(\frac{1}{v-b} + \frac{3}{2}\frac{b}{(v-b)^2} + \frac{1}{2}\frac{b^2}{(v-b)^2} - \frac{1}{v}\right) - \frac{1}{RT}\frac{a}{v^2}$$
(5.89)

where v is the molar volume. This can be further simplified to

$$\frac{P}{RT} = \frac{a_o}{v} + \frac{a_1}{v-b} + \frac{a_2}{(v-b)^2} + \frac{a_3}{(v-b)^3} - \frac{a}{RTv^2}$$
(5.90)

where,

$$a_{o} = 1 - \frac{db}{b} + \frac{(d)(db_{1})}{b^{2}} - \frac{(d)^{2}(db_{2})}{b^{3}} + r$$
 (5.91)

$$a_{t} = \frac{db}{b} - \frac{(d)(db_{1})}{b^{2}} + \frac{(d)^{2}(db_{2})}{b^{3}} - r$$
(5.92)

$$a_{2} = \frac{(d)(db_{1})}{b} - \frac{(d)^{2}(db_{2})}{b^{2}} - \frac{3}{2}br$$
 (5.93)

$$a_3 = \frac{(d)^2 (db_2)}{b} - \frac{1}{2} b^2 r$$
 (5.94)

Note that  $a_0 = 1 - a_1$ .

The Helmholtz free energy of a pressure explicit equation of state can be obtained from the following equation (Prausnitz et al., 1986),

$$A(T, V, n_i) = \sum_{i=1}^{n_c} n_i A_i^{\circ}(T) + \int_{V}^{\infty} (P - \frac{nRT}{V}) dV + RT \sum_{i=1}^{n_c} n_i \ln \frac{n_i RT}{V}$$
(5.95)

The Helmholtz free energy from PHSC EOS is

$$\frac{\Delta A}{RT} = (na_1) \ln \frac{V}{V - nb} + \frac{(n^2 a_2)}{V - nb} + \frac{1}{2} \frac{(n^3 a_3)}{(V - nb)^2} - \frac{n^2 a}{RTV} + \sum_{i=1}^{n} n_i \ln \frac{n_i RT}{V}$$
(5.96)

The chemical potential of component k is given by the following equation

$$\frac{\Delta \mu_{k}}{RT} = \ln \frac{V}{V - nb} \frac{\partial}{\partial n_{k}} (na_{1}) + \frac{na_{1}}{V - nb} \frac{\partial}{\partial n_{k}} (nb)$$
$$+ \frac{1}{V - nb} \frac{\partial}{\partial n_{k}} (n^{2}a_{2}) + \frac{(n^{2}a_{2})}{(V - nb)^{2}} \frac{\partial}{\partial n_{k}} (nb)$$
$$+ \frac{1}{2} \frac{1}{(V - nb)^{2}} \frac{\partial}{\partial n_{k}} (n^{3}a_{3}) + \frac{(n^{3}a_{3})}{(V - nb)^{3}} \frac{\partial}{\partial n_{k}} (nb)$$
$$- \frac{1}{RTV} \frac{\partial}{\partial n_{k}} (n^{2}a) + \ln \frac{n_{k}RT}{V} + 1$$

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(5.97)	
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#### **CHAPTER 6**

# **Model Performance**

# 6.0 Introduction

This Chapter demonstrates the capability of the models discussed in Chapter 5 for correlating and/or predicting the phase behaviour of some pure components and some binary and pseudo-binary systems. The first section shows a comparison of experimental and calculated vapor pressures and saturation densities for n-hexane, carbon dioxide and methylcyclohexane. The subsequent section compares the model performance versus the experimental data for the methylcyclohexane +  $CO_2$  system. Next, the performance of the models is evaluated for the system polyethylene + n-hexane. Both cases, (i) when the polymer is treated as monodisperse, and, (ii) when the polydispersivity of the polymer is taken into account, are covered. Finally the attempts made at correlating the cloud points for the system polystyrene + methylcyclohexane are shown.

# 6.1 Pure component phase behavior

# 6.1.1 n-hexane

Figure (6.1) shows a comparison of experimental and calculated vapor pressures from the three models discussed in Chapter 5. The parameters reported by the authors (Sanchez and Lacombe, 1978; Kennis et al., 1990; Song et al., 1996) were used for the



Figure 6.1. n-hexane vapor pressures. (•) Data Vargaftik (1975).

these calculations. The parameters were obtained by least squares fitting of selected vapor pressure and liquid density data without any regard for the critical point. The n-hexane parameters are contained in Tables (6.1) to (6.3). Figure (6.1) shows that the models fit the experimental vapor pressure data well at the lower temperatures but significant deviations are present at higher temperatures. The equation of state critical points for nhexane are compared with the data in Table (6.4). Figure (6.2) shows a comparison of experimental and calculated saturation densities.

#### Table 6.1. Sanchez-Lacombe EOS.

	d	ε/R (K)	$v (cm^3/mol)$
n-hexane	8.356	476	13.28
CO <sub>2</sub>	8.565	273	3.64
methycyclohexane	8.622	514	14.43

\* Sanchez and Lacombe (1978).

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	m	α	γ	β <sub>01</sub>	β <sub>02</sub>
n-hexane	5.6567	1.0475	-0.49924	-1.3177	660.72
CO <sub>2</sub>	1.29	0.9265	-1.299	-2.635	1183.8
CO <sub>2</sub>	1.4874	-4.2235	-0.12683	2.1505	1173.72
methyl- cyclohexane	4.641	0.06369	-0.29045	-0.5351	871.98

 $v_0 = 25 \text{ cm}^3/\text{mol.}$ 

\* Kennis et al. (1990).  $v_0 = 20 \text{ cm}^3/\text{mol.}$ \*\* Beckman et al. (1987).  $v_0 = 25 \text{ cm}^3/\text{mol.}$ 



Figure 6.2. n-hexane saturation densities. (•) Data Vargaftik (1975).

Table 6.3. PHSC EOS

	r	ε/k <sub>B</sub> (K)	σ (A <sup>°</sup> )	
n-hexane	3.446	235.6	4.084	
methylcyclohexane	2.968	283.7	4.336	
methylcyclohexane	5.256	206.7	3.472	
CO <sub>2</sub>	3.930	126.1	2.482	

\* Song et al. (1996).

model	T <sub>c</sub> (°C)	P <sub>C</sub> (bar)
Sanchez-Lacombe	253.25	36.17
MFLG	243.61	41.73
PHSC (1996)	263.31	34.7
data	234.7	30.31

#### Table 6.4. n-hexane critical points.

# 6.1.2 Carbon dioxide

In the case of carbon dioxide, the pure component parameters for PHSC model are not available in the literature. Kiszka et al. (1988) report CO, parameters for the Sanchez-Lacombe equation of state. The parameters were obtained by fitting vapor pressures and saturation volumes of CO<sub>2</sub>. Beckman et al. (1987) report carbon dioxide parameters for Kleintjens-Koningsveld model. Beckman et al. obtained the CO<sub>2</sub> parameters by minimizing errors in vapor pressures, liquid saturation densities and the critical point. The parameters reported by these authors are contained in Table (6.2). Figure (6.3) shows a comparison of the experimental and calculated vapor pressures for the Kleintjens-Koningsveld equation of state using the parameters reported by Beckman et al. Figure (6.4) shows a comparison of the experimental and calculated saturation values for the It these figures that, although same. can be seen from the fit to



Figure 6.3. CO<sub>2</sub> vapor pressures. (▲) Data Vargaftik (1975). (---) MFLG EOS. Parameters Beckman et al. (1987).



Figure 6.4. CO<sub>2</sub> saturation volumes. (▲) Data Vargaftik (1975). (---) MFLG EOS. Parameters Beckman et al. (1987).

the saturation volume data is good, the calculated vapor pressures lie consistently below the experimental values.

In this work, carbon dioxide parameters were regressed for all the models using the minimization algorithm of Nelder and Mead (1965). The approach to parameter estimation was, however, different from what has been the trend in the literature for these models. The parameters for the MFLG and PHSC models were obtained by minimizing an objective function (OF) of the form given by

$$OF = C_1 \sum_{i=1}^{ndata} \frac{1}{ndata} \left[ \frac{P_s(calc) - P_s(exp)}{P_s(exp)} \right]^2 + C_2 \left[ \frac{P_c(calc) - P_c(exp)}{P_c(exp)} \right]^2 + C_3 \left[ \left( \frac{\partial P}{\partial v} \right)_T \right]^2$$
(6.1)

 $C_1$ ,  $C_2$  and  $C_3$  are appropriate weighting factors.  $P_S$  and  $P_C$  are the vapor pressure and the critical pressure respectively.

The model  $P_C$  and  $(\partial P/\partial v)_T$  were evaluated at the experimental critical temperature. The volume used for the evaluation of these quantities was obtained by solving the following equation at the experimental critical temperature.

$$\left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{v}^2}\right)_{\mathrm{T}} = 0 \tag{6.2}$$

This equation is one of the critical point criteria for a pure component. The other is

$$(\partial \mathbf{P}/\partial \mathbf{v})_{\mathrm{T}} = \mathbf{0}.\tag{6.3}$$

By choosing  $C_2$  and  $C_3$  large, the model critical pressure is forced towards the experimental value.

The Sanchez-Lacombe model  $T_C$  and  $P_C$  can be obtained analytically from the critical point criterion mentioned above and the pressure equation and are given by the following equations.

$$T_{c} = \frac{2\varepsilon_{11}}{R} \frac{d_{1}}{(1+\sqrt{d_{1}})^{2}}$$
(6.4)

$$P_{c} = \frac{RT_{c}(1 - \sqrt{d_{1}})}{d_{1}v_{11}} - \frac{RT_{c}}{v_{11}} \ln \left[\frac{\sqrt{d_{1}}}{(1 + \sqrt{d_{1}})}\right] - \frac{\varepsilon_{11}}{v_{11}} \frac{1}{(1 + \sqrt{d_{1}})^{2}}$$
(6.5)

In the case of the Sanchez-Lacombe equation of state, the third term in the objective

function was replaced by 
$$C_3 \left[ \frac{T_C(calc) - T_C(exp)}{T_C(exp)} \right]^2$$
.

For all three models, no attempt was made to force the saturation densities. In the author's opinion, it is better to lay emphasis on correlation of the vapor pressures rather than fitting of liquid densities to obtain model parameters. For instance, in vapor-liquid equilibrium calculations the phase diagrams are anchored by the pure component vapor pressures. In the case of vapor-liquid-liquid equilibria involving binary or pseudo-binary polymer systems, the three phase condition is close to the solvent vapor pressures and hence, for such types of phase behavior, a good correlation of the vapor pressures is more desirable. Also, accurate representation of pure component critical points will give a better vapor-liquid critical locus and as a consequence the model phase behavior at higher pressures will be better.

The new estimated parameters for  $CO_2$  in the three models are contained in Tables (6.1) to (6.3). Figure (6.5) shows a comparison of the experimental and model vapor



Figure 6.5. CO<sub>2</sub> vapor pressures. ( $\blacktriangle$ ) Data Vargaftik (1975). (---) MFLG EOS. (----) Sanchez-Lacombe EOS. (----) PHSC EOS.

pressures. The fit is the best for MFLG Lattice-Gas model with the magnitude of the first term in the objective function ( $C_1 = 1$ ) equal to 0.1615\*10<sup>-4</sup>. The fit for the Sanchez-Lacombe equation of state is satisfactory with the magnitude of the first term in the OF equal to 0.21373\*10<sup>-3</sup>. Forty two data points were employed for the regression with the temperature ranging from 220 K up to the critical temperature. The model results for the PHSC equation of state are the least accurate of the three models with the magnitude of the first term in OF equal to 0.994\*10<sup>-3</sup>. The parameter estimation was done over a limited range of temperatures (273.15 K up to 300 K). Eighteen data points were employed for regression. The model critical points for CO<sub>2</sub> are compared with the experimental critical points in Table (6.5). For the two lattice gas models, the forced critical points are good with the representation better for the MFLG model. The PHSC equation of state critical point is not as satisfactory as the other two models. Figure (6.6) shows a comparison of experimental and calculated saturation volumes. The predictions are satisfactory. In all cases the predictions are shifted to slightly higher saturation volumes.

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model	T <sub>C</sub> (K)	P <sub>C</sub> (bar)	
Sanchez-Lacombe	304.21	73.73	
MFLG	304.19	73.81	
PHSC (1996)	305.76	74.37	
data	304.19	73.8	

Table 6.5. CO<sub>2</sub> critical points.

#### 6.1.3 Methylcyclohexane



Figure 6.6. CO<sub>2</sub> saturation volumes. ( $\blacktriangle$ ) Data Vargaftik (1975). (--) MFLG EOS. (---) Sanchez-Lacombe EOS. (---) PHSC EOS.

PHSC parameters for methylcyclohexane are available in the literature (Song et al., 1996). The parameters were obtained by fitting vapor pressure and saturated liquid density data in the range 0.5  $T_C < T < 0.9 T_C$ . The model vapor pressures are compared with data in Figure (6.7). It can be seen that there are significant deviations at higher temperatures. Figure (6.8) shows a comparison of model and experimental liquid saturation densities. From the two figures it is obvious that the model completely misses the experimental  $T_C$  and  $P_C$ .

Methylcyclohexane parameters were regressed for the three models following the strategy outlined in the previous sub-section. The methylcyclohexane parameters for the three models are contained in Tables (6.1) to (6.3). Figure (6.9) shows a comparison of experimental and calculated vapor pressures for the three models. The fit is satisfactory for the Sanchez-Lacombe equation of state with the magnitude of the first term in OF equal to 0.67\*10<sup>-3</sup>. The representation of the data is also good for the Kleintjens-Koningsveld equation of state with the magnitude of the first term equal to  $0.172 \times 10^{-4}$ . Again the magnitude of the first term in the objective function is the largest for PHSC equation of state and is equal to 0.393. The bulk of the error lies at lower temperatures where the vapor pressure is very small. In all cases, thirty data points were employed for regression of parameters with the temperature ranging from 0° C up to the critical temperature. These errors are larger than those for carbon dioxide. However, the temperature range involved is also larger in this case. The experimental and calculated liquid saturation densities are compared in Figure (6.10). The predictions from the



Figure 6.7. Methylcyclohexane vapor pressures. ( $\Delta$ ) Data Vargaftik (1975). (---) PHSC EOS. Parameters Song et al. (1996).



Figure 6.8. Methylcyclohexane saturation densities. ( $\blacktriangle$ ) Data Vargaftik (1975). (---) PHSC EOS. Parameters Song et al. (1996).



Figure 6.9. Methylcyclohexane vapor pressures. (▲) Data Vargaftik (1975). (---) MFLG EOS. (---) Sanchez-Lacombe EOS. (----) PHSC EOS.



Figure 6.10. Methylcyclohexane saturation densities. (A) Data Vargaftik (1975). (---) MFLG EOS. (---) Sanchez-Lacombe EOS. (----) PHSC EOS.

Kleintjens-Koningsveld model are the best and the match is quite good at lower temperatures. The Sanchez-Lacombe predictions are shifted to lower densities. The fit for the PHSC equation of state is not very good either. The model and data critical temperature and pressure are compared in Table (6.6).

model	T <sub>C</sub> (℃)	P <sub>c</sub> (bar)
Sanchez-Lacombe	299.25	34.69
MFLG	299.1	34.75
PHSC (1996)	299.43	34.82
data	299.1	34.7

Table 6.6 Methylcyclohexane critical points.

For the three compounds investigated in this work it seems that the performance of the PHSC EOS is not as good as that of the other two models. However, the reason for this could be an inadequate temperature dependence in the model. Perhaps this is one area in which further work will yield a better parametrization of this equation of state.

# 6.2 Carbon dioxide + methylcyclohexane system

Figures (6.11) to (6.13) show a comparison between the experimental data and the model results for the system carbon dioxide and methylcyclohexane. Two sources of experimental data are shown. One is the measurements made in this work over a limited composition range. The other is the data reported by Ng and Robinson (1979), measured over the entire composition range for a few temperatures. Ng and Robinson obtained their data by the analytical method or, in other words, the equilibrium phases were sampled. It is to be noted that the bubble point pressures measured in this work are higher than those



Figure 6.11. Methylcyclohexane/CO<sub>2</sub> system P-x sections. (▲) Data Ng and Robinson (1979), T = 37.85 °C. (●) Data Ng and Robinson (1979), T = 65.75 °C.
(■) Data T = 38 °C. (▼) Data T = 65.75 °C. Curves Sanchez-Lacombe EOS.



Figure 6.12. Methylcyclohexane/CO<sub>2</sub> system P-x sections. (▲) Data Ng and Robinson (1979), T = 37.85 °C. (●) Data Ng and Robinson (1979), T = 65.75 °C.
(■) Data T = 38 °C. (▼) Data T = 65.75 °C. Curves MFLG EOS.



Figure 6.13. Methylcyclohexane/CO<sub>2</sub> system P-x sections. (▲) Data Ng and Robinson (1979), T = 37.85 °C. (●) Data Ng and Robinson (1979), T = 65.75 °C.
(■) Data T = 38 °C. (▼) Data T = 65.75 °C. Curves PHSC EOS.

reported by Ng and Robinson. An effort was made to locate the source of this discrepancy in the two sets of data but the source of the discrepancy could not be ascertained. At the same time there is no reason to believe that the measurements made in this work are in error.

For the calculations shown in Figures (6.11) to (6.13), the pure component parameters estimated in this work were employed. The mixture parameters, or the binary interaction parameters, were obtained by fitting these to one or two binary data points measured in this work. Figure (6.11) is for the Sanchez-Lacombe equation of state for a binary interaction parameter of 0.11. The experimental data point chosen was at 65.75  $^{\circ}$ C, which explains the better agreement between the model results and data at this temperature. The model predictions at 38  $^{\circ}$ C lie below the data. A probable reason for this is that the model parameters are temperature independent. Overall the model predictions versus the data are reasonable.

Figure (6.12) is for the Kleintjens-Koningsveld model. The mixture parameters employed for the calculations are:

 $\alpha_{12} = 0.5$  and  $g_{12}[T(K)] = -1.021018 + 425.036609/T$ 

These were obtained by matching the model results at two bubble point pressures at the two temperatures of 38 °C and 65.75 °C. The model matches the data measured in this work very well. Overall the fit is very satisfactory.

Figure (6.13) is for the PHSC equation of state for a binary interaction parameter of 0.14. This was obtained in a manner similar to that for the Sanchez-Lacombe model. The model fits the data measured in this work well. The overall picture is also satisfactory.

# 6.3 n-hexane + polyethylene system

The experimental data reported by Kennis (1988) and Kennis et al. (1990) were used to evaluate the performance of the models. The data were measured in the vicinity of the lower critical solution temperature (LCST). The polyethylene had a number average molar mass of 8,000 g/mol and a weight average molar mass of 177,000 g/mol. The temperature and pressure ranges involved cross the n-hexane vapor pressure curve and, as a consequence, both liquid n-hexane and vapor n-hexane can play a role in the equilibrium and three-phase vapor-liquid-liquid equilibria (VLLE) can occur. The threephase behaviour occurs near a lower critical solubility condition, and, together, these phenomenon present significant modelling challenges.

Parameters for polyethylene are available in the literature and are presented in Table (6.7). These parameters were obtained by fitting P-V-T data for polyethylene.

Kennis et al. (1990) report binary interaction parameters for polyethylene + nhexane system in the MFLG equation of state. The polymer is treated as monodisperse. The parameters are  $\alpha_{12} = -0.25$  and  $g_{12} = -0.10$ . Kennis at al. (1990) computed only the spinodal curves at three pressures and selected the interaction parameters to match the minimum temperatures on the spinodal curves to the minimum temperatures on the three cloud point isobars.

#### Table 6.7. Polyethylene parameters.

Sanchez-Lacombe	
(Sanchez and Lacombe,	
1978)	
ε/R (K)	659
d	M/11.47
v (cm <sup>3</sup> /mol)	12.7
MFLG, $v_0 = 20 \text{ cm}^3/\text{mol}$	
(Kennis et al., 1990)	
m	M/16.66
γ	-0.95446
αο	0.96874
β <sub>o</sub>	-0.9711
βι	342.9
β <sub>2</sub>	247500
PHSC (Song et al., 1996)	
r	0.04939 M
σ (A <sup>°</sup> )	3.825
ε/k <sub>B</sub>	324.1
M = molar mass of the poly	mer.

Binary interaction parameters had to be determined for the Sanchez-Lacombe and the PHSC equations of state. In the fitting done in this work, the interaction parameter(s) were chosen to give 126.7 °C as the LCST at 6 bar. For the Sanchez-Lacombe equation a  $k_{ii} = -0.04144$  was estimated.

For the PHSC model, two binary interaction parameters are available: (i) an interaction parameter in the energy term,  $k_{ij}$ , and (ii) a "size reduction parameter",  $\zeta$ , for the polymer segment number in the perturbation term (Song et al., 1996). In this case, the summation "a" in the perturbation term is given by  $\Sigma\Sigma x_i x_j \zeta_i r_i \zeta_j r_j a_{ij}$ . In this work,  $k_{ij}$  was fixed at -0.1 and  $\zeta$  was estimated at 0.89538 to get the desired LCST. The use of two
parameters was necessary because with  $k_{ij}$  alone the model could not fit the LCST well. Perhaps the LCST can be fitted with the use of  $\zeta$  alone keeping  $k_{ij} = 0$ .

It is to be noted that the binary interaction parameters presented so far only hold for the case when the polymer is treated as monodisperse. The modelling results for the monodisperse case are discussed in the next sub-section. The effect of polydispersivity of the polymer on phase equilibrium computations is discussed in a later sub-section for the Sanchez-Lacombe equation of state.

# 6.3.1 Monodisperse polyethylene

Figures (6.14)-(6.17) show calculated VLE and LLE cloud-points (solid lines) and spinodal curves (dashed lines) for the HDPE/n-hexane system at 6, 25 and 50 bar. Figures (6.14) and (6.15) are for the Kleintjens-Koningsveld MFLG equation and Figures (6.16) and (6.17), respectively, are for the Sanchez-Lacombe and PHSC (1996) equations. The vapor phase composition, which is essentially pure hexane, is not distinguishable from the temperature axis.

Figure (6.14) includes polymer compositions up to 80 mass %, far beyond the range of the Kennis et al. (1990) data, in order to give a fuller picture of the phase behavior obtained from by the models. The 6 and 25 bar isobars show the presence of three-phase lines where the slopes are discontinuous. The lower sections represent LLE equilibria. These curves intersect VLE phase boundaries and, from the sharp edge onwards, the curves correspond to a liquid in equilibrium with a vapor-like hexane-rich



Figure 6.14. Calculated VLE, LLE and spinodals from MFLG EOS for the system n-hexane + HDPE.



Figure 6.15. Experimental cloud point curves and calculated VLE, LLE, spinodals from MFLG EOS for the system n-hexane + HDPE



Figure 6.16. Experimental cloud point curves and calculated VLE, LLE, spinodals from Sanchez-Lacombe EOS for the system n-hexane + HDPE



Figure 6.17. Experimental cloud point curves and calculated VLE, LLE, spinodals from PHSC EOS for the system n-hexane + HDPE

phase. The three-phase condition is at a temperature very close to the boiling temperature of n-hexane (as given by the EOS model) because this is the condition where pure nhexane liquid and vapor phases can be in equilibrium. The pressure of 50 bars is above the EOS critical pressure of n-hexane and no three-phase condition is indicated in the calculations.

The spinodal curves fall well inside the phase boundaries and do not provide an accurate picture of the equilibria. Furthermore, the LLE curve does not correctly represent the model behavior at temperatures above the three-phase line. A calculated LLE at higher temperature will represent a metastable equilibrium whereas the correct equilibrium solution will be a VLE condition with significantly different compositions and densities of the phases. At a pressure of 6 bar one may extend the LLE phase boundaries to temperatures far above the three-phase condition, into a region where the correct equilibrium involves a liquid solution and almost pure hexane vapor.

Figures (6.15)-(6.17) compare the calculated LLE and VLE cloud points with the Kennis et al. (1990) experimental cloud-point data. The n-hexane/polymer interaction parameters used in the calculations were adjusted to obtain a LCST at 6 bar that was in line with the data. As will be seen in Figure (6.15), Kennis et al. (1990) succeeded with their parameterization in placing the minimum points on the spinodal curves for the three isobars near the experimental minimum temperatures (i.e., the LCST points in the binary models). The critical temperatures on the 25 and 50 isobars for the Sanchez-Lacombe model (Figure 6.16) and the PHSC model (Figure 6.17) appear a bit low, with the

Sanchez-Lacombe results farther from the apparent experimental values. (The interaction parameters were fitted to the 6 bar isobar.)

The critical solubilities from all three models are displaced to higher mass fractions of polymer than the data indicate. The Sanchez-Lacombe calculations show a flatter coexistence curve with critical compositions not as close to the data as the other two models.

#### 6.3.1.1 Three-Phase Equilibria

The existence of three phase equilibria has implications on the ability of the models to match the data. Metastable LLE curves could be computed at higher temperatures but would be well inside the cloud point boundaries that are the correct equilibrium conditions according to the models. Parameter estimation procedures must take into account the different kinds of equilibria that can occur.

Figure (6.18) shows some details of the three-phase equilibrium calculated from the Sanchez-Lacombe equation. Several metastable coexistence lines that are shown in the Figure were found through two-phase flash procedures. Also indicated is the region of equilibrium between n-hexane rich vapor and liquid phases that lies below the threephase temperature.

The densities of the n-hexane-rich liquid and vapor phases that coexist on the three-phase line can be quite different, depending on the pressure. For example, the densities of the three phases we calculate from the Sanchez-Lacombe equation at 6 bar



Figure 6.18. Calculated VLE, LLE, metastable VLE and LLE, and the three-phase line from Sanchez-Lacombe EOS for the system n-hexane + HDPE.

are  $0.0171 \text{ g/cm}^3$  for the vapor,  $0.524 \text{ g/cm}^3$  for the middle liquid and  $0.572 \text{ g/cm}^3$  for the more polymer-rich liquid. The mass fraction of polymer in the middle liquid is 0.00467, obviously very small but not negligible. The mass fraction of polymer in the second liquid is 0.135. The composition at the LCST (from the model) is 0.04 mass fraction polymer.

The consequence of the presence of a three-phase line on the experiments to determine the cloud point curve are interesting. If the polymer mass fraction lies between the LCST composition and 0.135, the new phase formed as the coexistence curve is crossed will be a second liquid phase. However, if the polymer mass fraction exceeds 0.135, the new phase will be a solvent-rich vapor of a much different density from the polymer rich liquid.

The thesis by Kennis (1988) contains data for the three-phase cloud-point temperature and pressure at a series of mass fractions of the polyethylene in n-hexane. Figure (6.19) shows the temperature-pressure three-phase line data of Kennis (1988) and the computed three-phase lines from the EOS models. Also shown in Figure (6.19) are the calculated liquid-liquid critical lines for the three models. These lines intersect the three-phase lines at a lower critical end-point. The n-hexane + polyethylene system, when characterized as a binary mixture, is apparently type IV or type V in the general classification scheme for critical behavior.

The three-phase lines from the EOS models are very close to the n-hexane vapor pressure curves produced by these models and differ from each other because the vapor



Figure 6.19. Calculated three-phase and critical lines. Comparison with data of Kennis (1988).

pressure predictions differ. The Kennis (1988) data lie above the n-hexane vapor pressure curve; the probable cause for the difference being that the polymer is polydisperse, not monodisperse as is assumed in the EOS calculations.

The three-phase lines in Figure (6.19) locate the boundary between vapor-liquid equilibrium (below the line) and liquid-liquid equilibria (above the line). Metastable vapor-liquid equilibria can be calculated at pressures above the line. Similarly, metastable liquid-liquid separations can be calculated at pressure below the critical end-point pressure. Calculations must be done with caution to avoid accepting these metastable states as the true equilibrium.

Figure (6.20) shows the three-phase cloud point temperature against the mass fraction of polymer in the liquid phases. The three models and the Kennis (1988) data have very nearly the same critical end-point temperature (where the two liquid phases in equilibrium with the n-hexane rich vapor are critical), principally because the hexane/polymer interaction parameters were fitted to a low pressure critical temperature. The compositions of the polymer-rich liquid phases, as given by the models, deviate from the Kennis (1988) data at the lower temperatures. The MFLG model and the PHSC model are somewhat better than the Sanchez-Lacombe model in this regard. The polymer mass fraction at the minimum three-phase temperature in the Kennis (1988) data is somewhat uncertain but appears to be at a considerably lower value than is given by any of the models. This character may also be due to the polydisperse nature of the polymer. Overall, the three models represent these complex phenomena reasonably.



Figure 6.20. Liquid phase compositions and temperature along the three-phase lines. Comparison with data of Kennis (1988).

# 6.3.1.2 Equilibrium Calculation Methods

We used flash calculations to obtain the various cloud-point lines and the threephase conditions. That was possible because the polyethylene was treated as a monodisperse polymer with a number average molar mass of 8000, following the treatment of Kennis et al. (1990).

These calculations were problematic for more than one reason. Problems arise due to the extreme asymmetry in the vapor-liquid equilibria and are compounded by the large differences in the molar masses of the polymer and solvent. Extremely small fugacities and mole fractions for the polymer must be calculated, particularly in a solventrich vapor-like phase. In some cases, the numbers pass the "underflow" limits of typical computers.

Using the Sanchez-Lacombe equation, it was possible to obtain convergence of the flash calculations requiring equality of the chemical potentials, even of the polymer, in all the phases. This was true even though the mole fractions of the polymer fell to the order of  $10^{-200}$ . With the other two equations, however, underflow would occur in the mole fraction of polymer in the vapor. This problem was dealt with by freezing the equilibrium ratio ( $K \equiv y/x$ ) whenever the polymer mole fraction became lower than  $10^{-75}$ . The difference in chemical potential between the phases was then dropped from the convergence criterion.

A different kind of numerical problem is that the successive substitution algorithm itself can become oscillatory and divergent. The analysis of Heidemann and Michelsen (1995) show that this kind of instability of successive substitution can occur whenever any of the equilibrium phases shows strong negative departures from ideality. In successive substitution procedures, ratios of mole fractions (K factors) are used in an inner loop to find phase amounts and mole fractions. The K factors are updated in an outer loop until conditions of equal chemical potentials in all coexisting phases are reached. Heidemann and Michelsen (1995) suggested a simple "damping" procedure in the K factor updating algorithm that would result in a convergent process.

For binary systems around critical points (including the n-hexane/polyethylene systems at temperature just above the LCST) damping proves unnecessary and monotonic convergence to a solution is possible, even if slow. These conclusions also follow from the Heidemann and Michelsen (1995) analysis. A consequence is that VLE and LLE computations can behave differently. Away from critical points the behaviors are dictated by the negative deviations in the liquid phases.

Most of the calculations done involved looking only for two-phase VLE or LLE equilibrium. For VLE, the hexane-rich phase was assigned the larger of two volume roots from the equation of state (if two could be found). For LLE, liquid-like volume roots were used for both phases. The *K*-value updating scheme employed is;

$$\ln K_i^{k+1} = \ln K_i^k - \frac{1}{m} \left( \frac{\mu_i^{II}}{RT} - \frac{\mu_i^{I}}{RT} \right)^k$$
(6.6)

where *m* is the "damping factor" needed to obtain a convergent process.

For multi-phase calculations, we employed a slight modification of a scheme presented by Abdel-Ghani (1995) and Abdel-Ghani et al. (1994). There are possibly many phases, each with its own set of K-factors defined as  $K_{ij} = x_{ij} / \hat{x}_i$ . The reference mole fraction is arbitrary but could be the composition of the mixture being flashed; i.e.,  $\hat{x}_i = z_i$ . The inner loop calculates phase amounts and mole fractions consistent with the mass balances, using an algorithm based on a proposal by Michelsen (1994).

This inner loop algorithm is quite robust and capable of returning the mole fractions of any number of phases, including some that might have zero amounts in the mixture. (The amount of phase j is  $\beta_j$ .) Within the subroutine, the normalizing factors for the mole fractions in the phases are calculated,  $\sum_{i} X_{ij}$ . When the phase amount is

zero  $(\beta_i = 0)$ , then the normalizing factor is less than 1.0 ( $\sum_i X_{ij} < 1$ ).

In the outer loop, the equilibrium ratios are updated through;

$$\ln K_{ij}^{k+1} = \ln K_{ij}^{k} - \frac{1}{m} \left( \frac{\mu_{ij}}{RT} - \frac{\hat{\mu}_{i}}{RT} - \ln \sum_{i} X_{ij} \right)$$
(6.7)

In this equation, the reference chemical potential is calculated as a weighted average in the phases present; i.e.,  $\hat{\mu}_i = \sum_j \beta_j \mu_{ij}$ . The compositions of phases not present, once the

outer loop has converged, locate phases that lie above the plane tangent to the Gibbs free energy surface that defines the multiphase equilibrium. The tangent plane distance is, in fact, a minimum at these compositions. Equation (6.7) may look unfamiliar but it follows directly from the "tangent plane stability test" proposed by Michelsen (1982). It has been modified here by inclusion of the damping factor, m, which is needed to obtain convergence.

Table (6.8) and Table (6.9). demonstrate the effect of m on the iteration count at different temperatures in VLE and LLE calculations, respectively, using the two-phase algorithm and equation (6.6). (As noted, when a mole fraction for substance i was less than  $10^{-75}$ , the  $K_i$  value was not changed.) These results are for the Sanchez-Lacombe EOS at a pressure of 6 bar with a feed at the LCST composition of four mass percent polymer. If a specified maximum iteration count was exceeded, then either the calculations were oscillatory non-convergent or the damping factor was too large.

Table (6.8), for VLE calculations, shows that as m is decreased from 30 to 20 the iteration count decreases as expected. In this region of the Table, the actual number of iterations shown is quite small, mainly because the K value for the polyethylene becomes fixed after a few iterations and the polymer chemical potential difference between the two phases does not enter the convergence criterion. For smaller damping factors the iteration count shows an increase, again suggesting the occurrence of oscillations in computations. For a value of 11 for m, at the higher temperatures shown, the maximum iteration count is exceeded and the calculations fail to converge.

m=30	<i>m</i> =20	m=15	<b>m=</b> 13	m=11
T (C) I.C.	T (Ĉ) I.C.	Т(С) І.С.	Т (С) І.С.	T (C) I.C.
150.00 15	150.00 10	150.00 17	150.00 35	150.00 20001
149.00 15	149.00 10	149.00 17	149.00 33	149.00 20001
148.00 15	148.00 10	148.00 17	148.00 26	148.00 20001
146.00 15	146.00 10	146.00 17	146.00 28	146.00 20001
146.00 15	146.00 10	146.00 16	146.00 27	146.00 446
145.00 14	145.00 10	145.00 15	145.00 25	145.00 128
144.00 14	144.00 10	144.00 13	144.00 22	144.00 68
143.00 14	143.00 10	143.00 11	143.00 18	143.00 44
142.00 16	142.00 10	142.00 8	142.00 14	142.00 28
141.00 18	141.00 10	141.00 8	141.00 9	141.00 17
140.00 22	140.00 13	140.00 8	140.00 7	140.00 9
139.00 37	139.00 24	139.00 17	139.00 14	139.00 11

Table 6.8. Iteration Count with Various Damping Factors. VLE Calculations.

The iteration counts for LLE calculations are shown in Table (6.9). In all these calculations, the polymer mole fractions in the two phases are of similar orders of magnitude and the polymer chemical potentials are driven toward equality. Table (6.9) shows, as is expected, that damping is not required at temperatures near the LCST but, rather, retards convergence. However, away from the LCST there is an optimum value for m that minimizes the number of iterations required for convergence.

Tables (6.8) and (6.9) show that the optimum value of m is a function of temperature, pressure and composition. The optimization of m is a problem that needs to be addressed in order to have an efficient algorithm for these kinds of equilibrium computations. Heidemann and Michelsen (1995) have suggested alternatives to successive substitution for systems where successive substitution can become unstable. Chen, et al. (1993) propose a Newton-Raphson scheme for LLE equilibria in polymer/solvent systems.

<b>m=</b> 30	<i>m</i> =20	<i>m</i> =10	m=5	<i>m</i> ≈1
T(C) I.C.	T(C) I.C.	Г (C) І.С.	Т(С) І.С.	Г (С) І.С.
150.00 548	150.00 364	150.00 180	150.00 87	150.00 20001
148.00 564	148.00 374	148.00 185	148.00 90	148.00 20001
146.00 585	146.00 389	146.00 192	146.00 94	146.00 20001
144.00 613	144.00 407	144.00 202	144.00 99	144.00 20001
142.00 651	142.00 433	142.00 214	142.00 105	142.00 20001
140.00 703	140.00 467	140.00 232	140.00 114	140.00 155
138.00 777	138.00 516	138.00 256	138.00 126	138.00 30
136.00 886	136.00 589	136.00 293	136.00 144	136.00 25
134.00 1062	134.00 707	134.00 352	134.00 174	<b>134.0</b> 0 31
132.00 1389	132.00 925	132.00 461	132.00 229	132.00 43
130.00 2219	130.00 1478	130.00 738	130.00 367	130.00 71
128.00 13100	128.00 8733	128.00 4366	128.00 2182	128.00 436

Table 6.9. Iteration Count with Various Damping Factors. LLE Calculations.

The three-phase temperature was located using a modification of the algorithm proposed by Abdel-Ghani et al. (1994) that was described above. Flash calculations were initiated with four phases; i.e., a hexane-rich vapor, a hexane-rich liquid, the feed composition (4.0 mass percent polymer) as a liquid, and a polymer-rich liquid. At temperatures near the three-phase condition, a solution was found with two phases in finite amounts and a third (incipient) phase with  $\sum_{i} X_{ij} < 1$ . The three-phase temperature was the unique temperature (at 6 bar) where  $\sum_{i} X_{ij} = 1$  for three phases. Equality of chemical potentials was obtained for both the polymer and the n-hexane in all three phases in these calculations with the Sanchez-Lacombe equation.

Figure (6.21) is a blown up version of Figure (6.18) with emphasis on the hexane rich region. In Figure (6.21) the relation between metastable equilibrium, minimum



Figure 6.21. Calculated VLE, LLE, metastable VLE and LLE, and the three-phase line from Sanchez-Lacombe EOS. Also shown is the minimum tangent plane phase composition.

tangent plane phase composition (Michelsen, 1982) and the spinodal is shown. Our calculations show the expected behavior that, in general, both the metastable VLE and the minimum tangent plane phase compositions can be extended to the spinodal but no further. These characteristics indicate that computations looking for three-phase equilibria have to be performed with care.

# 6.3.2 Polydisperse polyethylene

Koningsveld and Staverman (1968), Solc (1970) and Kang and Sandler (1988) among others have shown that the polydisperse nature of the polymer can have a significant effect on phase equilibrium computations for polymer-solvent systems. These authors used various activity coefficient models for their phase equilibrium computations at low pressure. In this work the effect of the polydispersivity of polyethylene was investigated on the phase behaviour of the n-hexane + polyethylene system. The Sanchez-Lacombe equation of state was chosen for this investigation because of its relative simplicity and as shown above, its ability to give a satisfactory qualitative representation of the data when the polymer is treated as monodisperse. The polyethylene was chraracterised employing the method discussed in section 4.5 of Chapter 4. The molar mass distribution of the polymer was assumed to follow the log-normal distribution.

# 6.3.2.1 Characterisation of polyethylene

The polyethylene sample used by Kennis et al. (1990) had experimental  $M_w$  and  $M_n$  of 177,000 g/mol and 8000 g/mol respectively which give a polydispersivity index of 22.125. These values were used for estimating the parameters of the distribution function ( $\beta = 2.489$  and  $M_o = 1700.78$ ). With a choice of ten pseudocomponents for the polymer the calculated  $M_w$  and  $M_n$  were 176,089 g/mol and 8000 g/mol respectively. Since the calculated numbers give a good representation of the experimental values the number of pseudocomponents was assumed to be sufficient. The mole fractions, weight fractions and the molar masses of the ten pseudocomponents are reported in Table (6.10).

Table 6.10. Characterisation of Polyethylene into Pseudocomponents.					
mole fraction	weight fraction	molar mass			
0.43106526E-05	0.17711912E-09	0.32870960E+00			
0.75807093E-03	0.29502981E-06	0.31134796E+01			
0.19111581E-01	0.51311335E-04	0.21478635E+02			
0.13548370E+00	0.21830609E-02	0.12890470E+03			
0.34464233E+00	0.31211579E-01	0.72449782E+03			
0.34464233E+00	0.17200389E+00	0.39926350E+04			
0.13548370E+00	0.38003627E+00	0.22440263E+05			
0.19111581E-01	0.32173378E+00	0.13467594E+06			
0.75807093E-03	0.88038079E-01	0.92907479E+06			
0.43106526E-05	0.47417360E-02	0.88000331E+07			

While doing computations for the polydisperse polymer, the first three pseudocomponents were left out as their molar masses are unrealistically small. The seven remaining weight fractions were then normalized and used with the corresponding molar masses. The weight- and number-average molar masses obtained in this way were 176098 and 8162, respectively, which is a fairly good representation of the experimental values of these quantities.

# 6.3.2.2 Cloud point curves for the polydisperse case

The cloud points were calculated using the scheme described in section 4.3 of Chapter 4. In this scheme the non-linear equilibrium equations are solved by a Newton method.

Figure (6.22) shows the calculated cloud point curve for the system polyethylene and n-hexane at 6 bar. The solid curve is the cloud point curve or, in other words, the phase boundary. The dotted curve is the locus of equilibrium incipient phases, also called the shadowpoint curve. The parameters used for generating this figure were the same as that for the monodisperse case. The same binary interaction parameter was used for nhexane and all segments of polyethylene, i.e.,  $k_{ij}$  was set at -0.04144 irrespective of chain length. Figure (6.22) in comparison with Figure (6.16) shows that the lowest point on the cloud point curve is moved to a much lower temperature, approximately 97 °C, and it is very close to the temperature axis.

An interesting feature is the location of the critical point and the nature of the cloud point curve in the vicinity of the critical point. Figure (6.23) is a blown up version of Figure (6.22) highlighting the cloudpoint curve in the vicinity of the model critical point. The cloud-point curve shows a cusp with metastable branches. The point on the outside where the two cloud point curves intersect is a three phase point where three



Figure 6.22. Cloud and shadow point curves from Sanchez-Lacombe EOS for the system n-hexane + HDPE.  $k_{ij} = -0.04144$ . P = 6 bar.



Figure 6.23. Cloud and shadow point curves from Sanchez-Lacombe EOS for the system n-hexane + HDPE in the vicinity of the critical point.  $k_{ij} = -0.04144$ . P = 6 bar.

liquid phases are in equilibrium. The critical point is no longer the lowest point on the phase boundary, as would be the case for a binary system. Rather, it is located on the right hand tip of the cusp of the cloud point curve and is unstable in nature. Solc (1970) reports similar results for calculations with a Flory-Huggins type activity coefficient model when the molar mass distribution of the polymer is chosen to be log-normal.

In order to get a better quantitative representation of the data, the binary interaction parameter, k<sub>ii</sub>, was re-estimated. This was done, as for the monodisperse case, by roughly fitting the spinodal to the lowest temperature on the experimental cloud point curve at 6 bar. Note, the same k<sub>ii</sub> was used to characterise the interactions between the solvent and all fractions of polyethylene and the pure component parameters used were the same as before. The new estimated  $k_{ii}$  was -0.1297. The calculated cloud point curves, spinodals and experimental data are contained in Figure (6.24) for this system. Figure (6.24) retains the same features as Figure (6.22) but the results are quantitatively far superior. The calculated results are fairly satisfactory vis a vis the experimental data. It is obvious that the lowest temperature on the experimental curves is missed at higher pressures, but the slopes of the calculated curves are similar to the experimental curves. Also, the match between the compositions for the lowest temperatures on the calculated spinodals and experimental cloud point curves is better. Note that this is definitely not the case for the monodisperse calculations as shown in Figure (6.16). Hence, with one adjustable parameter fitted to one experimental temperature, significant quantitative improvement results when the polydisperse nature of the polymer is taken into account in



Figure 6.24. Cloud point curves and spinodals from Sanchez-Lacombe EOS for the system n-hexane + HDPE.  $k_{ij} = -0.1297$ . Data Kennis (1990).

phase boundary calculations. However, there is the added complication of the type of complex behaviour shown in detail in Figure (6.22). It is possible that this a consequence of the type of molar mass distribution employed to discretize the polymer.

#### 6.4 Polystyrene ( $M_N = 29100$ ) + methylcyclohexane system

The phase behavior of the system polystyrene (29100) + methylcyclohexane proved to be difficult to correlate with any of the models employed in this work. Some attempts at correlating this set of data are presented. The models used were the Sanchez-Lacombe and PHSC equations of state as in this case it was possible to get a qualitative representation of the data. It is possible that the modification employed for the Sanchez-Lacombe equation of state may yield at least qualitatively correct phase behavior for the MFLG model. However, this approach was not explored as there are already a fairly large number of model parameters.

The fit with the Sanchez-Lacombe equation of state is shown in Figure (6.25). The polystyrene parameters are contained in Table (6.11). The methylcyclohexane parameters are contained in Table (6.1). The calculated cloud point curves are narrow and the critical compositions are lower than the experimental values. In order to get the fit shown in Figure (6.25) an empirical modification had to be made to the attractive term as given by

d (polymer in the attractive term) = 
$$d \bullet \zeta$$
 (6.8)



Figure 6.25. Isobars for the system Polystyrene(29100)/Methylcyclohexane. Pressure (MPa): (+) 1, (+) 2, ( $\Delta$ ) 5, (O) 10, ( $\blacktriangle$ ) 14. (---) Sanchez-Lacombe EOS, P =1 MPa. (---) Sanchez-Lacombe EOS, P = 10 Mpa.

This was done following the suggestion of Song et al. (1996) and Hino et al. (1996) for the PHSC equation of state. The value of  $\zeta_1$  (for the solvent ) was set at unity and, for the polymer  $\zeta_2 = 0.7389$  was obtained by fitting the upper critical solution temperature at 10 bar.  $k_{ij}$  was set at zero. A modification of this kind is equivalent to changing the energy parameter for the polymer. The polymer density obtained from this modification will not be the same as that to which the model parameters were originally fitted and it is in fact smaller in magnitude.

#### Table 6.11. Polystyrene parameters.

Sanchez-Lacombe (Sanchez and Lacombe, 1978) 735 ε (K) đ 1540  $v (cm^3/mol)$ 17.1 PHSC (Lambert et al., 1995) 546.207 r  $\sigma$  (A°) 4.336 253.7  $\epsilon/k_{\rm B}({\rm K})$  $k_{ii} = 0.01582$ 

Kiran and coworkers (Kiran, 1994) report that, in order to correlate high pressure behavior of polyethylene + n-pentane system with the Sanchez-Lacombe model, they had to alter the polymer parameters. They used a smaller interaction energy parameter in order to correlate their data with a non-zero  $k_{ij}$ . Their approach is equivalent to the one used here. Wang et al. (1996) report correlation results using the Sanchez-Lacombe equation of state for the system polystyrene + acetone. The experimental data shows

simultaneous occurrence of LCST and UCST type behavior. These researchers used the original pure component parameters as reported by Sanchez and Lacombe (1976, 1978). The data were correlated with the use of a binary interaction parameter  $(k_{12})$  alone. For LCST type behavior, they found that the minimum temperatures are in the right region for the isobar fitted. However, the critical compositions are smaller than the experimental values and the calculated spinodal curves appear to be narrower. Wang et al. (1996) did not calculate the binodals for the Sanchez-Lacombe model. Also, the pressure dependence of LCST temperatures is too small. The UCST spinodal curve calculated by Wang et al. (1996) for the polystyrene + acetone system is approximately 100° C lower than the experimental values. The curves appear to be narrower than the experimental data and are shifted to lower compositions. Similar results were obtained by Wang et al. (1996) for the system polystyrene + n-hexane. This system also showed simultaneous occurrence of UCST and LCST type phase behavior. For the system polyisobutylene + n-pentane. Wang et al. report satisfactory correlation of LCST behavior with the Sanchezlacombe model. It is to be noted that the energy and volume parameters reported by Wang et al. (1996) for the Sanchez-Lacombe equation of state are interchanged. It is assumed in this discussion that the correct parameters were used in the calculations.

Figure (6.26) shows a comparison of the experimental data and calculations from the PHSC equation of state for the system polystyrene(29100) + methylcyclohexane. The parameters were obtained from the paper of Lambert et al. (1995). The polystyrene parameters are contained in Table (6.11). The methylcyclohexane parameters are the



<u>т (</u>к)

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same as reported by Song et al. (1996) and are contained in Table (6.3). Lambert et al. (1995) argue that a quantitative correlation of liquid-liquid equilibrium data with polymer parameters obtained from polymer PVT data has been largely unsuccessful regardless of the model used. These researchers obtained polystyrene parameters by fitting these to low pressure LCST and UCST data for a number of polystyrene + methylcyclohexane systems. Calculations in Figure (6.26) with these parameters show that the critical compositions are lower than the experimental values. Also, the model gives the wrong pressure dependence as the 10 MPa cloud point curve lies above the 1 MPa curve. For the record, it is to be noted that by using the original polystyrene parameters as reported by Song et al. (1996), and the modification given by equation (6.8), it is possible to get qualitatively correct phase behavior for the system polystyrene(29100) + methylcyclohexane.

Hino et al. (1996) have compared theoretical coexistence curves from the PHSC model with the experimental coexistence curves for the systems polystyrene + methylcyclohexane at low pressures. These authors employed the modification given by equation (6.8) [ $\zeta = 0.771$ ,  $k_{ij} = 0.0216$ ]. The calculated UCST binodals are narrower than the experimental binodals. Also, the critical compositions are much smaller than experimental values. They report a similar trend for LCST binodals.

Beckman et al. (1990), in their conclusions, mention that for the MFLG model, use of modifications to account for non-randomness of mixing may improve the description of phase behavior for systems such as polystyrene + cyclohexane and polystyrene + toluene. The accurate modeling of both the solvent-rich and polymer-rich phases remains a problem. Beckman et al. (1990) do not show any results for these systems but refer to the Ph.D. thesis of Beckman (1988). It seems from the paper of Beckman et al. (1990) though, that these authors obtained polystyrene parameters by fitting polystyrene density data.

It is apparent from the results obtained in this work and the work of other research groups that solutions of polystyrene are difficult to correlate irrespective of which equation of state is used.

The Chapter is concluded with an observation regarding the success of Wang et al. (1996) in correlating simultaneous LCST and UCST phase behavior for the system polystyrene + acetone with the Panayiotou and Vera (1982) version of a lattice-fluid model. Although the fit for this system is not excellent, the model is able to give a semiquantitative fit to data with one binary interaction parameter. It is to be noted that Wang et al. (1996) obtained the polymer parameters from functional group parameters which in turn were obtained by fitting vapor pressures and saturated liquid densities for low molar mass compounds. Perhaps a group-contribution approach followed by Wang et al. (1996) is better for estimating polymer parameters than fitting polymer densities. However, at the same time, the results of Wang et al. (1996) for this one system show that the pressure dependence of LCST and UCST phase behaviors is quite inadequate. The model results show only very little dependence on pressure.

#### **CHAPTER 7**

#### Conclusions

### 7.0 Introduction

Significant progress has been made in the equation of state modeling of polymer solution phase behavior. Equations of state such as the Sanchez-Lacombe model (Sanchez and Lacombe, 1976), the Kleintjens-Koningsveld model (Kleintjens and Koningsveld, 1980), the Panayiotou-Vera model (Panayiotou and Vera, 1982), the PHSC model (Song et al., 1994a) and the SAFT model (Chapman et al., 1990; Huang and Radosz, 1990), to name the prominent ones, are available for the correlation and/or prediction of phase behavior in mixtures containing both small and large molecules.

### 7.1 Pure component behavior

The models used in this work have been shown to be capable of modeling the phase behavior of small molecule systems. The results are perhaps not as good as those from cubic equations of state [ Soave-Redlich-Kwong EOS (Soave, 1972); Peng-Robinson EOS (Peng and Robinson, 1976); Trebble-Bishnoi-Salim EOS (Salim, 1990)], but show promise. It has been claimed (Song et al., 1994a) that the cubic equations of state are not applicable to polymeric systems.

The quantitative agreement between data and theory can perhaps be made better by small modifications, such as modifying the temperature dependence of the attractive term. For instance, the Sanchez-Lacombe model has no explicit temperature dependence in the attractive part.

# 7.2 Polymer Solutions

The results for polymer solutions are mixed. For the polyethylene + n-hexane system examined, the models gave a fairly satisfactory representation of complex phase behavior. The results for the polystyrene + methylcyclohexane system are not as good and only a qualitative representation of the data was obtained. This could be a difficult system as discussed in the final section of the previous Chapter. Also, it is possible, as pointed out by Lambert et al. (1995) and Hino et al. (1996), that this may be a consequence of the polymer parameters. This raises an important question regarding the methodology employed to obtain polymer parameters.

Usually the polymer parameters are obtained by fitting the polymer density data. However, there are indications that perhaps this is not the best way of estimating polymer parameters. The experience in this work (also that of Hino et al., 1996) was that the polymer parameters so obtained can sometimes push the LCST branch to much lower temperatures and an agreement between the theoretical and experimental curves cannot be obtained by the use of a binary interaction parameter alone. However, it cannot be said with certainty whether this is a consequence of the form of the model equation or a consequence of the methodology for estimating the polymer parameters. Also, the density data for the relevant polymer sample is not always available. Wang et al. (1996) and Lee and Danner (1996) have had considerable success at correlating and/or predicting phase behavior of polymer mixtures by obtaining polymer parameters by a group contributions approach, where the group parameters were obtained by fitting the VLE data of small molecule systems. These researchers employed the Panayiotou-Vera (1982) version of the lattice-fluid model. Shen et al. (1992) have used SAFT to model phase behavior of poly(ethylene-propylene) and low molar mass compound mixtures using generalized correlations to obtain polymer parameters. The parameters were correlated against molar mass for many compounds having similar structure. Their experience was that the polymer parameters obtained by fitting PVT data of PEP samples were not as reliable as those obtained from the generalized correlations.

Dohrn and Prausnitz (1990) have shown for the Carnahan-Starling hard-sphere reference equation of state (Carnahan and Starling, 1969) that, the use of a perturbation term other than the van der Waals term gives better agreement between data and theory. This line of research might be pursued to develop equations of state for polymer solutions with improved correlating powers. An alternative is to employ a shift of volume to match experimental polymer density data while fitting other parameters to mixture behavior.

# 7.3 Computational methods

The models present significant computational challenges owing to their complexity. For instance, unlike cubic equations of state, even solving for volume roots is not straightforward. In this work, some computational problems associated with the use
of these models have been addressed. It is shown that the conventional successive substitution flash calculation procedure can be made to converge with a simple modification proposed by Heidemann and Michelsen (1995). The same holds for the multiphase successive substitution procedure of Abdel-Ghani et al. (1994). A scheme is presented for doing phase boundary calculations that accounts for the polydispersivity of the polymer. The issue of polydispersivity of polymer in phase-equilibrium computations with equations of state for polymer solutions is not a well-addressed area in the literature.

#### 7.4 Experimental data

A considerable amount of pressure-temperature-composition data is available for polymer solutions and efforts are under way to generate more data by various groups around the world. Polymer solution phase behavior can be quite complex and sometimes show unexpected trends as seen for polystyrene(29100) + methylcyclohexane + carbon dioxide system in this work. At certain conditions of pressure, temperature and composition the solubility of polystyrene was higher in the mixed solvent than in either of the two solvents taken separately. Hence, the experiments have to be performed with care and the investigations have to be performed in detail so that no unexpected trends in the phase behavior are missed.

#### 7.5 Recommendations

Several possible lines of future research are suggested by the discussion in the preceding sections.

The ability of the lattice-gas and PHSC equations of state to fit pure component behavior or equilibria in mixtures of small molecules might be enhanced by modifications to the temperature dependence of parameters.

The equation of state parameters for pure polymers might be fit to the mixture data with a volume shift introduced to improve calculated liquid polymer density. Otherwise, alternatives can be sought for the perturbation terms.

The convergence behavior of the flash calculation procedures used in the thesis might be improved.

The effect of polydispersivity in phase boundary calculations requires further examination.

There is a continuing need for high quality experimental data on polymer-solvent phase behavior, particularly in regions of multiphase behavior.

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#### **APPENDIX** A

#### Phase Equilibrium and Stability

#### A.0 Introduction

In the first section of this Appendix the criteria for equilibrium in closed systems are presented. This is followed by a brief discussion regarding the fundamental equations for both open and closed systems. The subsequent section deals with conditions for equilibrium in heterogeneous systems. This is followed by a section about Tangent Plane Criterion. The Appendix A is concluded with some results regarding the limits of stability.

#### A.1 Criteria for equilibrium in closed systems

The first law of thermodynamics for a closed system, i.e. a system that does not exchange mass with the surroundings, is (Moore, 1972)

$$\Delta U = Q + W \tag{A.1}$$

 $\Delta U$  is the change in the internal energy of the system. Q and W refer to the heat and work transfer across the boundaries of the system respectively. The heat and work transferred into the system are considered positive quantities and vice-versa. The differential form of the first law is

$$dU = dQ + dW \tag{A.2}$$

If the work involved is only of the form PdV, where P and V are pressure and total volume respectively, then this equation can be expressed as

$$dU = dQ - PdV \tag{A.3}$$

-PdV is the work done on the system.

A statement of the second law is the inequality of Clausius (Moore, 1972) given by

$$dS \ge dQ / T$$
, or,  $dQ \le TdS$  (A.4)

S is the entropy and T is the temperature. The equality holds for a reversible process.

Combining equation (A.3) and inequality (A.4) we get

$$dU \le TdS - PdV \tag{A.5}$$

If the total volume and the total entropy are held constant

$$(\mathrm{dU})_{\mathrm{S},\mathrm{V}} \le 0 \tag{A.6}$$

Therefore at constant total S and V, for any change in the variables of the closed system the internal energy decreases and the equilibrium corresponds to the state of the lowest value of internal energy. Hence, the equilibrium condition in terms of a virtual displacement from equilibrium  $\delta U$  becomes

$$(\delta U)_{s,v} \ge 0 \tag{A.7}$$

The equilibrium criterion can be expressed in terms of enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G) as given below (Moore, 1972).

The enthalpy is defined as

$$\mathbf{H} = \mathbf{U} + \mathbf{P}\mathbf{V} \tag{A.8}$$

The equilibrium condition in terms of a virtual displacement from equilibrium  $\delta H$  is

$$(\delta H)_{S,P} \ge 0 \tag{A.9}$$

The Helmholtz energy is defined as

$$A = U - TS \tag{A.10}$$

The equilibrium condition in terms of a virtual displacement in this case is

$$(\delta A)_{T,V} \ge 0 \tag{A.11}$$

The Gibbs free energy is defined as

$$G = H - TS \tag{A.12}$$

The equilibrium criterion in terms of G is

$$(\delta G)_{\mathsf{T},\mathsf{P}} \ge 0 \tag{A.13}$$

## A.2 Fundamental equations

Assuming that dQ = TdS, i.e. the processes involved are reversible, the fundamental equations for a closed system are

$$dU = TdS - PdV \tag{A.14}$$

$$\mathbf{dH} = \mathbf{T}\mathbf{dS} + \mathbf{V}\mathbf{dP} \tag{A.15}$$

$$dA = -SdT - PdV \tag{A.16}$$

$$dG = -SdT + VdP \tag{A.17}$$

These equations are fundamental equations because all the thermodynamic information can be obtained from each one of them. For instance,

$$\mathbf{P} = -\left(\frac{\partial \mathbf{A}}{\partial \mathbf{V}}\right)_{\mathrm{T}} \tag{A.18}$$

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Equation (A.14) contains all the information obtained from basic laws. Equations (A.15-A.17) are derived from it and contain no new information. However, one of these equations maybe more convenient to work with than others depending on the application. For instance, while working with an equation of state model it is convenient to work with the fundamental equation in terms of A.

A closed system at equilibrium may be homogeneous or heterogeneous. That is, the system may comprise of one phase or the system content maybe distributed among a number of homogeneous phases. For each of the homogeneous phases the mole numbers of various components present are variables. In this section equations are developed for U, H, A and G that account for the variability of composition. The treatment here is very brief and the reader is referred to Denbigh (1981) for a comprehensive discussion.

Consider a homogeneous phase with nc components. U for the phase can be expressed as

$$U = U(S, V, n_1, n_2, ...., n_{nc})$$
(A.19)

where,  $n_1$ ,  $n_2$ ,...,  $n_{nc}$  are the mole numbers of the components present. The total differential of U is

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{nc} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_i} dn_i$$
(A.20)

For constant amounts

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$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_1}$$
(A.21)

and

$$\mathbf{P} = -\left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}}\right)_{\mathbf{S},\mathbf{n}_{i}} \tag{A.22}$$

and defining  $\mu_i$  as

$$\mu_{i} = \left(\frac{\partial U}{\partial n_{i}}\right)_{s, V, n_{i}}$$
(A.23)

we get

$$dU = TdS - PdV + \sum_{i=1}^{nc} \mu_i dn_i$$
 (A.24)

 $\mu_i$  is the chemical potential of component i. This is the fundamental equation for an open system. As before the fundamental equations can be derived in terms of H, A and G and are given as

$$dH = TdS + VdP + \sum \mu_i dn_i$$
 (A.25)

$$dA = -SdT - PdV + \sum \mu_i dn_i$$
 (A.26)

$$dG = -SdT + VdP + \sum \mu_i dn_i$$
 (A.27)

with

$$\mu_{i} = \left(\frac{\partial U}{\partial n_{i}}\right)_{S,V,n_{j}} = \left(\frac{\partial H}{\partial n_{i}}\right)_{S,P,n_{j}} = \left(\frac{\partial A}{\partial n_{i}}\right)_{T,V,n_{j}} = \left(\frac{\partial G}{\partial n_{i}}\right)_{T,P,n_{j}}$$
(A.28)

The definitions of the chemical potential are equivalent. Again, the use of a particular definition is a matter of convenience.

By integration of fundamental equations at constant temperature, pressure and composition it can be shown (Denbigh, 1981) that the following equations are also valid for a phase. The derivation of these equations requires the physical knowledge that the intensive variables are independent of the size of the phase, whereas, the extensive properties are directly proportional to the size of the system. Extensive properties like U, V, A etc. are homogeneous functions of order 1 (McQuarrie, 1976).

$$U = TS - PV + \sum_{i=1}^{nc} \mu_i n_i$$
 (A.29)

$$H = TS + \sum \mu_i n_i \tag{A.30}$$

$$\mathbf{A} = -\mathbf{P}\mathbf{V} + \sum \mu_i \mathbf{n}_i \tag{A.31}$$

$$G = \sum \mu_i n_i \tag{A.32}$$

This section is concluded by the derivation of the form of Gibbs-Duhem equation that relates variations in temperature, pressure and chemical potentials of the components present in the phase. The total derivative of equation (A.29) is given by

$$dU = TdS + SdT - PdV - VdP + \sum \mu_i dn_i + \sum n_i d\mu_i$$
(A.33)

The total derivative of U is also given by equation (A.24). Equating right hand sides of equations (A.29) and (A.24) we get the desired form of Gibbs-Duhem equation given below.

$$SdT - VdP + \sum n_i d\mu_i = 0$$
 (A.34)

#### A.3 Conditions for equilibrium in heterogeneous systems

The conditions for equilibrium in heterogeneous systems will be developed using the criterion given in the inequality (A.7). As mentioned above, this criterion states that when the total entropy and volume of the system are held constant, equilibrium is the state corresponding to the lowest possible value of the internal energy.

We assume that the system content associates itself into homogeneous masses or phases and that no reactions take place in the system. In other words the total number of moles of each species is conserved. Each of the phases is described by an internal energy function of the form

$$U_{i} = U_{i}(S_{i}, V_{i}, n_{1}, n_{2},...)$$
 (A.35)

The internal energy of the system as a whole has to be minimized with respect to the constraints of constant total volume, constant total entropy, constant moles of each species. This can be done with the method of Lagrangian multipliers. The Lagrangian function for the system is

$$L = \sum_{j=1}^{x} U_j(S_j, V_j, n_{ij}) - \hat{T}[\sum_{j=1}^{x} S_j - S^\circ]$$

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$$+\hat{P}[\sum_{j=1}^{\pi} V_{j} - V^{\circ}] - \sum_{i=1}^{n_{c}} \hat{\mu}_{i} [\sum_{j=1}^{\pi} n_{ij} - n_{i}^{\circ}]$$
(A.36)

 $\hat{T}$ ,  $\hat{P}$  and the set of  $\hat{\mu}_i$  are the Lagrangian multipliers.  $\pi$  is the number of phases. The conditions for a stationary point of the total internal energy are:

$$\frac{\partial \mathbf{L}}{\partial \mathbf{V}_{j}} = \left(\frac{\partial \mathbf{U}_{j}}{\partial \mathbf{V}_{j}}\right) + \hat{\mathbf{P}} = -\mathbf{P}_{j} + \hat{\mathbf{P}} = 0 \tag{A.37}$$

οг,

$$P_1 = P_2 = \dots = P_n = \hat{P}$$
 (A.38)

This is the condition for mechanical equilibrium, i.e. the pressures in all the phases are equal.

$$\frac{\partial L}{\partial S_{j}} = \left(\frac{\partial U_{j}}{\partial S_{j}}\right) - \hat{T} = -T_{j} + \hat{T} = 0$$
(A.39)

or,

$$T_1 = T_2 = \dots = T_{\pi} = \hat{T}$$
 (A.40)

This is the condition for thermal equilibrium, i.e. the temperatures in all the phases are equal.

And,

$$\frac{\partial L}{\partial n_{ij}} = \left(\frac{\partial U_j}{\partial n_{ij}}\right) - \hat{\mu}_i = \mu_{ij} - \hat{\mu}_i = 0$$
(A.41)

or, for every phase j where the species i is present

$$\mu_{ij} = \hat{\mu}_i \tag{A.42}$$

This is the condition for diffusional equilibrium. The chemical potentials of component i in each phase are equal.

#### A.4 Tangent Plane criterion

In this section the Tangent Plane Criterion of Gibbs (Gibbs, 1961) is derived and its geometrical significance is briefly discussed. The derivation presented here is due to Michelsen (1982).

At a given temperature ( $T^{o}$ ) and pressure ( $P^{o}$ ) consider a n component phase with mole numbers ( $n_1, n_2, ..., n_n$ ). The Gibbs energy of this phase is

$$G^{\circ} = \sum n_i \mu_i^{\circ} \tag{A.43}$$

Consider the divison of this mixture into two phases k and j with mole numbers  $(n_1-\delta n_1, n_2-\delta n_2,..., n_n-\delta n_n)$  and  $(\delta n_1, \delta n_2,..., \delta n_n)$  respectively. The amount of phase j ( $\delta n$ ) is infinitesimal. The change in Gibbs energy is given by

$$\Delta G = G^{k} + G^{j} - G^{o} \tag{A.44}$$

A Taylor series expansion of G<sup>I</sup> to the first order terms gives

$$G(\overline{n} - \overline{\delta n}) = G(\overline{n}) - \sum \delta n_i \left(\frac{\partial G}{\partial n_i}\right)$$
(A.45)

Using this result equation (A.44) can be expressed as

$$\Delta G = \sum \delta n_i (\mu_i^j - \mu_i^\circ)$$
 (A.46)

A necessary condition for the stability of the original mixture is that this quantity be positive and this condition is expressed as

$$\mathbf{D} = \sum \delta \mathbf{n}_i (\boldsymbol{\mu}_i^j - \boldsymbol{\mu}_i^\circ) \ge 0 \tag{A.47}$$

The geometrical interpretation of this inequality is that the phase evaluated at the <sup>o</sup> point is stable with respect to phase II if the distance (tangent plane distance D) between the energy hypersurface and the tangent plane at <sup>o</sup> point is greater than zero. This is the **Tangent Plane Criterion of Gibbs**. For an equilibrium, all the equilibrium phases have the same temperature and pressure, and, the chemical potential of component i is same in all the phases. Therefore, all equilibrium phases have a common tangent plane and the equality sign holds in expression (A.47). If this expression has a negative sign for a trial phase relative to any one of the equilibrium phases, then the equilibrium is unstable and a new distribution of phases is required. A zero or positive tangent plane distance for a stable phase also implies that at the point of evaluation, the curvature of the energy hypersurface has to be positive.

This section is concluded with a brief discussion regarding a computational application of inequality (A.47) also due to Michelsen (1982).

Inequality (A.47) can be written as

$$D = \sum_{i=1}^{n_{c}} n_{ij} (\mu_{ij} - \mu_{i}^{o}) \ge 0$$
 (A.48)

where i and j are component and phase indices respectively.  $n_{ij}$  are the mole numbers in phase j. Now D will be positive for all sets of  $\{n_{ij}\}$  if it is positive at the stationary points

of D. The condition of stationarity can be obtained with the constraint  $(\sum_{i=1}^{n_{c}} n_{ij} = n_{Tj})$  by

the method of Lagrangian multipliers.

The Lagrangian in this case is

$$L = D - \theta_{j} \left( \sum_{i=1}^{n_{c}} n_{ij} - n_{\tau_{j}} \right)$$
 (A.49)

The condition of stationarity is

$$\frac{\partial L}{\partial n_{kj}} = \frac{\partial D}{\partial n_{kj}} - \theta = 0$$
 (A.50)

Now,

$$\frac{\partial D}{\partial \mathbf{n}_{kj}} = \mu_{kj} - \mu_{k}^{o} + \sum_{i=1}^{n} n_{ij} \frac{\partial \mu_{ij}}{\partial \mathbf{n}_{kj}}$$
(A.51)

The summation in this expression is zero from Gibbs-Duhem equation at constant temperature and pressure. Therefore, at a stationary point

$$\mu_{kj} - \mu_k^o = RT \ln \frac{f_{kj}}{f_k^o} = \theta_j$$
(A.52)

irrespective of the component index. At a stationary point D is given by

$$\mathbf{D} = \boldsymbol{\theta}_{j} \mathbf{n}_{\mathsf{T}j} \tag{A.53}$$

or if one is dealing with mole fractions in the phase j

$$\mathbf{D} = \boldsymbol{\theta}_{i} \tag{A.54}$$

Hence for a phase to be stable with respect to the addition of the phase j,  $\theta_j$  has to be greater than zero. If  $\theta_j=0$ , then the phase j is part of the equilibrium and a negative value of  $\theta_j$  implies instability.

## A.5 Limits of stability

This chapter is concluded with a brief discussion about the spinodal and critical points. The reader is referred to the monograph of Heidemann (1994) and the paper by Heidemann and Khalil (1980) for a comprehensive review of this topic.

We begin with inequality (A.47) written as

$$G(T^{o}, P^{o}, n_{1}, n_{2}, ...) - \sum_{i=1}^{n_{c}} n_{i} \mu_{i}^{o} \ge 0$$
 (A.55)

This inequality can also be expressed in terms of A as

$$A(T^{o}, V, n_{1}, n_{2}, ...) - \sum_{i=1}^{n_{c}} n_{i} \mu_{i}^{o} + P^{o} V \ge 0$$
 (A.56)

The stability of the ° phase is to be tested. Consider a variation around the ° point given by

$$\mathbf{n}_i = \mathbf{n}_i^\circ + \mathbf{d}\mathbf{n}_i \tag{A.57}$$

and

$$\mathbf{V} = \mathbf{V}^{\circ} + \mathbf{dV} \tag{A.58}$$

Let us work with the Gibbs free energy first. Expanding G at T<sup> $\circ$ </sup> and P<sup> $\circ$ </sup> in a Taylor series around G<sup> $\circ$ </sup> we get

$$G = \sum_{i=1}^{nc} n_i^o \mu_i^o + \sum_{i=1}^{nc} \mu_i^o dn_i + \frac{1}{2} \sum_{j=1}^{nc} \sum_{i=1}^{nc} \left( \frac{\partial^2 G}{\partial n_i \partial n_j} \right)^o dn_i dn_j$$
$$+ \frac{1}{6} \sum_{i=1}^{nc} \sum_{j=1}^{nc} \sum_{k=1}^{nc} \left( \frac{\partial^3 G}{\partial n_i \partial n_j \partial n_k} \right)^o dn_i dn_j dn_k$$
(A.59)

Substituting in inequality (A.55) from equation (A.59) we get

$$G - \sum_{i=1}^{nc} n_i \mu_i^{\circ} =$$

$$\frac{1}{2} \sum_{j=1}^{nc} \sum_{i=1}^{nc} \left( \frac{\partial^2 G}{\partial n_i \partial n_j} \right)^{\circ} dn_i dn_j + \frac{1}{6} \sum_{j=1}^{nc} \sum_{i=1}^{nc} \sum_{k=1}^{nc} \left( \frac{\partial^3 G}{\partial n_i \partial n_j \partial n_k} \right)^{\circ} dn_i dn_j dn_k + O(dn^4) \ge 0 \quad (A.60)$$

Hence, <sup>o</sup> phase is stable if the quadratic form is greater than zero. The variation for which the quadratic form (QF) is equal to zero defines the spinodal. When the quadratic form is zero, the cubic form (CF) has to be zero for a phase to be stable. This can be seen as follows. If QF=0 for a variation  $\overline{dn}$ , it is also zero for a variation  $-\overline{dn}$ . However, if CF is positive for  $\overline{dn}$ , it is negative for  $-\overline{dn}$ , and, vice-versa. A negative CF implies instability. Also, for stability, the first non-zero higher order term must be of even order and positive. The conditions CF=QF=0 along with the restrictions on higher order terms define a stable critical phase. A critical phase is a stable phase at the limit of stability.

Now some familiar results for a binary system are derived using inequality (A.55). Consider one mole of a binary mixture with the molar Gibbs free energy given by  $g=G/(n_1+n_2)$ . Let,  $x=n_1/(n_1+n_2)$  be the mole fraction of component 1. We take x as the independent composition variable. For this case (A.55) can be written as

$$g(T^{\circ}, P^{\circ}, x) - x\mu_{1}^{\circ} - (1 - x)\mu_{2}^{\circ} \ge 0$$
(A.61)

Consider a variation in x given by

$$\mathbf{x} = \mathbf{x}^{\circ} + \mathbf{d}\mathbf{x} \tag{A.62}$$

Expanding g at T<sup>o</sup> and P<sup>o</sup> in a Taylor series around g<sup>o</sup> we get

$$g = x^{\circ}\mu_{1}^{\circ} + (1 - x^{\circ})\mu_{2}^{\circ} + \left(\frac{\partial g}{\partial x}\right)^{\circ} dx + \frac{1}{2}\left(\frac{\partial^{2}g}{\partial x^{2}}\right)^{\circ} dx^{2} + \frac{1}{6}\left(\frac{\partial^{3}g}{\partial x^{3}}\right)^{\circ} dx^{3} + \dots \quad (A.63)$$

Note,

$$g = x\mu_1^{\circ} + (1 - x)\mu_2^{\circ}$$
 (A.64)

Therefore,

$$\left(\frac{\partial g}{\partial x}\right)^{\circ} = \mu_1^{\circ} - \mu_2^{\circ}$$
 (A.65)

since the summation involving the derivatives of the chemical potentials is zero from Gibbs-Duhem equation. Substituting from equations (A.63) and (A.65) in inequality (A.61) we get

$$\left(\frac{\partial g}{\partial x}\right)^{\circ} dx + \frac{1}{2} \left(\frac{\partial^2 g}{\partial x^2}\right)^{\circ} dx^2 + \frac{1}{6} \left(\frac{\partial^3 g}{\partial x^3}\right)^{\circ} dx^3 + \dots \ge 0$$
 (A.66)

Hence, for a molar binary mixture the criterion for phase stability and the spinodal is given by

$$\left(\frac{\partial^2 g}{\partial x^2}\right)^{\circ} \ge 0 \tag{A.67}$$

The greater than sign is the criterion for the stability of the <sup>o</sup> phase and the equal to sign gives the equation of the spinodal. If the quadratic form is equal to zero, then the limit of stability for the <sup>o</sup> phase, this phase being critical now, is given by

$$\left(\frac{\partial^3 g}{\partial x^3}\right)^\circ = 0 \tag{A.68}$$

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And furthermore for stability we require

$$\left(\frac{\partial^4 g}{\partial x^4}\right)^{\circ} > 0 \tag{A.69}$$

Figure (A.1) demonstrates the geometric interpretation of expressions (A.68) and (A.69) for a binary system on a molar basis. In Figure (A.1 a) the quadratic form is always greater than zero or in other words the curvature is always greater than zero and all the phases on the curve are stable. In Figure (A.1 b) the onset of instability (on an exaggerated scale) is shown. Figure (A.1 c) shows the case where two equilibrium phases are present (having a common tangent plane). Also shown in this figure are the two spinodal phases or points where the curvature or the second derivative of the G-x curve is zero. A phase located between an equilibrium phase and the spinodal phase is locally stable. A phase located between the two spinodal phases is unstable and cannot exist as a single phase.

In terms of Helmholtz free energy the Taylor series expansion gives

$$\frac{1}{2}\sum_{j=1}^{nc}\sum_{i=1}^{nc} \left(\frac{\partial^2 A}{\partial X_i \partial X_j}\right)^{\sigma} dX_i dX_j + \frac{1}{6}\sum_{j=1}^{nc}\sum_{i=1}^{nc}\sum_{k=1}^{nc} \left(\frac{\partial^3 A}{\partial X_i \partial X_j \partial X_k}\right)^{\sigma} dX_i dX_j dX_k + O(dX^4) \ge 0$$
(A.70)

where

$$\overline{\mathbf{X}} = (\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{V})^{\mathrm{T}}$$
(A.71)

Now some familiar results for a molar amount of a pure component are derived using inequality (A.70). In this case only variations in the volume are considered. So dX=dV.





Figure A.1. g-x diagram showing the onset of instability in a binary system.

Also,  $-\left(\frac{\partial A}{\partial V}\right)_{T} = P$ . Therefore, in terms of P and V the criterion for the spinodal of a

pure component is

$$\left(\frac{\partial P}{\partial V}\right)_{T} = 0 \tag{A.72}$$

This equation along with the following equation defines the critical point for a pure component.

$$\left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{V}^2}\right)_{\mathrm{T}} = 0 \tag{A.73}$$

Note that a variation of the type

$$\frac{\mathrm{dX}_{\mathrm{i}}}{\mathrm{X}_{\mathrm{i}}} = \mathrm{k}; \quad \mathrm{all}\,\mathrm{i}. \tag{A.74}$$

does not qualify as a variation in phase. This merely corresponds to an increase in the size of the phase. When working in terms of A this can be avoided by setting dV=0.

A necessary condition for a point on the spinodal is that the matrix  $\overline{Q}$  with elements  $q_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)$  (variation dV = 0) should have a zero determinant (Q=0). The

spinodal temperature for a fixed composition phase at a given pressure can be found by treating Q as a function of temperature and then solving for Q(T)=0 using Newton's method.

$$T = T - \frac{Q(T)}{Q'(T)}$$
(A.75)

The temperature derivatives of Q can be obtained numerically.

$$C = \sum_{i=1}^{nc} \sum_{j=1}^{nc} dn_i dn_j \left( \sum_{k=1}^{nc} dn_k \frac{\partial Q_{ij}}{\partial n_k} \right) = \sum_{i=1}^{nc} \sum_{j=1}^{nc} dn_i dn_j Q_{ij}^* = \overline{dn}^T \overline{\overline{Q}}^* \overline{dn}$$
(A.76)

where

$$Q_{ij}^{\bullet} = \frac{\partial Q_{ij}(\bar{n} + s\bar{dn})}{\partial s}$$
(A.77)

where s is a dummy variable.  $Q_{ij}^{*}$  is obtained by expanding  $Q_{ij}$  in a Taylor series as

$$Q_{ij}(\overline{n} + s\overline{dn}) = Q_{ij}(\overline{n}) + \sum_{k=1}^{nc} sdn_k \left(\frac{\partial Q_{ij}}{\partial n_k}\right)_{\overline{n}}$$
(A.78)

Partially differentiating with respect to s we get

$$\partial Q_{ij}(\bar{n} + s\bar{dn}) / \partial s = \sum_{k=1}^{nc} dn_k \left(\frac{\partial Q_{ij}}{\partial n_k}\right)_{\bar{n}} = Q_{ij}^*$$
 (A.79)

Use of this suggestion avoids the evaluation of the third derivative.  $Q_{ij}$  can be evaluated numerically.

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		Mass	percent Po	lystyrene	(29100)		
3.23 mass %		4.94 mass%		7.26 mass %		8.82 mass %	
T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)
299.38	1.05	301.3	1.05	302.53	1.05	303.46	1.05
298.99	3.05	301.01	2.05	302.29	2.05	303.19	2.05
298.58	5.05	300.78	3.05	302.04	3.05	302.93	3.05
298.25	7.05	300.6	4.05	301.82	4.05	302.72	4.05
297.92	9.05	300.41	5.05	301.61	5.05	302.47	5.05
297.6	11.05	300.22	6.05	301.41	6.05	302.27	6.05
297.34	13.05	300.03	7.05	301.25	7.05	302.1	7.05
		299.85	8.05	301.05	8.05	301.9	8.05
		299.68	9.05	300.88	9.05	301.79	9.05
		299.5	10.05	300.73	10.05	301.52	10.05
		299.19	12.05	300.42	12.05	301.24	12.05
		<b>298.9</b> 5	14.05	300.13	14.05	300.9	14.05

## Appendix B.1. Liquid-Liquid Equilibria in the system Polystyrene(29100)/Methylcyclohexane: P-T isopleths at given mass percent polystyrene.

## Appendix B.1 (continued).

Mass percent Polystyrene (2	291	00)
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10.97 mass %		12.81 m	mass % 15.19 mass %		nass %	18.21 mass %	
T (K)	P(MPa)	T(K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)
304.05	1.05	304.44	1.05	305.03	1.05	305.45	1.05
303.48	3.05	303.88	3.05	304.44	3.05	304.41	5.05
303.06	5.05	303.45	5.05	304	5.05	304	7.05
302.69	7.05	302.97	7.05	303.53	7.05	303.53	9.05
302.25	9.05	302.56	9.05	303.11	9.05		
301.88	11.05	302.24	11.05	302.62	11.05		
301.52	13.05	301.93	13.05	302.35	13.05		
		301.68	14.05	302.17	14.05		

Mass percent Polystyrene (29100)								
20.6 mass %		22.51	mass %	26.34 mass %				
T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)			
305.42	1.05	305.43	1.05	305.03	1.05			
304.95	3.05	304.96	3.05	304.44	3.05			
304.53	5.05	304.35	5.05	303.9	5.05			
303.89	7.05	303.91	7.05	303.51	7.05			
303.52	9.05	303.45	9.05	303.02	9.05			
303.15	11.05	303.08	11.05	302.7	11.05			
302.8	13.05	302.75	13.05	302.32	13.05			

## Appendix B.1 (continued).

## Appendix B.2. Liquid-Liquid Equilibria in the System Polystyrene(64000)/Methylcyclohexane:

P-T isopleths at given mass percent polystyrene.

2.11 mass %		3.30 mass %		5.11mass %		6.48 mass %	
T (K	P(MPa)	T(K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)
329.81	3.95	330.76	2.40	330.91	1.45	330.11	2.00
329.35	4.90	330.37	3.15	330.35	2.40	330.09	2.00
328.5	6.55	329.87	4.00	329.46	3.95	329.04	3.90
327.87	7.95	329.01	5.65	328.62	5.60	328.98	4.00
327.24	9.25	328.09	7.60	327.71	7.60	327.83	6.30
326.63	10.85	327.43	9.05	326.91	9.50	326.85	8.60
		326.35	11.80	326.23	11.30	326.37	9.75
				325.75	12.60	325.83	11.15
						325.26	12.85

## Mass percent Polystyrene

## Appendix B.2 (continued).

Mass percent Polystyrene							
9.71 m	ass %	13.60 mass %					
T (K)	$\Gamma(K) P(MPa)$		P(MPa)				
329.34	1.60	328.36	1.50				
328.59	3.05	328.29	1.60				
327.81	4.55	327.68	3.00				
327.05	6.10	327.33	3.50				
326.3	7.70	326.63	4.85				
325.47	<b>9.8</b> 0	325.86	6.55				
324. <b>8</b> 6	11.55	325.15	8.25				
		324.47	10.10				
		323.9	11.75				

## Appendix B.3. Liquid-Liquid Equilibria in the System Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>: P-T isopleths at different mass percent CO<sub>2</sub> and almost constant polystyrene concentration (4.79-5.0 mass %.).

Mass percent Polystyrene								
<b>4.95</b> 1	mass %	4.94 r	nass %	4.94 m	ass %	4.96 m	ass %	
			Mass per	cent CO <sub>2</sub>				
3.77 n	nass %	7.75 r	nass %	11.22 mass %		12.21 mass %		
T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)	T(K)	P(MPa)	
295.91	12.05	298.28	2.95	299.37	3.00	299.99	3.30	
296.4	9.75	297.38	4.45	298.28	4.30	298.16	5.45	
296.73	8.50	296.4	6.60	<b>296.7</b> 3	6.60	296.85	7.15	
296.86	8.025	295.88	7.75	295.36	8.80	295.73	8.80	
297.16	7.25	295.36	9.05	294.38	10.60	294.96	10.05	
297.55	5.40	294.84	10.40	293.52	12.35	294.14	11.50	
297.77	4.65	294.4	11.55	293.24	12.90	293.59	12.45	
298.34	2.85	294	12.90			293.07	13.55	
298.4	2.70							

# Appendix B.3 (continued).

	Mass percent Polystyrene								
4.91 mass %		4.94 п	nass %	4.79 mass %		4.95 mass %			
			Mass per	cent CO <sub>2</sub>					
14.79	mass %	18.12	mass %	20.95	mass %	21.14	mass %		
T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)		
303.92	3.25	315.8	4.60	313.3	11.65	313.3	12.55		
302.89	3.95	314.29	5.10	316.29	10. <b>6</b> 0	315.33	11.8		
301.48	5.20	311.86	6.05	319.01	9.80	318.33	10.85		
299.33	6.95	308.28	7.70	323.61	8.80	323.33	9.65		
298.4	8.00	305.83	9.05	328.91	7.95	326.28	9.1		
296.32	10.30	304.29	10.05	348.36	7.30	328.32	8.9		
295.36	11.45	302.28	11.50	354.03	7.50	330.35	8.6		
294.43	12.80	300.64	12.80	358.95	7.80	333.33	8.35		
				363.49	8.10	336.34	8.15		
				368.48	8.55	338.37	8.05		
						341.34	8		
						344.34	7.95		
						347.4	8		
						352.44	8.15		
						359.02	8.5		
						367.47	9.15		

## Appendix B.4. Liquid-Liquid Equilibria in the System Polystyrene(29100)/Methylcyclohexane/CO<sub>2</sub>: P-T isopleths at different mass percent CO<sub>2</sub> and almost constant polystyrene concentration (10.9-11.0 mass %.).

10.99 mass % 10.9 mass % 10.97 mass % 10.91 mass % Mass percent CO <sub>2</sub> 2.42 mass % 4.28 mass % 5.08 mass % 7.42 mass %		
Mass percent $CO_2$ 2.42 mass %4.28 mass %5.08 mass %7.42 mass %	6	
2.42 mass % 4.28 mass % 5.08 mass % 7.42 mass %		
	7.42 mass %	
T(K) P(MPa) T(K) P(MPa) T(K) P(MPa) T(K) P(MPa	'a)	
301.62 2.25 300.92 2.05 301.04 1.95 301.05 1.85		
301.06 4.1 300.19 4 300.41 3.45 301 1.95		
300.09 7.65 299.56 5.75 299.66 5.25 300.3 3.1		
<b>299.52</b> 10.1 <b>298.81 8.1 298.8</b> 7.6 <b>299.44</b> 4.65		
299.22 11.45 298.35 9.65 298.31 9.1 298.56 6.4		
298.98 12.65 297.85 11.5 297.68 11.15 297.44 8.85		
297.5 12.95 297.12 13.05 296.56 11.05		
295.89 12.85		

## Appendix B.4 (continued).

Mass percent Polystyrene									
10.98 mass %		10.95 mass %		10.95 mass %		10.96	mass %		
			Mass per	rcent CO <sub>2</sub>	2				
10.37	mass %	11.67	mass %	14.57	mass %	16.57	mass %		
T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)	T (K)	P(MPa)		
302.29	2.85	303.57	3.1	310.79	3.825	320.65	4.325		
301.38	4	303.17	3.5	310.28	4.075	317.06	5.325		
300.25	5.4	301.87	4.8	309.28	4.625	312.3	7.175		
299.14	7	300.72	6.2	308.35	5.175	309.34	8.625		
298.18	8.5	299.33	7.95	305.77	6.875	307.24	9.925		
297.1	10.3	297.62	10.45	303.74	8.425	305.58	11		
296.18	12.1			302.83	9.2	303.32	12.75		
				301.73	10.25				
		_		299.37	12.7				







TEST TARGET (QA-3)







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