To my parents Jesús and Marilú,
my sister Clara & my uncle Luis.
In this work, the validity of two thermodynamic models, the Sanchez-Lacombe equation of state [SL EoS] and the UNIFAC-free volume [UNIFAC-FV] activity coefficient model, in predicting the phase behaviour of polymer solutions, was analysed. For this, liquid-liquid and vapour-liquid equilibrium data were measured for polystyrene [PS] and poly(methyl methacrylate) [PMMA], in solution with a common solvent, cyclohexanol. A block and a random copolymer were also investigated in this solvent. Cloud-point curves [CPC] were measured by thermo-optical analysis using a turbidimeter, which was constructed to measure, as a function of temperature and composition, changes in transmitted light intensity through the aforementioned solutions. Measurements were carried out in solutions containing up to ~25% polymer by weight, in the temperature range 290-523K and at the solvent vapour pressure. Solvent activity coefficients were measured in the temperature range 383.15-493.15K using inverse gas chromatography. Data was collected at infinite dilution and at finite concentrations of solvent (up to ~30% by weight), the latter using the elution on a plateau technique.

The SL EoS correctly predicted the observed UCST behaviour in all systems and the molecular weight dependence of the CPCs. Quantitative agreement of the critical temperatures was achieved by fitting the binary interaction parameter \(k_{12}\); however it was not possible to simultaneously fit the critical compositions. In contrast, UNIFAC-FV fails to predict a phase-split in the PMMA or copolymer solutions and over-predicts the UCST of the PS system. Despite this, UNIFAC-FV is superior in predicting the observed decrease in solvent activity coefficients as a function of increasing temperature and solvent concentration. Finally, an enhanced solubility with respect to its homopolymers, is observed in the random copolymer, owing to increased molecular interactions. This cannot be predicted by either model.
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$a$</td>
<td>Activity</td>
</tr>
<tr>
<td>$a_{ij}$</td>
<td>Interaction parameter between groups $i$ and $j$</td>
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<td>$A$</td>
<td>Helmholtz free energy</td>
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<td>$B_{11}$</td>
<td>Second virial coefficient</td>
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<td>$c$</td>
<td>Concentration</td>
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<td>$c_i$</td>
<td>External degrees of freedom of component $i$</td>
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<td>$D_g$</td>
<td>Diffusion coefficient in gas phase</td>
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<td>Poynting factor, flowrate</td>
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<td>Partition function</td>
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<tr>
<td>$Q_k$</td>
<td>Surface area parameter for group $k$</td>
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<td>$r$</td>
<td>Number of mers (or chain segments)</td>
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<td>$R$</td>
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<td>Mole fraction of component $i$</td>
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Subscripts

A  Atmospheric
av  Average
b  Binodal
CP  Cloud-point
c  Critical
FV  Free-volume
int  Internal
kin  Kinetic
liq  Liquid
m  Molar
max  Maximum
min  Minimum
mix  Mixture
n  Number average
SL  Sanchez-Lacombe
sp  Spinodal
trans  Translational
vap  Vapour
w  Weight average

Superscripts

c  Critical
comb  Combinatorial
fv  Free volume
id  Ideal
L  Liquid
pg  Perfect gas
res  Residual
V  Vapour
Characteristic property
Pure state
Standard conditions
Saturation
Infinite dilution

Greek symbols

α  Thermal expansion coefficient
β  Isothermal compressibility
χ_{12}  Flory-Huggins interaction parameter
δ  Flexibility parameter
δ_i  Solubility parameter of component i
ε_{12}  Interaction energy between molecules of type 1 and 2
ϕ_i  Volume fraction of component i, fugacity coefficient of component i
γ  Activity coefficient (mole fraction based)
κ_{12}  Enthalpy parameter between molecules of type 1 and 2
μ  Chemical potential
π  Number of phases
θ  Flory's theta temperature
ϕ  Site fraction of molecules of type i
ρ  Density
σ  Symmetry number
τ  Film thickness
ω  Acentric factor
\( \Omega \)  Total number of configurations

\( \Omega_i \)  Weight fraction activity coefficient

\( \psi_{12} \)  Entropy parameter between molecules of type 1 and 2

\( \Gamma_k \)  Residual activity coefficient of group \( k \)
Chapter I

INTRODUCTION

1.1 — Polymers

Studies on polymers and especially on their physical properties started during the 1920's and 1930's. It was Staudinger (Staudinger, 1920) and his collaborators who established the concept of "macromolecules". After extensive work on the physical chemistry of polymers during the 1940's and 1950's, polymer solutions were examined. These were first approached by the application of the basic fundamentals of low-molecular-weight solutions. In this way, relations between chemical potential, polymer concentration and molecular weight were established. P. J. Flory (1953), E. A. Guggenheim (1952) and M. L. Huggins (1941) were very important contributors to the field. The research on polymer solution thermodynamics was further extended to vapour-liquid equilibria and it was found that polymer solutions deviate substantially from the ideal solution law used to describe small molecule systems, as embodied in Raoult's Law. Only at the very extreme of dilution where the ideal law must be approached as an asymptotic limit, do they behave close to ideality. These abnormalities motivated the development of a thermodynamic theory specific to polymer solutions.

There are several properties that differentiate polymers from "small molecules" and that need consideration when developing a theory. Firstly, unlike
small molecules that have a fixed structure and molecular formula, polymers consist of a large number of repeat units (segments) covalently bonded together to form a chain. Polymers can either be linear, where all the segments are joined to form a long continuous chain, or they can form complicated networks thereby making them fairly insoluble in common solvents. They can consist of a backbone with segments attached on only one side (isotactic), or have segments attached on both sides alternatively (syndiotactic), or have segments randomly placed on either side (atactic). Furthermore, a polymer chain may consist of two or more types of segments, forming a copolymer. Depending on the order in which the segment types are found, the copolymer is known as random, alternating or block copolymer. The difference between the latter two is that the homopolymers A and B will form either an -ABABABABA- alternating structure or an -AAABBAABBBB- block structure. Such a wide range of possible structures complicates the thermodynamic behaviour of polymer containing systems and thus thermodynamic models should be able to account the effect of structural differences on thermodynamic and physical properties. Secondly, the size of a polymer is usually much larger than that of the solvent giving rise to small and non-ideal entropies of mixing due to the fewer number of arrangements that are possible in the solution. This will influence to a great extent the thermodynamic behaviour. Thirdly, when polymers are produced as a result of a polymerisation reaction, they contain molecules of different chain lengths, i.e. a distribution of molecular weights. This polydispersity affects the phase behaviour depending on what the content of the different chain lengths is. Finally, polymers in the condensed phase can exist in three different physical states: as melts, amorphous solids or semi-crystalline solids. Depending on their state they will respond in different ways to the effect of temperature, this being observed in physical properties such as the density and the viscosity.

1.2 - Polymers in Solution

In order to understand polymer solution thermodynamics one needs to understand what happens physically when a polymer is dissolved in a small-molecular-weight solvent. Initially, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer-polymer interactions are high due
to, for example, cross-linking or strong hydrogen bonding, then this swelling is all that will occur. On the other hand, if polymer-solvent interactions are high enough then the gel will disintegrate and the polymer will dissolve into a “true” solution. Once in solution, the polymer is typically a randomly coiling mass whose conformations occupy many times the volume of its segments alone. In a thermodynamically ‘good’ solvent, the coils are extended, whereas in a ‘poor’ solvent or at a sufficiently low temperature it is possible to achieve the condition where the chains attain their unperturbed dimensions, the polymer molecules distribute themselves over the volume and they exert no net forces on one another. The temperature at which this occurs is known as the theta temperature, below which the polymer molecules will attract one another and the polymer will precipitate out. Solubility relations in polymer systems are therefore more complex than in “small molecule” systems. They are function of the size differences between solvent and polymer, the molecular weight and the topology of the polymer.

Understanding polymer solution phase behaviour is not only of importance from a purely scientific point of view, but also from a production point of view. Polymers are contained in many commercial products, from plastics to paints and coatings. Knowledge of how polymers behave in solution at different temperatures and pressures is essential during the design of polymerisation processes. Chemical engineers rely extensively on process simulation and require powerful and accurate tools for predicting physical properties. Steady-state and dynamic simulations of a process require the solution of mass and energy balances which in turn require calculation of phase equilibria, i.e. the number and composition of coexisting phases formed among the component presents. For example, liquid-liquid phase separation influences the final characteristics of the polymer products (Saraiva et al, 1995) as is the case in the production of low-density polyethylene (LDPE), where it is sometimes desirable to have a two-phase reaction that will yield a narrow molar mass distribution, giving the polymer superior film properties. Alternatively, LDPE can also be produced using the high-pressure polyethylene process where only one-phase is present, making heat removal from the highly exothermic polymerisation reaction much easier (Folie & Radosz, 1995). This high dissipation of heat is just one of the difficulties sometimes encountered in the production of polymers. Another is the high viscosities of some reaction mixtures. This is the case in some bulk chain-
polymerisation reactions. To solve this problem one could work at low conversions or alternatively a solution polymerisation process can be employed. A solvent is chosen so that both the monomer and the polymer are soluble in it. Using this method, better thermal control, lower viscosities and good mixing are achieved, the disadvantage being the cost of the solvent and its subsequent removal. The removal of the low molecular weight components left at the end of the process (any monomer, co-solvent, additives) to obtain the pure polymer or to meet health and safety regulations is normally achieved by devolatilization or steam stripping (McHugh & Guckes, 1985), although the latter is rather energy consuming. For the design of the necessary process equipment for these processes, information on vapour-liquid equilibria, i.e. solvent activities, is required (Kontogeorgis et al, 1995). Alternatively, a lower critical solution temperature (LCST) phase split could be used (Seckner et. al, 1988). Eventhough LCST's are normally high and this would also be a high energy consuming method, the temperature can be lowered with the addition of a third component, such as a supercritical fluid (Mc Hugh & Guckes, 1985; Seckner et. al, 1988; Kennis et. al, 1990). Moreover, the addition of a co-solvent can enhance polymer solubility. If the solvent is highly expanded, the addition of a dense co-solvent reduces the free volume differences between the solvent and the polymer, hence reducing the pressure of the single phase (Kirby & Mc Hugh, 1999). All these examples described require knowledge of the phase behaviour of polymer-solvent systems.

Since, it is implausible to measure all polymer/solvent systems possibly encountered, chemical engineers require good modelling tools that will replicate accurately the thermodynamic behaviour of such systems. Modelling polymer solutions is a relatively new endeavour and the task of selecting an appropriate thermodynamic method and model parameters is challenging. The phase behaviour of polymer/solvent systems can be simulated by using one of two methods: an activity coefficient model or an equation of state. The latter treats the system pressure as a function of temperature, molar density and mixture composition and all thermodynamic properties can then be derived from exact thermodynamic relations. Examples are Flory's equation of state, the Sanchez-Lacombe equation of state and the polymer version of Soave-Redlich-Kwong equation. On the other hand, activity coefficient models correct the ideal solution assumption of Raoult's Law by introducing activity coefficients. These activity coefficients are strong functions of
temperature and composition and generally not so dependent on the system pressure. Examples of polymer activity coefficient models are the well-known Flory-Huggins model or the predictive group contribution model, UNIFAC.

1.3 – Motivation and Overview of this Work

This work stems as a result of the growing need for understanding how these long chain structures behave in the presence of low-molecular weight solvents and for developing models that are able to accurately describe their behaviour. Although there is a rather large number of thermodynamic models available in the literature, no consensus exists on which one is the best for any particular system. The accuracy and validity of these theories is still to be tested on a large number of systems with respect to both liquid-liquid and vapour-liquid equilibrium data. The purpose of this work was to investigate a few polymer/solvent systems. Experimental liquid-liquid phase diagrams (cloud-point curves) as well as temperature and composition dependences of activities of a common solvent, cyclohexanol, in two well-known vinyl polymers, polystyrene (PS) and poly(methyl methacrylate) [PMMA] were measured. Polystyrene is an inexpensive and hard plastic and probably only poly(ethylene) is more common in our everyday lives. It has many uses, amongst others expandable PS is used for light packaging and SBS (a copolymer with butadiene) used for things like the soles of shoes and car tyres. PMMA is a hard plastic which is more transparent than glass and is used as an alternative to glass in many instances. Another application is in paints where it is suspended in water. In addition to these two polymers, their copolymer in the same solvent has also been studied in this work, stretching the capability of two chosen thermodynamic models, the Sanchez-Lacombe equation of state and the group contribution UNIFAC-free volume model for polymers.

The remainder of the thesis is organised as follows. Chapter II gives a detailed explanation on the thermodynamics of polymer solutions, what types of phase behaviour are possible and the issues associated with the behaviour for these systems. In this chapter, the Flory-Huggins' theory (Flory, 1953) is derived. Chapter III presents thermodynamic models which have been developed since 1953 for the prediction of the experimentally observed phase behaviour. Emphasis is placed on
the two models that will be explored in detail in this work. Chapter IV starts with a brief introduction to the experimental techniques available for measuring thermodynamic behaviour and describes in detail the methods of turbidimetry and inverse gas chromatography used in this work to measure liquid-liquid phase separation and vapour-liquid equilibria respectively. Experimental results from both techniques are presented and discussed in Chapter V. The experimental data are compared to model predictions in Chapter VI, where detail is given of the computational algorithm used for the implementation of these models and issues that arise when dealing with polymer/solvent systems are considered. In Chapter VII conclusions from this work are drawn and some recommendations are given for future work.
2.1 — Introduction

In this chapter, some basic thermodynamic concepts are reviewed briefly and the main features observed in the phase equilibria of polymer solutions are discussed. Some examples of liquid-liquid and vapour-liquid equilibrium in polymer solutions are given. After a preliminary discussion on the ideal solution, the first important theory developed to explain polymer solution thermodynamics, the Flory-Huggins' theory, is presented and its limitations are discussed.

2.2 — Basic Thermodynamics

Consider a closed system with only one phase and no chemical reactions. The fundamental equation for the total Gibbs free energy of a system as a function of temperature $T$ and pressure $P$ is:

$$d(nG_m) = (nV_m) dP - (nS_m) dT$$  \hspace{1cm} (2.1)
where \( n \) is the total number of moles in the system, \( G_m \) is the molar Gibbs free energy, \( V_m \) is the molar volume and \( S_m \) is the molar entropy. From this equation, the following partial derivatives can be written:

\[
\left( \frac{\partial (nG_m)}{\partial P} \right)_{T,\sigma} = nV_m \quad \text{and} \quad \left( \frac{\partial (nG_m)}{\partial T} \right)_{P,\sigma} = -nS_m
\] (2.2)

Now, consider an open system that can exchange material with its surroundings, still consisting of only one phase. For a system with more than one component, the following expression holds:

\[
nG_m = f(P,T,n_1,n_2,\ldots,n_\ldots)
\] (2.3)

where subscript \( i \) refers to species \( i \). A similar expression to (2.1) results:

\[
d(nG_m) = \left( \frac{\partial (nG_m)}{\partial P} \right)_{T,\sigma} dP - \left( \frac{\partial (nG_m)}{\partial T} \right)_{P,\sigma} dT + \sum_{i} \left( \frac{\partial (nG_m)}{\partial n_i} \right)_{T,P,\sigma} dn_i
\] (2.4)

where the summation is over all species \( i \). Substituting expression in (2.2) into the above gives:

\[
d(nG_m) = (nV_m) dP - (nS_m) dT + \sum_{i} \left( \frac{\partial (nG_m)}{\partial n_i} \right)_{T,P,\sigma} dn_i
\] (2.5)

where the quantity being summed in equations (2.4) and (2.5) is defined as the chemical potential of species \( i \) in a mixture \( \mu \). The chemical potential of a molecule in a mixture is thus given by the increase of the Gibbs free energy of the system when one molecule is added to the system and \( P, T \) and the numbers of the other species are kept constant under the condition that the system remains in thermodynamic equilibrium. Equation (2.5) can be rewritten as:

\[
d(nG_m) = (nV_m) dP - (nS_m) dT + \sum_{i} \mu_i dn_i
\] (2.6)

31
or in terms of the mole fractions as:

\[ dG = (nV_m) dP - (nS_m) dT + \sum_{i}^{N} \mu_i d\chi_i \]  

(2.7)

where \( G = f(P, T, x_1, x_2, \ldots, x_j, \ldots) \). Equation (2.7) forms the basis for the thermodynamic theory of solutions.

Further consider a closed system with two phases, each of which is open and can exchange material with the other. Two equations like (2.6) can be written, one for each phase,

\[ d(nG_n)^I = (nV_n)^I dP - (nS_n)^I dT + \sum_{i}^{N} \mu_i^I d\chi_i^I \]  

(2.8)

\[ d(nG_m)^II = (nV_m)^II dP - (nS_m)^II dT + \sum_{i}^{N} \mu_i^II d\chi_i^II \]  

(2.9)

where superscripts I and II represent each of the two phases. The change in the total Gibbs free energy of this two-phase system is the sum of these two equations such that:

\[ d(nG_m) = d(nG_n)^I + d(nG_m)^II \]

\[ = (nV) dP - (nS) dT + \sum_{i}^{N} \mu_i^I d\chi_i^I + \sum_{i}^{N} \mu_i^II d\chi_i^II \]  

(2.9)

At equilibrium, temperature and pressure are constant and therefore:

\[ \sum_{i}^{N} \mu_i^I d\chi_i^I + \sum_{i}^{N} \mu_i^II d\chi_i^II = 0 \]  

(2.10)

where \( d\chi_i^I \) and \( d\chi_i^II \) refer to the material transfer between phases and because mass has to be conserved,

\[ d\chi_i^I = -d\chi_i^II \]  

(2.11)
which means that:

\[ \sum_{i} (\mu_{i}^{n} - \mu_{i}^{l}) \Delta n_{i}^{n} = 0 \]  
(2.12)

and this can only be true if and only if:

\[ \mu_{i}^{l} = \mu_{i}^{n} \]  
(2.13)

This equality can be extended to a system containing up to \( \pi \) phases such that at equilibrium:

\[ \mu_{i}^{l} = \mu_{i}^{n} = ... = \mu_{i}^{\pi} \]
\[ T_{l} = T_{n} = ... = T_{\pi} \]
\[ P_{l} = P_{n} = ... = P_{\pi} \]  
(2.14)

In some cases the chemical potential is not a convenient quantity for engineering calculations, so equilibrium is expressed in terms of the fugacity which is directly related to the chemical potential by:

\[ d\mu_{i} = RT \ln f_{i} \]  
(2.15)

and so at equilibrium:

\[ f_{i}^{l} = f_{i}^{n} = ... = f_{i}^{\pi} \]  
(2.16)

The fugacity of component \( i \) can be written in terms of the system pressure, \( P \), the mole fraction \( y_{i} \) and the fugacity coefficient, \( \phi_{i} \),

\[ f_{i} = \phi_{i} y_{i} P \]  
(2.17)
which can be calculated from a thermodynamic model using the following expression:

\[ \ln \phi_i = -\frac{1}{RT} \int_{V_m}^{\infty} \left( \frac{\partial P}{\partial n_i} \right)_{T,p,V-m} \left( -\frac{RT}{V_m} \right) dV_m - \ln Z \]  

\( (2.18) \)

2.2.1 – Thermodynamics of Solutions

The simplest model available to treat solutions is the ideal solution. For these, the fugacity coefficient is unity and the fugacity in equation (2.17) can be replaced by the partial pressure of component \( i \) in the solution. This is essentially Raoult's Law which states that the partial pressure of each component in a mixture is equal to the product of the mole fraction of that component in the mixture and the saturated vapour pressure of the component in its pure state. Raoult's Law is expressed as:

\[ P_i = y_i P_i^0 \]  

\( (2.19) \)

In terms of the Gibbs free energy, ideal solution behaviour results in the following equation:

\[ G_m^i = G_m^0 + RT \ln x_i \]  

\( (2.20) \)

where \( G_m^i \) is the partial molar Gibbs free energy of component \( i \) in the ideal solution and \( G_m^0 \) is the partial molar Gibbs free energy of pure component \( i \) at the same conditions of temperature, pressure and physical state. This equation can be extended to real solutions, by introducing the concept of activity \( a_i \). Thus for a real solution,

\[ G_m = G_m^0 + RT \ln a_i \]

\[ = G_m^0 + RT \ln x_i y_i \]  

\( (2.21) \)
where $\gamma_i$ is the activity coefficient. For an ideal solution $\gamma_i$ has a value of 1 and in this case the activity of component $i$ equals its mole fraction at specified temperature and pressure. The activity coefficient serves as a measure of the differences in shape, size and interactions between molecules in the system that are responsible for the deviations from ideality found in real solutions.

2.3 — Phase Equilibria

It has already been stated that in a multiphase system at equilibrium the chemical potential of each component $i$ in each of the phases must be the same. Furthermore, a system in equilibrium is characterised by the condition that at constant temperature and pressure, the Gibbs free energy of mixing must be at its minimum. A typical diagram of $\Delta G_{mix}$ versus mole fraction for a binary mixture is plotted in figure 2.1. First of all, for two components to mix at a fixed temperature and pressure, the total Gibbs free energy of the system should decrease such that:

$$G = nG_m < \sum_{i}^{N_i} \eta_i G_{m,i}$$  \hspace{1cm} (2.22)

$$G - \sum_{i}^{N_i} x_i G_i < 0$$  \hspace{1cm} (2.23)

$$\Delta G_{mix} < 0$$  \hspace{1cm} (2.24)

where $G$ is the total Gibbs free energy of the system. If the last criterion is not satisfied it means that the components are completely immiscible with one another and they will separate into two pure phases. This is the case shown by curve II in figure 2.1. If equation (2.24) is satisfied, the components may either be completely miscible or partially miscible in one another. If $\Delta G_{mix}$ shows a positive curvature with respect to all compositions, the system will be thermodynamically stable and the mixture will exist as one homogeneous phase. This is shown by curve I. Finally curve III, shows a region of negative curvature bounded by $x_{op}^\alpha$ and $x_{op}^\beta$, known as the spinodal compositions of component $i$ in phases $\alpha$ and $\beta$ respectively. These are the points of inflexion of the curve. Drawing a number of similar curves at different
temperatures and joining the spinodal compositions of each of these curves, will result in a spinodal curve as shown in figure 2.2. At any composition within this spinodal curve the system is thermodynamically unstable and any small fluctuation in concentration will lower the Gibbs free energy of mixing leading to it separating into two coexisting phases each containing a certain amount of both components. The compositions of the coexisting phases are \( x_i^a \) and \( x_i^b \) which are referred to as the binodal compositions. This mechanism by which the components phase separate is called spinodal decomposition. Similar to the spinodal curve, a binodal curve can also be drawn by joining the binodal compositions at different temperatures. The region between the binodal and spinodal curves is called the metastable region. The alternative mechanism for phase separation is associated with this region. It is known as nucleation and growth. Within this region, there is a negative change in the Gibbs free energy of mixing and a positive curvature in the curve, so a small change in concentration will not spontaneously lead to a decrease in \( \Delta G \), An activation energy is required to generate a nucleus of the second phase. Once formed, this nucleus will grow until phase separation is complete due to the diffusion of the components.

Finally, the point at which the binodal and spinodal curves meet is called the critical point. This will occur at the critical solution temperature and at the critical composition. Mathematically, at the critical point,

\[
\left( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x_i^2} \right)_{T,P,x_i} = \left( \frac{\partial^3 \Delta G_{\text{mix}}}{\partial x_i^3} \right)_{T,P,x_i} = 0
\]  

(2.25)

In terms of \( \Delta G_{\text{mix}} \), for a phase to be stable the following must be true:

\[
\left( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x_i^2} \right)_{T,P,x_i} > 0
\]

(2.26)
Figure 2.1 — Possible forms of $\Delta G_{\text{mix}}/RT$ as a function of the mole fraction of component $i$ for a binary mixture. Curve I represents a completely miscible system, curve II a completely immiscible system and curve III a partially miscible system with phases $\alpha$ and $\beta$.

Figure 2.2 — Phase diagram for a system showing upper critical solution temperature behaviour. Temperature is plotted against the volume fraction of the polymer in solution. --- denotes the spinodal curve and — denotes the binodal curve.
2.3.1 - Liquid-Liquid Equilibrium (LLE)

Binary LLE is usually represented with temperature-composition diagrams, like that in figure 2.2 which show the binodal curves (or coexistence curves) separating the one-phase region from the two-phase region. One of the six phase diagrams may be encountered. They are shown in figure 2.3. In case (a), the system exhibits an upper critical solution temperature (UCST) above which the system will exist as one phase and below which it will phase separate. It is the interactions between the components that give a positive enthalpy of mixing which cause demixing. This behaviour is very widely observed in polymer solutions. Some examples include polyethylene (PE)/ethylene (Koak et al., 1999), poly(isobutylene)/di-isobutyl ketone (Shultz and Flory, 1952) and poly(α-methylstyrene)/methyl cyclohexane (Pruessner et al., 1999). In case (b), the opposite behaviour is observed. Above the lower critical solution temperature (LCST), the solution separates into two phases and below it, it exists as one homogeneous phase. The negative enthalpy of mixing overcomes the negative entropy of mixing and is responsible for phase separation. This behaviour is observed in solutions of PE and poly(isobutylene) in various n-alkanes (Hamada et al., 1973 and Liddell et al., 1970 respectively) as well as in PS/benzene and PS/methyl ethyl ketone (Saeki et al., 1973) systems. The case where both LCST and UCST behaviour are observed is shown in case (c). For temperatures between the LCST and the UCST, the system is miscible in all proportions, but at higher and lower temperatures there will be compositions that are not thermodynamically stable. This type of behaviour is observed for example in PS/cyclohexane as shown in figure 2.4 (Saeki et al., 1973). Three important characteristics of polymer solution coexistence curves can be pointed out from this plot. First of all, polymer solution coexistence curves are highly asymmetric as a function of composition. Secondly, as compared with small molecule mixtures the coexistence curves are very flat near the critical solution temperature region. Finally, the plot shows that the both critical solution temperatures are dependent on the molecular weight of the polymer. This type of behaviour is not only observed in other polystyrene systems such as in solutions with methyl acetate (Saeki et al., 1974) and ethyl formate (Konno et al., 1975), but also in systems like cellulose acetate/aceton (Cowie et al., 1971) and poly(styrene-co-α-methylstyrene)/cyclohexane (Hino et al., 1996). Case (d) shows a type of behaviour known as closed-loop behaviour, which is observed in some highly
Figure 2.3 — Possible liquid-liquid phase diagrams.
Figure 2.4 – Phase curves observed in LLE for PS/cyclohexane binary systems of indicated molecular weights (g/mol) measured by turbidimetry by Sacki et al., 1973.
polar systems (Siow et al., 1972). Both a LCST and a UCST exist and the two-phase region is that enclosed by the loop. Examples of systems that exhibit this behaviour are poly(butyl methyl acrylate)/methyl ethyl ketone and poly(styrene-co-butyl methyl acrylate)/methyl ethyl ketone (Kyoumen et al., 1990). Finally, case (e) shows a system where the UCST and LCST merge to form an hourglass-shaped phase diagram, and case (f) shows a system that has neither a UCST nor a LCST. In these systems, either the LCST is smaller than the freezing point of the mixture or the UCST greater than the boiling point. This behaviour has been observed in PS/acetone solutions and some PS/diethyl ether solutions (Siow et al., 1972), and in poly(butadiene)/n-hexane (Bogdanic and Vidal, 2000).

Although the examples used are all polymer-solvent systems, these phase diagrams are general liquid-liquid phase diagrams and not specific to polymer solutions. There are many more polymer solutions whose phase behaviour has been studied over the years and those mentioned above are only a set of examples. A more extensive compilation of experimental LLE data for polymer solutions can be found in the Polymer Solution Collection (Hao et al., 1992). Several methods are available to determine phase separation curves in polymer solutions, almost all based on light changes through the solutions. The two most commonly used techniques are turbidimetry and light scattering techniques, but it has also been measured by differential refractometry or by using a differential scanning calorimeter (DSC) which is more commonly employed for determining polymer glass transition temperatures. In all these cases what is measured is the so-called cloud-point curve which is the curve that separates a completely clear solution from a cloudy one. Starting from the latter of the mentioned techniques, DSC can be used to measure the onset of cloudiness in polymer solutions by mixing known quantities of polymer and solvent in a cell and cooling it rapidly to obtain a semi-rigid material. The solution is then heated at a constant rate and the cloud-point curve can be detected with a DSC as an endotherm at a certain temperature (UCST). If on the other hand there is a phase change upon cooling an exotherm will result (LCST). In general, DSC is hardly used because the heat effect is small and tends to disappear easily with baseline shift.

All other techniques are based on measuring a change in light intensity, either transmitted through the solution or scattered by the solution, as it changes from being one phase to being two phases. In the case of differential refractometry, two prism-shaped containers (one for the pure solvent and the other for the polymer
solution) are built in the differential cell. He-Ne laser light is shone parallel through both the pure solvent and the solution and the difference between the two refracted beams is measured as a function of the refractive indices. A relationship between this difference and the weight fraction of solvent in the solution can be used to calculate the concentration of the solution at the particular temperature. A drawback of this method is that calibration is necessary prior to conducting the experiment, with a solution of known composition at a particular temperature. This method was used by Bazuaye and Huglin (1979) to measure the effect of temperature and solvent concentration on the unperturbed dimensions of polystyrene chains. They measured specific refractive index increments at the \( \theta \) temperature in a differential refractometer calibrated with an aqueous KCl solution. In addition, these authors also used light scattering on these solutions. Light scattering techniques are most commonly used for looking at phase separation in polymer blends but are also used for solutions, especially for determining theta temperatures. Cloud-point temperatures can be determined by measuring changes in the intensity of scattered light from a polymer solution as the temperature is raised or lowered. As the solution becomes cloudy there will be a sudden increase in scattered light. Normally the light source is a He-Ne laser beam and scattering is measured at a number of angles with respect to the beam's axis. With the concentration of the solutions known prior to the start of the experiment, cloud-point temperatures are measured and the phase separation curve can be drawn. Many authors have used this method and only a couple will be mentioned here. Liquid-liquid demixing curves have been measured for PS/cyclohexane and PS/methyl cyclohexane using light scattering techniques as a function of pressure (Szydlowski and van Hook, 1998; van Hook et al., 1999).

Lastly, but by far the most commonly used to determine liquid-liquid phase splits, are turbidimetry techniques. Here, the polymer and solvent are mixed in known quantities into a solution cell. The solution is then heated or cooled to a temperature where it will be in the one-phase state and stirred for a certain amount of time to ensure solution homogeneity. The temperature is then cooled or heated respectively until a phase change is observed, at which point the solution will become cloudy. This change in appearance at a particular temperature can either be measured visually or using a photoelectric device. Measurements using this technique have been carried out for example by Saeki et al. (1973, 1974) on solutions.
of PS in a number of solvents where they obtained measurements of polymer concentrations up to 25% by weight in the solutions. They employed flame sealed solution cells in a water bath for UCST determination and a silicone oil bath for LCST determination, both controlled to ± 0.01K and a He-Ne laser beam as the light source. Phase separation curves of the poly(α-methyl styrene)/methyl cyclohexane system were measured by Pruessner et al. (1999) by placing the solutions in a water bath and inspecting the cloudiness transition visually. Turbidimetry methods can also be used for measurements at high pressures by designing an appropriate high-pressure solution cell. This was done by Meilchen et al. (1991) who designed a variable-volume high-pressure cell for measurements up to 2000 bar and reported cloud-point data for poly(ethylene-co-methacrylate) in solutions of propane and chlorodifluoromethane.

In this work, the technique of turbidimetry has been chosen to perform LLE experiments. It is a simple, rapid and convenient method, no calibration is necessary and a simple light source can be used. Details of the design and experimental procedures employed for this purpose are presented in chapter IV.

2.3.2—Vapour-Liquid Equilibrium (VLE)

Vapour-liquid equilibrium is in some ways a simpler subject than liquid-liquid equilibrium at least in respect of polymer solutions. This is because polymers are non-volatile substances. In a polymer solution where a vapour phase is present, this phase will consist solely of pure solvent. VLE in polymer solutions is normally studied by looking at the activity and activity coefficients of the solvent in the polymer solution, at a specified temperature. A typical result is shown in figure 2.5. Similar diagrams have been measured for many other polymer solvent systems (Hao et al., 1992). Plots like these are useful for obtaining information about the compatibility of the polymers with the solvents and this is very useful especially in the production of polymers where they are in most cases in the presence of solvents. VLE in polymer solutions is also important in a number of other applications including polymer devolatilization (High and Danner, 1990), membrane separation processes and pervaporation (Maeda et al., 1991).
Figure 2.5 – VLE of the polydecene-1 (M<sub>n</sub> = 94,900 g/mol)/toluene binary system. The symbols represent the experimental data at 303.15 K by Tait and Livesey (1970); the solid line corresponds to ideal solution behaviour.

Reliable VLE data is essential for the design and optimisation of industrial processes involving polymers and are required over a wide range of temperatures, pressures and concentrations. Several techniques are available to measure vapour-liquid thermodynamics of polymer solutions. Among these methods, the most prominent are osmotic pressure measurements, gravimetric sorption, differential vapour pressure measurements and inverse gas chromatography. Others which are seldom used are light scattering techniques, ultracentrifuge and viscosity measurements. In addition, Zielinski et al (2001) have very recently developed a new analytical technique based on vapour-phase infrared spectroscopy which allows multiple samples to be measured at one time and higher operating pressures can be achieved compared to the other techniques. For measurements at pressures above atmospheric, other methods are available like for example pressure decay sorption (Danner et al., 2001) but these will not be considered in this work. Each method has its advantages and disadvantages depending on the concentration range of interest and on the magnitude of the solubilities being measured. All the aforementioned techniques were developed some years ago and although the fundamental principles have not changed with time, instrumentation has been improved. Reviews have been presented by a number of authors including Bonner (1975), Eichinger et al. (1975),
Hao et al. (1992a), Wolfarth (1994) and High and Danner (1993), and so only a brief summary will be given here.

Osmotic pressure measurements can be used to obtain activities and second order virial coefficients by having a polymer solution separated from pure solvent by a semi-permeable membrane, through which only solvent molecules can pass. Due to the difference in solvent activity in the pure state and that in the polymer solvent solution, solvent molecules will diffuse through the membrane leading to a difference in liquid level, and consequently a hydrostatic pressure difference or osmotic pressure, can be measured. This is directly related to the solvent activity. In the early days, Flory and co-workers (1968) used high-pressure osmometry to measure VLE of poly(isobutylene)/n-alkane systems with up to 50% solvent, and Kuwahara and co-workers (Kuwahara et al., 1968; Sugamiya et al., 1974) used this technique to measure poly(dimethylsiloxane) in several solvents. More recently, Fernández-Berridi et al. (1983) used osmometry to obtain vapour pressures for the poly(isobutylene)/benzene system at temperatures in the range of 35°C - 200°C and up to 40% solvent.

More suitable for concentrated solutions are vapour sorption methods. Typically this method uses a microbalance in which a sample of polymer is suspended from a calibrated quartz spring and exposed to solvent vapour. The entire apparatus is contained in a constant temperature bath. As the polymer absorbs the solvent, the weight on the spring increases. The spring extension is measured with a cathetometer and is related to the vapour pressure of the solvent and hence its activity. This method has two main disadvantages, the first being that a substantial amount of polymer is necessary and secondly, that the low diffusivity of solvents in polymers results in each experiment taking hours, days or even weeks to be completed, and furthermore requires very good temperature control. This method is actually very useful for measuring diffusivities (High and Danner, 1993). Prager and co-workers (Prager and Long, 1951; Prager et al., 1953) used this technique to obtain sorption isotherms for poly(isobutylene)/hydrocarbon systems, and Nakajima et al. (1959) measured vapour pressures of poly(vinyl acetate) solutions. In 1970, Tait and Livesey used this method to study the thermodynamic properties of concentrated solutions of poly(α-olefins) in toluene and further in 1977, Tait and Abushida compared results using this method and a gas chromatographic technique on PS, poly(vinyl chloride) and PMMA in several solvents. They found very good
agreement between the two methods but concluded that the chromatographic technique was much quicker and could be used with a wider range of temperatures. Furthermore, experimental errors were encountered in both the low concentration regions, where the measured pressures are very small, and the high concentration regions were the measured pressure is approaching the vapour pressure of the pure solvent.

A different type of vapour sorption apparatus uses a piezoelectric detector. Instead of measuring a change in weight, a change in the oscillation frequency of the quartz crystal is measured, as the polymer absorbs the solvent. The change in frequency is directly proportional to the mass of gas sorbed by the polymer film. The quartz crystal is covered with a thin polymer film and therefore the experiment requires much shorter equilibration times. The drawback is that the film has to be uniform for good results. Bonner and Cheng (1975) used this method for measurements of the system low-density PE/nitrogen at 125°C and at pressures up to 120 bar. Finally, the difference in vapour pressures between the pure solvent and a polymer solution at a fixed temperature can be measured directly. Bawn et al. (1950) measured vapour pressure of PS solutions in toluene and methyl ethyl ketone at different temperatures using a U-tube connected to a mercury reservoir at the bend. One arm of the tube is connected to a flask containing the polymer solution and the other leading to a vacuum line sealed off with a calibrated tube containing pure solvent. Both flasks are immersed in a constant temperature bath. Measurements of up to 0.95 solvent weight fraction were achieved.

A much faster but equally reliable technique is inverse gas chromatography. Smidrod and Guillet (1969) applied the technique of gas chromatography for measuring thermodynamic properties such as activity coefficients and enthalpies of solution. The chromatographic process is based on the separation of the components in a sample, owing to their differences in solubility or adsorption in a stationary phase of material. When applied to polymer solutions, the polymer becomes the stationary phase and because it is the phase of interest and does not act as a separating agent, the technique is referred to as inverse gas chromatography. As the solvent, travelling with the carrier gas, is swept through the column containing the polymer, it encounters resistances from the longitudinal diffusion in the gas phase and from the mass transfer into the polymer phase. Because equilibrium does not occur instantaneously, the solvent lags behind and the retention time is measured.
This is related to the polymer-solvent interactions and hence to the solvent activity in the polymer. Since 1969, extensive work has been carried out using this technique. It is the method chosen for this work and therefore a detailed discussion is presented in Chapter IV.

2.3.3 – Effect of Polydispersity

As mentioned previously (section 1.1), polydispersity is an important characteristic of polymers. A polymer is normally composed of a distribution of chain lengths. This will undoubtedly affect their phase behaviour in solution. The systems are essentially multi-component mixtures, so a change in the shape of the phase diagrams will be expected. Although the effect is not highly significant in VLE, it is in LLE. Polydispersity has been observed to shift both the critical solution temperature and the critical solution composition (McMaster, 1973).

An application where polydispersity is of great importance is in polymer fractionation where the light ends of the polymer distribution are separated with the polymer-lean phase and the bulk of the polymer is in the polymer-rich phase. The distribution of molecular weights becomes important when trying to model these systems. A common way to deal with this problem is to divide the polymer into pseudo-components and solve the phase equilibrium as a mixture of discrete pseudo-components. The higher the number of pseudo-components, the better the polymer representation. Koningsveld and co-workers (Koningsveld and Staverman, 1968 and Koningsveld et al., 1970) have carried out an extensive analysis using this procedure, using the Flory-Huggins model with a composition dependent binary interaction parameter. In addition, Söl (1970, 1975) looked at the effect of the molecular weight distribution function of polymers on cloud-point curves and went on further to study the possibility of finding multiple critical points in polydisperse polymer solutions (Söl et al., 1984). This method of defining the polymer as a multi-component mixture has also been used by Folie (1996) to represent the fractionation of poly(ethylene vinyl acetate).

There is an alternative method for studying polydisperse polymers in solution, whereby continuous thermodynamics is used to define thermodynamic functions. “Expressions for the chemical potentials, spinodals and critical points
were derived using functional theory, where high-order variations were obtained by using the Lagrange method of undetermined multipliers for minimizing the second-order differential of the Gibbs energy" (Hu et al., 1995). It is beyond the scope of this work to explain the details of this method or discuss the phase behaviour of polydisperse polymers in solution and so will not be treated further. Furthermore, all the polymer samples used for LIE experiments in this work were monodisperse (where $M_w/M_n$ was always less than 1.12).

2.4 – A Thermodynamic Theory for Polymer Solutions

Starting with an ideal binary solution, the entropy of the system can be calculated by representing the fluid as a lattice containing both solvent and solute molecules, as shown in figure 2.6 (Fried, 1995). The coloured dots represent molecules of one low molecular weight fluid, while the white dots represent the molecules of a second low molecular weight fluid.

![Figure 2.6 – Molecules of a simple fluid in a solvent.](image)

The entropy of the system is given by Boltzmann’s equation,

\[ S = k \ln \Omega \]  

(2.27)
where \( k \) is Boltzmann's constant and \( \Omega \) is the total number of ways of arranging \( N_1 \) identical molecules of solvent and \( N_2 \) identical molecules of solute on a lattice which comprises of a total of \( N_0 = N_1 + N_2 \) available sites. The expression for \( \Omega \) is,

\[
\Omega = \frac{N_0!}{N_1!N_2!}
\]  

(2.28)

and the entropy is then:

\[
S = k \left( \ln N_0! - \ln N_1! - \ln N_2! \right)
\]  

(2.29)

Using Stirling's approximation,

\[
\ln N! \approx N \ln N - N
\]  

(2.30)

the following expression for the entropy of mixing results:

\[
\Delta S_{\text{mix}} = k \left[ (N_1 + N_2) \ln (N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2 \right]
\]  

(2.31)

Assuming that for an ideal mixture \( \Delta H_{\text{mix}} = 0 \) and using \( \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \), the expression for the Gibbs free energy becomes:

\[
\Delta G_{\text{mix}} = kT \left[ N_1 \ln x_1 + N_2 \ln x_2 \right]
\]  

(2.32)

in terms of mole fractions. This expression can be written under a number of assumptions. Firstly, there is no volume change upon mixing. Secondly, molecules have equal sizes so that they can interchange freely. Thirdly, all possible arrangements have the same energy, this being equal to the sum of the interaction energies of all the nearest-neighbour pairs. Finally, the motion of the components about their equilibrium position remains unchanged upon mixing.
2.4.1 – Flory-Huggins Theory

Ideal solutions have no enthalpy or volume change on mixing and all the excess properties are zero. Real solutions, which deviate from the ideal behaviour as expressed by Raoult's Law, can be divided into three types. Those solutions that have no excess volume or entropy change but do have an enthalpy change on mixing are known as regular solutions. The second type is referred to as athermal solutions and these have no enthalpy change on mixing but do have a finite entropy of mixing. Finally, irregular solutions deviate from ideal behaviour in both $\Delta S_{\text{mix}}$ and $\Delta H_{\text{mix}}$ and the deviation increases with increasing molecular weight. Polymer solutions are classified as being non-ideal and irregular and it is only at extreme dilutions where they approach ideality as an asymptotic limit. The most important reasons for these deviations are the size differences between solvent and polymer molecules that give rise to small entropies of mixing and the finite heat arising from mixing. Polymers are regarded as long chains of small segments bonded covalently and the interactions between these segments as well as the way that they can arrange themselves with solvent molecules on a lattice similar to that shown in figure 2.7, can be used to explain the observed deviation from ideality. This constitutes the basis of the theory of Flory-Huggins for polymer solutions.

When a polymer, initially as a solid, dissolves in a solvent, it immediately gains freedom of movement and arranges itself in a way dependent on the polymer flexibility and on the interactions between the polymer and the solvent. Flory (1942) and Huggins (1942) independently considered that the formation of a polymer solution depended on two important factors:

1. The transfer of a pure polymer chain from a pure ordered state to a state of disorder, allowing the chain to position itself in a random place on a lattice.
2. The mixing process of the chains with the solvent molecules.

Flory made two further assumptions:

1. Molecules in a lattice consist of large number of chain segments, $r$, each of equal length.
2. The solution is concentrated enough so that the occupation of the lattice sites is distributed at random rather than finding separated regions of \( r \) occupied sites.

### 2.4.2 — Entropy of Mixing

Consider a lattice with a total number of cells \( N_b = N_1 + rN_2 \), where \( N_1 \) is the number of solvent molecules, \( N_2 \) is the number of monodisperse polymer molecules and \( r \) is the degree of polymerisation. The lattice arrangement for a polymer in solution is shown in figure 2.7 (Fried, 1995). The coloured dots represent the polymer chain segments, while the white dots represent the solvent molecules. All lattice sites must be occupied because no vacancies are allowed in this model. After placing a first molecule \( i \), the number of vacant cells left which can accommodate the next \((i+1)\) molecule will be \((N_i-n)\).

![Figure 2.7 — Lattice model for a polymer solution.](image)

Also, the first segment can occupy any empty cell but the second is restricted to the immediate near neighbours surrounding the first (chain connectivity). This can be given by a co-ordination lattice number \( z \). Furthermore, the cell has to be empty before a segment can be placed there. Let \( p_i \) be the probability that a neighbouring cell is empty and be expressed as,
\[ p_i = \frac{(N_0 - r)}{N_0} \]  

(2.33)

and valid for large values of \( \xi \). It then follows that the expected number of empty cells available for the second segment is \( \xi_0 \), and the third is \( \xi_0^3 p_0 \). Hence the total number of ways in which the \((i+1)\) molecule can be placed on the lattice is:

\[
\Omega_{i+1} = (N_0 - ri)z(z-1)^r \left[ \frac{N_0 - ri}{N_0} \right]^{-1} = (N_0 - ri)^r z(z-1)^r \left( \frac{1}{N_0^r} \right)
\]

(2.34)

This gives the possible number of ways in which the \((i+1)\) molecule can be placed on the lattice. Consequently, the product of all the possible ways gives the total number of ways of accommodating all \(N_2\) molecules. Moreover, because all polymer molecules are identical, the number of ways of adding all \(N_2\) molecules becomes,

\[
\Omega = \prod_{i=1}^{N_2} \Omega_i
\]

\[
= \frac{1}{N_2!} \left[ \frac{z(z-1)^r}{N_0^{r-1}} \right]^{N_2} \prod_{i=1}^{N_2} \left[ N_0 - r(i-1) \right]^{r-1}
\]

\[
= \frac{1}{N_2!} \left[ \frac{z(z-1)^r}{N_0^{r-1}} \right]^{N_2} r N_2 \prod_{i=1}^{N_2} \left[ \frac{N_0}{r} \right]^{r-1} \left[ \frac{N_i}{r} \right]^{r-1}
\]

(2.36)

Adding the solvent molecules to the lattice can now only be done in one way, so that there are no more contributions to the entropy of the system. So, finally using Boltzmann's formula for the entropy, \( S = k \ln \Omega \) and Stirling's approximation \( \ln N! \approx N \ln N - N \), the following expression for the entropy is obtained:

\[
\frac{S}{k} = -N_1 \ln \left( \frac{N_1}{N_0} \right) - N_2 \ln \left( \frac{r N_2}{N_0} \right) + N_2 \left( r - 2 \right) \ln (z-1) - (z-1) + \ln rz
\]

52
The fraction of sites occupied by the solvent and the polymer, \( \theta_1 \) and \( \theta_2 \) respectively, are defined as,

\[
\theta_1 = \frac{N_1}{N_0} = \frac{N_1}{N_0 + rN_2}
\]

\[
\theta_2 = 1 - \theta_1 = \frac{rN_2}{N_0 + rN_2}
\]

Therefore, in terms of the site fractions the entropy can be written as,

\[
\frac{S}{k} = -N_1 \ln \theta_1 - N_2 \ln \theta_2 + N_1 [(r - 2) \ln(z - 1) - (r - 1) + \ln rz]
\]

(2.39)

For the pure solvent, \( N_2 = 0 \) and so \( S_1 = 0 \). On the other hand, for the pure polymer \( N_1 = 0 \) which gives an expression for the entropy of the polymer which is embodied in equation (2.40):

\[
S_2 = N_2 [(r - 2) \ln(z - 1) - (r - 1) + \ln rz]
\]

(2.40)

The entropy of mixing is calculated using,

\[
\Delta S_{\text{mix}} = S_{\text{mix}} - S_1 - S_2
\]

(2.41)

and so,

\[
\Delta S_{\text{mix}} = -k \{N_1 \ln \theta_1 + N_2 \ln \theta_2\}
\]

(2.42)

In terms of the volume fractions for the solvent and polymer respectively, \( \phi_1 \) and \( \phi_2 \),

\[
\Delta S_{\text{mix}} = -k \{N_1 \ln \phi_1 + N_2 \ln \phi_2\}
\]

(2.43)
assuming that the number of sites occupied by the polymer is proportional to the volume. This expression represents the combinatorial entropy of mixing of an athermal polymer solution.

2.4.3 — Enthalpy of Mixing

When Flory derived the expression for the entropy of mixing, he assumed that it was equal to the entropy of an athermal solution hence neglecting any possible influence of the interaction energies between molecules on the entropy of mixing. He considered that any interaction between neighbouring components led solely to an enthalpy of mixing. The enthalpy of mixing $\Delta H_{\text{mix}}$ is considered as the energy arising from the formation of a polymer-solvent (1-2) contact on mixing, by replacing some of the (1-1) and (2-2) contacts. It can be treated as a quasi-chemical reaction that has energy associated with it,

$$\frac{1}{2}(1-1) + \frac{1}{2}(2-2) \rightarrow (1-2)$$

$$\Delta U_{\text{mix}} = \Delta \varepsilon_{12} = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} - \varepsilon_{22})$$  \hspace{1cm} (2.44)

where $\varepsilon_{ij}$ are the contact energies and $\Delta U_{\text{mix}}$ is the internal energy of mixing. This can be replaced by the enthalpy of mixing because the volume change upon mixing is assumed to be zero. The enthalpy is given by,

$$\Delta H_{\text{mix}} = P_{12} \Delta \varepsilon_{12}$$  \hspace{1cm} (2.45)

where $P_{12}$ is the number of new contacts estimated by assuming that the probability of a cell being occupied by a solvent molecule is equal to the volume fraction $\phi_i$. Each polymer molecule will then be surrounded by $(\phi_i r_0^2)$ solvent molecules such that,

$$\Delta H_{\text{mix}} = N_1 \phi_i r_0 z \Delta \varepsilon_{12} = N_1 \phi_2 z \Delta \varepsilon_{12}$$  \hspace{1cm} (2.46)
where \( rN_2\phi_1 = N_1\phi_2 \) from the definition of the volume fraction. This last equation is the Van Laar equation applied to polymer solutions. To eliminate \( z \), Flory defined a dimensionless parameter \( \chi_{12} \) per solvent molecule such that,

\[
\Delta H_{\text{mix}} = kT\chi_{12}N_1\phi_2 = RT\chi_{12}x_1\phi_2
\]

(2.47)

\( \chi_{12} \) is called the Flory-Huggins interaction parameter (or the chi parameter) and is defined as:

\[
\chi_{12} = \frac{z\Delta \epsilon_{12}}{kT}
\]

(2.48)

For \( r \to \infty \), if \( \chi_{12} > 0.5 \) the polymer could be partially miscible with the solvent and if \( \chi_{12} < 0.5 \) the polymer will be totally miscible in the solvent.

**2.4.4 — Gibbs Free Energy of Mixing and the Chemical Potential**

Going back to the expression from the Gibbs free energy of mixing we can now write,

\[
\Delta G_{\text{mix}} = kT[N_1\ln \phi_1 + N_2 \ln \phi_2 + N_1\phi_2\chi_{12}]
\]

(2.49)

or

\[
\Delta G_{\text{mix}} = RT[x_1\ln \phi_1 + x_2 \ln \phi_2 + x_1\phi_2\chi_{12}]
\]

(2.50)

where the first two terms represent the combinatorial contribution and the last term represents the enthalpic contribution. This expression is valid provided that the configurational entropy change represents the total entropy change on mixing, neglecting possible contributions arising from specific interactions between neighbouring molecules which will only give rise to the enthalpy of mixing.

An expression for the molar chemical potential of the solvent \( \mu_r \) relative to its chemical potential (per molecule) in the pure liquid \( \mu^o_r \) can be obtained by
differentiating the above equation with respect to \( N \), the number of solvent molecules, and multiplying by Avogadro's constant. So, using

\[
\mu_i - \mu_i^0 = \left( \frac{\partial \Delta G_{\text{mix}}}{\partial N_i} \right)_{N, T, r}
\]

the following is obtained:

\[
\mu_i - \mu_i^0 = RT \left[ \ln (1 - \phi_i) + (1 - \gamma_i) \phi_i + \chi_{12} \phi_i^2 \right]
\]  

(2.52)

From this expression it can be seen that the chemical potential depends on the polymer chain length, represented by \( r \), especially at low concentrations of polymer. A similar expression holds for component 2:

\[
\mu_2 - \mu_2^0 = RT \left[ \ln \phi_2 + (1 - r)(1 - \phi_2) + \chi_{12} r (1 - \phi_2^2) \right]
\]

(2.53)

At equilibrium, the chemical potential must be equal in all phases and two expressions that are functions of the binodal compositions can be written (at fixed temperature and pressure) and solved and solved:

\[
f_1 = \ln \left[ \frac{1 - \phi_{1,b}^*}{1 - \phi_{2,b}^*} \right] - \left( \phi_{1,b}^* - \phi_{2,b}^* \right) \left[ \chi_{12} \left( \phi_{1,b}^* + \phi_{2,b}^* \right) + (1 - 1/r) \right] = 0
\]

(2.54)

\[
f_2 = \ln \left[ \frac{\phi_{1,b}^*}{\phi_{2,b}^*} \right] - \left( \phi_{1,b}^* - \phi_{2,b}^* \right) \left[ (1 - r) + 2 \chi_{12} r - \chi_{12} \left( \phi_{1,b}^* - \phi_{2,b}^* \right) \right] = 0
\]

(2.55)

From the chemical potential expression one can also calculate the critical composition, at which point the first and second derivatives of the chemical potential with respect to composition are equal to zero. In doing this the following two equations result:

\[
-\frac{1}{(1 - \phi_2)^2} + 2 \chi_{12} = 0
\]

(2.56)
$$\frac{-1}{(1-\phi_1^2)} + \left(1 - \frac{1}{r}\right) + 2\chi_{12}\phi_2 = 0$$  \hspace{1cm} (2.57)$$

Eliminating $\chi_{12}$ gives an expression for the critical composition as a function of $r$:

$$\phi_{2,c} = \frac{1}{1 + r^{0.5}}$$  \hspace{1cm} (2.58)$$

Finally, the activity of the solvent in the polymer for a binary mixture from this model is:

$$\ln a_i = \ln(1-\phi_1) + (1 - \chi)\phi_2 + \chi_{12}\phi_2^2$$  \hspace{1cm} (2.59)$$

### 2.4.5 – Application of the Flory-Huggins Theory

Figure 2.8 shows an example of the Flory-Huggins theory applied to the liquid-liquid phase behaviour of the PS/cyclohexane system whose phase curves have already been presented in figure 2.4. Plotted are the upper critical solution temperatures as a function of the critical concentrations of the polymer. Each of these corresponds to a different molecular weight of PS. As can be seen the agreement is very poor. The model predicts critical compositions that are significantly lower than the experimental data.

The model can also be applied to vapour-liquid phase behaviour and a typical result is shown in figure 2.9 where the activity of cyclohexane has been measured in polystyrene solutions of differing molecular weights ($M_\text{w} = 25,100$ g/mol and 440,000 g/mol) at 307.15K (Krigbaum and Geymer, 1959). The prediction of the Flory-Huggins equation with the best-fitted chi parameter is shown as the solid line for the lowest molecular weight system. The prediction is not too bad although it is far from the experimental data at higher concentrations of polymer.

These are only two examples of the application of this theory which has become the starting point for describing polymer solutions thermodynamics. It is still widely used as a first approximation to real behaviour but unfortunately has several limitations that have been recognised and that have been improved upon by
Figure 2.8 – UCST's as a function of critical composition for PS/cyclohexane. Points are experimental data from Saeki et al. (1973), the solid line is the prediction of Flory-Huggins' model.

Figure 2.9 – VLE of PS/cyclohexane. Points are experimental data at 307.15 K for (●) $M_n = 25,100$ g/mol and (●) $M_n = 440,000$ g/mol. Data are from vapour pressure measurements of Krigbaum and Geymer (1959). The solid line is the prediction from the Flory-Huggins model.
various authors over the years. In deriving the equation for the Gibbs free energy of mixing and applying the theory, the following assumptions were made:

1. The positioning of the segments in the lattice is random but this is only true assumption if $\Delta \varepsilon_{12}$ is equal to zero.
2. The flexibility of the chains remains unchanged as the polymer comes into contact with the solution therefore restricting the entropy of mixing to a combinatorial contribution only.
3. Any polymer-solvent interactions which lead to a change in chain orientation is neglected, hence polar solutions will not be correctly described.
4. A uniform segment density lattice is assumed and this only holds for concentrated solutions.
5. Lattice sites are assumed to be equal in size for polymer and solvent molecules.
6. The model assumes no volume changes upon mixing.

As a result of these assumptions, the Flory-Huggins theory does not describe very well, amongst other things, dilute solution behaviour. Furthermore, it fails to predict lower critical solution behaviour in polymer solutions and this inability is closely related to an important weakness of the theory, in that it treats the mixture as incompressible. This inability will be explained in what follows.

In equation (2.26) the necessary condition for phase stability was presented which said that the Gibbs free energy of mixing must have a positive curvature with respect to composition at a specified temperature and pressure, such that any fluctuation in composition will cause an increase the mixture's free energy. For a closed system at constant temperature and pressure, the first and second laws of thermodynamics states that:

$$dU = dQ + dW = TdS - PdV$$  \hspace{1cm} (2.60)
An important quantity in thermodynamics is the Helmholtz free energy which is defined as $A = U - TS$. Differentiating and using equation (2.60) the following results:

$$dA = dU - TdS - SdT = -PdV - SdT$$  \hspace{1cm} (2.61)

from which,

$$\frac{\partial A}{\partial T} = -S \quad \text{and} \quad \frac{\partial A}{\partial V} = -P$$  \hspace{1cm} (2.62)

Not only is $A$ a function of $T$ and $V$ but also of the composition $x$. The derivative can be written in terms of these three variables:

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,x} dT + \left(\frac{\partial A}{\partial V}\right)_{T,x} dV + \left(\frac{\partial A}{\partial x}\right)_{T,V} dx$$  \hspace{1cm} (2.63)

The Gibbs free energy is related to the Helmholtz free energy by $G = A + PV$ and the derivative is then $dG = dA + PdV + VdP$. Using this and equations (2.62) and (2.63) we arrive at:

$$dG = A_x dx - SdT + VdP$$  \hspace{1cm} (2.64)

where the subscript refers to the first derivative with respect that variable. From equation (2.64) it can be seen that at constant $T$ and $P$, $G_x = A_x$. Further, using equation (2.63) for the second derivative of $A$,

$$d(G_x) = d(A_x) = A_{x,T} dx + A_{x,T} dT + A_{x,V} dV$$  \hspace{1cm} (2.65)

and at constant temperature,

$$G_{xx} = A_{x,T} + A_{x,T} \left(\frac{\partial V}{\partial x}\right)_{T,P}$$  \hspace{1cm} (2.66)

Now, the isothermal compressibility of a system is defined as
and so, the stability criterion can be re-written as

\[ G_{xx} = \Delta H_{xx} - \frac{V}{\beta} \Delta A_{xx}^2 = \Delta H_{xx} - V\beta p_x^2 > 0 \]  

(2.68)

In this equation, the second term accounts for the compressibility of the mixture and it is an unfavourable contribution to phase stability. The failure of the Flory-Huggins equation to predict LCST’s can be explained based on this stability criterion. The Flory-Huggins model treats the mixture as incompressible meaning that the second term is zero and so only UCST’s can be predicted. At all temperatures above this, the model predicts a stable homogeneous mixture. For some polymer solutions though, the isothermal compressibility increases with temperature and at a high enough temperature, namely the lower critical solution temperature, the second term is large enough to overcome the positive first term leading to phase induced separation.

2.4.6 - Extensions of the Flory-Huggins' Theory

Following this failure of the theory, extensions to try and “fix” weaknesses such as this one have been developed by several authors. As mentioned above, the Flory-Huggins' lattice model considers a uniform lattice and therefore at best only holds for concentrated solutions. Flory and Krigbaum (1950) modified the lattice theory so that it could be applied to dilute polymer solutions. The new lattice consisted of regions or domains of individual polymers chains surrounded by regions of pure solvent, therefore abandoning the uniform density lattice idea. When the concentration of the polymer molecules is so small that they are far apart from each other and separated by regions of solvent, the concentration of segments must be larger in the neighbourhood of the molecules and zero in the regions between them. The segments occupy a finite volume and tend to exclude all others from this volume they occupy. Within such excluded volume occur long-range interactions between
molecules whose thermodynamic functions can be derived. For a dilute solution, the expression for the activity of the solvent becomes:

\[
\ln a_i = (\kappa_1 - \psi_1)\phi_i^2
\]  

with which they define two new parameters, an enthalpy parameter and an entropy parameter, \( \kappa_{12} \) and \( \psi_{12} \) respectively. The temperature at which these parameters become identical in value is known as the theta temperature or the Flory temperature and is defined as:

\[
\theta = T \frac{\kappa_1}{\psi_1}
\]

At this temperature, the excluded volume effects disappear and the polymer chain is unperturbed. Above this temperature the polymer chains expand creating interactions with the solvent and below it, the polymer segments act as though they attract one another, the excluded volume becomes negative and eventually phase separation occurs. This temperature can be obtained from phase separation experiments. Referring back to figure 2.4, if a line were to be drawn connecting the UCST's at increasing molecular weights of polymer and extrapolated to zero polymer concentration, the temperature at which this line crosses the \( y \)-axis, corresponds to the theta temperature. The theta temperature is equivalent to the UCST of a solution of a polymer of infinite molecular weight.

Two years after Flory and Huggins published their theory, Guggenheim (1944) presented a similar lattice theory for athermal polymer solutions. He considered a lattice with a smaller number of nearest neighbouring sites and also considered the possibility of there being multiple demands for one particular site. His results showed that Flory’s derivation neglects the effect of the finite co-ordination number because he assumed that the probability of occupying a site is independent of the knowledge of how a neighbouring site has been occupied. Guggenheim worked further on this with McGlashan (1950) and developed expressions for solutions of monomers with triangular trimers, square and tetrahedral tetramers. Along the same lines, Staverman (1950) and Tompa (1952) modelled solutions of \( r \)-mers occupying more-than-singly-connected set of sites. This is a set
of sites in which a single cut between two adjacent sites does not necessarily separate into two disconnected sets.

As already mentioned, polymer solutions are classified as irregular solutions as the excess volume, entropy and enthalpy upon mixing, are all non-zero. Nevertheless, Hildebrand (1947) used the concept of regular solutions and presented an alternative derivation for the entropy of mixing. Instead of assuming that the lattice sites for the solvent and the polymer are equal in size, he assumed that the free volume available per unit volume of solution is identical for the solvent and the polymer. Hildebrand and Scott (1962) then introduced the concept of a solubility parameter as a measure of the interaction energies between molecules, which can be used to estimate the $\chi_{12}$ parameter for the polymer solution. This solubility parameter is related to the cohesive-energy density, i.e. the amount of energy per unit volume that keeps the solution in the liquid state and it is defined as its square root. They wrote,

$$\chi_{12} = \frac{\nu_1}{RT} (\delta_1 - \delta_2)$$

(2.71)

where $\nu_1$ is the molar volume of the solvent and $\delta_1$ and $\delta_2$ are the solubility parameters of the solvent and polymer respectively. The optimum condition for solubility is when the two parameters are equal in value making $\chi_{12}$ equal to zero.

A few years later in 1968, Koningsveld and Staverman included molecular weight dependence in the expression for the Gibbs free energy of mixing. In the original Flory-Huggins theory, the interaction between the polymer segments and the solvent were accounted for in the interaction energy term which was assumed to be constant and independent of molecular weight and temperature. Through experiments and through theories (reviewed by Staverman, 1962), this assumption was proved to be rather unrealistic.

Nevertheless, the most dramatic change made to the lattice theory was made by Sanchez and Lacombe in 1976. They incorporated the concept of compressibility into the derivation of the Gibbs free energy of mixing thereby allowing the prediction of LCST behaviour in polymer solutions. The details of this model and the resulting equations are explained in full in Chapter III as well as all other major developments on polymer solution thermodynamic theories since the Flory-Huggins' model.
3.1 – Introduction

There is no doubt that engineers and scientists require tools to predict the phase behaviour of polymer solutions. Ideally, well-founded and accurate thermodynamic models are needed, able to describe the behaviour of these mixtures in the widest range of operating conditions. A useful model should be able to describe mixtures containing components of differing sizes and molecular interactions, in the simultaneous presence of both vapour and liquid phases. It should also be able to describe all the different types of phase equilibria that are observed experimentally. For the specific case of polymer-solvent systems, the first systematic approach to describing the thermodynamic and phase behaviour was developed by Flory and Huggins (Flory, 1953); this approach has been described in detail in the preceding chapter. Many other models have been developed for polymer solutions. Initially, these theories attempted to overcome the limitations of the Flory-Huggins approach but subsequently other models founded on different principles have emerged.

In this chapter, following an introduction on basic statistical thermodynamic concepts, an overview is given of the most important models
developed since the pioneering work of Flory and Huggins. The discussion has been divided into two, thereby reflecting the two general approaches which can be used to describe mixture phase behaviour. Most emphasis is placed on two particular models, which are described fully in sections 3.5 and 3.6. These are the Sanchez-Lacombe equation of state (Sanchez and Lacombe, 1976) and the unified activity coefficient free volume (UNIFAC-FV) model of Oishi and Prausnitz (1978). These will be used later to model the liquid-liquid equilibria and vapour-liquid equilibria of the polymer-solvent systems investigated experimentally.

3.2 — Statistical Thermodynamics

In order to understand modern thermodynamics, some basic statistical mechanics and thermodynamic concepts need to be introduced. The utility of statistical mechanics is that it links the microscopic and macroscopic descriptions of a system by means of a single statistical quantity, the partition function, \( Q \). This function relates the most probable distribution of energy states in a system to the macroscopic thermodynamic properties of that system. In deriving the partition function, we consider a collection of very large number of \( N \) systems, referred to as the canonical ensemble, which replicate a macroscopic thermodynamic system of \( N \) molecules in a volume \( V \) at temperature \( T \). Even though all systems in the ensemble have the same values of \( N \), \( V \) and \( T \) they are not equal microscopically. It can be shown (Reed and Gubbins, 1973) that the probability \( P_i \) of finding one system selected at random in a quantum state labelled \( i \) varies exponentially with the energy \( E_i \) associated with that state such that:

\[
P_i(E_i) \propto \exp\left(-\frac{E_i}{kT}\right) \tag{3.1}
\]

where \( k \) is Boltzmann’s constant. Since the probability of the system being in some state is unity, \( \sum_{i=1}^{N} P_i E_i = 1 \) and therefore:

\[
P_i(E_i) = \frac{\exp\left(-\frac{E_i}{kT}\right)}{Q} \tag{3.2}
\]
where

\[ Q(N, V, T) = \sum_{i=1}^{N} \exp(-E_i / kT) \]  

(3.3)

This is called the canonical partition function and although has no well-defined physical meaning is a tool in terms of which all thermodynamic properties can be obtained. As an example, the internal energy of the system is given by,

\[ U = \sum_{i=1}^{N} E_i P_i = \frac{1}{Q} \sum_{i=1}^{N} \exp(-E_i / kT) \]  

(3.4)

Which following from the definition of \( Q \) can be written as:

\[ U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \]  

(3.5)

All other thermodynamic variables can be derived in a similar way. The results are given in the table below (Assael et al., 1996):

<table>
<thead>
<tr>
<th>Thermodynamic Property</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helmholtz free energy</td>
<td>( A = -kT \ln Q )</td>
</tr>
<tr>
<td>Entropy</td>
<td>( S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k \ln Q )</td>
</tr>
<tr>
<td>Pressure</td>
<td>( P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} )</td>
</tr>
<tr>
<td>Gibbs free energy</td>
<td>( G = kTV \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} - kT \ln Q )</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>( H = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)<em>{N,V} + kTV \left( \frac{\partial \ln Q}{\partial T^2} \right)</em>{N,V} )</td>
</tr>
<tr>
<td>Chemical potential per molecule</td>
<td>( \bar{\mu} = -kT \left( \frac{\partial \ln Q}{\partial N} \right)_{T,V} )</td>
</tr>
</tbody>
</table>

Table 3.1 – Definition of thermodynamic properties in terms of the partition function \( Q \).
To evaluate the partition function, it is convenient to recognise that the energy of a system is made of several contributions. The most important factorisation separates an internal energy contribution, $Q_{\text{int}}$, due to rotational and vibrational degrees of freedom (so-called internal degrees of freedom), from the translational contribution, $Q_{\text{trans}}$, due to the positions and motions of the centres of mass of the molecules. Thus, $Q$ factorises into two terms:

$$Q = Q_{\text{int}}(N,T)Q_{\text{trans}}(N,V,T) \quad (3.6)$$

Separating the terms in this way implies that the internal energy of each molecule is independent of the position of any molecule, $Q_{\text{int}}$ is independent of the volume of the system. In the classical approximation, the translational contribution to the partition function is the product of two factors, one arising from the kinetic energy and the other from the potential energy. For a one-component system of $N$ molecules, $Q_{\text{trans}}$ is given by:

$$Q_{\text{trans}} = Q_{\text{kin}}(N,T)Z_{\pi}(N,T,V) \quad (3.7)$$

For a given number of molecules, $Q_{\text{kin}}$ depends solely on the temperature. The second factor, $Z_{\pi}$, called the configurational partition function, contains information about the interactions between the molecules in the system and is the only term in $Q$ that depends on volume. Therefore, from table 3.1, when solving for the system pressure we can write:

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = kT\left(\frac{\partial \ln Z_{\pi}}{\partial V}\right)_{N,T} \quad (3.8)$$

### 3.3 — Models for Thermodynamic Phase Behaviour

As previously mentioned, the partition function serves to provide an expression for the pressure of a system as a function of the temperature, volume (or density) and composition. This leads to the equation of state (EoS) approach which is one of the two approaches that can be taken to describe the phase behaviour of
thermodynamic systems. The other is by using an activity coefficient model (ACM). It would be useful if either approach described the thermodynamic behaviour of polymer solutions to the same accuracy, but unfortunately this is not the case. As it happens, certain models are more useful than others depending on the nature of the system being described and the conditions in question. As a general rule of thumb, ACM's are useful when describing systems at low to moderate pressures (about 10 bar) as they mostly do not account for the compressibility of fluids (Bokis et al., 1999).

3.3.1 — Equations of State

Equations of state are used to derive all thermodynamic properties of a system from an expression for the pressure of the system that has the following general form:

\[ P = f(T, \rho, x_1, x_2, ..., x_n) \]  

(3.9)

where \( \rho \) is the density and \( x_i \) is the mole fraction of component \( i \) in a mixture of \( n \) components. The functional form of an equation of state is normally arrived at by combining some theoretical analysis of molecular interactions with a number of parameters that are obtained by fitting the equation to experimental data for the pure components. It would be desirable if such equations of state would describe mixture behaviour with only these parameters, but in practice the addition of extra binary interaction parameters is necessary in order to obtain good qualitative and quantitative agreement between models and experimental data. Equations of state serve to describe both LLE and VLE Equations of state are very attractive tools as they serve to describe both small and large molecules and their mixtures, and correlate volumetric, calorimetric and phase behaviour.

The most famous is the van der Waals’ (VdW) cubic equation of state given by:

\[ P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]  

(3.10)
where $R$ is the universal gas constant, $V_m$ is the molar volume and $a$ and $b$ are two parameters that need to be adjusted to fit the critical properties, vapour pressures or other thermodynamic properties of a pure fluid. At a fixed temperature the function given in (3.10) has three solutions for the molar volume, the smallest corresponds to the liquid phase, the largest corresponds to the gas phase and the intermediate value corresponds to a root with no physical significance. As the temperature is increased towards its critical value, the three roots converge to one solution, which corresponds to the critical density.

To extend use of the equation to mixtures, a series of so-called mixing and combining rules are necessary. The former relates mixture parameters to pure components and interaction terms, whereas the latter relates interaction terms to pure component parameters and interaction parameters. Parameter $a$ in the VdW equation can be used to illustrate what this means. In a mixture, the composition dependent parameter $a$ is given by (mixing rule):

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij}$$

(3.11)

where $x_i$ and $x_j$ are the mole fractions of components $i$ and $j$ respectively, $n$ is the total number of components in the mixture and $a_{ij}$ contains information about the interactions between molecule of component $i$ and component $j$. Correspondingly, the combining rule, for $a_{ij}$, is usually assumed to be based on a geometric mean such that:

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}$$

(3.12)

where $k_{ij}$ is the so-called binary interaction parameter.

Describing polymer solution thermodynamics begun with the Flory-Huggins lattice theory and probably the most serious shortcoming of this theory is that it does not allow for the volume of the lattice to change as a function of pressure, hence making it unable to predict the thermally induced phase separation phenomena observed at high temperatures. A way to overcome this is by formulating an expression for the pressure in terms of temperature, volume and composition. In what follows, the basic ideas behind the equations derived over the
years for polymer solutions as well as their strengths and limitations will be briefly
described.

Following from the assumptions of Prigogine (1957), Flory and co-workers
(1964) developed one of the earlier equations of state for systems containing
copolymers. They considered a chain molecule to be made of a succession of segments
that do not necessarily correspond to the repeating unit. The motions of the chain
molecule can be unambiguously separated into internal (intra)molecular) and external
(intermolecular). They assumed that the intermolecular energy depends only on the
volume and a hard-sphere repulsive potential is used for the segments. Based on
these assumptions, they derived a partition function $Q$ consisting of three terms: a
combinatorial term, a free volume term and a configurational term. The free-volume
is defined as the difference between the total volume and the excluded volume,
which is that part of the molar volume which is not available to a molecule due to the
presence of others. Flory's equation of state contains three characteristic parameters
which are obtained from pure component experimental PVT data or thermodynamic
properties (such as the thermal expansion coefficient, the isothermal compressibility
or the thermal pressure coefficient). This equation provided an improvement to the
Flory-Huggins lattice theory, being able to predict LCST behaviour (Flory et al. 1964).
Unfortunately, it is only applicable to liquid polymer solutions since it does not
reduce to the ideal gas equation in the limit of zero pressure and infinite volume.
This defect leads to incorrect behaviour for systems at high pressure (Renuncio and
Prausnitz, 1976).

Beret and Prausnitz (1975) developed a similar EoS derived from a van der
Waals partition function that takes into account three factors. The first term comes
from the work of Carnahan and Starling (1969) and accounts for the free volume
effects. The second term accounts for contributions from vibrational and rotational
degrees of freedom and was postulated such that (i) it uses Prigogine's approximation
that at liquid-like densities all external degrees of freedom can be considered as
equivalent translational degrees of freedom, (ii) it satisfies the ideal gas limit and (iii)
it has a value of unity when there are no rotational or vibrational degrees of freedom.
The last term accounts for the interaction energies between the molecules in the
mixture and it is based on the molecular dynamic results of Alder et al. (1972).
Unfortunately, this equation of state is quite complicated and can be difficult to use
for multi-component mixtures.
In another attempt to correct the failure of Flory's EoS in the ideal gas limit, Holten-Andersen and co-workers (1987) extended the work of Prigogine (1957), Patterson (1967) and Flory (Flory et al., 1964 and Flory, 1970). The new partition coefficient contains two terms, an attractive contribution that accounts for the random intermolecular orientations and favoured intermolecular configurations, and a free volume term. Although the model has the form of a liquid-phase equation of state, the molecular parameters are not directly calculated from experimental data but using a group-contribution approach.

In 1990, Chen et al. revised the Holten-Andersen model and proposed a modified and simpler version, now known as the GC-Flory EoS. It combines the free-volume expression from the Flory EoS with a local composition expression for the energy of the system. The model is formulated as an expression for the activity of component \( i \) in the system and is calculated from the sum of three contributions. There is a combinatorial contribution, an interaction or enthalpic contribution and a free-volume contribution. They showed that the predictions from the equation were in good agreement with experimental data for pure solvent and polymer properties. Similarly, the agreement between solvent activities in polymer solutions was very good and often better than the predictions using the Holten-Andersen equation. In two consecutive papers, Bodganic and Fredenslund (1994) and Saraiva et al. (1995) revised pure component parameters and extended the range of solvents that can be predicted. They showed that the GC-Flory EoS performs well in predicting both VLE and LLE of an extensive range of polymer solutions. However they have found that the agreement was only qualitative.

The models described until now all use a volume-dependent energy term to account for compressibility and to achieve the prediction of LCST’s in polymer solutions. Alternatively, a lattice as used by Flory (1942) and Huggins (1942) can be used allowing partial occupation, i.e. allowing the existence of some unoccupied sites or \( \text{hoks} \). Several authors including Sanchez and Lacombe (1976), Kleintjens and Koningsveld (1980), and Panayiotou and Vera (1982) have developed equations based on this approach. Sanchez and Lacombe (1976) developed the so-called lattice-fluid model on the assumption of completely random distribution of molecules and vacant sites on the lattice. An expression for the Gibbs free energy of the system was derived which is the addition of two terms, an attractive energy term based on random mixing (i.e. the composition anywhere in the solution is equal to
the overall composition) and a combinatorial entropy term. They applied the more rigorous Guggenheim-Huggins-Miller (Guggenheim, 1952) approximation to enumerate the number of possible configurations of molecules and holes on a lattice similar to that used by Flory (1942) and Huggins (1942). The model contains three pure component parameters and one binary interaction parameter per pair of components. There are a number of reports in the literature that show the applicability of the model to describing phase behaviour in pure components (Sanchez and Lacombe, 1976) and polymer solutions (Koak and Heidemann, 1996; An and Wolf, 1998; Orbey et al., 1998b and Tao et al., 1999), including high pressure phase behaviour in ternary systems (Kiran et al., 1993; Xiong and Kiran, 1994 and 1995). For example, Bokis et al. (1999) tested the SL equation against VLE in a polyethylene/ethylene system and found the agreement with experimental data to be good, but when predicting the saturation curve of ethylene, it is found to over predict the critical pressure. An and Wolf (1998) have shown very good agreement between the calculated binodal curves and experimental data for systems containing different molecular weights of polystyrene with trans-decalin (C_{10}H_{18}) at atmospheric pressure. This is one of two models studied in this work and will be described in full detail in section 3.5.

Kleintjens and Koningsveld (1980, 1985) developed a similar equation to that of Sanchez and Lacombe, which is known as the Mean Field Lattice Gas (MFLG) model. A pure component is considered as a pseudo-binary mixture of occupied and vacant sites distributed randomly on a lattice. Changes in volume with pressure or temperature are modelled by changes in the concentration of the vacant sites (holes). The molar volume per lattice site is kept constant and independent of temperature and pressure and also, instead of using a constant lattice coordination number, interacting contact surface areas are assigned to each kind of site in the system. Further, molecules may occupy m lattice sites, where even fractional numbers are permitted for occupancy. The expression for the free energy of mixing consists of two terms. One term accounts for the energy of mixing and the other is the Flory-Huggins combinatorial term accounting for the entropy of mixing but with the addition of an empirical entropy correction. For the internal energy expression, only nearest-neighbour interactions contribute. Therefore, when calculating VLE, the equilibrium is considered as an equilibrium between two fluid phases of differing hole concentration only, such that a change in hole concentration will change the
number of contacts between the occupied sites and with that the total internal interaction energy. Unfortunately, this model can have five or more parameters for the pure components, some being temperature dependent, making it unattractive. Nevertheless, the model has shown to be useful in describing both pure component and multi-component phase behaviour (Kleintjens and Koningsveld, 1980; Beckman et al., 1987 and Kennis et al., 1990).

Another important variation of the lattice fluid approach is the EoS derived by Panayiotou and Vera in 1982. Their model is also similar to the SL equation but differs in two aspects: (i) the average mer volume of each lattice site is fixed to \(9.75 \times 10^{-3}\) \(\text{m}^3\) \(\text{kmol}^{-1}\) (based on good PVT predictions of polyethylene) and (ii) there is a correction for non-random mixing which arises from the interaction energies between molecules. Fixing the volume of the lattice avoids having to mix different pure components lattice volumes for a mixture. Moreover, a chain segment or a molecule is allowed to occupy a fraction of a unit cell. They used the quasi-chemical approach for the non-randomness of the molecules in the mixture and for binary mixtures, the quasi-chemical expressions reduce to a quadratic equation with one unknown. In the case of a multi-component mixtures, the resulting equations are a coupled set of quadratic equations (Kumar et al., 1987). A Taylor expansion on these expressions around the point where there are no interaction energies (random mixing) can be used to aid computation.

Similar to the way that Chen et al. (1990) modified the Flory EoS, High and Danner (1989, 1990) modified the Panayiotou and Vera EoS by using a group contribution approach in the calculation of the molecular parameters. The group contributions are calculated from saturated liquid densities and vapour pressure data of small molecules. Furthermore, to apply the High-Danner equation to mixtures, only one binary parameter is required. This model known as the group contribution lattice fluid (GCLF) EoS, was initially tested against pure component thermodynamics including polymer PVT data (Parekh and Danner, 1995), mixtures of small molecule mixtures and polymer solution VLE. Unfortunately, predictions for only a few polymer solutions were found to be in very good agreement with experimental data (High and Danner, 1989). In an attempt to improve the model, Lee and Danner (1996a) added more groups and provided better temperature dependencies of the interaction energies. This modified GCLF has yielded very good predictions for activity coefficients at both infinite dilution and at finite
concentrations of solvents in polymers, including in some copolymer systems (Lee and Danner, 1996b). In a second publication, Lee and Danner (1996c) showed that the equation can predict UCST's (PMMA/tert-butyl alcohol), LCST's (high density PE/2,4-dimethylpentane) and hour-glass shaped liquid-liquid phase separation curves (polyethylene glycol/tert-butyl acetate). The LLE predictions were made with the same group-contribution parameters as used for the prediction of VLE.

An alternative way of dealing with the thermodynamics of polymer solutions through statistical mechanics is to look closely at the molecular structure of the components in the mixtures and at interactions between molecules. If the resulting equations of state are applied to systems of small molecules then the parameters describing molecular geometry can be fitted experimentally and mixing rules can be used to extend the equations to mixtures including polymer solutions. In this perturbation models, a reference system is assumed (in the case of the ones presented here, this is a system of athermal hard spheres) and corrective terms attributed to chain connectivity and bonding are introduced to describe the real system. Application to polymer chains results in the Perturbed Hard-Sphere-Chain Theory (PHSCT) of Song et al. (1994a, 1996). The polymer is considered as a long chain of hard spheres that are chemically bonded together and that interact with their neighbouring molecules. The equation developed is the sum of two terms, a reference part (Chiew, 1990) and a van der Waals type attractive or perturbation term. In this model, each pure solvent or homopolymer is characterised by three molecular parameters, one accounting for the chain length, one for the hard-sphere diameter and a third for the interaction energy. As is usual, the parameters are obtained by fitting the EoS to vapour pressures and densities. For each pair of unlike segments, two binary parameters are used. The PHSCT equation has been used to calculate PVT behaviour of pure components and polymer solution VLE (Gupta and Prausnitz, 1995, 1996) and LLE (Song et al., 1994b,c, 1996; Lambert et al., 1995 and Hino et al, 1996). The predictions are acceptable but the equation is of a fairly cumbersome form. Furthermore, the equation fails to accommodate for specific interactions such as those arising from hydrogen bonding.

An improvement has been achieved with the Statistical Associating Fluid Theory (SAFT) developed by Chapman et al. (1989, 1990) and Huang and Radosz (1990, 1991). SAFT is a perturbation theory based on the theory of associating fluids developed by Wertheim (1984a, b; 1986a, b). Molecules are represented as covalently
bonded chains of segments that contain sites and which can form associative complexes. The new equation contains separate terms for the different types of interactions between molecules, namely three contributions to the residual Helmholtz free energy added together: term one, accounts for the connectivity of the hard segments in the main chain and term two accounts for the presence of site-site specific interactions between the segments. Terms three and four account for the energy of site-site interactions of the segments with themselves or other segments. The first three terms form the reference equation and the fourth one is the perturbation term. The hard-sphere term is calculated as originally proposed by Carnahan and Starling (1969) but extended to mixtures. The mean-field attractive energy or dispersion term can be determined from that given by Cotterman et al. (1986). This model has a total of five parameters, three pure component parameters and two binary parameters. SAFT has been used to calculate the phase behaviour of associating and non-associating polymer solutions. Chen and co-workers have applied SAFT to non-hydrogen bonding polyolefin solutions (Chen et al., 1992 and 1993; Condo and Radosz, 1996), and Lee et al. (1996) used it to model the cloud-point behaviour of binary mixtures of PE, poly(ethylene-o-co-acrylic acid) and poly(ethylene-o-co-methyl acrylate) copolymers in non-polar alkanes. Their investigation led to the conclusion that a lot of work is still needed in accounting for polarity effects in systems containing polymers. Other theories based on the same principles are the generalized Flory dimer equation (Bolds et al., 1994; Wu et al., 1996), the polymer chain of rotators EoS (Sy-Siong-Kiao et al., 1996) and the EoS for chainlike molecule fluids (Hu et al., 1999).

In recent years, there have been efforts to apply the well-known and useful cubic equations of state to systems containing polymers. In 1989, Sako et al. proposed a three-parameter cubic equation of state applicable to high-pressure VLE of the PE/ethylene system, but the method to obtain equation of state parameters for the polymers was very unclear. A method was proposed by Kontogeorgis and co-workers (Kontogeorgis et al., 1994b and Harismiadis et al., 1994) which involved fitting them to volumetric data at zero pressure. They applied the van der Waals equation to correlate VLE of some PE and poly(isobutylene) solutions. Although the prediction was satisfactory, the equation performed poorly in predicting volumetric behaviour of polymers and also yielded very high vapour pressures for these. Further in 1994, Orbey and Sandler used the Flory-Huggins equation with a
modified Peng-Robinson (PR) EoS to correlate VLE in polymer solutions. They obtained the two parameters for the polymer by fitting them to one density datum and setting the polymer vapour pressure to $10^{-7}$ bar. Unfortunately, they found that calculated excess volumes of mixing were very large compared to experimental findings and this was attributed to poor volume predictions of the PR equation (Liu and Wong, 1996). Furthermore, a pair of parameters is needed for each molecule of polymer. Orbey and co-workers (1998c) went further and used the modified PR equation of state and when extending it to mixtures, included a two term expression for the excess Gibbs free energy. It consists of a Flory-Huggins entropic contribution and a residual term that accounts for the existence of specific interactions between molecules. The equation was tested against several polymer solutions. Only in some cases was it possible to use the equation as a predictive one (i.e. where no binary interaction parameters are necessary).

Louli and Tassios (2000) have recently also used the PR EoS to model VLE in polymer solutions and used polymer PVT data to fit the two parameters independently of polymer molecular weight. Also, they tested the effect of using different mixing rules for the mixture parameters. They used (i) the Van der Waals one fluid mixing rule with the BertheJot combining rule and the arithmetic mean for $a_p$, and the Lorentz rule for $b_p$, (ii) the one of Zhong and Masouka, and (iii) the modified Huron-Vidal first order (by coupling the cubic equation to the FH model). All involve just one interaction parameter. This equation proved to be useful although they did not agree on one choice of mixing rule.

Orbey et al. (1998b) also applied another cubic EoS, that of Soave-Redlich-Kwong (SRK) with mixing rules based the FH equation. They tested the model with several polymer solutions and found that there was a very good agreement between experimental activity coefficients and the model results. Volumetric predictions were not so good and two alternative relationships to calculate the polymer “critical” constants were proposed. These improved the density predictions but worsened agreement for the VLE of polyethylene (of high molecular weights) in ethylene.

A very similar approach was taken by Bertucco and Mio (1996) who used a group contribution model to calculate the activity coefficients at infinite-pressure whilst keeping the SRK form of the equation. To fit the parameters they required one density value of the pure polymer at the temperature of interest and one activity coefficient of the solvent in the polymer solution. They have shown good
predictions of VLE in a series of polymer solutions including PS/chloroform, poly(vinyl acetate)/n-propanol and PS/acetone. Poor predictions were found though for the system PE-ω-poly(vinyl acetate) (50/50) with chloroform, which they attributed to possible hydrogen bonding between the acetate and the chloroform groups.

3.3.2 – Activity Coefficient Models

The alternative to modelling phase behaviour involves using activity coefficient models. These are usually empirical in nature and serve to predict the activity coefficient of a component in a mixture. The activity coefficient $\gamma$ represents a deviation from the ideal behaviour described by Raoult's Law, for which $\gamma \to 1$. The general equation for determining activity coefficients using this approach is (Assael et al., 1996):

$$\gamma_i = \left( \frac{x_i}{\gamma_i} \right) \left( \frac{P}{P_i^\sigma} \right) \left( \frac{\phi_i^{(v)}}{\phi_i^{(s)}} \right) \left( \frac{1}{F_i} \right)$$  \hspace{1cm} (3.13)

where $\gamma_i$ and $x_i$ are the mole fractions of component $i$ in the vapour phase and liquid phase respectively, $P$ is the pressure, $P_i^\sigma$ is the saturated pressure of pure $i$, $\phi_i^{(v)}$ is the fugacity coefficient of component $i$ at the vapour-phase composition, $\phi_i^{(s)}$ is the fugacity coefficient of the pure saturated vapour and $F_i$ is the Poynting factor. Activity coefficients tend to be strong functions of temperature and composition but not of pressure. At low pressures, vapour phases usually approximate ideal gases for which $\phi_i^{(v)} = \phi_i^{(s)} = 1$ and the Poynting factor becomes insignificant, such that the equation reduces to:

$$\gamma_i = \left( \frac{x_i}{\gamma_i} \right) \left( \frac{P}{P_i^\sigma} \right)$$  \hspace{1cm} (3.14)

which reduces to Raoult’s law when $\gamma_i \to 1$. 

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Two approaches are employed to obtain values for the parameters in these models. The first involves fitting the ACM to experimental VLE data normally at one temperature for a binary system. Once parameters have been fitted to all pairs of components in a multi-component mixture, prediction of thermodynamic behaviour can be achieved. Alternatively, parameters can be calculated via a group-contribution method. In this approach, the mixture is considered as being made up of the structural units of the components in the mixture, rather than being made up of the molecules as such. These structural units are referred to as sub-groups and parameters are characteristic of each of these sub-groups. Activity coefficients do not only depend on the sub-group properties but also on interactions between sub-groups. Here, similar sub-groups are assigned to a main group and all sub-groups belonging to a main group are considered identical with respect to group interactions. Therefore parameters characterising group interactions are identified with pairs of main groups.

The first activity coefficient model to be developed for polymer solutions (described in section 2.4) was that independently derived by Flory (1942) and Huggins (1942). Since then, another important correlative ACM has been developed, the polymer-Non-Random Two-Liquid model (Chen, 1993), which is an extension of the NRTL model of Renon and Prausnitz (1968) for small molecule systems. On the other hand, predictive models based on group-contributions such as the UNIFAC-FV model (Oishi and Prausnitz, 1978) have been derived specifically for polymer/solvent systems. This is the second of the studied models in this work and will be described in full detail in section 3.6.

The concept of local composition was first introduced by Wilson (1964) in deriving the Wilson equation for small molecules. It is recognised that due to intermolecular interactions between like and unlike molecules within a solution, the composition at a particular point in the solution will not be equal to the overall composition. This concept was also used to develop the original NRTL equations that have been used extensively to correlate phase equilibria in systems of small molecules of all kinds. To extend the model to systems containing polymers, Chen (1993) replaced the combinatorial entropy of mixing term by that given by Flory and Huggins and kept the original energetic mixing term that accounts for the weak local physical interactions that exist between solvent and polymer chain segments. The resulting equation therefore contains two contributions and reduces to the well-
known NRTL equation (Renon and Prausnitz, 1968) if no polymers are present. In a polymer/solvent system, the local composition concept is applied to interactions between solvent and polymer segments as opposed to polymer chains. This polymer version of NRTL model requires two binary interaction parameters for each of the solvent-solvent, polymer segment-solvent and polymer segment-polymer segment pairs. Chen (1993) tested the equation by correlating activities at 298.15 K for several polystyrene solutions (PS in acetone, chloroform, n-propyl acetate and toluene) and found excellent agreement with experimental data. Unfortunately, this model cannot predict LCST behaviour in polymer solutions neither can it accommodate for hydrogen bonding or free-volume effects.

The second type of ACM's are models derived from the original group contribution method developed by Fredenslund et al. (1975), UNIFAC, and are all predictive models. The activity of a component in a mixture is the sum of two contributions, a combinatorial contribution due to differences in molecular sizes and a residual or energetic contribution due to molecular interactions. These contributions are calculated from the sole knowledge of the molecular structure of the components in the mixture. The main advantage is that no input parameters are required and this potentially proves useful for systems where no experimental data is available. The original expression for the activity coefficient of component \( i \) in a mixture is given by the sum of two contributions. The first is a combinatorial contribution developed by Stavermann (1950) and the second is a residual term taken from Guggenheim’s quasichemical theory. All parameters are the result of fitting the equation to thermodynamic data of mixtures of small molecules and values are found in a number of publications (Fredenslund et al., 1977; Oishi and Prausnitz, 1978 and Hansen et al., 1991). Although UNIFAC has proved to be a convenient and easy way of calculating activities in small molecule systems, is it not that powerful for systems containing macromolecules (Oishi and Prausnitz, 1978; Tseng and Lloyd, 1984; Zhong et al., 1996). Following their findings, Oishi and Prausnitz (1978) recognised that an extra contribution to the activity coefficients is necessary for polymer/solvent systems, a contribution that accounts for the free-volume effects which arise due to molecular size differences between polymer and solvent molecules. The free-volume term was derived from Flory’s EoS assuming a zero value for Flory’s chi parameter. When first tested against experimental activity coefficients, Oishi and Prausnitz (1978) reported a reduction of 30% in the average
error in the activity coefficients for fourteen tested systems. Two main problems with UNIFAC-FV have been recognised, the first being that the evaluation of the free-volume term requires prior knowledge of the pure components' specific volumes at the temperature in question and the second being the assignment of a value to the \( c \) parameter which is introduced in the FV term. This parameter represents the external degrees of freedom of component \( i \) and for small molecules, it has been set to a value of 1.1 following earlier results from Flory (1970) and Beret and Prausnitz (1975). For larger molecules, Oishi and Prausnitz (1978) already had pointed out that "...a large value of \( c \) might be needed", but they gave no such value. For these reasons, Iwai et al. (1985) proposed a new expression for the free-volume term derived from a partition function applicable to polymer/solvent systems and used an EoS to calculate the specific volumes of the pure components. They successfully predicted Henry's constants for systems of PS/xylene, natural rubber/benzene and poly(styrene-\( o \)-butadiene)/octane at several temperatures (Iwai and Arai, 1989). Furthermore, they used this modified model to predict LLE of polystyrene with cyclopentane and cyclohexane (Iwai et al., 1993). The agreement was very good but only after fitting both the interaction parameters and the \( c \) parameter to cloud-point data.

UNIFAC-FV became the starting point for the application of UNIFAC-based models to polymer solutions and since then a series of UNIFAC-based equations has been developed. Kontogeorgis et al. (1993) developed the Entropic-FV model. It consists of two contributions to the activity coefficient, a combined combinatorial and free-volume contribution term presented by Elbro et al. (1990) and a residual term taken from the original UNIFAC equation. In contrast to UNIFAC-FV, the interaction parameters are temperature dependent and the combinatorial-free volume term is much simpler (for example, the \( c \) parameter is removed). Lee and Danner (1997) have shown that this model results in the over prediction of activity coefficients at infinite dilution especially for polymers in weakly polar solvents, although it performs well in predicting activity coefficients in systems containing strongly polar solvents. Similar results were found by Kontogeorgis et al. (1993) who studied a large range of polymer solutions. Average deviations between experimental and predicted values of the infinite dilution activity coefficient at a series of temperatures varied from 2.4% (poly(iso butylene)/n-hexane) to 7.6% (low density PE/n-hexane) for athermal solutions, and between 1.2% (PE/benzene) to
27% (poly(butadiene)/methanol) for polymer solutions with specific interactions. Results compare well to predictions from UNIFAC-FV and the GCLF theory. The disadvantage of this model is that an accurate knowledge of solvent and polymer volumes is necessary. Kontogeorgis et al. (1995) also tested the model against LLE data and although it was capable of qualitatively predicting UCSTs, LCSTs and hourglass shape phase diagrams and even the correct molecular weight dependence of the critical solution temperatures, the quantitative agreement was not so good. Furthermore, it fails to predict LCST behaviour in athermal solutions like PE and poly(iso butylene) in n-alkanes. The combinatorial term yields positive entropies of mixing implying complete miscibility.

Fairly recently, Bodganic and Vidal (2000) developed a segment-based thermodynamic model by modifying the entropic-FV model and applied it to LLE of polymer solutions. The interactions considered are between segments (repeating units of polymer or copolymer) and the solvent molecules, as opposed to between the polymer and the solvent or functional group interactions. New values of the interaction parameters were obtained by fitting with experimental LLE data. They tested a large number of monodisperse polymer/solvent systems and found very good agreement both qualitative and quantitative, with systems exhibiting LCST, UCST, hour-glass shaped phase diagrams and even closed-loop behaviour.

3.4 — Choice of Thermodynamic Models

In the next two sections, the two thermodynamic models chosen for study in this work will be described in detail, the Sanchez-Lacombe equation of state and the UNIFAC-FV model. Out of all the available models, why choose these two? First of all, it is the aim of any thermodynamic model to be able to describe correctly both VLE and LLE behaviour. The purpose of this work is to look at one example of each of the two types of thermodynamic approaches that are available to model polymer solutions. That is to say, choose one equation of state and one activity coefficient model and test their power in correlating or prediction both types of phase behaviour. But which EoS and which ACM? The Sanchez-Lacombe equation of state and UNIFAC-FV were chosen for a number of reasons. First, they have proved to be well-founded models and are fairly uncomplicated in terms of working
equations making them good candidates for easy use. Further, there are still are significant gaps in testing these two models. There is a fair amount of literature where the SL equation has been tested against liquid-liquid coexistence curves and similarly, due to its convenient nature, the UNIFAC-FV model has been used in calculating activity coefficients of solvents in polymers and comparing these to experimental measurements. On the contrary, little emphasis has been given to activity coefficient calculations from the SL equation or to the prediction of binodal curves using the UNIFAC-FV model. For all these reasons, these two models seemed the most attractive.

3.5—Sanchez-Lacombe Lattice-Fluid Model

Conceptually the lattice-fluid theory developed by Sanchez and Lacombe (Sanchez and Lacombe, 1976; Lacombe and Sanchez, 1976; Sanchez and Lacombe, 1977 and Sanchez and Lacombe, 1978;) is very similar to that derived independently by Flory (1942) and Huggins (1942). The lattice used by these two authors to describe the thermodynamics of polymer solutions is rigid and allows no density changes, as well as having all lattice sites occupied by either a solvent or a polymer molecule. Consequently this leads to a failure of the model when trying to predict lower critical solution temperature behaviour. To overcome this problem, Sanchez and Lacombe relaxed the assumption of a rigid lattice by allowing the existence of vacancies (or holes). They initially developed the theory for pure fluids (Sanchez and Lacombe, 1976) but the aim subsequently was to develop an expression for the Gibbs free energy of mixing at specified temperature and pressure. This can be defined in terms of the entropy, energy and volume of mixing as shown:

$$G = U + PV - TS$$  \hspace{1cm} (3.15)

An expression for the entropy can be derived following a similar methodology as that used for the derivation of the Flory-Huggins equation. The full derivation is presented in appendix A. A lattice is used to count the number of configurations \( \Omega \) available to a system of \( N_1 \) \( r_1 \)-mers, \( N_2 \) \( r_2 \)-mers, ..., \( N_k \) \( r_k \)-mers and \( N_0 \) empty sites (holes), where an \( n \)-mer is defined as a molecule that occupies \( r \) sites
on a lattice of co-ordination number $\xi$. The entropy of the system is given by Boltzmann's equation $S = k \ln \Omega$ and therefore for the large $\xi$ approximation, the following expression results,

$$S = krN \left[ (1 - \bar{\rho}) \ln(1 - \bar{\rho}) - \frac{1}{r} \ln \bar{\rho} - \sum_{i=1}^{k} \phi_i \ln \left( \frac{\phi_i}{\bar{\rho}} \right) \right]$$  \hspace{1cm} (3.16)

This is the expression for the entropy of mixing for the system where $k$ is Boltzmann's constant, $r$ is the total number of mers in the system, $N$ is the number of occupied sites (excluding the number of holes), $\bar{\rho}$ is the fraction of sites occupied by all molecules ($=1/\bar{V}$) or reduced density, $\phi_i$ is the site fraction of molecules if type $i$ in the absence of vacancies and $\omega_i$ is a term that contains information about mers of type $i$.

According to Sanchez and Lacombe, the energy of the lattice only depends on the nearest neighbour interactions. The model being described here contains only holes and mers so that the only non-zero pair interaction energy is the one from the non-bonded mer-mer. Assuming random mixing of holes and molecules, the following expression for the energy results:

$$U = -rN\bar{\rho} \sum_{i=1}^{k} \sum_{j=1}^{k} \phi_i \phi_j \varepsilon^*_{ij} = -rN\bar{\rho} \varepsilon^*$$ \hspace{1cm} (3.17)

where,

$$\varepsilon^* = \sum_{i=1}^{k} \sum_{j=1}^{k} \phi_i \phi_j \varepsilon^*_{ij} = \sum_{i=1}^{k} \phi_i \varepsilon^*_i - \sum_{i=1}^{k} \sum_{<j} \phi_i \phi_j kT\chi_{ij}$$ \hspace{1cm} (3.18)

$$kT\chi_{ij} = \varepsilon^*_i + \varepsilon^*_j - 2\varepsilon^*_{ij}$$ \hspace{1cm} (3.19)

where $\varepsilon^*_{ij}$ is the pair interaction energy between components $i$ and $j$ and $\chi_{ij}$ is the classical thermodynamic interaction parameter. This is the only parameter that is necessary to characterise a binary mixture. It is often assumed that interaction energies can be estimated by using the Berthelot formula (the geometric mean). In this work interaction energies will be expressed in terms of a dimensionless
parameter $k_y$ which is a measure of the deviation of the interaction energy from the geometric mean, such that:

$$
\varepsilon_y^* = (1 - k_y) \sqrt{\varepsilon_u \varepsilon_y^*} 
$$

(3.20)

The expression for the volume of a lattice fluid is derived assuming additivity of the close-packed volumes, i.e. such that the average mer volume $v^*$ is given by,

$$
v^* = \sum_{i=1}^{4} \phi_i v_i^* 
$$

(3.21)

and $v_i^*$ is the volume associated with one mer of molecules of type $i$. The total volume of a lattice fluid is then given by:

$$
V = N_i v^* = \bar{v} r N v^* 
$$

(3.22)

Then, using these expressions and equation (3.15), the expression for the Gibbs free energy of mixing is obtained:

$$
G = rN \left\{ -\bar{\rho} \varepsilon^* + P \bar{v} + kT \left[ (\bar{v} - 1) \ln (1 - \bar{\rho}) + \frac{1}{r} \ln \bar{\rho} + \frac{1}{r} \sum_{i=1}^{4} \phi_i \ln \left( \frac{\phi_i}{\omega_i} \right) \right] \right\} 
$$

(3.23)

From this, an expression for the chemical potential for component $i$ in the mixture can be obtained by simply differentiating the Gibbs free energy with respect to $N_i$ to give:

$$
\frac{\mu_i}{RT} = \ln \frac{\phi_i}{\omega_i} + \left( 1 - \frac{r_i}{r} \right) + r_i \bar{\rho} \left[ \sum_{j=1}^{4} \phi_j \chi_{ij} - \sum_{i=1}^{4} \phi_i \phi_j \chi_{ij} \right] 
$$

$$
+ \frac{1}{r} \ln \bar{\rho} + \frac{\bar{P} \bar{v}}{\bar{T} r_i} + \frac{1}{r_i} \ln \bar{\rho} + (\bar{v} - 1) \ln (1 - \bar{\rho}) 
$$

(3.24)

where $\bar{T}$ and $\bar{P}$ are the reduced temperature and pressure respectively given as:
For thermodynamic equilibrium, the Gibbs free energy has to be at a minimum with respect to all possible changes at given temperature and pressure, which yields the Sanchez and Lacombe equation of state:

\[ \tilde{T} = \frac{T}{T^*} = \frac{kT}{\varepsilon} \]  
(3.25)

\[ \tilde{P} = \frac{P}{P^*} = \frac{P\nu^*}{\varepsilon} \]  
(3.26)

For thermodynamic equilibrium, the Gibbs free energy has to be at a minimum with respect to all possible changes at given temperature and pressure, which yields the Sanchez and Lacombe equation of state:

\[ \tilde{\rho}^2 + \tilde{P} + \tilde{T}\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho} = 0 \]  
(3.27)

This equation has three characteristic parameters which define every pure component, \( T, P \), and \( \rho^* \), and they are related to each other and to the size parameter \( r \) and the molecular weight \( M \) by the following expression:

\[ r = \frac{M}{\rho^* \nu^*} = \frac{MP^*}{\rho^* kT^*} \]  
(3.28)

This expression is valid for pure fluid components as well as for mixtures of components. Tables with values of the characteristic parameters for both simple fluids and polymers can be found in the literature (Sanchez and Panayiotou, 1994). They have been determined experimentally from measurements of thermodynamic properties. For simple fluids they used saturated vapour pressures and for polymers they carried out a simple non-linear least-squares fitting with experimental liquid densities. Once the parameters are known, as with any EoS, it can be used to derive other thermodynamic properties.

Equation (3.24) is the expression for the chemical potential of species \( i \) in a mixture according to the SL EoS. Now, in a perfect gas mixture, the chemical potential per molecule of component \( i \) is given by:

\[ \mu_i^{\text{PG}} = \mu_i^0(T) + kT \ln \left( \frac{P_i}{P^0} \right) \]  
(3.29)
where $\mu_i^0(T)$ is the chemical potential of pure $i$ at standard temperature and pressure, $P_i^0$, and $T$ is equal to $N_i kT/V$ for a perfect gas where $N_i$ is the number of molecules of component $i$. According to the Sanchez-Lacombe model, the chemical potential per molecule of pure component is given by,

$$
\mu_{i,SL}^0 = r_i kT \left[ -\frac{\tilde{p}_i}{T_i} + \frac{\bar{P}_i \bar{\rho}_i}{T_i} + \frac{1}{r_i} \ln \tilde{\rho} + (\bar{\rho}_i - 1) \ln (1 - \tilde{\rho}_i) \right]
$$

(3.30)

where $Z_i$ is the compression factor of component $i$ defined as $\bar{P}_i \bar{\rho}_i r_i / \bar{T}_i$. In the perfect gas limit (approaching zero density and $Z_i \to 1$), the above equation reduces to:

$$
\mu_{i,SL}^{\text{per}} = kT \left[ 1 - r_i + \ln (1 - \tilde{\rho}_i) \right] = kT \left[ 1 - r_i + \ln \left( \frac{r_i N_i \rho_i^*}{V} \right) \right]
$$

(3.31)

Therefore, in the perfect gas limit equations (3.29) and (3.31) should be equal such that:

$$
\mu_{i,SL}^{\text{per}}(T) = kT \left[ 1 - r_i + \ln \left( \frac{r_i N_i \rho_i^*}{kT} \right) \right]
$$

(3.32)

and substituting into equation (3.29) gives:

$$
\mu_{i,SL}^{\text{per}} = kT \left[ 1 - r_i + \ln \left( \frac{r_i N_i \rho_i^*}{V} \right) \right]
$$

(3.33)

The Gibbs free energy of a perfect gas mixture of $N_i$ molecules of each component $i$ as given by the SL model is:

$$
G_{\text{per}} = \sum_i N_i \mu_{i,SL}^{\text{per}} = N kT \left[ 1 - r_i \sum_i \frac{\phi_i}{r_i} \ln \left( \frac{r_i N_i \rho_i^*}{V} \right) \right]
$$

(3.34)
where \((N_i/N) = r\phi_i/r\) from the definition of \(\phi_i\). For a real gas mixture, the expression for the Gibbs free energy given by the SL model is:

\[
G = NkT \left[ -\frac{r\bar{\rho}}{T} + Z + r(\bar{v} - 1)\ln(1 - \bar{\rho}) + \ln \bar{\rho} + r \sum_i \left( \frac{\phi_i}{r_i} \right) \ln \phi_i \right]
\]  

(3.35)

Using equation (3.22) the above can be rearranged to:

\[
G = NkT \left[ -\frac{r\bar{\rho}}{T} + Z + r(\bar{v} - 1)\ln(1 - \bar{\rho}) + r \sum_i \left( \frac{\phi_i}{r_i} \right) \ln \left( \frac{r_iN_i\nu_i^*}{V} \right) \right]
\]  

(3.36)

Subtracting the Gibbs free energy for the perfect gas mixture from this expression give the residual Gibbs free energy:

\[
G^\text{res} = NkT \left[ -\frac{r\bar{\rho}}{T} + (Z - 1) + r(\bar{v} - 1)\ln(1 - \bar{\rho}) - r + r \sum_i \left( \frac{\phi_i}{r_i} \right) \ln \left( \frac{\nu_i^*}{v_i} \right) \right]
\]  

(3.37)

or in terms of the mole fractions (where \(x_i = r\phi_i/r\)):

\[
G^\text{res} = NkT \left[ -\frac{r\bar{\rho}}{T} + (Z - 1) + r(\bar{v} - 1)\ln(1 - \bar{\rho}) - r + r \sum_i x_i \ln \left( \frac{\nu_i^*}{v_i} \right) \right]
\]  

(3.38)

As the perfect gas mixture limit is approached, i.e. as \(\bar{\rho} \to 0\), this last equation should tend to a value of zero. This is actually not the case meaning that the equation is not generally consistent with the correct form of the Gibbs free energy of a perfect gas mixture. The reason for this discrepancy is that in equation (3.38) the average mer volume \(\bar{v}^*\) contains the volume contributions of both the holes and the vacated sites, whereas in equation (3.34) only the contribution of vacated sites is present. This inconsistency could lead to errors when computing phase equilibrium through the use of the residual properties.
3.5.1 — Solving the SL Equation

Due to the non-linear nature of the equation of state, an iterative method must be used to solve it. The details of the computational method used in this work to solve for the reduced density as a function of reduced temperature, reduced pressure and composition, and the relevant equations will be discussed in Chapter VI. In general though, the equation has three solutions, where the lowest and the highest values of the reduced density correspond to two minima in the Gibbs free energy function and the intermediate value corresponds to a maximum. Furthermore, the highest value corresponds to a liquid density and the lowest value to a vapour density. The temperature and pressure at which the two minima become equal correspond to the saturation temperature and pressure of the system. As these saturation temperatures and pressures increase, there comes a point where the liquid and vapour density become equal, the critical point. At this point the following two conditions are satisfied (Sanchez and Lacombe, 1976):

\[
\frac{\partial f(\tilde{\rho})}{\partial \tilde{\rho}} = 1 \tag{3.39}
\]

\[
\frac{\partial^2 f(\tilde{\rho})}{\partial \tilde{\rho}^2} = 0 \tag{3.40}
\]

where the function \( f(\tilde{\rho}) \) is obtained by rearranging the equation of state as shown:

\[
\tilde{f}(\rho) = 1 - \exp \left[ -\frac{\tilde{\rho}^2}{\tilde{T}} - \left( 1 - \frac{1}{r} \right) \tilde{\rho} - \frac{\tilde{P}}{\tilde{T}} \right] = \tilde{\rho} \tag{3.41}
\]

Applying the two conditions, expressions for the critical variables can be obtained and as can be seen they are uniquely a function of the \( r \)-size parameter. The reduced critical density, the reduced critical temperature, the reduced critical pressure and the reduced critical compression factor respectively, are given below:

\[
\tilde{\rho}^c = \frac{1}{1 + r^{0.5}} \tag{3.42}
\]

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\[ \tilde{T}^e = \frac{2r}{(1 + r^{0.5})^2} \] (3.43)

\[ \bar{P}^e = \left[ \frac{2r}{(1 + r^{0.5})^2} \right] r \ln \left( 1 + \frac{1}{r^{0.5}} + 0.5 - r^{0.5} \right) \] (3.44)

\[ Z^e \equiv \frac{P^e V^e}{RT^e} = r \frac{\bar{P}^e \tilde{T}^e}{T^e} = \left[ 1 + r^{0.5} \right] \left[ r \ln \left( 1 + \frac{1}{r^{0.5}} + 0.5 - r^{0.5} \right) \right] \] (3.45)

Inspecting these equations, one can see that \( \tilde{T}^e \) increases with \( r \), whereas \( \bar{P}^e \) decreases. Also, \( \bar{P}^e \) tends to zero, as \( r \) becomes very large. For an infinitely long chain, for which there will only be one unique solution to the EoS, a phase transition from liquid to vapour is not possible. This means that the equilibrium vapour pressure of an infinitely long chain is zero, which agrees with the fact that polymers do not have a vapour pressure.

### 3.5.2 - Phase Stability

Due to the complexity of the expression for the chemical potential according to the SL equation, no analytical solution exists to the phase equilibrium problem and an iterative method is required. The stability of each of the phases solved for needs to be checked. A negative free energy of mixing is a necessary but not sufficient condition for miscibility. For a binary mixture at a given temperature and pressure, the necessary and sufficient condition for miscibility is that the first derivative of the chemical potential must be positive over the entire composition range, i.e. \( (d\mu/d\phi) > 0 \). When applied gives:

\[ kT \left[ \frac{1}{r_1 \phi_1} + \frac{1}{r_2 \phi_2} - 2\bar{\rho} \chi_{12} \right] - \frac{\bar{V}}{v_t} \beta \left[ \bar{\rho}^2 [\epsilon_{11}^* - \epsilon_{22}^* + (\phi_1 - \phi_2) kT \chi_{12}] + P (v_1^* - v_2^*) - kT \bar{\rho} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \right] > 0 \] (3.46)
which can be further simplified to:

\[
\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} > 2\tilde{\rho}\chi_{12} + \tilde{T}\psi^2 \rho^* \tilde{\rho}
\]  

(3.47)

where

\[
\chi_{12} = \left(\epsilon^{\cdot,11} + \epsilon^{\cdot,22} - 2\epsilon^{\cdot,12}\right)/kT
\]

(3.48a)

\[
P^* \beta = \tilde{\nu}^2 \left[\left(1/\tilde{\nu} - 1\right) + 1/r\right] - 2
\]

(3.48b)

\[
\psi = \tilde{\rho}\lambda_{12} - \left(1/r_1 - 1/r_2\right) + \left(P\tilde{\nu}/kT\right)(\nu_1 - \nu_2)
\]

(3.48c)

\[
\lambda_{12} = \left(1/kT\right)(\partial \epsilon^*/\partial \phi^*)
\]

(3.48d)

In the inequality (3.47) three terms should be recognised. The term on the left-hand side represents the combinatorial entropy contribution, the first term on the right-hand side is the energetic contribution and the last term is the contribution due to equation of state effects. If the stability condition is not satisfied it means that the solution is thermodynamically unstable and consequently, it will separate into two phases. Figure 3.1 shows the stability regions in a hypothetical system that shows UCST behaviour. At all compositions outside the binodal, the system is unstable and so it will exist as one homogeneous phase. On the other hand, at all compositions inside the spinodal, the system will be unstable and will phase separate into two coexisting phases whose compositions are the binodal compositions. At any composition inside the region encompassed by the spinodal and binodal curves, the system exits in a metastable state where any small composition fluctuation will cause it to phase separate.

Up to now only LLE using the SL has been discussed. In terms of VLE in polymer solutions, the activity of the solvent in the polymer is referred to, via the activity coefficients that can be obtained experimentally as will be shown in Chapter V. An expression for the activity of the solvent (normally weight fraction based activity coefficients when dealing with polymer systems) can be easily derived from the chemical potential:

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Figure 3.1 – Phase diagram for a system showing UCST behaviour. — denotes the spinodal curve and — denotes the binodal curve.

\[
\ln \alpha_i = \frac{\mu_i}{RT} - \frac{\mu_i^c}{RT}
\]

(3.49)

and so

\[
\ln \alpha_i = \ln \phi_i + \left(1 - \frac{r_i}{\bar{r}}\right) + r_i \bar{\rho} \phi_i^2 \chi_{12} \\
+ r_i \left[-\frac{\bar{\rho} + \bar{\rho}_1 + \bar{r}_i (\bar{\nu}_1 - \bar{\nu}_i)}{\bar{r}_1} + \frac{1}{r_i} \ln \frac{\bar{\rho}}{\bar{\rho}_1} + (\bar{\nu} - 1)\ln(1 - \bar{\rho}) - (\bar{\nu}_1 - 1)\ln(1 - \bar{\rho}_1)\right]
\]

(3.50)

where

\[
\phi_i = \frac{\sum r_i x_j}{\sum r_i w_j / M_j} = \frac{r_i w_j / M_j}{\sum r_i w_j / M_j}
\]

(3.51)

As the pure solvent side is approached, such that \( \phi_i \rightarrow 1 \), all terms on the right-hand side tend to zero and therefore the activity of the pure solvent tends to a value of 1. At the other end of the composition range, i.e. when the system tends to all polymer
and $\phi_i \rightarrow 0$, the activity of the solvent tends to a value of zero. The special case of this equation is when the system is at infinite dilution, i.e. when there is an infinitesimally small amount of solvent in the system. Activity coefficients at infinite dilution are calculated using a similar equation to that shown above, but to avoid the calculation of the logarithm of $(\phi_i/w_i)$ which would blow up, this term is manipulated into the logarithm of $(r_i M_i / r_2 M_i)$ where $M_i$ is the molecular weight of component $i$.

3.5.3 - Application of the SL equation

In their first publication, Sanchez and Lacombe (1976) tested the equation of state against pure fluid phase behaviour. For small molecule fluids, like n-heptane, very good agreement with experimental saturated vapour pressures was obtained (much better than using the van de Waals model for example). Similarly, values of the orthobaric densities were also well correlated, as well as other thermodynamics properties such as the thermal expansion coefficient, the isothermal compressibility or the enthalpy of vaporisation. In the case of pure polymers, they calculated liquid densities of poly(vinyl acetate) in the range 308.15 – 373.15 K and 0 – 800 MPa with a mean error or less than 0.1%. A year later Sanchez and Lacombe (1977) fitted the equation to a large number of polymer density data to obtain the characteristic parameters and found the maximum error in any calculated density to be 1.2%. For mixtures, the equation was capable of predicting the liquid-vapour phase transition in simple fluids, even in systems exhibiting azeotropic behaviour (such as the carbon disulfide/acetone system) or polar/polar systems like phenol/2,6-dimethylpyridine (Lacombe and Sanchez, 1976). They have also shown that the equation can correlate both UCSTs and LCSTs depending on the value of the interaction parameter. For polymer/solvent systems Sanchez and Lacombe (1978) have presented good agreement between calculated and experimental data of several thermodynamic quantities including enthalpies of mixing and volumes of mixing for poly(iso butylene) solutions.

Since then, many authors have used this equation of state for comparison with experimental findings but only some will be covered here. A considerable amount of work has been carried out on polyethylene/n-alkanes solutions. Kiran and
co-workers (1993) used this model to predict high-pressure phase behaviour of solutions of PE in n-pentane and in n-pentane/carbon dioxide systems. Using the characteristic parameters from the literature for the polymer and solvent they found that calculated binodals did not agree well enough with the experimental cloud-point curves, even after varying the interaction parameter. Re-fitting of $T^*$ for polyethylene helped a great deal. Using the new proposed value of $T^*$, the binodals for the binary systems were in very good agreement even as a function of PE molecular weight. The model also predicted the correct change from LCST behaviour to UCST behaviour that results from increasing the CO$_2$ content in the n-pentane/CO$_2$ system.

Koak and Heidemann (1996) looked at polymer-solvent phase behaviour near the solvent's vapour pressure curve where VLLE is possible. They used the SL equation among others and found a maximum deviation of 5% in vapour pressures calculated for n-hexane and also that the fit was better at low temperatures. VLE and LLE were studied for HDPE/n-hexane and calculated binodals appear fairly far from the experimental findings. Moreover, although the curves are quite flat (as compared to results from other models), the critical compositions are displaced to higher mass fractions than found experimentally. Orbey et al. (1998) have also looked at PE solutions, especially with its monomer ethylene and have found that predictions were not too good. They report poor agreement if the interaction parameter is set to zero and if tuned, correlation is better but still not excellent. The addition of a second interaction parameter for the characteristic volume of the mixture also helps. Koak et al. (1999) also investigated this system found good agreement between calculations and experiments only when a temperature-dependent binary interaction parameter was used.

An and Wolf (1998) studied the system PS/trans-decalin. Introducing a molecular weight dependence on the interaction energy between mers, gave excellent agreement between calculated binodal curves and measured cloud-point curves (both critical solution temperatures and compositions) at 1 MPa. Also, including pressure dependence gave a very good correlation of the cloud point curves as a function of pressure.

Gas solubilities in polymers from inverse gas chromatography experiments have been correlated by the SL equation (Sanchez and Rodgers, 1990). The agreement was very good for PS in alkanes, for poly(1-butene) in alkanes, cyclic
hydrocarbons, aromatic hydrocarbons and even chlorinated hydrocarbons, and polypropylene with the latter solvents. In all these systems, the average percentage error is around 12%. For two polar polymers studied, poly(vinyl acetate) and poly(methyl acrylate), solubilities of non-aromatic gases are largely overestimated but polar and aromatic gases are represented well. To overcome the non-polar/polar combinations, Rodgers and Sanchez (1993) suggested using Hansen's empirical solubility parameters to calculate the cohesive energy density. This improved the correlation of the experimental data. The application of the SL equation to predict solubilities has also been presented by Sato et al. (2000). A very good agreement between calculation and experiment is reported for hexane in polypropylene and ethylene in an impact polypropylene copolymer.

The Sanchez-Lacombe equation of state has been extended to systems were specific interactions such as hydrogen bonding are present, by Sanchez and Balazs in 1989, where they compared the SL calculations with experimental data for a poly(vinyl methylether)/polystyrene blend. The model gives a quantitative description of the phase behaviour in this blend, but there are new three interaction parameters that need to be fitted: (i) a parameter $\delta_{12}$ accounting for the non-specific interactions (ii) a $\delta_{S}$ parameter accounting for the specific interactions and (iii) an entropic parameter $q$. The model was further modified by combining Flory's model for polydisperse polymer solutions with the SL equation (Panayiotou and Sanchez, 1991), giving rise to the Lattice Fluid Association model (LFAS). It has been derived for pure fluids that can self-associate through hydrogen bonding and form linear association complexes by varying length.

3.6 – UNIFAC-FV model

In section 3.3.2 the most important UNIFAC-based models have been discussed. As already pointed out, the beauty of these models is not only that they are purely predictive and no user input parameters are required but also they are fairly uncomplicated expressions to use. The UNIFAC-FV model of Oishi and Prausnitz (1978) triggered the application of UNIFAC-based models to polymer solutions. The equations require no prior experimental data and are simple to use. Oishi and Prausnitz (1978) reported that solvent activities for polymer solutions
calculated using these two contributions only are lower than those found experimentally and recognised that in order to apply the UNIFAC equation to systems containing large molecules, an extra term was necessary to account for the significant differences in size between molecules in these systems. Accordingly, they added a so-called free-volume term to the expression for the activity coefficient as shown below:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} + \ln \gamma_i^{\text{fv}} \quad (3.52)$$

When referring to phase equilibria in polymer solutions, due to the molecular weight differences between polymer and solvent, it is more convenient to write expressions in terms of weight fractions rather than mole fractions. Consequently it becomes more appropriate to talk about weight fraction activity coefficients (WFACs) as opposed to mole fraction activity coefficients. Henceforth, all equations will be written in terms of weight fraction ($w$). Thus re-writing equation (3.52) in terms of the WFAC of component $i$, $\Omega_i$:

$$\ln \Omega_i = \ln \frac{a_i}{w_i} = \ln \frac{x_i \gamma_i}{w_i} = \ln \Omega_i^{\text{comb}} + \ln \Omega_i^{\text{res}} + \ln \Omega_i^{\text{fv}} \quad (3.53)$$

The contributions are (i) the combinatorial expression developed by Stavermann (1950), (ii) the residual term from Guggenheim's quasi-chemical theory and (iii) a free volume term derived from the chemical expression resulting from Flory's equation-of-state (1970) and setting Flory's chi parameter equal to zero. The equations are given in table 3.2. They are all analytical equations containing parameters that have been fitted to activities of small molecule systems. It should be noted that the expression for the combinatorial contribution needs to be re-written for the specific case of infinite dilution (i.e. when the mixture is almost all polymer except for the presence of an infinitely small amount of solvent), or else the logarithms will fail to compute. The compositions in the two logarithmic terms are re-written as:

$$\frac{\phi_i}{w_i} = \frac{r_i/M_i}{\sum_j r_j/M_j} \quad \text{and} \quad \frac{\theta_i}{\phi_i} = \frac{\sum_j r_j w_j/M_j}{\sum_i q_i w_i/M_i} \quad (3.54)$$
<table>
<thead>
<tr>
<th>COMBINATORIAL</th>
<th>RESIDUAL</th>
<th>FREE-VOLUME</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln \Omega_{i}^{\text{comb}} = \ln \frac{\phi_{i}}{w_{i}} + 5 q_{i} \ln \frac{\theta_{i}}{\phi_{i}} + l_{i} - \frac{\phi_{M_{i}}}{w_{i}} \sum_{j \neq i} w_{j} l_{j} / M_{j} )</td>
<td>( \ln \Omega_{i}^{e} = \sum_{k} v_{i}^{(k)} \left[ \ln \Gamma_{k} - \ln \Gamma_{k}^{(i)} \right] )</td>
<td>( \ln \Omega_{i}^{f} = 3 \gamma_{i} \left[ \ln \left( \frac{\tilde{v}<em>{i}}{v</em>{i}^{(i)} \tilde{v}<em>{mix}} \right) - \gamma</em>{i} \left( \frac{\tilde{v}<em>{i}}{v</em>{i}^{(i)} \tilde{v}_{mix}} - 1 \right) \right] )</td>
</tr>
</tbody>
</table>

where:

- \( \phi_{i} \) = molecular volume fraction of component \( i \)
- \( \theta_{i} \) = molecular volume fraction of component \( i \)
- \( r_{i} \) = volume parameter of molecule \( i \)
- \( q_{i} \) = surface area parameter of molecule \( i \)
- \( v_{i}^{(k)} \) = number of groups of type \( k \) in molecule \( i \)
- \( Q_{k} \) = surface area parameter\(^1\) for group \( k \)
- \( M_{i} \) = molecular weight of component \( i \)
- \( \Gamma_{i}^{(k)} \) = residual activity coefficient of group \( k \) in a ref. solution containing pure component \( i \)
- \( \Gamma_{k} \) = residual activity coefficient of group \( k \) in a mixture at specified temperature
- \( \theta_{n} \) = group surface area fraction of group \( m \)
- \( X_{n} \) = mole fraction of group \( m \)
- \( \psi_{mk} \) = interaction parameter for group \( m \) with group \( k \)
- \( a_{mk} \) = interaction parameter\(^2\) for group \( m \) with group \( k \)

\( l_{i} = 5(r_{i} - q_{i}) - (r_{i} - 1) \), \( r_{i} = \sum_{k} v_{i}^{(k)} Q_{k} \)

\( q_{i} = \sum_{k} v_{i}^{(k)} Q_{k} \)

\( \Gamma_{i}^{(k)} \) = residual activity coefficient of group \( k \) in a ref. solution containing pure component \( i \)

\( \Gamma_{k} \) = residual activity coefficient of group \( k \) in a mixture at specified temperature

\( \theta_{n} \) = group surface area fraction of group \( m \)

\( X_{n} \) = mole fraction of group \( m \)

\( \psi_{mk} \) = interaction parameter for group \( m \) with group \( k \)

\( a_{mk} \) = interaction parameter\(^2\) for group \( m \) with group \( k \)

\( \gamma_{i} \) = external degree of freedom parameter

\( b = 1.28 \)

\( \tilde{v}_{i} = \frac{v_{i} M_{i}}{0.01517 b r_{i}} \)

\( \tilde{v}_{mix} = \frac{\sum_{i} v_{i} w_{i}}{0.01517 b \sum_{i} r_{i} w_{i} / M_{i}} \)

\( \tilde{v}_{i} = \) reduced volume of component \( i \)

\( \tilde{v}_{mix} = \) reduced volume of the mixture

\( v_{i} = \) specific volume of component \( i \)

\( b = 1.28 \)

\( \gamma_{i} = \) external degree of freedom parameter

\( b = 1.1 \) for solvents

\(^{1}\) Tabulated in Oishi and Prausnitz (1978)

\(^{2}\) Tabulated in Fredenslund et al. (1977)

Table 3.2 – Equations for the UNIFAC-FV model of Oishi and Prausnitz (1978).
The combinatorial and residual terms can be evaluated with the sole knowledge of the tabulated parameters for the specific groups making the molecules in the system. On the other hand, the free-volume term requires specific volumes for all components in the mixture, at the temperatures at which the calculation of the activity coefficients is done. In addition, the value of the external degrees of freedom parameter \( c \), which for solvents is equal to 1.1, needs to be calculated for polymers. Oishi and Prausnitz (1978) stated that the value should be larger than 1.1 for larger molecules, but did not quote a specific value. Belfiore et al. (1988) suggested calculating \( c \) (i.e. that for the polymer) by using the Flory EoS definition in terms of the characteristic properties \( P^* \), \( T' \) and \( V^* \) (parameter values for some common polymers can be found in that publication):

\[
c_2 = \frac{P^*V^*M_2}{RT^*}
\]

These represent the characteristic potential energy density, the potential energy per external degree of freedom and the hard-core specific volume respectively. Also, \( M_2 \) is the molecular weight of the monodisperse polymer. Iwai et al. (1993) also have suggested an alternative way of calculating \( c \). For the solvent, instead of assuming a value of 1.1, they proposed a calculation based on the knowledge of experimental heats of vaporisation. For the polymer, this expression cannot be used and so they calculated it by assigning \( c_k \) values for each group \( k \) in each component and then used a group-contribution scheme to calculate the polymer \( c \) value. They also use a group-contribution method to calculate the specific hard-core volume. In this work, the UNIFAC-FV of Oishi and Prausnitz (1978) will be tested using values of 1.1 for the solvent and values calculated using equation (3.55) for the polymers.

This work is concerned especially with the application of the thermodynamic model to predict phase equilibria, both VLE and LLE in several polymer solutions that were studied experimentally. In terms of vapour-liquid equilibrium, an activity coefficient model is easy to use as it provides a direct means of calculating activity coefficients or activities or equilibrium pressures (as a function of composition and temperature), which give us information on the VLE of the solution. With regards to liquid-liquid equilibrium, analysis is also simple. Having analytical expressions for the activities of both polymer and solvent, all one needs to
do is solve the equilibrium equation (the activity in each phase for every component is equal) with no other equations required.

\[ a_i' = a_i'' = \ldots = a_i^n \]  

(3.56)

3.6.1 — Application of the UNIFAC-FV model

Several authors have calculated activity coefficients for a number of polymer solutions and tested its applicability in predicting phase behaviour. All of them have considered VLE phase behaviour and only a publication by Iwai and Arai (1989) have used it to look at LLE behaviour in the polystyrene-cyclohexane-cyclopentane system, as has already been mentioned above. Patwardhan and Belfiore (1986) have also studied LLE in some polystyrene solutions. The model gives a good qualitative description of the complete miscibility of PS melt in ethylbenzene, the nearly complete immiscibility of PS in methanol and the partial miscibility observed in the PS/acetone system.

Oishi and Prasunitz (1978) themselves tested the new equation against a large number of polymer systems including poly(isobutylene), polystyrene, polyheptene, poly(ethylene oxide), poly(propylene oxide) and poly(vinyl acetate) in a number of solvents including benzene, toluene, acetone, cyclohexane, propyl acetate, ethyl acetate and methyl ethyl ketone. UNIFAC-FV predicted solvent activities to within ± 10% of the experimental values. Sorensen et al. (1990) compared calculated values of activity coefficients at infinite dilution of n-alkanes, benzene and toluene in poly(ethylene glycol) at three different molecular weights and at temperatures in the range 333 — 373 K. They found predictions with UNIFAC-FV to be qualitatively correct and the model was useful to understand variation in activity coefficients with temperature and polymer molecular weight. Quantitatively agreement was somewhat poorer although a constant value for the pure component densities was used in all calculations.

Kontogeorgis et al. (1993) report average deviations in infinite dilution activity coefficients from 3.5 % in a poly(isobutylene)/cyclohexane solution to 27.5% for a low-density polyethylene/n-hexane solution. For solutions with specific interactions, average deviations range from 0.5 % for a polyethylene/toluene solution
to 31.7% in a polybutadiene/acetonitrile solution. Molecular weight seems to play an important role, as for example there is an average deviation of 6.1% for a polystyrene ($M_w = 3,524 \text{ g/mol}$) in benzene whereas the deviation for the polystyrene ($M_w = 86,700 \text{ g/mol}$) solution is 21.5%. In a later publication, Kontogeorgis et al. (1994a), report better agreement for PS solutions, with average absolute deviations between experimental and predicted equilibrium pressures of 4.7% for a PS/methyl ethyl ketone and 9% for a PS/toluene solution. Kikic et al. (2000) used the model to predict WFACs at infinite dilution (almost all solvent in the polymer solution) as a function of temperature on paraffinic/polycarbonate solutions and aromatic/polycarbonate solutions. They report deviations of 13.3% and 9.3% respectively.
Chapter IV

EXPERIMENTAL METHODS

4.1 — Introduction

Phase behaviour in polymer solutions has been measured extensively over the years and collections of data are available in the literature. A good compilation of both LLE data and experimental activities and solubilites of solvents in polymers may be found in Hao et al. (1992b). Other useful sources include Danner and High (1993) and Wohlfarth (1994). Several experimental methods are available for determining liquid-liquid and vapour-liquid phase behaviour in polymer solutions and a summary was presented in chapter II. By far the most common method of measuring immiscibility in these systems is by using an optical device to determine the temperature at which a polymer solution of known composition undergoes phase separation. This is the method of turbidimetry used for LLE determination and chosen for this work. For VLE measurements, the technique of inverse gas chromatography (IGC) has been employed. Obtaining VLE data can be very time consuming by conventional gravimetric techniques and IGC has proved a fast and reliable method for measuring solvent activities.

This chapter is divided into two sections, LLE and VLE determinations. In both sections, a detailed description of the apparatus used for the purpose is
presented. Experimental procedures are described as well as any other important aspects of the measurement. The results on the chosen systems will be presented in Chapter V.

4.2 — Liquid-Liquid Equilibria by Turbidimetry

As already pointed out, by far the most commonly used methods to determine liquid-liquid phase splits are turbidimetry techniques. Here, the polymer and solvent are mixed in known quantities in a solution cell. The solution is then heated or cooled to a temperature where it will exist as one-phase and stirred for a certain amount of time. This is to ensure phase homogeneity. The temperature is then varied until a phase transition is observed, which results in the solution turning cloudy. The temperature at which this happens is called the cloud point temperature and corresponds to a point on the binodal curve at the specified composition. This change in appearance at a particular temperature can either be detected visually or using a photoelectric device. This was the technique chosen for this work as it is a simple, rapid and convenient method (no calibration is necessary and a simple light source can be used). The description of the turbidimeter follows.

A turbidimeter was designed and built to measure cloud-point temperatures of polymer solutions at temperatures ranging from 290 K to 523 K and to withstand pressures up to 30 MPa. Due to the fact that a coexistence curve is a function of both temperature and concentration, it is convenient to measure more than one concentration in a single experimental run, i.e. more than one point on the phase diagram. Consequently, the turbidimeter was designed to have five sample cells, each to be filled with a polymer solution of different but known composition. As the temperature of the cells was varied a change in the transmitted light through the solutions was measured from which cloud-point temperatures were obtained.

Figure 4.1 shows a schematic block diagram of the turbidimetry apparatus. There was a constant power supply of 9V dc to the five light emitting diodes (shown as the red blocks). To these were connected five optical fibres which were screwed into the turbidimeter cell block and aligned so that the light shone directly through the centre of each of the sample solution cells. The light beams were made parallel using equi-convex lenses which ensure maximum incident intensity of the cells. The
Figure 4.1 — Schematic block diagram of the turbidimetry set-up.
transmitted light was collected using another set of five optical fibres (and lenses), also correctly aligned and the optical intensities were measured by five photodetectors (shown as the blue boxes). The dc voltage generated by the photodetectors was measured using a multiplexer and operated under "HP bench logger" software running on a PC. The cell block was heated using two cartridge heaters and the temperature monitored with two calibrated platinum resistance thermometers that ran along the length of the cell block. Also running along the length was a 1/16 in. OD tube stainless steel through which nitrogen gas flowed to provide the cooling. The line entered the cell block through one side and returned to come back out through the same side. The entire cell block was connected to a motor arrangement that was used to rock the turbidimeter ± 180° from the axis. This rocking mechanism provided the stirring of the sample cells.

4.2.1 Cell Block

Figure 4.2 shows a 3D isometric view of the cell block. The block consisted of an I-section aluminium block which was 95 mm long, 35 mm wide and 54 mm high. The centre of the I-piece was 8 mm thick. Bored out of the centrepiece were 5 rectangular shaped holes, 14 mm high and 8 mm wide. The five holes were evenly distributed along the length and the height of the block. The centre of the two end cells was at a distance of 11.5 mm from the edge of the block and the distance between each cell centre was 18 mm. Also, the centre of the cells was half way between the top and bottom of the block. Figures 4.3, 4.4 and 4.5 give the dimensions of the cell block and its parts. Figure 4.3 shows the front view of the block where the five cells are shown. Also shown in this view are twelve clearance holes to accommodate M3 socket head cap screws that hold this centrepiece to the lens holder arrangement and close the sample cells as will be explained further on. Both lines of six screw holes were at a distance of 16.5 mm from the top and bottom of the block and so they were 21 mm between them. Along the length of the block, the screw holes were placed as evenly as possible and the distances are given in figure 4.3.
Figure 4.4 shows the bottom view of the cell block. Drilled through the bottom were two holes used to accommodate the two platinum resistance thermometers PT-100 (wire wound glass elements, resistance type P2, supplied by Hartmann & Braun UK Ltd.). One was used to monitor the temperature and was connected to the multiplexer and the other was connected to the temperature controller. The holes were 5 mm in diameter, and 12 mm in depth and were placed half way along the width of the block and at 54 mm from each other.

Looking from the top, there were five holes going through to the sample cells and these were fitted with five screw caps, also made of aluminium, which were used to close the cell. Once the entire turbidimeter was assembled the materials were introduced through these holes. The screw caps and holes have been designed to accommodate one Viton\(^1\) o-ring size 008 each, supplied by Mecro Ltd. (4.47 ± 0.13 mm inside diameter and 1.78 ± 0.08 mm section). The dimensions are given in figure 4.6. The screw caps were placed half way along the width of the block, i.e. at 17.5 mm from the edges. Also shown in figure 4.3 is the side view which not only shows

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\(^1\) Viton is the trade name for hexafluoropropylenevinylidene fluoride copolymer.
Figure 4.3 – Technical drawing of the centre piece: front view, side view and top view.
Figure 4.4 – Technical drawing of the turbidimeter centre piece: cross sectional view through a sample cell and bottom view.
Figure 4.5 – Technical drawing of the turbidimeter centre piece: Cross sectional view along the length of the cell block.
Figure 4.6 – Detailed technical drawing of the heating and cooling arrangements in the turbidimeter's centre piece.
the I-shape of the block but also four holes corresponding to where the heating rods and the cooling tube are placed. They were placed evenly in the block and the distances are given in figure 4.4 in the diagram showing a cross-section through one of the sample cells.

4.2.2 — Cooling and Heating

Cooling of the block was achieved using a nitrogen gas supply which was fed from a cylinder through a stainless steel tube of internal and outside diameters 0.031 in. and 1/16 in. respectively (purchased from TW Metals Ltd., UK). The tube was connected to the cell block using Swagelok P-NPT connectors for 1/16 in. tubing. The nitrogen gas flowed through the top right hand hole (see figure 4.7), leaves and returned via an external loop to the cell block again on the bottom, so that the gas exited through the bottom left hand hole. The nitrogen gas was switched on manually and was continually flowing when the experiments were running and the heaters were on.

Heating was achieved using two 50W, 120V Firerod cartridge heaters purchased from Watlow Ltd., UK. Both were of 1/8 in. diameter and 2 in. length. They were both introduced through the right hand side of the cell block, so that the four leads all come out on the same side. One cartridge heater had a 513 K thermal fuse soldered to it. They were connected together in series with the mains power output (230V ac) of the temperature controller and driven by mains current. A schematic of the heater arrangement is shown in figure 4.8.

4.2.3 — Light Source, Photodiode and Lens Assembly

The light sources used were five photoemitters purchased from Farnell UK which shine red light. They were 200 and 250 μm inside and outside diameter glass fibre leads manufactured from tight jacket cable and all with metal SMA connectors. Each fibre was connected to a piece referred to as a lens holder via an SMA connector. On the other end of the optical fibre was either a SMA emitter or a SMA detector (also obtained from Farnell, UK). Detailed specifications of the fibres,
Figure 4.7 – Detailed drawing of the hexagonal screw caps for sealing the sample cells from the top.
Figure 4.8 — Electrical diagram for the turbidimeter: Light emission and detection and temperature measurement and control (not drawn to scale).
emitters and detectors can be found in appendix B1. The emitters were run by the power supply and the detectors were connected to the multiplexer as shown in figure 4.8. The maximum current that can be passed through the light emitting diodes (LED's) is 50 mA, making it necessary to place a resistance between the power supply and the LED as shown. For a 9V power supply, resistors of 150 Ω were used (see appendix B2 for the calculation). Figure 4.8 shows the electrical circuits more clearly. The power supply fed the five LED's via the resistors as shown. From the LED's, the lines represent the optical fibres which were connected to the block via the co-called lens holder that will be described next. The light shone through the sample cells and travelled through another set of five optical fibres to the photo detectors. The detected voltage was recorded in the multiplexer (the numbers represent the different channels where the variables are recorded).

The light emitted from the end of the optical fibres diverges in a conical shape and needed to be made into a parallel beam using a convex lens. The lenses used were 4 mm in diameter and 1.9 mm thick (supplied by Coherent UK as equi-convex micro-lenses). The focal length was 6 mm and to obtain a parallel beam, the lens must be placed at a distance from the object, i.e. the end of the fibre optic, equal to the focal length. A lens holder arrangement was designed and made out of brass. The distance from the end of the fibre optic to the centre of lens was fixed at 6 mm and the lenses were kept in place with silicone glue. The distance between the centre of the lens and the sample cell was adjustable. Figure 4.9 shows a 3D image of the lens holder pin-pointing the position where the lens was held. Figures 4.10 and 4.11 give detailed dimensions of the separate components. The first piece represents the SMA connector and has been drawn as a cylinder without representation of the thread. Piece number 2 is a hollow brass cylinder which served to join pieces 1 and 3 together (both stainless steel) and hold the lens sandwiched in between them. Piece 3 was actually threaded entirely until the end of the piece. Piece 4 is another brass component and was used for connecting the lens holder to an aluminium piece that is then screwed to the cell block using twelve M3 socket head cap screws. This aluminium piece is shown in figure 4.12. The entire lens holder was introduced through one of the holes in the Al piece in the direction into the page. Part 5 is a ring of polytetrafluoroethylene (PTFE) inside diameter 6 mm, outside approximately 11.95 mm and thickness 5 mm. In order to achieve a variable distance between the centre of the lens and the sample cell, parts 3 and 4 are threaded to allow rotatory
movement. On one of the edges of part 3 a dent was cut out 12 mm from the edge (as shown in figure 4.11 and marked (6) in the diagram above). Once the distance was chosen a small stainless steel pin was inserted into the hole marked 6 to lock the position of all the components.

Figure 4.9 — 3D view of the lens holder (1) representation of the SMA connector for the fibre optic (2) brass hollow piece holding pieces 1 and 3 together with lens inside (3) threaded SS piece (4) brass piece connecting lens holder to Al piece (fig.4.10) (5) PTFE ring with hole bored for a pin which fixes the cell to lens distance (6) pin-holes.

Five of these holders were placed on the emitting side of the cell block and connected to the optical fibres and another five were placed on the detecting side and are also connected to the other five optical fibres. Figure 4.13 gives the dimensions of the aluminium piece used one on each side. The Al piece is 28 mm high, 8 mm wide and 95 mm long. It has five circular holes bored through with their centres aligned with the centres of the sample cells.
Figure 4.10 – Detailed drawing of the lens holder arrangement. An equi-convex micro-lens is sandwiched between parts I and III and fixed using silicone glue. Part II covers the lens arrangement.
Figure 4.11 — Drawing showing the dimensions of the PTFE ring and the brass piece connecting the lens holder to the Al piece.
Figure 4.12 — Aluminium piece to connect the lens holders and light arrangement to the cell block.

Figure 4.13 — Detailed drawing of aluminium piece connecting the lens holders and light arrangement to the cell block.
4.2.4 – Sealing of Cells

As explained previously in section 4.2.1, the sample cells were sealed at the top with screw caps and Viton o-rings, but they also had to be closed on the sides. The sample cells were closed with glass windows through which the light from the optical fibres passed through. A cushioning material was necessary between the aluminium pieces and the glass and also a sealing material between the glass and the centre piece (the cell block). These two materials were chosen to withstand temperatures up to 523.15 K and to have good chemical resistance. Initially, a 2mm thick PTFE sheet was used as the cushion followed by a 3mm thick sheet of borosilicate glass and a Viton sheet of 1.5 mm thickness as the sealing material. A sketch is shown in figure 4.14 (a). One single flat glass window was used with notches carefully cut out to accommodate the 12 screws. The window was cut out as shown in figure 4.15 (a) (which is not drawn to scale although the correct dimensions are shown). It was very difficult to cut out the notches in the glass window at the correct distance from each other and of correct width and depth. Furthermore, this arrangement for sealing the cells proved to be unsuccessful. Several problems were encountered after assembling the turbidimeter and subjecting it to high temperatures and pressures (up to 523.15 K and approximately 3 MPa), in tests with the sample cells partially filled with cyclohexane.

Firstly, the glass window cracked at several points on the sheet, the cracks originating at the notches. Bending moments were created when the screws were tightened up and the stresses concentrated at these notches. As shown in figure 4.14, the centre piece and the two Al pieces which hold the lens holders and the optical fibres are assembled together using twelve M3 steel socket head cap screws (40 mm long), washers and nuts. The screws are tightened following the sequence shown in figure 4.16 and each one is tightened half a turn each time to ensure equal pressures (and to excessive pressures) are applied at each point. The stress caused by the tightening of the screws and the increase of pressure pushing out from the fluid in the cells, were responsible for the glass breakage. This problem was solved by using five individual windows on each side of the cell block of shape shown in figure 4.15 (b). The corners were cut off to leave enough space for the screws to go through without touching the windows. Although all the windows are not exactly the same size, the average width was 18 mm so that they cover the entire cell. They were
Figure 4.14 — Sketch showing the cross-section of the turbidimeter arrangement (a) Al-PTFE-Glass-Viton, (b) Al-O-ring-Glass-Viton.

Figure 4.15 — Sketch showing the glass window (a) original design: one window with cut out notches, (b) new design: five separate small windows.

Figure 4.16 — Sealing Viton sheet (95 × 28 × 1.5 mm). Not drawn to scale. Aligned with cell block. Also shown is the sequence for tightening up the M3 screws for assembly of the turbidimeter.
placed alongside each other along the length of the block.

The second problem was that PTFE is a soft material and deforms and flows under pressure, and this problem worsens with increasing temperature. The PTFE sheets were found to be deformed after the block was exposed to high temperature and pressure. As a consequence of this and the breaking of the windows sealing of the sample cells was not achieved. The PTFE was replaced by Viton o-rings exactly the same as those used in the caps at the top of the cell block. These where carefully glued to the PTFE ring in the lens holder ensuring not to obstruct the light passageway, using a silicone rubber sealant. The o-ring is shown in figure 4.14 (b).

Finally, at the higher temperatures near 523 K, the Viton gasket, which was cut as shown in figure 4.16, was found to crack, expand and slightly disintegrate especially near the edges. The Viton sheet purchased from Goodfellow Cambridge Ltd. has an upper working temperature range of 493 to 573K and a thermal expansivity of $160 \times 10^{-6} \text{ K}^{-1}$. Also, although chemical resistance is good at room temperature, this deteriorates as temperature increases. For experiments at higher temperatures, a material capable of withstanding higher temperatures such as the perfluoroelastomer Kalrez (purchased from James Walker & Co. Ltd., UK) should be used. It has excellent chemical resistance to almost all chemicals and even after long-term exposure to temperatures up to 589 K, retains its elasticity and recovery properties.

A test run was carried out again with the new arrangement of single windows, the o-rings as cushions and the Viton gasket as the seal. The sample cells were filled with cyclohexane and the temperature was raised to around 523 K. Unfortunately, the system still leaked although the windows were intact. The reason for the non-sealing of the gasket was found to be the sealing surface on the cell block. A small test piece was made as shown in figure 4.17 and different surface finishes were tried on the sealing face. The test cell was a cylindrical cavity of approximately 0.4 cm$^3$ filled about two thirds of the way with cyclohexane. The cell was assembled and bolted up and placed into an oven. The temperature was raised to about 503 K and kept at this temperature for about 30 minutes after which time the test piece was cooled and inspected.
Different sealing surface finishes were tried and sketches are shown in figure 4.18. In case (a) where there are several grooves of 0.5 mm thickness and 0.5 mm depth, the glass cracked and the cyclohexane leaked and evaporated. In case (b), a single raised lip of 0.5 mm depth and 1.0 mm width was used. The window did not crack but the cell leaked and the Viton was damaged in the inner edge. The test was repeated and unfortunately even the Viton cracked. In case (c) the depth was increased to 1 mm and the width increased to 2 mm, still keeping a single raised bit.
The cell leaked and the lip cut through the Viton in some places implying that the lip was maybe too high. In case (d) the depth was reduced to 0.2 mm and two raised lips were made. The first was 2 mm wide and the second was 1 mm wide with a groove in between of 1.5 mm width. The test was run and no leak or glass cracks were observed. The test was repeated twice to make sure that it was sealing properly.

From these tests, it appeared that using design (d) cause no leak or rupture of the glass and this was therefore used as the sealing pattern on both sealing surfaces of the cell block. Due to practical difficulties, the dimensions of the raised lips had to be modified slightly. The first raised lip was changed to 1.5 mm wide. A template in brass was made, the pattern drawn using an engraving machine and all sharp edges removed to ensure no damage to the Viton sheet when sealing. A sketch of the cell block is shown below and the final dimensions of the sealing surfaces are presented in figures 4.20 and 4.21.

Figure 4.19 — 3D isometric view of the cell block showing the sealing surface finish.

4.2.5 — Turbidimeter Assembly

The two aluminium pieces holding the lens holder were bolted to the cell block as explained previously. A photograph of the assembled turbidimeter is shown in figure 4.23. To minimise the temperature gradient in the block and to reduce heat
Figure 4.20 — Detailed drawing of the sealing surface on the cell block showing a front view and depth of grooves.
Figure 4.21 — Detailed drawing of the sealing surface on the cell block showing the dimensions of the sealing surface.
losses, the turbidimeter was enclosed in white expanded silicone sponge of 25.4 mm thickness. The sponge was cut out in order to accommodate those parts that stuck out such as the lens holders. The entire insulated assembly was further enclosed in an aluminium box of wall thickness 5 mm and internal dimensions 155 x 110 x 95 mm, made up of 6 plates bolted together. The arrangement is shown in figure 4.22.

Stirring of the solutions was achieved by rocking the entire turbidimeter enclosed in the Al box as can be seen in figure 4.22. A stainless steel ball of 5 mm diameter was introduced in each cell to stir the solutions ensuring that the mixtures are homogeneous in their one phase state before the commencement of an experimental run. The size of the ball was chosen to be as big as possible without it blocking the light path in any way when sat at the bottom of the sample cells. A suitable mechanism was designed to rock the turbidimeter at varying angles. The rocking mechanism components were a white delrin spur rack and spur gear, two Igubal® sliding female M6 bearings, two 8 mm diameter radial flanged bearings, a single reduction worm gear unit motor (Parvalux motor speed 3000 rpm, DC shunt wound, final rpm = 42, voltage 220V) and a variable speed controller (purchased from CJ Controls, UK).

The turbidimeter could be rocked at variable speeds (depending on the viscosity of the solutions) with an amplitude of up to ± 180° from the central axis. The controller was switched on and off and the speed set manually as and when required.

4.2.6 — Temperature Measurement and Control

As already explained in section 4.2.2, the turbidimeter was heated with two cartridge heaters wired in series placed inside the aluminium cell block and incorporating a 513 K thermal fuse. They were driven by a Eurotherm temperature controller (model number 2416). The controller was suitable for a temperature range of 273.15 K to 523.15 K (displays at 0.01 K) and was connected to a computer via an RS232 communications port. It is set for an RTD/PT 100 thermometer as the temperature-measuring device. Before the experiments were run the controller was tuned, whereby in order to obtain good control, the characteristics of the controller are matched to those of the process being controlled. This means that there is stable
Figure 4.22 — Photograph of assembled turbidimeter.

Figure 4.23 — Photograph of the experimental set-up: the turbidimeter, an optical fibre and an LED plus resistor, the Al enclosure, the rocking mechanism including the motor.
control of the set point temperature (without significant fluctuations), that there is an acceptable overshoot or undershoot of the temperature set point after adjustment and that there is a fast response to any deviation from the set point caused by possible external disturbances. The controller was tuned using its automatic tuning function, which works by switching the output on and off to induce an oscillation in the measured value and from the amplitude and period of the oscillation calculates optimal values for the tuning parameters. Tuning was only performed at the commissioning stage of the apparatus and there was no need to do it again throughout the course of the experimental campaign. Also, it was tuned at ambient temperature as advised by the manufacturers as this allowed the tuner to calculate more accurately the low and high cutback values that restrict the amount of overshoot or undershoot. Temperature stability was checked at different temperatures and deviations from the set point were found to be extremely small. An example is shown in figure 4.24 for the stability at $T_{\text{set point}}$ of 333.35 K. The maximum deviation is $\pm 10 \text{ mK}$.

![Figure 4.24 — Performance of the temperature controller at $T = 333.35 \text{ K}$](image)
For cloud-point determinations an initial temperature was set in the controller such that the polymer solution was in one phase and the temperature was then either lowered or raised at a specified rate. The controller was programmed using its ramp and dwell functions to offset this reference temperature. The ramp rate or the ramp time and the target set point must be specified. On the other hand, the dwell function is where the set point remains constant for a specified period. The controller was capable of storing up to four programs and has up to 16 segments per program. Various time periods (in hrs, mins or secs from 0.1 to 999.9) and temperature ranges can be preset on the ramp, enabling the rate of change of temperature to be varied. Moreover, the direction of this temperature change can also be chosen allowing controlled heating or cooling runs.

The temperature of the cell block was measured using two four-wire platinum resistance thermometer (PRT), one for control and one for recording. The thermometers were calibrated at the ice point of water and by comparison at other temperatures with a PRT standard from the National Physical Laboratory (NPL). The ice-point cell used for the two PRT's consisted of a dewar vessel filled with a mixture of distilled water and crushed ice (also prepared from distilled water). The PRT was placed inside a glass tube filled with dodecane, which is liquid at 0 °C, and this tube inserted into the dewar. The ice/water mixture was continuously stirred to maintain a constant temperature throughout the bath. Resistances were measured during a 30 min period, where the last 10 mins were monitored closely to ensure stability of readings (readings taken every half a minute). The resistance of the standard was also measured at the ice point of water to check if the standard, which was used for comparison, was still accurately calibrated. The set-up was different though. A resistance bridge was used to measure the ratio of the resistance of the thermometer to that of a 25 Ω standard resistance every minute for a 40 min period.

Calibration was carried out at temperatures of −20 °C, 40 °C, 80 °C, 120°C and 160°C. A temperature-controlled bath was used for this purpose and at each temperature the resistance of the PRT measured. Readings were taken every 10 minutes for a one hour period. In the case of the standard thermometer, the resistance bridge was used again although now a 50 Ω standard was used. The same frequency of readings was used.

The calibration equation for a PRT takes the following form depending on the temperature range (NPL Certificate of Calibration, 1990; Preston-Thomas, 1990):
Above 0 °C: \[ W - W_{\text{ref}} = a(W - 1) + b(W - 1)^2 \] (4.1)

Below 0 °C: \[ W - W_{\text{ref}} = a(W - 1) \] (4.2)

where \( a \) and \( b \) are the calibration constants obtained by fitting using a least squares method and \( W \) is the resistance ratio defined as

\[ W = R(T) / R(0.01^\circ \text{C}) \] (4.3)

where \( R(T) \) is the resistance at temperature \( T \) and \( R(0.01^\circ \text{C}) \) is the resistance at the triple point of water. The temperatures corresponding to the measured resistances are calculated using the following two equations depending on the temperature range being measured:

Above 0 °C (\( T \) accurate to ±0.00013°C):
\[ T(\degree \text{C}) = D_0 + \sum_{i=1}^{9} D_i \left[ (W_{\text{ref}} - 2.64) / 1.64 \right]^i \] (4.4)

Below 0 °C (\( T \) accurate to ±0.0001°C):
\[ T(\text{K}) = B_0 + \sum_{i=1}^{15} B_i \left[ (W_{\text{ref}}^{1/6} - 0.65) / 0.35 \right]^i \] (4.5)

where \( D_i \) and \( B_i \) are constants for the equations (NPL Certificate of Calibration, 1990), and \( W_{\text{ref}} \) values are calculated for the PRT's in question from equations (4.1) and (4.2) once \( a \) and \( b \) have been determined.

The full details of the calibration and the experimental data are given in appendix B4. The values of \( a \) and \( b \) are given in table 4.1 for both thermometers used in this apparatus.

<table>
<thead>
<tr>
<th>Temperatures above 0 °C</th>
<th>Temperatures below 0 °C</th>
</tr>
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<tbody>
<tr>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>PRT 1</td>
<td>-1.8076 \times 10^2</td>
</tr>
<tr>
<td>PRT 2</td>
<td>-1.9875 \times 10^2</td>
</tr>
</tbody>
</table>

*Table 4.1 — Calibration constants for platinum resistance thermometers in the turbidimeter, where PRT 1 is connected the controller and PRT2 is used to record the temperature in the cell block.*
4.2.7 — Data Logger and Acquisition of Data

All five photodetectors and one of the PRT's were connected to a multiplexer (HP 34901A 20 two-wire channel general-purpose multiplexer module) integrated in a data acquisition/switch unit (HP 34970A). Collected signals from each of the 6 channels used were switched one at a time and displayed on the screen of the data acquisition box. Each channel was programmed to read either a DC voltage (in the case of the photodetectors) or a resistance (in the case of the 4-wire PRT), both with a 6.5-digit multimeter accuracy. The multimeter enabled us to log measurements either directly or by automatically scanning at specified intervals during a given period of time. The data acquisition unit was linked to a PC via an IEEE-488 cable and the data logged and monitored numerically and graphically using HP Benchlink Data Logger software.

4.2.8 — Materials

Three systems were chosen for cloud-point determination, two common homopolymers and one copolymer, all three in the common solvent cyclohexanol. Monodisperse samples were used of polystyrene, poly(methyl methacrylate) and a copolymer of the two which in actual fact is as block copolymer. It has been previously explained that polymer molecular weight is a very important factor in liquid-liquid equilibria and it causes a shift in cloud-point temperatures. Consequently, not only were monodisperse samples used in these experiments, but also the effect of molecular weight on the LLE of the homopolymer/solvent systems was investigated. Three different molecular weights were investigated for each homopolymer/solvent system. Unfortunately, only one copolymer/solvent system could be studied.

Cyclohexanol with 99% purity was purchased from Aldrich co., UK and has a melting point of 293.15-295.15 K, a boiling point of 433.15-434.15 K and a liquid density at ambient temperature of 0.963 g/cm³. The polymers were analysed by gel permeation chromatography (GPC) for molecular weight and molecular weight distribution and in the case of the copolymer it was also analysed using nuclear magnetic resonance (NMR) for composition. The results from these analyses and
the suppliers are given in table 4.2 where \( M_w \) is the average molecular weight, \( M_n \) is the number average molecular weight and PDI is the polydispersity index defined as \( M_w/M_n \). Included in this table are all the polymers used for this work, both for testing purposes and for the objective measurements. Additionally, some preliminary test-runs of the apparatus were carried out using a solution of the well-documented system, polystyrene /cyclohexane. The cyclohexane used of 99.9 % purity was obtained from Aldrich co., UK (boiling point of 353.85 K and much less viscous than cyclohexanol).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_w ) (g/mol)</th>
<th>( M_n ) (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 4(^{(a)})</td>
<td>( 4.215 \times 10^3 )</td>
<td>( 3.95 \times 10^3 )</td>
<td>1.07</td>
</tr>
<tr>
<td>PS 79(^{(a)})</td>
<td>( 7.88 \times 10^4 )</td>
<td>( 7.03 \times 10^4 )</td>
<td>1.12</td>
</tr>
<tr>
<td>PS 28c(^{(b)})</td>
<td>( 2.86 \times 10^5 )</td>
<td>( 1.30 \times 10^5 )</td>
<td>2.2</td>
</tr>
<tr>
<td>PS 850(^{(c)})</td>
<td>( 8.49 \times 10^5 )</td>
<td>( 5.86 \times 10^5 )</td>
<td>1.45</td>
</tr>
<tr>
<td>PMMA 68(^{(d)})</td>
<td>( 6.80 \times 10^4 )</td>
<td>( 6.61 \times 10^4 )</td>
<td>&lt; 1.03</td>
</tr>
<tr>
<td>PMMA 280(^{(d)})</td>
<td>( 2.80 \times 10^5 )</td>
<td>( 2.63 \times 10^5 )</td>
<td>&lt; 1.06</td>
</tr>
<tr>
<td>PMMA 992(^{(d)})</td>
<td>( 9.922 \times 10^5 )</td>
<td>( 9.389 \times 10^5 )</td>
<td>&lt; 1.06</td>
</tr>
<tr>
<td>S(48.7%)-b-MMA(^{(d)})</td>
<td>( 5.85 \times 10^4 )</td>
<td>( 5.52 \times 10^4 )</td>
<td>&lt; 1.06</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Purchased from Polymer Laboratories Ltd., Shrewsbury, UK who provided the GPC and NMR results.
\(^{(b)}\) Provided by Imperial College London, UK. GPC results from RAPRA Technology Ltd., UK.
\(^{(c)}\) Purchased from Phase Separations Ltd., Clayd, UK who provided the GPC results.
\(^{(d)}\) Purchased from Polymer Standards Service, Mainz, Germany who provided the GPC results.

Table 4.2 — Characteristics of polymers used for cloud-point determinations.

4.2.9 — Preparation of Samples

Polymer solutions were prepared in situ, i.e. inside the sample cells. Having five cells, solutions of five different concentrations could be prepared for one experimental run. An experimental run was always started at a temperature at which the polymer solution was in one phase, i.e. at a temperature above the LLE phase separation curve. For these systems theta temperatures have been reported by
Kotaka et al. (1970) using light scattering as $\theta_{b} = 356.15$ K, $\theta_{PMMA} = 351.95$ K and $\theta_{(50\%)-b-MMA} = 353.95$ °C. Similar values were obtained by Froelich and Benoit (1966) of $\theta_{b} = 356.65$ K, $\theta_{PMMA} = 350.75$ K. Due to these high temperatures, the samples were prepared inside the sample cells.

The turbidimeter cell was assembled first making sure that the stirring balls were placed inside the empty sample cells. The assembly was then weighed using a balance capable of measuring to ± 0.001 g and the weight of the empty block noted. Having calculated the necessary mass of both polymer and solvent required for a specified solution concentration, the necessary amount of polymer was then carefully introduced in the first sample cell using a pre-weighed glass funnel. All polymers were of a powdery nature and so care was essential when filling the cells. The new weight of the cell block was recorded and the next cell was filled. This process was repeated until all five cells were filled. Without removing the turbidimeter from the balance, the required amount of solvent was introduced into the first cell using a pipette, then weighed and immediately sealed with the pre-weighed screw cap and o-ring. This process is repeated until all five cells are filled. The sample cells were not filled completely although there was enough to have the light path covered with solution. All weights were recorded and concentrations of the solutions were recorded as weight fractions.

4.2.10 — Experimental Procedure

With the polymer solutions sealed in the turbidimeter, the apparatus was assembled and then left to settle for a few hours during which time the polymer started swelling and dissolving in the solvent. The motor was started and the rocking speed and angle set manually. These settings depended on the viscosity of the solutions, which in turn depends on the concentration of polymer in the mixture. The volume of the cell actually was a limitation on the amount of polymer in a sample solution especially if the polymers were very flaky, since they could occupy a substantially high volume compared to the solvent. Several concentrations of solutions were prepared in test tubes previous to carrying out any experiments in the turbidimeter to get a feel for the viscosity of the solutions.
As soon as stirring was started the temperature was ramped from room temperature to a temperature 20-40 K greater than the theta temperature, at a rate of 0.1 K/min. It was left at the set point temperature for at least two hours before starting the experiments. The motor was then stopped when the turbidimeter returned to its starting position and the transmitted light intensity signal monitored during some time (normally around one hour) until a constant value of the signal was obtained. In the one phase region of the phase diagram, the solution should be transparent and the detected signal should be at its highest. A rate of cooling and a final temperature were programmed into the temperature controller and the transmitted signal from the photodetectors recorded in the PC.

The steps here described are those for a typical run of a polymer solution exhibiting UCST behaviour. An almost identical procedure was followed for an LCST system. First of all the polymer solution was taken to a temperature where there is a one-phase region. The temperature was increased further and the signal monitored to check for changes. If there was sudden drop, implying that there is LCST behaviour, the temperature was lowered at a very slow rate to 20-40 K below the approximate phase transition temperature, whilst stirring. The motor was then stopped when the turbidimeter returned to its original position and left to settle until the recorded signal from the photodetectors became constant. A heating ramp was programmed into the temperature controller and the experiment started. Note that all experiments were carried out at the vapour pressure of the solvent.

4.3 – Vapour-Liquid Equilibria Using Inverse Gas Chromatography

In 1969, Smidrod and Guillet were the first to use gas chromatography as a method of measuring thermodynamic properties such as activity coefficients and enthalpies of solution. The chromatographic process is based on the separation of the components in a sample, owing to their differences in solubility or in adsorption in a stationary phase of material (either a liquid or a solid). A typical chromatographic system consists of a number of components as shown in figure 4.25. A sample is introduced at the injection point where it mixes with the carrier gas and is carried into the column. Chromatographic separation takes place and the detector responds to each component in the gas by yielding an electrical signal. The
carrier gas typically nitrogen or helium, is called the *moving phase* and should be non-interacting with the sample. The *stationary phase* is usually a material impregnated on a support. This phase is packed inside a chromatographic column, which is a length of either coiled glass or metal tubing. The entire assembly is contained in an oven with which the temperature is monitored.

**Figure 4.25** - Sketch of the main components of a gas chromatographic system.

The signal is usually detected by one of four main types of detectors: a flame ionisation detector (FID), a thermal conductivity detector (TCD), an electron capture detector (ECD) or a flame photometric detector (FPD). The most commonly used are the first two. The FID works on the basis that, when organic compounds are burnt in a flame, ions are produced. A pair of polarized electrodes inside the detector collects these ions thereby creating a signal. On the other hand, in a TCD, a thin wire that forms part of a Wheatstone bridge circuit is heated electrically. The thermal conductivity of the gas changes with composition and this in turn affects the heat loss from the wire; hence the temperature and the resistance of the wire change.

**4.3.1 – Inverse Gas Chromatography (IGC)**

In gas chromatography applied to polymer solutions, the polymer becomes the stationary phase and because this phase is the phase of interest and does not act
as the separating agent, the technique is referred to as *inverse gas chromatography*. As the solvent, travelling with the carrier gas, is swept through the column containing the polymer, two important resistances are encountered. The first is the longitudinal diffusion in the gas phase and the second is the mass transfer into the polymer phase. Because equilibrium does not occur instantaneously, the solvent lags behind resulting in an elution peak. The retention time of the solvent, which is the time required for the centre of mass of the solvent to move along the column, is a function of the time it spends in both the mobile phase and the polymer stationary phase. This is directly related to the fundamental variable of gas chromatography, the partition coefficient $K$. It is defined as the ratio between the concentrations of solvent in the stationary polymer phase to that in the mobile carrier gas. The shape of the elution curve and the partition coefficient give us information not only about polymer-solvent interactions, i.e. the thermodynamic properties of the polymer solution (such as the solvent activity coefficient) but also about the transport properties such as the diffusion coefficient of the solvent in the polymer.

Since 1969, extensive work has been carried out using gas chromatography for the measurement of thermodynamic properties of polymer solutions however this has been mainly at infinite dilution of the solvent, i.e. when the solution consists of nearly all polymer. Surprisingly it was also in 1969, that Conder and Purnell (1968a, 1968b; 1969a, 1969b) in a series of papers developed the mathematical expressions for the application of GC to the finite concentration region. It was Brockmeier et al. (1972a, 1972b; 1973) that adapted the work to systems involving polymers, obtaining weight fraction activity coefficients for concentrations of up to 60% by weight of various hydrocarbon vapours in polystyrene, amorphous polyethylene and atactic polypropylene. Since then, only a few workers have used this technique. Amongst others, Leung and Eichinger (1974a, 1974b) investigated poly(isobutylene) with hydrocarbons, Cheng and Bonner (1975a, 1975b) measured the activities of benzene in poly(ethylene oxide), Lau et al. (1982) have investigated polybutadiene with benzene and cyclohexane and Sørensen et al. (1990) measured infinite dilution activity coefficients in poly(ethylene glycol) with n-alkanes, benzene and toluene. Kontominas et al. (1994) have looked at solutions of polystyrene in n-alkanes and Kikic et al. (2000) measured activity coefficients at infinite dilution using this method. Furthermore, Danner and co-workers (Tihminlioglu et al., 1997 and 2000; Tihminlioglu and Danner, 1999 and 2000; Surana et al., 1997 and 1998; Danner
et al., 1998) have been working extensively with this method and have investigated several solutions of polystyrene and poly(vinyl acetate).

All in all, inverse gas chromatography has proved over the years to be a fast, convenient and reliable method of measuring activity coefficients. Measurements can be achieved in a matter of minutes, changes in solvent temperature can be achieved quickly and furthermore detectors can detect very small amounts of injected solvent, thus enabling measurements to be taken at infinite dilution. For all these reasons, this technique has been chosen for this work. Full details of the experimental apparatus used in these experiments and the issues associated with this method will cover the rest of this chapter.

4.3.2 — Chromatographic Columns

There exist two types of column that can be used for the chromatographic process, packed columns or capillary columns. In the majority of apparatus used where the polymer has been the stationary phase, packed columns have been typically used. In these columns, the polymer is coated onto a solid support by mixing a weighed amount of support material with a solution of polymer (a suitable solvent must be chosen). The solvent is then evaporated (by passing nitrogen gas through it for example) and the support is then dried in a vacuum oven at a high temperature. The amount of polymer coated on the support is found by weighing before and after. Loading is usually around 10% polymer by mass. The column is finally packed with the stationary phase by means of a mechanical vibrator. The most commonly used support materials are Fluoropak and Chromosorb P, G or W (all flux-calcinated supports) either acid washed or treated with dimethyldichlorosilane. Newman and Prausnitz (1972) observed that the former produced nearly symmetric peaks with polar solvents and eliminated the dependence of retention time on sample size. These findings were also supported by Romdhane and Danner (1991) who found that although surface adsorption of non-polar solvents on Fluoropak was around 10 times greater than that on Chromosorb, for polar solvents adsorption was much smaller using Fluoropak, there was no dependency of retention times on sample sizes and peak symmetry was far superior. The specifications of the columns are generally
similar in all experiments: 0.6 cm diameter aluminium or stainless steel tubes of around 1.5 m in length.

The alternative to a packed column is a capillary column and these are being used more regularly. In these, the polymer is coated onto the inside wall of a small-bore tube and no granular material is used. The typical coating thickness is about $10^4-10^5 \, \text{Å}$ comparable to $10^2-10^3 \, \text{Å}$ thickness in packed columns (the same order of magnitude as the length of the polymer molecules). Lichtenthaler et al (1974) questioned whether the polymer-solvent interactions in such a thin polymer layer would be the same as those in the bulk polymer and wanted to investigate the performance of both types of columns. They carried out some experiments on several solvents with poly(isobutylene), poly(vinyl acetate) and poly(dimethylsiloxane), to compare retention volumes and values of Flory's interaction parameter using both types of columns. They observed that in fact, the values were somewhat different, sometimes by as much as 20%. In general, retention volumes obtained using packed columns were lower than those obtained with capillary columns, however Flory's interaction parameter resulting from capillary column studies agreed better with results from experiments using static methods. Another observation was the tailing in the elution peaks using capillary columns. Reasons for this are possible surface adsorption which can be examined by taking measurements with columns of different loading, and possible non-equilibrium probably caused by the slow diffusion of the solvent vapour in the stationary phase. If there is an observable difference in retention volumes with gas flow rate then one can extrapolate to zero flow rate.

In the experiments carried out in this work, capillary columns were used. Not only is it possible to obtain thermodynamic data for the systems studied, but the IGC technique can also be used to obtain data on the diffusivity of the solvent in the polymer. One of the difficulties with making packed columns is obtaining a uniform distribution of the polymer on the column and to obtain good data in packed columns, it is essential that there are no interactions between any exposed area of solid support and the solvent. For this reason, capillary columns are advantageous as a much more uniform film thickness can be achieved.
4.3.3 – IGC at Finite Concentrations

To perform experiments at finite concentrations, four different techniques are available as originally described by Conder and Purnell (1969). The main characteristics of these are presented by Conder and Young (1979). These are frontal analysis, frontal analysis by characteristic point, elution by characteristic point and elution on a plateau. The latter has been used very successfully by researchers to measure thermodynamic data mainly because it does not require detector calibration (Price and Guillet, 1986; Brockmeier et al., 1972a, 1972b; Conder and Purnell 1968, 1969; Tihminlioglu and Danner, 1999). It has proved to be the most convenient although its main disadvantage is that the presence of the solvent in the carrier gas can lead to scatter in the results which will increase as the activity of the solvent increases.

In the technique of elution on a plateau, the carrier gas is passed through a gas saturator where it mixes with the solvent before entering the column. The mixed gas leaves through a well-insulated pipe and is fed into the gas chromatograph and into the column to equilibrate with the polymer. The vapour pressure of the solvent at the saturator temperature and the total pressure determine the composition of the mixed gas. After the GC reaches steady state (constant temperature, flowrate and pressure), the detected signal becomes the baseline for the measurements. A plateau is therefore set at a constant concentration. Good temperature control and a small pressure drop are required to make fluctuations as small as possible. An injection is then made into the column, of either marker gas or solvent. In general, experiments should be carried out at different gas flowrates and different sample sizes to ensure that there is negligible effect from adsorption or concentration. Finally the temperature in the saturator is changed in order to achieve a new concentration of solvent in the carrier gas.

In frontal analysis techniques, there is a continuous switchover between a stream of mixed carrier gas and solvent and a stream of pure carrier gas. This produces two boundaries, a frontal boundary when the solvent concentration increases and a rear boundary when the solvent concentration decreases. Breakthrough of the boundary at the column outlet depends on how much solvent has been absorbed by the polymer. In the frontal analysis by characteristic point technique, the sorption isotherm is obtained by measuring retention volumes along
the breakthrough curve at different characteristic points of concentration. The frontal analysis technique is fast and a complete isotherm can be measured in a single experiment, but this method requires detector calibration, especially at high gas phase concentrations (Danner et al., 1998). Furthermore, the signals are very sensitive to gas non-ideality, temperature and permeability effect (Conder and Purnell, 1969).

Following these arguments and based on good agreement between results from both methods as shown by Danner et al. (1998), it was decided that for this work the elution on a plateau technique would be used. It has proved more accurate although somewhat more time consuming.

4.3.4 - Experimental Apparatus

A diagram of the apparatus used is shown in figure 4.26. This set-up is a modified version of that used by Conder and Purnell (1969) and by Price and Guillet (1986). It had been constructed previous to this work at the Centre for the Study of Polymer Solvent Systems (CSPSS) at the Pennsylvania State University, University Park, Pennsylvania, USA. Two different set-ups were used for the experiments where the gas chromatographs where Varian Models 3400 and 3600 equipped with flame ionisation detectors, column injectors and circulating air ovens. One set-up (gas chromatogram Varian 3600), used for most of the measurements at infinite dilution, was similar to that shown in figure 4.26 but without the saturator, such that the carrier gas is directly fed into the column and through to the detector. Ultra-high purity helium was used as the carrier gas in both apparatus and this carried the injected solvent into the column inside the oven. Furthermore, it was used as the make-up gas, which bypasses the column, to provide an adequate flow into the detector and reduce mixing effects at the end of the column produced by pushing the column gas into the detector at high velocities. Additionally, to maintain a constant carrier flowrate, the pressure upstream of the column is regulated with a flow controller. The fire in the flame ionisation detector was lit up with dry-grade air and high-purity hydrogen. For the marker gas, air or methane is commonly used but because the FID will not detect air, methane was used. It was very important to maintain the temperature of the injector and the detector were kept always well above the column temperature (at least 30 K higher) to ensure volatilisation of the
Figure 4.26 - Schematic of the experimental set-up.
solvent and therefore avoid any possible condensation at any point throughout the system. The oven is equipped with a digital control unit with which the temperature of the injector, detector and columns can be adjusted with a resolution of 1.0 K. Additionally, the oven has a large diameter, high-speed air fan at the back to help with temperature uniformity.

In the case of the finite concentration experiments, the apparatus shown in figure 4.26 was used. Two photographic views of the set-up are shown in figures 4.27 and 4.28. For the elution on a plateau technique, the helium gas is passed through the gas saturator before entering the chromatographic column. The saturator consists of a stainless steel vessel of approximately 1.7 litre capacity, sealed with an O-ring. The vessel is filled with solvent and tightly sealed. A leak-sealed stirrer (lightning G3S53R, 300-1800rpm) and a gas-diffusing stone are used to ensure thorough mixing and uniform diffusion of the gas into the liquid. The vessel is heated using an immersion heater and cooled simultaneously to achieve good temperature control, by placing it on a cold plate. A proportional controller is used to maintain the saturator at a constant temperature (± 0.1 K). The system is entirely sealed to ensure no leakage of gas or solvent vapour and the gas leaves through a surge tank to minimise any fluctuations in the carrier gas. Both the vapour space on the upper part of the vessel (just below the lid) and all the lines leading to the gas chromatograph were well insulated with heating tapes and kept at least 20 K above the saturator temperature, to ensure no condensation and avoid any cold spots. Thermocouples were placed at five different points in the set-up to monitor the temperature. Temperature control is critical in the experiment, as this is what determines the concentration of solute going into the column. Finally, a pressure transducer was placed just before the entrance to the column to monitor the pressure drop. The carrier gas-solvent vapour mixture leaves the saturator and flows through the column where it equilibrates with the polymer.

The data was recorded with a frequency ranging between 4 and 11 Hz, on an IBM PC through an RS232 port. The raw data was then processed using the Capillary Column Inverse Gas Chromatography (CCIGC) model which will be explained in the next chapter. The maximum file size was limited to 1024 points which Pawlisch et al. (1987) showed provided a good resolution.
Figure 4.27 — Set-up for Inverse Gas Chromatography Experiments at Fenske Lab, Pennsylvania State University.
Figure 4.28 — Set-up for Inverse Gas Chromatography Experiments at Fenske Lab, Pennsylvania State University.
4.3.5 — Samples and Columns

The solvent used for all experiments was cyclohexanol (99% purity from Aldrich, UK). To ensure that experiments were carried out at conditions approaching infinite dilution, solvent sample sizes were always kept as small as possible but without compromising measured signal. A compromise was reached between samples being too small to be detected and too large and giving ill-defined peaks. Measurements were carried out with different sample sizes of cyclohexanol and a value of 0.1 µl cyclohexanol was appropriately chosen (see section 5.3.6.1). The marker gas injections were 10 µl in volume. Moreover, cyclohexanol retention times were found to be independent of sample size over the range of temperatures investigated.

Experiments were performed with the three polymers already mentioned, polystyrene, poly(methyl methacrylate) and a PS-PMMA copolymer of 40% styrene. The polymers were obtained from Aldrich co. (UK) and their molecular weights and glass transition temperatures are given in table 4.3. For both the polystyrene sample and the copolymer sample no polydispersity index was available although they were known to be polydisperse samples.

All capillary columns were prepared by the CSPSS at Penn State, using a static polymer coating technique as described by Jennings (1980). The polymer is dissolved in chloroform or dichloromethane to form a viscous solution, which is then pushed into and completely fill a fused silica column. Once the column has been filled, one end is carefully sealed with an epoxy and the other is used for the removal of the solvent under vacuum, in a constant temperature bath. As the solvent evaporates, the meniscus of the filled column travels form one end of the column to the other leaving a thin polymer film deposited on the inner walls of the column. The final thickness of the polymer coating is calculated from the parameters of the solution used as explained in appendix C1. The capillary column specifications are given in table 4.4. The columns were carefully installed in the GC ovens ensuring that there were no leaks in the system, and conditioned for a minimum of 12 hours at the highest temperature to which they would later be subjected thereby eliminating the possibility of any residual volatile components in the polymer affecting experimental results. This involved heating the column up at a very low rate, namely 1 K/min.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w \times 10^3$ (g/mol) (a)</th>
<th>Polydispersity (a)</th>
<th>$T_g$ (K) (b)</th>
</tr>
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<tbody>
<tr>
<td>PS</td>
<td>200</td>
<td>Not available</td>
<td>375.57</td>
</tr>
<tr>
<td>l-PMMA</td>
<td>15</td>
<td>1.67</td>
<td>365.20</td>
</tr>
<tr>
<td>h-PMMA</td>
<td>996</td>
<td>9.67</td>
<td>393.45</td>
</tr>
<tr>
<td>PS-co-PMMA</td>
<td>125</td>
<td>Not available</td>
<td>378.14</td>
</tr>
</tbody>
</table>

*Table 4.3 – Specifications of polymers studied.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Column length, $L \pm 0.5$ (cm)</th>
<th>Column inner diameter, $D \pm 0.001$ (cm)</th>
<th>Film thickness, $r \pm 5 \times 10^{-5}$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1335.5</td>
<td>$5.3 \times 10^2$</td>
<td>$5.12 \times 10^4$</td>
</tr>
<tr>
<td>l-PMMA</td>
<td>1281.5</td>
<td>$5.3 \times 10^2$</td>
<td>$3.0 \times 10^4$</td>
</tr>
<tr>
<td>h-PMMA</td>
<td>1317.5</td>
<td>$5.3 \times 10^2$</td>
<td>$3.0 \times 10^4$</td>
</tr>
<tr>
<td>PS-co-PMMA</td>
<td>1299.3</td>
<td>$5.3 \times 10^2$</td>
<td>$3.0 \times 10^4$</td>
</tr>
</tbody>
</table>

*Table 4.4 – Capillary column specifications.*

### 4.3.6 – Experimental Procedures

Once the chromatographic column had been installed properly and conditioned, the set-up was ready for a run. For the measurement of activity coefficients at infinite dilution, a run consisted of the following steps. First, the flame in the detector was lit, and the injector and detector temperatures were set. Once these temperatures were attained, the required column temperature was set. The recorder signal was monitored and once it showed a steady baseline signal and the GC had reached steady-state operation (i.e. constant temperature and carrier gas.

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(1) Data provided by Aldrich co., UK.
(2) Results from DSC analysis by T. Rattana at the Pennsylvania State University, USA.
(3) Specifications from H. Betz at the Pennsylvania State University, USA.
flowrate), a sample of methane gas (the marker gas) was injected as a pulse. Data collection was started manually at the time of the sample injection. From the retention time in the resulting elution peak, the velocity of the carrier gas was calculated. The magnitude of the signal with respect to the baseline is proportional to the concentration of methane in the outlet stream, and so the carrier flowrate can be adjusted to obtain an easily detectable signal. A second marker gas injection was done before the solvent injection. A similar injection to that of the methane gas was done but now with the solvent under study. The recorder produces an elution peak from which the retention time was noted and the profile saved for data analysis using the CCIGC model. A further two injections of methane gas were made after the solvent injection, so as to be in no doubt that the carrier gas velocity had not changed during the experiment. The column temperature was increased or decreased to the next set-point and the apparatus left to equilibrate for 15-20 minutes at the new temperature.

For the finite concentration experiments, the steps were essentially the same although a few extra actions were necessary. Again, once the columns were installed, checked for leaks and conditioned, the injector and detector temperatures were set. Next, not only the column temperature was set but also the saturator was heated to and maintained at a constant temperature, which would then provide the plateau concentration of solvent in the carrier gas. The recorder signal was monitored for a steady baseline signal. The waiting time (equilibration time) was more than for the infinite dilution runs. Especially at the higher concentration plateaus, i.e. at the higher temperatures of the saturator, a few hours were necessary for a steady baseline. Once the recorded signal was steady, all the temperatures in the system and the pressure reading were checked for stability, and if reached the system was said to have achieved steady state. At this point a sample of methane gas (the marker gas) was injected. The retention time was noted. Actually two marker gas injections were made before the solvent injection and two afterwards. In the finite concentration experiments, three solvent pulse injections were carried out to check on the repeatability. After the two methane injections, the next saturator temperature was set, consequently changing the concentration of solvent entering the column. All retention times were noted and the solvent elution peaks were saved for analysis using the CCIGC model.
Chapter V

EXPERIMENTAL RESULTS

5.1 — Introduction

In this chapter, the experimental results obtained using the techniques described in the previous chapter are presented. The chapter is divided into two main sections, the first concerning turbidimetric measurements (LLE) and the second concerning the results from the inverse gas chromatography apparatus (VLE). In both cases, two homopolymers in solution with cyclohexanol have been studied: PS and PMMA. In the case of LLE, a block copolymer S-b-MMA (with 48.7% PS by weight) was used. For the IGC experiments a random copolymer S-α-PMMA (40 % PS by weight) was used.

5.2 — Turbidimetry Results

Cloud point curves have been measured using the turbidimeter and the results are presented in this section. Before taking measurements on the systems under study, the stability of the light from the optical fibres and LEDs was investigated. Additionally, some preliminary runs on the well documented
polydisperse PS/cyclohexane system were carried out to ensure that the apparatus was functioning properly.

5.2.1 – Stability of the Light Source and Photodiodes

Light emitting diodes connected in series to a stabilised power supply were used as the light sources in the turbidimeter and photodiodes (which are more sensitive towards the red wavelength end of the spectrum) were used as the photodetectors. To test the stability of the light source and detectors, the turbidimeter was assembled with the sample cells empty and the signals in all five cells monitored during a period of an hour. First though the magnitude of the background noise in each channel was recorded.

The average value of the fluctuations in each of the channels is given below:

<table>
<thead>
<tr>
<th>LED #</th>
<th>Variation in DC Voltage (V) with no light</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>± 0.0002</td>
</tr>
<tr>
<td>2</td>
<td>± 0.0005</td>
</tr>
<tr>
<td>3</td>
<td>± 0.0005</td>
</tr>
<tr>
<td>4</td>
<td>- 0.0004 ≤ V ≤ 0.0008</td>
</tr>
<tr>
<td>5</td>
<td>- 0.0004 ≤ V ≤ 0.0010</td>
</tr>
</tbody>
</table>

Table 5.1 – Approximate peak-to-peak background noise for each channel monitored during a 5 min period. The values are averaged from three test runs.

The LEDs were then turned on and the signal through the empty cells was monitored during a one hour period. This test was performed twice on two consecutive days. The results show that there was an initial period that the LED needed before the signal was constant, on one day it was around 20 mins and in the second it was around 40 mins. During this "warming-up" time the signal fell by around 1.0 % from its initial value for LEDs 1-4. Another observation was the
The difference in the value of the signal between day 2 and day 1, which ranged between 1.0 and 2.5%. On average, the stable voltages at full light power from the LEDs were around 250 mV as given in table 5.2, except for LED 5 that showed a lower value of around 140 mV. Also, the decrease in signal from its initial value to the stabilised value was approximately 3% on day one and 3.7% on day two, for all cells. These observations were associated with the windows being dirty, therefore causing some obstruction to the light path. The windows cleaned thoroughly before every experiment. It should be mentioned that the optical fibres needed to be tightly screwed onto the lens holder, since looseness could result in the fibres being misaligned.

<table>
<thead>
<tr>
<th>LED #</th>
<th>$V_a$ (mV)</th>
<th>Av. % change in $V$ before stabilisation</th>
<th>% deviation from $V_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>246.6</td>
<td>-0.89</td>
<td>±0.02</td>
</tr>
<tr>
<td>2</td>
<td>250.8</td>
<td>-1.10</td>
<td>±0.02</td>
</tr>
<tr>
<td>3</td>
<td>257.0</td>
<td>-1.00</td>
<td>±0.03</td>
</tr>
<tr>
<td>4</td>
<td>273.4</td>
<td>-0.98</td>
<td>±0.02</td>
</tr>
<tr>
<td>5</td>
<td>136.2</td>
<td>-3.34</td>
<td>±0.11</td>
</tr>
</tbody>
</table>

*Table 5.2—Stability of LED/photodetector pairs at full light power.*

As can be seen from table 5.2, once the signal had reached a steady value, fluctuations in the voltage were very small. Moreover, the large values of $V_a$ compared to the background noise and the fact that phase separation caused changes in transmitted signals as large as $V_a$, meant that the background noise could be considered to be negligible.

### 5.2.2 — Polystyrene/Cyclohexane

Some initial test runs were carried out with a polydisperse PS sample (PS 286) and cyclohexane as the solvent. Saeki et al. (1973) have reported cloud point
curves for several molecular weights of monodisperse PS in solution with cyclohexane. This system exhibits both UCST and LCST behaviour and using their data (which was presented in Chapter II), a PS sample of $M_w = 286,000$ g/mol should show one phase change at a temperature around 298 K and another at a temperature around 498 K.

5.2.2.1 – Test I: 1% by weight PS 286 in cyclohexane

The turbidimeter was set-up and the sample cells filled with a 0.94% by weight solution of PS 286 in cyclohexane. The solution was heated up from room temperature 290 K to 328 K at a rate of 10 K/min, stirring at all times. Once at 328 K, the temperature was maintained for an hour stirring continuously. The motor was then switched off and the sample left to cool naturally whilst recording the transmitted light intensity. The results are shown in figure 5.1 where the transmitted signal is plotted against temperature. The progress of the experiment was from right to left as the temperature decreased.

![Graph showing transmitted light signal as a function of temperature for PS 286 in cyclohexane](image)

**Figure 5.1** – Transmitted light signal as a function of temperature for a 0.94% by weight solution of PS 286 in cyclohexane in cell 2. Cloud-point temperature (CPT) is 23.92°C.
As can be seen from the plot, at the higher temperatures the signal was constant and large because the solution was in one phase and therefore transparent. As the temperature was decreased, the polymer solution underwent a phase change and became cloudy, leading to a sharp fall in the transmitted light (detected as a voltage). The temperature at which this happened i.e. the cloud point temperature ($T_{cp}$) was calculated by drawing two straight lines through the graph as shown and finding the temperature at which they intersect (as shown). For this sample it was 23.92 °C (297.07 K). As the temperature dropped further below the $T_{cp}$, the voltage decreased and as can be seen the magnitude of the drop was quite large. In the same figure, the voltage was plotted for the entire cooling process in order to show that the transmitted signal was extremely constant as a function of temperature through the transparent one phase PS solution. When phase separation occurred, the signal reached a lower limit. The signal then started increasing and rose up actually higher than its initial value. Once the two phase system had reached thermodynamic equilibrium, the two phases separated and the cloudy one (polymer rich phase) fell to the bottom of the sample cell. The polymer lean phase was transparent and so the transmitted signal increased sharply. A possible reason for it being higher than that for the one phase system was that there could have been some bubbles in the one phase solution caused by the continuous stirring upon heating.

5.2.2.2 — Test II: PS286 in cyclohexane at varying concentrations

The turbidimeter was set-up and the sample cells filled with solutions of PS 286 in cyclohexane of differing concentrations. Four samples were made up and a maximum concentration of 5 % PS by weight was achieved due to the nature of the polymer. The samples were simultaneously heated up to a high enough temperature, around 333 K, to be in the one phase region of the phase diagram. At this temperature they were stirred for an hour, the motor was then stopped and the solutions left to settle for half one hour, before finally turning the heaters off so that the solutions cooled down to room temperature at a natural rate. This experiment was carried out twice and the results are tabulated below (included in this table is the result from test I):
Table 5.3 – Cloud-point temperatures for PS 286 (polydisperse) with cyclohexane.

<table>
<thead>
<tr>
<th>% by weight PS 286</th>
<th>$T_{CP, \text{RUN} 1}$ (K)</th>
<th>$T_{CP, \text{RUN} 2}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30</td>
<td>297.95</td>
<td>298.70</td>
</tr>
<tr>
<td>1.94</td>
<td>299.02</td>
<td>298.95</td>
</tr>
<tr>
<td>2.27</td>
<td>299.00</td>
<td>298.38</td>
</tr>
<tr>
<td>4.80</td>
<td>298.35</td>
<td>298.45</td>
</tr>
<tr>
<td>0.94</td>
<td></td>
<td>297.07</td>
</tr>
</tbody>
</table>

Figure 5.2 shows the measured cloud-point curve (UCST behaviour) for this system and is compared to the results from Saeki et al. (1973). The plotted values are the average of the two measurements and the error bars show the deviation from the average values. There is good agreement between the data taking into account the difference in polydispersity between our samples and theirs.

5.2.2.3 – Test III: 5% by weight PS286 in cyclohexane, UCST and LCST behaviour

Again, four solutions of PS 286 in cyclohexane were made up in the turbidimeter. This time all four samples had approximately 5% by weight PS. In this way, we compared the repeatability of results from cell to cell. In these experiments both UCST and LCST behaviour were investigated. For the former, the same procedure was used as in the previous experiments. For the latter, the temperature was raised to 513 K whilst stirring and then maintained at this temperature for approximately one hour. The motor was then switched off and the solutions left to settle in the cells. At this temperature the solutions were still in one phase. When the signal was constant, a heating ramp was programmed in the temperature controller and the experiment started. The results from these experiments are given in Table 5.4. Results show that there is good agreement between cells. The cloud point temperatures for UCST compare well with those for the solution of similar concentration measured in the previous test (section 5.2.2.2). The average $T_{cp}$s for UCST behaviour are 298.64 K and 298.35 K at cooling rates of 0.042 K/min and 0.018 K/min respectively and the reproducibility is ± 0.19 K and ± 0.13 K respectively. For LCST, $T_{cp}$s are 495.15 K for both heating rates with a
Figure 5.2 — Cloud point curves for the UCST behaviour of PS/cyclohexane samples. Points represent experimental data, solid lines represent best polynomial fit. • This work with polydisperse PS samples and • Saeki et al. (1973) with monodisperse PS samples.
reproducibility of ± 1.78 K and ± 1.15 K respectively. In general though, these LCST values compare well to those from Saeki et al. (1973). The bigger deviations in results from cell to cell for this LCST behaviour might be due to the higher heating rates used. An effect of cooling rate, although very slightly, was observed in the measurements of UCST behaviour. $T_{\text{CP}}$s measured at the slower cooling rate were approximately 0.3 K lower than those for the faster cooling rate. However, the values are just within the reproducibility range and so the effect of cooling rate was considered as negligible. It is not very clear if heating and cooling rates do influence the phase separation process and hence the cloud point temperatures, and if this influence if system dependant. Bae et al. (1991) measured cloud-points by thermo-optical analysis for monodisperse PS ($M_w = 100\text{kg/mol}$)/cyclohexane solutions at three different cooling rates (0.1, 0.3 and 0.5 K/min) and found the same CPT for all three cooling rates. In contrast though, Szydlowski and Van Hook (1998) have talked about a possible effect of the quenching rate on cloud-point temperatures, as the cloud-point in a solution is kinetically and not thermodynamically defined. Furthermore, too fast a rate of change of temperature could produce thermal lags and non-equilibrium phase separation whereas too slow a rate might encourage polymer degradation. The latter effect though should be accounted for in the error resulting from the reproducibility of the experiments. For each system in this work, at least two rates of change of temperature were measured. If a significant difference in the resulting cloud point temperatures was observed, values are extrapolated to infinitely slow rates.

Another observation for this system from the plots of voltage versus temperature was that the rate of drop in transmitted light signal was very similar for

<table>
<thead>
<tr>
<th>Heating/cooling rate (K/min)</th>
<th>$T_{\text{CP, CELL 1}}$ (K)</th>
<th>$T_{\text{CP, CELL 2}}$ (K)</th>
<th>$T_{\text{CP, CELL 3}}$ (K)</th>
<th>$T_{\text{CP, CELL 4}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.042</td>
<td>UCST</td>
<td>298.55</td>
<td>298.45</td>
<td>298.65</td>
</tr>
<tr>
<td>0.018</td>
<td>UCST</td>
<td>298.30</td>
<td>298.20</td>
<td>298.40</td>
</tr>
<tr>
<td>4.0</td>
<td>LCST</td>
<td>496.15</td>
<td>493.65</td>
<td>493.65</td>
</tr>
<tr>
<td>2.1</td>
<td>LCST</td>
<td>496.15</td>
<td>494.15</td>
<td>494.15</td>
</tr>
</tbody>
</table>

Table 5.4 — Cloud-point temperatures for 5 % by weight solutions of PS 286 in cyclohexane. Data for both LCST and UCST behaviour.
each sample cell. This was expected. Differences can be attributed to environment differences between cell and cell, such as the presence of impurities, differences in wall roughness, scratches on the windows or different extents of homogeneity of the one-phase solutions. Any of these factors can be enough to cause the activation of a nucleation site leading to phase separation of the solution.

5.2.3 — Polystyrene/Cyclohexanol

The cloud point curves of monodisperse samples of PS in cyclohexanol were measured using the turbidimeter. The procedure described earlier for carrying out an experimental run was followed. The specifications of the samples can be found in table 4.2. Three molecular weights of monodisperse PS were measured, $M_w = 4.21 \times 10^3$, $7.88 \times 10^4$ and $8.49 \times 10^5$ g/mol, samples PS 4, PS 79 and PS 850 respectively. The system was heated from room temperature to 513 K to check what phase changes occurred and near what temperatures. Only UCST behaviour was observed in this temperature range. The results are presented in the tables 5.5 — 5.7. Repeatability of the CPT’s varied between 0.2 and 0.8 K.

It was observed during these measurements that in some instances the signal at the beginning of the run was not as high as 250 mV which was the voltage measured with an empty cell. In some cases it was much lower than this. This was attributed to a possible misalignment of the optical fibre with respect to the centre of the cell (maybe caused by the rocking of the turbidimeter) or to dirt deposited on the surface of the lenses leading to a reduction in the intensity of the transmitted light. Nevertheless, a sharp decrease in the recorded signal voltage resulted when the phase change occurred.

The cloud point curves for the three molecular weight systems are plotted in figure 5.3. The results are as expected. The cloud point curves of this system are a function of the molecular weight of PS. The upper critical solution temperatures increase as the polymer becomes heavier and they appear to be converging to a constant value as the molecular weight of PS becomes very large. This converged value of the UCST would correspond to the theta temperature, which has been reported in the literature as 356.15 K (Kotaka et al., 1970). The curves are very flat as has been observed many times in polymer solutions.
The phase behaviour of this system was compared to that of the PS/cyclohexane system shown in figure 2.4. The first difference observed was that the presence of the alcohol led to no LCST behaviour (at least in the temperature range measured) and secondly, the miscibility gap for the same PS molecular weight was smaller in cyclohexanol than when dissolved in cyclohexane. This was as expected. Using the solubility parameter criteria as expressed by equation (2.71), the closer the solubility parameters of the solvent and the polymer, the more miscible. The concept of solubility parameter was introduced as a measure of the interactions between molecules in a solution and it is defined as the square root of the cohesive energy per unit volume that keeps the fluid in the liquid state. The solubility parameter of PS is 18.1 MPa$^{1/2}$ and that for cyclohexane and cyclohexanol are 16.8 and 23.3 MPa$^{1/2}$ respectively. The difference between the parameters of PS and cyclohexanol is greater than that for PS and cyclohexane, hence it is to be expected that PS will be more miscible in cyclohexane than in the corresponding alcohol.

![Figure 5.3 — Cloud-point curves for monodisperse PS of molecular weights $M_w = 4,210$ g/mol; 78,800 g/mol and 849,000 g/mol in solution with cyclohexanol.](image-url)
<table>
<thead>
<tr>
<th>% PS by weight</th>
<th>( T_{CP} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.271</td>
<td>300.87</td>
</tr>
<tr>
<td>1.969</td>
<td>304.72</td>
</tr>
<tr>
<td>3.353</td>
<td>310.42</td>
</tr>
<tr>
<td>4.050</td>
<td>312.91</td>
</tr>
<tr>
<td>5.220</td>
<td>315.01</td>
</tr>
<tr>
<td>8.696</td>
<td>321.04</td>
</tr>
<tr>
<td>10.05</td>
<td>320.24</td>
</tr>
<tr>
<td>12.52</td>
<td>319.39</td>
</tr>
<tr>
<td>15.07</td>
<td>318.54</td>
</tr>
<tr>
<td>20.26</td>
<td>317.91</td>
</tr>
</tbody>
</table>

*Table 5.5 - Cloud-point temperatures for PS 4 (monodisperse, \( M_w = 4,215 \) g/mol) in cyclohexanol.*

<table>
<thead>
<tr>
<th>% PS by weight</th>
<th>( T_{CP} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.701</td>
<td>347.14</td>
</tr>
<tr>
<td>1.110</td>
<td>347.39</td>
</tr>
<tr>
<td>1.933</td>
<td>348.89</td>
</tr>
<tr>
<td>1.946</td>
<td>349.30</td>
</tr>
<tr>
<td>3.338</td>
<td>350.04</td>
</tr>
<tr>
<td>4.125</td>
<td>351.65</td>
</tr>
<tr>
<td>4.691</td>
<td>351.80</td>
</tr>
<tr>
<td>8.393</td>
<td>351.73</td>
</tr>
<tr>
<td>9.629</td>
<td>351.82</td>
</tr>
<tr>
<td>12.14</td>
<td>351.95</td>
</tr>
</tbody>
</table>

*Table 5.6 - Cloud-point temperatures for PS 79 (monodisperse, \( M_w = 78,800 \) g/mol) in cyclohexanol.*

<table>
<thead>
<tr>
<th>% PS by weight</th>
<th>( T_{CP} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.836</td>
<td>353.29</td>
</tr>
<tr>
<td>1.897</td>
<td>353.50</td>
</tr>
<tr>
<td>3.581</td>
<td>353.34</td>
</tr>
<tr>
<td>3.994</td>
<td>353.20</td>
</tr>
<tr>
<td>5.499</td>
<td>353.27</td>
</tr>
</tbody>
</table>

*Table 5.7 - Cloud-point temperatures for PS 850 (monodisperse, \( M_w = 849,000 \) g/mol) in cyclohexanol.*
5.2.4 — Poly(methyl methacrylate)/Cyclohexanol

Solutions of three different molecular weights were prepared and measured in a similar way to the PS/cyclohexanol samples. Samples PMMA 68, 280 and 992 correspond to $M_w = 6.8 \times 10^4$, $2.8 \times 10^5$ and $9.922 \times 10^5$ g/mol. The temperature of the solutions was raised and lowered between room temperature and 513 K and only one phase transition was observed, also upper critical solution behaviour. The measured cloud point temperatures are presented in tables 5.8 — 5.10 and the cloud point curves are shown in figure 5.4. Due to the "flaky" nature of the PMMA sample and volume restrictions, the maximum concentration achieved of polymer in solution was 17 % by weight. Repeatability of the CPT's at the same cooling rate varied between 0.1 and 0.6 K. These solutions of PMMA were less cloudy (less opaque) than the PS solutions, resulting in higher final transmitted light intensities (~75 mV). It should also be mentioned that the PMMA-rich phase had a tendency to stick to both the aluminium block and the seal, and so thorough cleaning was required before filling it with new samples. The cell block was soaked in ethanol for a few hours, all residue sample removed and finally placed in an oven to dry and remove any possible solvent.

![Figure 5.4 — Cloud-point curves for monodisperse PMMA of molecular weights $M_w = 68,000$ g/mol; 280,000 g/mol and 992,200 g/mol in solution with cyclohexanol.](image_url)
<table>
<thead>
<tr>
<th>% PMMA by weight</th>
<th>$T_{cp}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.140</td>
<td>344.48</td>
</tr>
<tr>
<td>0.448</td>
<td>344.89</td>
</tr>
<tr>
<td>0.734</td>
<td>345.39</td>
</tr>
<tr>
<td>1.057</td>
<td>344.02</td>
</tr>
<tr>
<td>1.702</td>
<td>345.12</td>
</tr>
<tr>
<td>2.105</td>
<td>345.20</td>
</tr>
<tr>
<td>5.105</td>
<td>346.15</td>
</tr>
<tr>
<td>9.823</td>
<td>346.69</td>
</tr>
<tr>
<td>12.98</td>
<td>346.30</td>
</tr>
<tr>
<td>13.29</td>
<td>346.59</td>
</tr>
</tbody>
</table>

Table 5.8 – Cloud-point temperatures for PMMA 68 in cyclohexanol.

<table>
<thead>
<tr>
<th>% PMMA by weight</th>
<th>$T_{cp}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.139</td>
<td>347.39</td>
</tr>
<tr>
<td>0.263</td>
<td>347.42</td>
</tr>
<tr>
<td>0.678</td>
<td>348.72</td>
</tr>
<tr>
<td>1.379</td>
<td>349.02</td>
</tr>
<tr>
<td>2.336</td>
<td>349.06</td>
</tr>
<tr>
<td>5.233</td>
<td>350.85</td>
</tr>
<tr>
<td>7.880</td>
<td>350.12</td>
</tr>
<tr>
<td>10.05</td>
<td>350.25</td>
</tr>
<tr>
<td>11.02</td>
<td>350.38</td>
</tr>
<tr>
<td>11.63</td>
<td>350.73</td>
</tr>
</tbody>
</table>

Table 5.9 – Cloud-point temperatures for PMMA 280 in cyclohexanol.

<table>
<thead>
<tr>
<th>% PMMA by weight</th>
<th>$T_{cp}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.147</td>
<td>348.36</td>
</tr>
<tr>
<td>0.439</td>
<td>350.05</td>
</tr>
<tr>
<td>1.004</td>
<td>349.38</td>
</tr>
<tr>
<td>1.029</td>
<td>350.58</td>
</tr>
<tr>
<td>1.901</td>
<td>350.40</td>
</tr>
<tr>
<td>4.749</td>
<td>350.51</td>
</tr>
<tr>
<td>8.599</td>
<td>349.42</td>
</tr>
<tr>
<td>9.677</td>
<td>350.24</td>
</tr>
<tr>
<td>14.75</td>
<td>350.18</td>
</tr>
<tr>
<td>16.90</td>
<td>349.49</td>
</tr>
</tbody>
</table>

Table 5.10 – Cloud-point temperatures for PMMA 992 in cyclohexanol.
The cloud point curves for this system appear to be very flat, and for the molecular weights measured the solvent rich phase is nearly pure cyclohexanol. In addition, the cloud point temperatures for all three molecular weights are very close to each other. The results compare well to the theta temperature of 351.95 K measured by Kotaka et al. (1970).

5.2.5 — Poly(styrene-b-methyl methacrylate)/Cyclohexanol

Only one molecular weight of the copolymer was measured, $M_w = 58,500$ g/mol. The theta temperature was found to be 353.95 K (Kotaka et al., 1970) and so the cloud-point temperatures were expected at temperatures not too far below this. Measured cloud point temperatures are presented in table 5.11 for solutions of ten different compositions, up to a copolymer weight fraction of 18.3 % by weight in solution. Repeatability of the readings at the same cooling rate varied from ± 0.1 to ± 0.6 K. The cloud point curves are shown in figure 5.5. Also shown in that figure are the curves for the PS 79 and the PMMA 68 samples. In the temperature range studied only UCST was detected for the copolymer in solution with cyclohexanol. The phase boundary is very flat, similar to those for the PMMA solutions. Unfortunately, the same molecular weights of the homopolymers and the copolymers were not available and so direct comparison is not possible. Even so, looking at the phase diagram it appears that if measurements had been taken for homopolymers with a molecular weight of 58,500 g/mol, the copolymer cloud point curve could lie between the two homopolymer curves. This is indeed the behaviour found from the theta temperatures.

5.3 — Inverse Gas Chromatography Data

In the previous chapter the method of inverse gas chromatography (IGC) was described in detail. The basis of this method as a means to obtain vapour-liquid equilibrium data on polymer/solvent systems was discussed and a full description was given of the apparatus and procedures used. The following section starts with an explanation of how to analyse the elution profiles obtained from an IGC
<table>
<thead>
<tr>
<th>% S(48.7 %)-b-MMA by weight</th>
<th>$T_{cr}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.148</td>
<td>340.74</td>
</tr>
<tr>
<td>0.619</td>
<td>346.65</td>
</tr>
<tr>
<td>1.039</td>
<td>347.14</td>
</tr>
<tr>
<td>4.167</td>
<td>345.68</td>
</tr>
<tr>
<td>6.022</td>
<td>345.41</td>
</tr>
<tr>
<td>9.413</td>
<td>345.61</td>
</tr>
<tr>
<td>11.79</td>
<td>345.45</td>
</tr>
<tr>
<td>15.89</td>
<td>345.73</td>
</tr>
<tr>
<td>16.39</td>
<td>344.80</td>
</tr>
<tr>
<td>18.30</td>
<td>345.15</td>
</tr>
</tbody>
</table>

*Table 5.11* — Cloud-point temperatures for S(48.7 %)-b-MMA (monodisperse, $M_w = 58,500$ g/mol) in cyclohexanol.

*Figure 5.5* — Cloud-point curves for monodisperse S(48.7 %)-b-MMA (monodisperse, $M_w = 58,500$ g/mol) in cyclohexanol.
run and translate these into thermodynamic data such as the activity of the solvent in the solution. The analysis is different for experiments at infinite dilution and those at finite concentrations and so these will be considered separately. Following this, the results obtained from the measurements taken are presented.

5.3.1 - Infinite Dilution

A typical elution peak from an infinite dilution experiment is shown in figure 5.6. The data is recorded as a concentration curve as a function of time. From this plot, retention volumes, activity coefficients, Flory-Huggins interaction parameters and even diffusion coefficients can be calculated.

For a binary solution, the following relationship applies:

\[ P_i = \gamma_i x_i P_i^\sigma \]  

(5.1)
where $P_1$ is the pressure of the solvent above the solution, $\gamma_1$ is the activity coefficient of the solvent, $x_1$ the mole fraction and $P_1^\sigma$ is the saturation vapour pressure. At infinite dilution, where there is negligible solvent in the polymer, the activity coefficient can be related to chromatographic data and the vapour pressure by:

$$\gamma_1^\infty = \frac{T_0 R}{V_0^\infty P_1^\sigma M_1} \quad (5.2)$$

where $T_0$ is 273.15 K, $M_1$ is the molecular weight of the solvent and $V_0^\infty$ is the specific retention volume per gram of solvent reduced to standard conditions (273.15 K and 0.1013 MPa) defined as:

$$V_0^\infty = \frac{T_0 V^R}{T m_2} = \frac{V^T}{T} m_2 = \frac{V_N}{m} = \frac{K T_0}{\rho_2 T} \quad (5.3)$$

where $V^R$ and $V^T$ are the retention volume and specific retention volume at temperature $T$ respectively, $m_2$ is the mass of polymer, $V_N$ is the net retention volume, $K$ is partition coefficient and $\rho_2$ is the polymer density. Including a correction for the non-ideality of the carrier gas, the following relationship for the weight fraction activity coefficient at infinite dilution as a function of the specific retention volume can be derived (the derivation is given in appendix C2):

$$\ln \gamma_1^\infty = \ln \frac{RT}{P_1^\sigma V_0^\infty M_1} - \frac{P_1^\sigma (B_{11} - V_1)}{RT} = \ln \left( \frac{a_1}{w_1} \right)^\infty \quad (5.4)$$

where $B_{11}$ is the second virial coefficient of the solvent, $V_1$ is molar volume of the liquid solvent at temperature $T$ and $a_1$ is the activity of the solvent vapour.

The development of this last equation enables the calculation of activities at infinite dilution, which can be easily related to the existing theories used to describe polymer solution thermodynamics. Going back to the Flory-Huggins theory, the activity coefficient according to model is given by:

$$\ln a_1 = \ln \phi_1 + \left( 1 - 1/r \right) \phi_2 + \chi_{12} \phi_2^2 \quad (5.5)$$
where $\chi_{12}$ is the Flory-Huggins interaction parameter and $\phi_1$ and $\phi_2$ are the volume fractions of the solvent and polymer respectively. The parameter $r$ is defined as,

$$r = \frac{M_2 \rho_1}{M_1 \rho_2}$$

(5.6)

where $M_1$ and $M_2$ are the molecular weights of solvent and polymer respectively and $\rho_1$ and $\rho_2$ are the liquid densities at temperature $T$. At infinite dilution the $\chi_{12}$ parameter can be calculated from the following expression:

$$\chi_{12} = \ln \Omega^0 - \left(1 - \frac{1}{r}\right) + \ln \left(\frac{\rho_1}{\rho_2}\right)$$

(5.7)

5.3.2 - Capillary Column IGC Model (CCIGC)

Macris (1979) first introduced the CCIGC technique to measure polymer-solvent interactions at infinite dilution. He derived a relationship between the diffusivity of the solvent in the stationary phase and the width of the Gaussian elution curve, as expressed by its variance. Pawlisch (1985) then extended the model to account for the possible non-uniformity of the polymer coating on the column. However, he found that the diffusion coefficient did not show a strong dependence on the uniformity of the coating. Later on, Surana (1997), Tihminlioglu et al. (1997) and Tihminlioglu (1998) used Conder and Young's (1979) theoretical development to show that this model developed by Macris could be extended to analyse further results obtained in the finite concentration regime.

Figure 5.7 is a schematic which shows the progression of the solvent profile through the chromatographic process. The injection is made as an input pulse which travels through the capillary column, finally becoming an elution peak. In Macris' formulation, the capillary column is modelled as a straight cylindrical tube that contains an annular film of polymer deposited on its walls. As the solvent, carried by the carrier gas, travels through the column it encounters mass transfer resistances which causes a delay in the solvent peak and causes it to broaden as shown in the sketch.
For the model, a series of initial assumptions for the model are established:

(i) the system is isothermal
(ii) the carrier fluid is assumed to be an incompressible fluid
(iii) the carrier gas flow is steady laminar flow with a parabolic velocity profile
(iv) the polymer coating is uniform and homogeneous
(v) the polymer film thickness is much less than the radius of the column
(vi) the carrier gas is insoluble in the polymer
(vii) axial diffusion in the stationary phase is negligible
(viii) no chemical reactions occur between the carrier gas, the polymer or the solvent
(ix) no surface adsorption occurs at the polymer-gas interface or the polymer-column interface
(x) diffusion coefficients are concentration independent
(xi) the injected sample enters the column as a narrow pulse so that the inlet concentration profile can be modelled as an impulse function
(xii) the absorption isotherm is linear.

The continuity equation for the solvent in the gas phase is:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} + c \frac{\partial u}{\partial z} = D_g \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^2} \right]$$  \hspace{1cm} (5.8)

and for the solvent in the polymer phase:
\[
\frac{\partial c'}{\partial t} = D_p \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c'}{\partial r} \right) \right]
\]  \hspace{1cm} (5.9)

where \( c \) and \( c' \) are the concentration of solvent in the gas and polymer phases respectively, \( D_g \) and \( D_p \) are the diffusion coefficients of the solvent in the gas and polymer phases respectively, \( z \) and \( r \) are the axial and radial co-ordinates respectively and \( u \) is the mean velocity of the carrier gas. The term \( \epsilon \partial u/\partial z \) was introduced by Surana (1997) and Tihminlioglu (1998) to account for the sorption effect at higher concentrations. The initial and boundary conditions are the following:

\[
c(r, z, t) = c'(r, z, t) = 0 \quad \text{at } t = 0, \ z > 0 \hspace{1cm} (5.10)
\]
\[
c(r, z, t) = \delta(t)c_0 \quad \text{at } z = 0 \hspace{1cm} (5.11)
\]
\[
c(r, z, t) = \frac{c'(r, z, t)}{K} \quad \text{at } r = R \hspace{1cm} (5.12)
\]
\[
\frac{D_e}{r} \frac{\partial c}{\partial r} = \frac{D_p}{r} \frac{\partial c'}{\partial r} \quad \text{at } r = R \hspace{1cm} (5.13)
\]
\[
\frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \hspace{1cm} (5.14)
\]
\[
\frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \hspace{1cm} (5.15)
\]
\[
\frac{\partial c'}{\partial r} = 0 \quad \text{at } r = R + \tau \hspace{1cm} (5.16)
\]

where \( c_0 \) is the strength of the injected solvent pulse, \( K \) is the equilibrium partition coefficient, \( R \) is the radius of the gas-polymer interface (internal radius of the capillary column), \( \delta(t) \) is the Dirac function and \( \tau \) is the thickness of the polymer film (assumed constant). From these equations Pawlisch et al. (1987) developed an expression for the concentration profile at the outlet of the column in the Laplace domain,

\[
Z(s) = \frac{cL}{c_0 u} = \exp \left( \frac{1}{2\Gamma} \right) \exp \left[ - \left( \frac{1}{4\Gamma^2} + \frac{s}{\Gamma} + \frac{2\sqrt{s}}{\alpha\beta} \tanh(\beta\sqrt{s}) \right)^{1/2} \right] \hspace{1cm} (5.17)
\]

where \( \alpha, \beta \) and \( \Gamma \) are dimensionless quantities defined as:
\[ \alpha = \frac{R}{K\tau} \quad ; \quad \beta^2 = \frac{\tau^2}{D_p t_c} \quad ; \quad \Gamma = \frac{D_g}{uL} \] (5.18)

where \( L \) is the length of the capillary column, \( s \) is the Laplace operator and \( t_c \) is the residence time of the carrier gas. Thus, the elution profile is a function of three dimensionless quantities: \( \alpha \), a thermodynamic parameter, and \( \beta \) and \( \Gamma \) contain information on the polymer and gas phase transport properties respectively. Arnould (1989) and HadjRomdhane (1994) studied the effects of the solubility and diffusion coefficient parameters, i.e. \( \alpha \) and \( \beta \) respectively, on the shape of the retention peak. As the solubility increases, \( \alpha \) decreases giving a symmetric and broad peak. Similarly shaped peaks are obtained if \( \beta \) is small, i.e. if diffusion coefficients are high. On the other hand, as the mass transfer resistances increase and \( \beta \) increases, the retention peaks will become very asymmetric and will show tailing at the end.

A solution to equation (5.17) is found by using the moment generating property of Laplace transforms. The generalised expression for the \( k^{th} \) moment of the elution curve results (Macris, 1979):

\[ \mu_k = (t_c)^k (-1)^k \lim_{s \to \infty} \frac{d^k Z(t)}{ds^k} = \lim_{s \to \infty} \frac{\int_0^\infty t_c \epsilon(t) \, dt}{\int_0^\infty \epsilon(t) \, dt} \] (5.19)

where \( t_c \) is the residence time of the carrier gas. Therefore, the resulting pair of equations from the transform function for \( \mu_1 \), the first temporal moment or mean residence time and \( \mu_2 \), the second central moment or variance of the elution profile, are given by:

\[ \mu_1 = t_c \left( 1 + \frac{2\tau K}{R} \right) \] (5.20)

\[ \mu_2 = t_c^2 \left[ \frac{4\tau^3 K}{3t_c D_p R} + \frac{2D_g t_c}{L^2} \left( 1 + \frac{2\tau K}{R} \right)^2 \right] \] (5.21)
As can be seen from these two expressions, the first moment is only dependant on the thermodynamic properties of the polymer-solvent system, while the second moment is dependant on both the thermodynamic and transport properties. In actual fact, the equation for the second moment is composed of two contributions. The first term is the contribution to the peak dispersion of the slow diffusion in the stationary phase and the second term is the contribution due to axial molecular diffusion in the gas phase. This is such that the higher the solubility and also the lower the diffusion coefficient of the solvent in the polymer, the greater the peak spreading. By integrating the experimental elution curve, these moments can be calculated and hence $K$ and $D_r$ can be obtained. The correctness of using the first moment of the peak and not the peak maximum as the measure of retention for the calculation of polymer/solvent partition coefficients and thermodynamic interactions has been questioned and examined by several authors [Pawlisch et al. (1988); Arnould (1989); Wang and Charlet (1989). Romdhane et al. (1995) measured specific retention volumes, infinite dilution weight fraction activity coefficients and $X_{12}$ parameters for the PS/toluene system using both the first moment and the peak maximum retention times. They found that there was a difference in the trends. Whilst using the first moment yields a linear dependence of these three quantities with respect to temperature, using the peak maximum gives a z-shaped dependence with breaks above and below the glass transition temperature of PS. This difference was originally attributed to a physical change in the retention mechanism as the polymer undergoes a physical change at the glass transition temperature, but was later considered as a mere artefact of the inappropriate use of the retention parameter. At temperatures in the vicinity of the glass transition temperature, diffusion of the solvent into the polymer becomes much smaller causing a skewness of the peak. Thus, a shift in the time at which the elution peak maximum occurs with respect to the change in curvature of the first moment causes a difference in the temperature dependency of thermodynamic data using the two different approaches for calculation. This is also confirmed by the fact that at temperatures well above the glass transition temperature, the temperature dependence of the aforementioned quantities becomes linear using both approaches.

The calculation of these moments needs the elution curve to be symmetrical and as Pawlisch reported in 1988, results from asymmetric peaks could be inaccurate. To ensure a good fit even with these asymmetric and highly tailing peaks, the model
needs to be evaluated using a time-domain fitting procedure as described by Romdhane (1994). Using the initial \( K \) and \( D_p \) values obtained from the moment analysis as estimates, the equation for the response peak \( Z(t) \) is inverted numerically using a Fast Fourier Transform (FFT). The resulting theoretical response in the time domain is compared against the experimental elution profile and regressed using a non-linear least squares minimisation of the following objective function:

\[
I = \sum_{n=1}^{N} \left( f_{\text{theoretical}}(t) - f_{\text{experimental}}(t) \right)^2
\]

(5.22)

where \( N \) is the number of data points and \( f_{\text{theoretical}} \) and \( f_{\text{experimental}} \) are the elution profiles in the time domain respectively (subroutine LMDIF1 from the MINPAC-1 software product of the Applied Mathematical Division of the Argonne National Laboratory, Argonne, Illinois). The code uses a Levenberg-Marquadt algorithm and the regression results are optimum values of \( K \) and \( D_p \).

5.3.3 – Physical Properties for the CCIGC Model

In using the equations given in the previous two sections the values of several properties were necessary. Starting with equation (5.4), values for the second virial coefficient \( B_{11} \), the saturation pressure \( P_1^{sw} \) and the liquid density \( \rho_1 \) of cyclohexanol, as functions of temperature were required. The values used in this work were obtained from the AIChE DIPPR data compilation (DCAPPII) and the values are given in table 5.12. The equations and parameters used for these three properties are given in tables 5.13 (a), (b) and (c) respectively. Only the values of the vapour pressures used affect the calculation of the weight fraction of the cyclohexanol. The resulting percentage error is almost exactly the same as the percentage uncertainty in \( P_1^{sw} \), i.e. a 10% change in \( P_1^{sw} \) will lead to a 10% change in \( \Omega_t \). On the other hand the liquid density and the second virial coefficient have very little effect on the calculated \( \Omega_t \) (for the temperature range and systems studied, a maximum error of 0.2% and 1% in \( \rho_1, B_{11} \) respectively, for a 10% uncertainty in the input parameters).
For the calculation of Flory's interaction parameter, values of the polymer liquid densities were also required. The values used were those calculated from the Tait equation (most commonly used correlation for polymer PVT data). The form of the equation is given below and the parameters for each polymer and the range of validity are given in table 5.13 (d). They were obtained from Rodgers (1993). In all cases where liquid densities were necessary at temperatures outside the range of applicability of the parameters, the data were extrapolated. Finally, the diffusion coefficients of cyclohexanol in helium (the carrier gas) were necessary for the calculation of parameter $\Gamma$ in equation (5.18). Values of these as a function of temperature were obtained from the AIChE DIPPR data prediction manual and are presented in the table 5.12.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P_i^a$ (bar)</th>
<th>$\rho_i$ (gmol/cm³)</th>
<th>$B_\Pi$ (cm³/gmol)</th>
<th>$D_k$ (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>343.15</td>
<td>2.195 × 10²</td>
<td>9.062 × 10⁻³</td>
<td>-2.870 × 10³</td>
<td>0.33804</td>
</tr>
<tr>
<td>353.15</td>
<td>3.859 × 10²</td>
<td>8.971 × 10⁻³</td>
<td>-2.568 × 10³</td>
<td>0.35546</td>
</tr>
<tr>
<td>363.15</td>
<td>6.495 × 10²</td>
<td>8.879 × 10⁻³</td>
<td>-2.316 × 10³</td>
<td>0.37326</td>
</tr>
<tr>
<td>373.15</td>
<td>1.051 × 10³</td>
<td>8.786 × 10⁻³</td>
<td>-2.102 × 10³</td>
<td>0.39144</td>
</tr>
<tr>
<td>383.15</td>
<td>1.640 × 10³</td>
<td>8.691 × 10⁻³</td>
<td>-1.919 × 10³</td>
<td>0.40998</td>
</tr>
<tr>
<td>393.15</td>
<td>2.479 × 10³</td>
<td>8.595 × 10⁻³</td>
<td>-1.762 × 10³</td>
<td>0.42889</td>
</tr>
<tr>
<td>403.15</td>
<td>3.638 × 10³</td>
<td>8.497 × 10⁻³</td>
<td>-1.625 × 10³</td>
<td>0.44816</td>
</tr>
<tr>
<td>413.15</td>
<td>5.198 × 10³</td>
<td>8.398 × 10⁻³</td>
<td>-1.505 × 10³</td>
<td>0.46779</td>
</tr>
<tr>
<td>423.15</td>
<td>7.247 × 10³</td>
<td>8.296 × 10⁻³</td>
<td>-1.399 × 10³</td>
<td>0.48779</td>
</tr>
<tr>
<td>433.15</td>
<td>9.882 × 10³</td>
<td>8.193 × 10⁻³</td>
<td>-1.305 × 10³</td>
<td>0.50814</td>
</tr>
<tr>
<td>443.15</td>
<td>1.321</td>
<td>8.087 × 10⁻³</td>
<td>-1.221 × 10³</td>
<td>0.52885</td>
</tr>
<tr>
<td>453.15</td>
<td>1.732</td>
<td>7.980 × 10⁻³</td>
<td>-1.145 × 10³</td>
<td>0.54990</td>
</tr>
<tr>
<td>463.15</td>
<td>2.234</td>
<td>7.869 × 10⁻³</td>
<td>-1.1077 × 10³</td>
<td>0.57130</td>
</tr>
<tr>
<td>473.15</td>
<td>2.837</td>
<td>7.756 × 10⁻³</td>
<td>-1.015 × 10³</td>
<td>0.59310</td>
</tr>
<tr>
<td>483.15</td>
<td>3.552</td>
<td>7.641 × 10⁻³</td>
<td>-9.587 × 10²</td>
<td>0.61519</td>
</tr>
<tr>
<td>493.15</td>
<td>4.391</td>
<td>7.521 × 10⁻³</td>
<td>-9.071 × 10²</td>
<td>0.63765</td>
</tr>
</tbody>
</table>

Table 5.12 – Physical properties of cyclohexanol as a function of temperature.

169
Saturated vapour pressure of cyclohexanol

\[ P^*_{v} \text{bar} = \exp(a + bT^{-1} + c \ln T + dT^{-2}) \]

\begin{tabular}{|c|c|c|c|c|}
\hline
\(a\) & \(b\) & \(c\) & \(d\) & \(e\) \\
\hline
1.891 \times 10^{-2} & -1.4337 \times 10^{4} & -24.148 & 1.074 \times 10^{-5} & 2.0 \\
\hline
\end{tabular}

Valid for range 296.60K to 650.10K (extrapolated).

Equation fitted to data from Timmermans (1965) and Ambrose and Gilissen (1987)

Table 5.13 (a) – Calculation method of the DIPPR for \(P_{v}^*\) of cyclohexanol.

Liquid density of cyclohexanol

\[ \rho / \text{kmol.m}^{-3} = a b^{[\exp(-\rho^{-1})]} \]

\begin{tabular}{|c|c|c|c|}
\hline
\(a\) & \(b\) & \(c\) & \(d\) \\
\hline
8.243 \times 10^{-1} & 2.6545 \times 10^{-1} & -6.501 \times 10^{2} & 2.8495 \times 10^{-2} \\
\hline
\end{tabular}

Valid for range 296.60K to 650.10K (extrapolated).

Equation fitted to data from Friend and Hargreaves (1944) and Kuss (1955)

Table 5.13 (b) – Calculation method of the DIPPR for \(\rho\) of cyclohexanol.

Second virial coefficient of cyclohexanol

\[ B_{11} / \text{m}^{-3}.\text{kmol} = a + bT^{-1} + cT^{-3} + dT^{-8} + eT^{-9} \]

\begin{tabular}{|c|c|c|c|c|}
\hline
\(a\) & \(b\) & \(c\) & \(d\) & \(e\) \\
\hline
2.1683 \times 10^{-1} & -2.8146 \times 10^{2} & -6.1366 \times 10^{7} & -1.4803 \times 10^{20} & 1.4602 \times 10^{21} \\
\hline
\end{tabular}

Valid for range 325.05K to 1300K (extrapolated).

Equation fitted to data from Tsonopoulos (1978)

Table 5.13 (c) – Calculation method of the DIPPR for \(B_{11}\) of cyclohexanol.
Polymer liquid density (Tait equation)

\[ V(P, T) = V(0, T) \left[ 1 - c_1 \ln \left( 1 + \frac{P}{b(T)} \right) \right] \]

\[ V(0, T) = a_0 + a_1 T + a_2 T^2 \text{ or } V(0, T) = a_0 \exp(a_1 T) \]

\[ b(T) = b_0 \exp(b_1 T) \]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(a_0)</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(b_0) (bar)</th>
<th>(b_1) ((1/°C))</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA(1)</td>
<td>0.8254</td>
<td>0.00028383</td>
<td>7.792 \times 10^{-3}</td>
<td>2875</td>
<td>-0.004146</td>
<td>0.0894</td>
</tr>
<tr>
<td>PS(2)</td>
<td>0.9287</td>
<td>0.0005131</td>
<td>-</td>
<td>2169</td>
<td>-0.003319</td>
<td>0.0894</td>
</tr>
<tr>
<td>PS(40%)-co-PMMA(3)</td>
<td>0.8610</td>
<td>0.0003350</td>
<td>6.980 \times 10^{-3}</td>
<td>2610</td>
<td>-0.004611</td>
<td>0.0894</td>
</tr>
</tbody>
</table>

\((1)\) Valid for range 387.15K to 432.15K and 0bar to 2000bar

\((2)\) Valid for range 388.15K to 469.15K and 0bar to 2000bar

\((3)\) Valid for range 383.15K to 543.15K and 0bar to 2000bar

Table 5.13 (d) – Tait equation and its parameters for polymers used in this work.

5.3.4 - Sensitivity Analysis of the CCIGC Model

The CCIGC model works well in describing the elution peaks, although like most things it has its limitations. Arnould (1989) reported that certain values of \(a\) and \(\beta\) yield unreliable results for \(K\) and \(D_p\). Surana et al. (1997) carried out some simulations and found that \(\beta\) should lie between 0.03 and 50 in order to obtain reliable results with the model. They showed that below and above these limits respectively, simulated elution profiles (at constant values of \(a\) and \(\Gamma\)) gave the same curves, showing that the sensitivity to the value of \(\beta\) is lost. It was also pointed out that this range of \(\beta\) may vary to some extent from system to system. This limitation can be explained mathematically by examining the mass transfer equation. If the value of \(\beta\) is very small, i.e. at high diffusion coefficients \(\tanh(\beta \sqrt{s})\) reduces to \(\beta \sqrt{s}\). This cancels out the \(\beta\) term and the \(\Gamma\) parameter becomes dominant implying that diffusion in the gas phase, represented by \(D_p\), is the controlling process. In the other extreme, if \(\beta\) is very high and diffusion coefficients are low, then
\( \tanh(\beta \sqrt{s}) \) tends to 1. The model, in this case, cannot differentiate between the contributions of the two variables.

In the case of the sensitivity of the \( \alpha \) parameter, at high solubilities (i.e. high values of \( K \) and low values of \( \alpha \)), long elution times and a very large number of data points will result. This can be overcome by shortening the column length or increasing the gas flowrate, but these two variables also have their own limitations and might lead to other unwanted consequences. If, on the other hand, the \( \alpha \) parameter is high, i.e. at too low solubilities, adsorption on the capillary column might begin playing a significant role in the mass transfer process and distinguishing between the retention times of polymer and solvent becomes a problem. As a rule of thumb, \( K \) should be greater than 10.

5.3.5 - Experiments at Finite Concentrations

In the case of the analysis of the data obtained from the experiments at finite concentrations of solvent, the CCIGC model can also be used however it has to be modified to account for the ground concentration plateau that is built-up in the technique of elution on a plateau (Tihminlioglu et al., 1997). The final non-dimensional expression for the outlet concentration in the Laplace domain is:

\[
Z(s) = \left( \frac{c - c_{\text{plateau}}}{c_0 u} \right) \frac{L}{(c - c_{\text{plateau}})} = \exp \left( \frac{1}{2 \Gamma} \right) \exp \left[ - \left( \frac{1}{4 \Gamma^2} + \frac{s}{\Gamma} + \frac{2 \sqrt{s}}{\alpha \beta \Gamma} \tanh(\beta \sqrt{s}) \right) \right]^{1/2} (5.23)
\]

This expression is very similar to equation (5.17) used for the infinitely dilute region, and is regressed in the same way to obtain the diffusion coefficient \( D_p \) and a value of \( K \). It is important to note that following the development of equation (5.23), \( K \) is not defined as the partition coefficient. In this modified model it is equal to \( \frac{dc}{dc} \) (where \( c \) is the concentration of solvent in the polymer phase and \( c \) the concentration of solvent in the gas phase) and only equals \( \frac{c'}{c} \), the partition coefficient, at the infinite dilution limit.
Although the modified CCIGC model can be used effectively to calculate diffusion coefficients, this is not the one of the objectives of this work and a more rigorous method of analysis is necessary to determine the thermodynamic data. Theoretical relationships that were developed by Conder and Young (1979) and Price and Guillet (1986) can be used to calculate the retention volumes and sorption isotherms. The retention volume \( V_N \), is given by the expression

\[
V_N = V_s (1 - y_{true}) \frac{dc}{dt}
\]  

(5.24)

where \( V_s \) is the volume of stationary phase and \( y_{true} \) is the true mole fraction of solvent on the gas phase, which is corrected for gas non-ideality. By introducing the mass of polymer used \( W_2 \) and integrating the equation, the concentration of solvent in the polymer phase \( c' \) can be calculated,

\[
c' = \frac{j}{W_2} \int_0^1 \frac{V_N}{(1 - y_{true})} dc
\]  

(5.25)

where \( j \) is a correction factor for the compressibility effects due to a possible pressure gradient in the column. This correction factor can be calculated from

\[
j = J_3 \left[ 1 + \frac{y_0^2 P_0 B_{11} (1 - J_2 y_0)}{RT} \right]
\]  

(5.26)

where \( y_0 \) is the mole fraction of solvent in the carrier gas calculated from the saturated vapour pressure at the temperature of the saturator and the total pressure in the saturator:

\[
y_0 = \frac{P_1^*(T_{saturator})}{P^s_{saturator}}
\]  

(5.27)

Also in equation (5.26) \( B_{11} \) is the second virial coefficient of the solvent vapour at the column temperature and \( J_2' \) is given by:

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\[ J^n = \frac{n}{m} \left( \frac{P_i}{P_A} \right)^n - 1 \]  
\[ \left( \frac{P_i}{P_A} \right)^n - 1 \]  
(5.28)

where \( P_i \) is the pressure at the column inlet and \( P_A \) is atmospheric pressure. Also, a compressibility correction and a correction factor for the non-ideality of the gas (in experiments using capillary columns they are generally very small) are used to calculate the true mole fraction \( y_{true} \) as shown:

\[ y_{true} = a y_0 \]  
(5.29)

where

\[ a = \left[ \frac{1 + \frac{1}{2} a (1 - j_2 y_0)}{1 + \frac{1}{2} a (1 - j_2 y_0)} - 1 \right] \left[ \frac{2 y_0 B_1 P_0^0 (1 - y_0)}{RT} \right] \]  
(5.30)

and

\[ k = \frac{t_r - t_M}{t_M} \]  
(5.31)

where \( t_r \) and \( t_M \) are the retention times of the solvent and the marker gas respectively. Therefore in order to evaluate the isotherm, the integral in equation (5.25) is evaluated by measuring retention volumes at different solvent concentrations in the carrier gas, fitting a polynomial to the isotherm and integrating the polynomial at the appropriate concentration. The weight fraction of solvent in the polymer solution can be calculated from,

\[ \omega_1 = \frac{\varepsilon M_1}{1 + \varepsilon M_1} \]  
(5.32)

and finally the weight fraction activity coefficient can be calculated using the following expression:
\[
\Omega_1 = \frac{a_{11}}{u_1} = \frac{P_1(T_{saturator})}{P_1(T_{column})u_1}
\] (5.33)

Where \( P_1(T_{saturator}) \) and \( P_1(T_{column}) \) are the vapour pressures of the solvent at the saturator and column temperatures respectively.

In these finite concentration experiments, the solvent concentration in the polymer phase is a key parameter in the measurements. As already mentioned, it is calculated by integrating the sorption isotherms over a range of concentrations. Values of \( V_N/(1 - y_{true}) \) as a function of solvent concentration in the gas phase \( c \), are fitted to a second or third order polynomial and integrated. Following this methodology, in the case of the infinite dilution, the retention volume is equal to the product of the volume of stationary phase and the partition coefficient \( (V_N = V_s K) \), where the partition coefficient is the ratio of solvent concentration in the polymer phase to that in the gas phase \( (K = c'/c) \). As pointed out earlier, the retention volume at a given concentration is expressed not in terms of \( c' \) but of the derivative of \( c' \) with respect to \( c \) which is directly related to the slope of the tangent to the absorption isotherm [see equation (5.25)]. At very low concentrations, approaching infinite dilution, the tangent and the absorption isotherm overlap, giving rise to a simple linear relationship between the solvent concentrations in the polymer and gas phases. At higher concentrations however, the absorption isotherm is no longer linear and the slope to the tangent may vary depending on the temperature and concentration. A number of measurements in small steps of concentration of the solvent in the gas phase are necessary in order to define accurately the integral and, consequently the concentration of the solvent in the polymer.

5.3.6 — Results at Infinite Dilution

As already mentioned in section 4.3.5, it is advisable that before carrying out experiments, the effect of the size of injected solvent volume on the thermodynamic results is tested. The solution of low molecular weight poly(methyl methacrylate) with cyclohexanol was used as the test system. Results from this are presented first. After this, each of the three polymer solutions is considered in turn. At infinite
dilution, measurements were carried out at several column temperatures in order to study the dependency of the thermodynamic data on temperature. The results presented are partition coefficients, weight fraction activity coefficients and the Flory-Huggins interaction parameter.

5.3.6.1 — Low molecular weight PMMA/cyclohexanol

The choice of solvent sample size was tested using the PMMA (low molecular weight)/cyclohexanol system. A series of experimental runs was carried out using different injection volumes of cyclohexanol at temperatures of 423.15 K and 413.15 K. The resulting elution profiles are shown in figures 5.8 and 5.9 respectively. At 423.15 K chromatographic data were obtained for samples of 0.01 µl, 0.05 µl and 0.1 µl and as can be seen there is rather a lot of scatter in the profiles obtained with the two smallest sample sizes, the injected volumes being insufficient for the measurements. An injection of 0.1 µl gave a much more satisfactory curve. A similar comparison was done at 413.15 K where 0.01 µl, 0.10 µl and 0.20 µl were used.

The same severe scatter is seen with the smallest injection but for the other two, the curves are almost identical in both shape and size, indicating that at injection volumes higher than a certain value there is no significant difference in peak profile. The injected volume should however be kept as small as possible as the experiments are carried out at infinite dilution. From these results a value of 0.1 µl was chosen as the volume of cyclohexanol injected. Furthermore at both temperatures, the retention times of cyclohexanol were found to be independent of sample size. This agreed with previous results from Romdhane et al. (1995) and those of Romdhane and Danner (1991), who also showed no dependence of retention time on sample size for their systems.

Infinite dilution measurements were made for this system at temperatures ranging from 353.15 to 493.15 K in steps of either 10 K or 20 K. At temperatures of 353.15, 373.15 and 393.15 K, i.e. near the glass transition temperature of the PMMA sample, the peaks are very sharp. This can be seen in figure 5.10. The figure shows both the experimental points and the curve fitting using the CCIGC
Figure 5.8 – Effect of sample size on the peak shape for 1-PMMA /cyclohexanol at 423.15 K.

Figure 5.9 – Effect of sample size on the peak shape for 1-PMMA /cyclohexanol at 413.15 K.
model. The model shows unstable behaviour at these three temperatures. A possible reason for this is the lack of enough data points even at the highest data rate permitted experimentally. The model does not have enough points to yield a good fit for the $\beta$ parameter, generating values outside the $0.03 \leq \beta \leq 5.0$ range. Consequently values of $K$ are obtained which are not reproducible. For the three curves shown, the values of $\beta$ are $43.0 \pm 0.3$, $45.9 \pm 0.2$ and $56.8 \pm 0.3$. In contrast, also shown in this figure is the elution curve at 413.15 K for which the CCIGC model is well behaved. At this temperature $\beta$ is within the applicable range and for the case shown has a value of $2.3 \pm 0.1$. Surana et al. (1995) suggested that for temperatures in the vicinity of the glass transition temperature, the $K$ values should therefore be obtained by a different method. They used the method of Vrentas et al. (1993) involving extrapolation from the higher temperature results as in fact $\ln K$ is a linear function of $1/T$.

![Figure 5.10 - Elution profiles for l-PMMA/cyclohexanol at 353.15, 373.15, 393.15 and 413.15K. The points are experimental data and the line is that calculated with the CCIGC model.](image-url)
At temperatures of 413.15 K and above, the CCIGC model parameters were within the applicability range and the model performed well describing the elution profiles obtained experimentally, as is presented next. Figure 5.11 shows elution profiles for temperatures from 423.15 K to 493.15 K ascending in steps of 10K. Table 5.5 gives the values of the partition coefficients and the weight fraction activity coefficients at infinite dilution (calculated using equation 5.4) at these different temperatures. All the given values are the average of either three or four measurements (the complete set of experimental data can be found in appendix D1). The uncertainty in the values of $K$ from fitting the model, ranging from ± 0.03% to ± 0.5%, was very small compared with the irreproducibility of the experiment. In all cases repeatability ranged from ± 0.3% to ± 4.9%. Figure 5.12 shows that $K$ is strongly dependent on temperature and the dependence is linear for $\ln K$ as a function of $1/T$, behaviour that has been observed already in other polymer-solvent systems. The partition coefficient, the ratio of solvent in the polymer phase to that in the gas phase, increases as temperature decreases. Thus, the solubility of cyclohexanol in this PMMA sample is inversely related to the temperature of the system. The temperature dependence of the weight fraction activity coefficients at infinite dilution is shown in figure 5.13 and indicates that values decrease with temperature quite significantly. Finally, figure 5.14 shows the temperature dependence of the Flory-Huggins interaction parameter calculated using equation (5.5). Inspection of these values shows that at most of the measured temperatures, cyclohexanol is a good solvent for PMMA although following the Flory-Huggins approximation that at values of the chi parameter higher than 0.5, a liquid-liquid miscibility gap is to be expected at temperatures lower than around 433.15 K (see section 2.4.3).

5.3.6.2 — High molecular weight PMMA/cyclohexanol

Similar results are presented for a solution of higher molecular weight (996,000g/mol) PMMA, with a measured $T_g$ of 393.45 K, purchased from Aldrich co., UK. The column dimensions are given in table 4.2. For these experiments the same injection volume of 0.1 µl was used. Following the findings at temperatures near or below the glass transition temperature of the polymer using the CCIGC
Figure 5.11 - Elution profiles for l-PMMA/cyclohexanol for temperatures 423.15 - 493.15 K. The points are experimental data and the line is that calculated with the CCIGC model.
<table>
<thead>
<tr>
<th>$T$(K)</th>
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<th>$\chi_{12}^*$</th>
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<td>413.15</td>
<td>96.00</td>
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<td>0.7865</td>
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<td>423.15</td>
<td>75.33</td>
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<td>433.15</td>
<td>68.25</td>
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<td>493.15</td>
<td>22.27</td>
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<td>0.2646</td>
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*Table 5.14* – IGC results at infinite dilution for 1-PMMA/cyclohexanol at different temperatures.

*Figure 5.12* – Temperature dependence of $K$ at infinite dilution for 1-PMMA/cyclohexanol.
Figure 5.13 — Temperature dependence of $\Omega_1^\kappa$ for l-PMMA/cyclohexanol.

Figure 5.14 — Temperature dependence of $\chi_{12}^\kappa$ for l-PMMA/cyclohexanol.
model for the low molecular weight PMMA solution, experiments for this heavier polymer were carried out starting at a temperature above the glass transition: \( T = 423.15 \) K. Experiments were carried out again in steps of 10 K up to and including 493.15 K. Figure 5.15 shows that 423.15 K is still too low a temperature, resulting in a highly skewed peak. A complete set of the experimental data can be found in appendix D1. At this temperature the values of \( \beta \) obtained are 28, 31, 45 and 7.4 which are outside the applicability of the model and the resulting calculated partition coefficient values using the model are 174.4, 175.0, 216.9 and 83.9. The poor performance of the model is also reflected in the regression uncertainty for \( K \), which in these cases lies between \( \pm 30-35\% \) and as can be seen from the discrepancy between values. The last value is the only one that could be assumed to be correct as the value of \( \beta \) is just outside the limits of applicability of the model. The regression yields a \( K \) value \( \pm 2\% \). Furthermore, it is not until temperatures above 443.15 K that the elution curve starts showing less tailing. Also, the reduction of this tailing occurs at a higher temperature for this polymer than for the lower molecular weight polymer because of its higher glass transition temperature. Even so at all temperatures above 433.15 K the model parameters are within the validity. Table 5.15 gives the resulting values for \( K \), \( \Omega_{i}^{\infty} \) and \( \chi_{i}^{\infty} \). By inspection it can be seen that in fact the results at 150°C and 160°C do not follow the trend and due to the strong tailing of the peaks the results will be regarded as unreliable.

Shown in figure 5.16 is a plot of \( K \) as a function of the reciprocal of the temperature and as with the low molecular weight PMMA solution, the solubility of cyclohexanol decreases with increasing temperature. The regression gives uncertainties for \( K \) ranging between \( \pm 0.025\% \) and \( \pm 0.77\% \) and reproducibility of results varies between approximately \( \pm 0.25\% \) and \( \pm 2.25\% \).

Figure 5.17 shows that the weight fraction activity coefficient at infinite dilution for this heavier PMMA also decreases with increasing temperature. The activity coefficient is shown for both PMMA solutions are plotted and as can be seen there is a significant quantitative difference between the two curves. The average uncertainty in \( \Omega_{i}^{\infty} \) is around \( \pm 5\% \) and therefore the differences are beyond this experimental error. Similarly, there is a significant difference in the values of Flory-Huggins interaction parameters for both PMMA solutions as a function of temperature, as shown in figure 5.18. Unlike in liquid-liquid equilibrium experiments
Figure 5.15 - Elution profiles for h-PMMA/cyclohexanol for temperatures 423.15 - 493.15 K. The points are experimental data and the solid line is that calculated with the CCIGC model.
<table>
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<th>$T$ (K)</th>
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<th>$X_{12}^c$</th>
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<td>30.28</td>
<td>6.75</td>
<td>0.5621</td>
</tr>
<tr>
<td>473.15</td>
<td>25.70</td>
<td>6.43</td>
<td>0.5049</td>
</tr>
<tr>
<td>483.15</td>
<td>21.54</td>
<td>6.29</td>
<td>0.4741</td>
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<tr>
<td>493.15</td>
<td>18.31</td>
<td>6.15</td>
<td>0.4418</td>
</tr>
</tbody>
</table>

*Table 5.15 – IGC results at infinite dilution for h-PMMA/cyclohexanol at different temperatures.*

*Figure 5.16 – Temperature dependence of $K$ at infinite dilution for h-PMMA/cyclohexanol.*
Figure 5.17 — Temperature dependence of \( \Omega_1^{\infty} \) for both high and low \( M_w \) PMMA/cyclohexanol.

Figure 5.18 — Temperature dependence of \( \chi_{12}^{\infty} \) for both low and high \( M_w \) PMMA/cyclohexanol.
experiments, polymer molecular weight is believed to have a rather insignificant this
effect on the solubility and on the weight fraction activity coefficients. Interestingly,
is not the case here. From these results, it appears that indeed there is some
dependence with molecular weight, although to make any valid conclusions, a more
thorough investigation is required. Recently, Petri and co-workers (1995) used
several techniques to measure Flory's interaction parameters for the systems
poly(vinyl methyl ether)/cyclohexane and poly(dimethyl siloxane)/toluene and
showed that at regions of high polymer concentration there is actually a dependence
on polymer chain-length which goes beyond experimental error. For the effect at
infinite dilution they report the following: "Whether the curves at constant
temperature for different molecular weights meet at \( \varphi_2 \to 1 \) ... is uncertain owing to
the lack of data for \( \chi_{12} \equiv (M_c) \)... Tentatively, the influences of molecular weight on
\( \chi \) in the concentrated regime are attributed to changes in the dimensions of polymer
coils with composition – which according to experimental evidence and theoretical
considerations – should not be restricted to the dilute regime but should persist up to
large \( \varphi_2 \) values.” Furthermore, their results showed that the effects increase as the
temperature increase.

Finally, the dependence of the solubility on polymer molecular weight and
temperature is shown in figure 5.19. As might be expected the partition coefficient
of the solvent is smaller for the higher molecular weight polymer than for the
polymer of smaller chain lengths as the solvent is less soluble in the heavier polymer.
This is supported by the values of the diffusion coefficients at those temperatures for
the two molecular weight PMMA solutions. From the CCIGC model values for the
solvent diffusion coefficient \( D_p \) have been calculated and are plotted in figure 5.20.
The graph shows that as the polymer chain length increases, it becomes more
difficult for the solvent molecules to penetrate, leading to smaller diffusion
coefficients.

5.3.6.3 – Shape of the Elution Profile

As already shown, results from IGC are less reliable at temperatures in the
vicinity of the \( T_g \) and below. Not only is there a physical effect from measuring in
polymer solutions at these temperatures, but also the shape of the elution curve is
Figure 5.19 — Temperature dependence of $K$ at infinite dilution for both low and high $M_w$ PMMA/cyclohexanol.

Figure 5.20 — Temperature dependence of $D_0$ at infinite dilution for both low and high $M_w$ PMMA/cyclohexanol.
affected by these lower temperatures. It becomes less and less symmetric with decreasing temperature thus influencing the $K$ values calculated using the CCIGC model. As explained by Pawlisch et al. (1987) who obtained the same dependency of peak shape with temperature, in the case of asymmetric peaks, the unreliability of the data for these elution profiles can be associated with an incorrect application of the baseline correction. This can change the magnitude and extent of the tails, thus shifting the calculated mean residence time (first moment) and therefore also the partition coefficient. The baseline correction, which is required in order to calculate the true moments, is based on the measured detector signals at the beginning and at the end of the experimental run. The elution curve is integrated with respect to a hypothetical zero concentration baseline which is superimposed on the experimental elution curve. Due to random signal noise and possible baseline shifts, the baseline correction may be in error thereby giving rise to incorrect calculated values of the first moment. In a symmetric profile, any integration error arising from factors such as baseline drifts will tend to be cancelled out. This is because an error will result in the tail at the beginning of the peak but will be counteracted by an equal error in the tail at the end of the peak. In asymmetric peaks this cancellation does not take place.

5.3.6.4 — Polystyrene/Cyclohexanol

Examples of elution curves obtained for this system are shown in figure 5.21. Measurements at infinite dilution were taken for temperatures ranging from 403.15 K and 493.15 K in increasing steps of 10 K. Results are presented in table 5.16 (the raw data can be found in appendix D1). Like for the PMMA solutions, at temperatures close to the glass transition temperature (which is 375.55 K for this particular PS sample), the profiles are rather asymmetric with a sharp front and a tailing peak, but at temperatures well-above $T_g$ this asymmetry is removed. For this system, the model performs very well in fitting the elution curves. Partition coefficient values are regressed with an uncertainty not worse than about ± 0.2 % and reproducibility is much better than for the PMMA solutions, lying between ± 0.02 % and ± 1.2 %. Figures 5.22, 5.23 and 5.24 show the temperature dependence of $K$, $\Omega_1^\infty$ and $\chi_{12}^\infty$ respectively. For this system ln $K$ is also linearly dependent on
Figure 5.21 – Elution profiles for polystyrene/cyclohexanol for temperatures 403.15 – 493.15 K. The points are experimental data and the solid line is that calculated with the CCIGC model.
Table 5.16 – IGC results at infinite dilution for polystyrene/cyclohexanol at different temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K$</th>
<th>$\Omega^\circ$</th>
<th>$\chi_{12}^\circ$</th>
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<td>0.9237</td>
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<td>0.4327</td>
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Figure 5.22 – Temperature dependence of $K$ at infinite dilution for polystyrene/cyclohexanol.
Figure 5.23 — Temperature dependence of $\Omega_1$ at infinite dilution for polystyrene/cyclohexanol.

Figure 5.24 — Temperature dependence of $\chi_{12}$ at infinite dilution for polystyrene/cyclohexanol.
1/T, meaning that the solubility of cyclohexanol in PS decreases with temperature. In addition, both the weight fraction activity coefficient and the chi parameter are strongly dependent on temperature also. From the values of the chi parameter, liquid-liquid phase separation should take place at temperatures below around 473.15 K according to the Flory-Huggins theory. This suggests that cyclohexanol is only a good solvent for PS at very high temperatures.

5.3.6.5 — Poly(styrene-\omega-methyl methacrylate)/Cyclohexanol

Experiments using the copolymer were run at temperatures from 403.15 K to 493.15 K in steps of 10 K. Initially some runs were carried out at 383.15 K but the IGC model oscillated and gave values of $\beta$ that were too high, from which we could deduce that the calculated values of $K$ would be incorrect. Again this was associated with being at temperatures too close to the $T_g$ which is 378.15 K. Four experimental runs were carried out at this temperature and the resulting values of $K$ were 304.7, 218.5, 307.0 and 212.4. The average uncertainty from the regression was ± 27 % and repeatability is ± 20 %. Nevertheless, as can be seen from the plot of $K$ as a function of temperature, the average value of 260.6 for the partition coefficient at 383.15 K fits in very well with the trend. The same is observed in the other two plots. Figure 5.25 shows examples of the elution curves at each temperature measured and the values of $K$, $\Omega_1^\infty$ and $\chi_1^\infty$ are presented in table 5.17 (the raw data can be found in appendix D1). The temperature dependency of these three variables is plotted in figures 5.26, 5.27 and 5.28.

As with the two homopolymers, $\ln K$ is a linear function of 1/T at temperatures above the glass transition temperature. The model yields values of $K$ with an uncertainty between ± 0.09 % and ± 0.12 %, and the repeatability of the measurements lies between ± 0.15 % and ± 3.5 %. These uncertainties exclude the measurements at 383.15 K, which have already been discussed. Both the weight fraction activity coefficient of cyclohexanol in the copolymer and the chi parameter decrease with increasing temperature. According to the condition set by the Flory-Huggins theory, liquid-liquid immiscibility should occur for this copolymer solution at temperatures below approximately 433.15 K.
Figure 5.25 - Elution profiles for PS (40%)-α-MMA /cyclohexanol for temperatures 383.15 – 493.15K. The points are experimental data and the solid line is that calculated with the CCIGC model.
Figure 5.26 – Temperature dependence of $K$ at infinite dilution for PS (40%)-$\alpha$-MMA/cyclohexanol.

Table 5.17 – IGC results at infinite dilution for PS (40%)-$\alpha$-MMA/cyclohexanol at different temperatures.

<table>
<thead>
<tr>
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Figure 5.27 - Temperature dependence of $\Omega_0^*$ at infinite dilution for PS (40%)-co-MMA/cyclohexanol.

Figure 5.28 - Temperature dependence of $\chi_1^*$ at infinite dilution for PS (40%)-co-MMA/cyclohexanol.
5.3.6.6 – Homopolymer vs. Copolymer Solutions

Figures 5.29, 5.30 and 5.31 show the partition coefficients, cyclohexanol WFACs and Flory’s interaction parameters as a function of temperature for the two homopolymers and the copolymer. One would expect that the behaviour of the copolymer would be somewhere in between that of the two homopolymers. The results show that this is not the case. To be absolutely correct in making a comparison, if PS of $M_w = 200 \times 10^3$ g/mol and PMMA of $M_w = 15 \times 10^3$ g/mol are used, then the resulting copolymer with 40% styrene should have a $M_w$ of $89 \times 10^3$ g/mol. Unfortunately, this was not available and so a copolymer of $M_w$ of 100-150 $\times 10^3$ g/mol was used. The results show that at the temperatures measured at infinite dilution, cyclohexanol is more soluble the PS-PMMA copolymer than in the two separate homopolymers. Moreover, it is more soluble in PMMA than it is in PS. As the temperature is raised solubility decreases in all three polymers and it appears that at high enough temperature, the solubility tends towards a constant and common value for all three polymers. In addition, the weight fraction coefficient at infinite dilution was found to be lower for the copolymer than for the two homopolymers, confirming that the cyclohexanol solubility is higher for the copolymer. Again they appear to be tending towards a constant value as the temperature is increased far enough. Although it seems reasonable to think that for the copolymer solution, thermodynamic property values should lie somewhere in between those for the two constituent homopolymers, according to their composition, this is not always the case, as is observed here. Only one group has published similar behaviour in polymer/solvent systems: Gupta and Prausnitz (1995, 1996). They used a gravimetric sorption technique to measure VLE data for polymer-solvent binaries and copolymer-solvent binaries and found that although some copolymers, like the poly(ethylene-co-vinyl acetate) in cyclohexane and poly(styrene-co-butyl methacrylate) in chloroform have thermodynamic values lying in between those of the homopolymer solutions, there were other similar solutions of hydrocarbons with poly(butadiene-co-acrylonitrile) where this was not the case. Here, the effect from the acrylonitrile is much stronger than that from the copolymer composition leading to higher solubilities of the solvent in the copolymer than in the homopolymers.
Figure 5.29 — Temperature dependence of $K$ at infinite dilution for solutions of PS, PMMA and PS (40%)-α-MMA in cyclohexanol.

Figure 5.30 — Temperature dependence of $\Omega_1^*$ for solutions of PS, PMMA and PS (40%)-α-MMA in cyclohexanol.
To explain this effect, interactions between segments in the components have to be considered. In the systems measured here, the solubility of cyclohexanol in the P(S-co-MMA) copolymer is greater than that in PS or in PMMA. Figure 5.32 shows schematically the molecular structure of the components. Cyclohexanol is made up of two groups, a non-polar group aliphatic ring and a polar —OH group. In solution with polystyrene, the non-polar aromatic ring of styrene will “dislike” the polar group and similarly, in solution with PMMA, the ester groups in the polymer repeat unit will dislike the non-polar rings of the cyclohexanol. On the other hand in the poly(S-co-MMA) copolymer, both polar and non-polar groups are available for cyclohexanol hence making it more soluble in it. Moreover, due to the presence of —OH groups in cyclohexanol and there are available oxygen sites on the methyl methacrylate units, hydrogen bonding is possible making the attractive interactions very strong. If this reasoning is correct then results at finite concentrations should indicate that at the same value of the activity, the solvent absorption in the copolymer should be higher than that in its constituents.

Finally, from these VLE experiments using IGC, values for the diffusion coefficients of cyclohexanol in these polymers were calculated. Although this is not the focus of this work, the results are presented. Diffusion coefficients as a function of temperature are plotted in figure 5.33. It is not surprising to observe that the

Figure 5.31 – Temperature dependence of $\chi_{12}^*$ for solutions of PS, PMMA and PS (40%)-co-MMA in cyclohexanol.
Figure 5.32 — Schematic showing the molecular structure of (a) polystyrene, (b) poly(methyl methacrylate), (c) cyclohexanol and (d) copolymer P(S-co-MMA).
the diffusion coefficients of cyclohexanol in the copolymer lie in between those for
the two constituent homopolymers. This is expected as the glass transition
temperature of the copolymer lies in between the glass transition temperature of the
homopolymers. For a molecule to diffuse (or move) three main conditions need to
be fulfilled (Tihminlioglu et al., 1997):

(i) a large enough hole opens up for the molecule to move into
resulting from a local density fluctuation,
(ii) the molecule has enough energy to break from its neighbours and
move
(iii) another molecule jumps into the hole left by the moving molecule
before this one returns to its original position.

\[ 10^3/T (\text{K}^1) \]

\[ D_p (\text{cm}^2/\text{s}) \]

\[ 1.00E-05 \]
\[ 1.00E-06 \]
\[ 1.00E-07 \]
\[ 1.00E-08 \]
\[ 1.00E-09 \]
\[ 1.00E-10 \]

\[ \times \text{PS} \]
\[ \triangle \text{PS (40\%-co-MMA)} \]
\[ \circ \text{PMMA low Mw} \]
\[ \diamond \text{PMMA high Mw} \]

Figure 5.33 — Temperature dependence of \( D_p \) for cyclohexanol through the polymers PS, PMMA and
PS (40\%-co-MMA). Lines are only for visual purposes.

So, for solvent diffusion in a polymer, the key factor is that there is free volume
around the polymer that can be occupied by the solvent molecules, and the amount
of free volume is reflected by the glass transition temperature. This temperature is a
good indicator of how much and how quickly molecules can move or migrate. At
temperatures above the glass transition temperature, polymer chains can move around easily but as the temperature is lowered, this mobility is inhibited until the chains cannot move any longer and become stagnant in the glassy-polymer state. Since the $T_g$ of the P(S-co-MMA) falls in between that of the to parent polymers, it is expected that diffusion coefficients of the solvent in the copolymer lie in between those in the homopolymers.

5.3.7 – Results at Finite Concentrations

Experiments at finite concentrations have been carried out using the elution on a plateau technique and the data analysed as described in section 5.3.5. In the following section, retention volumes, absorption isotherms, weigh fraction activity coefficients and activities of the solvents are presented not only as a function of concentration of solvent in the solution, but also as a function of temperature.

Three systems have been investigated, the high molecular weight of PMMA, the PS and the random copolymer. For each polymer solution, measurements at two temperatures were carried out (i) PMMA/cyclohexanol at 453.15 K and 473.15 K, (ii) PS/cyclohexanol at 433.15 K and 453.15 K and (iii) PS-co-MMA/cyclohexanol at 433.15 K and 493.15 K. All the temperatures were chosen to be well above the glass transition temperatures of all the polymers to avoid asymmetric peaks and the possibility of obtaining values of $\beta$ outside the range of applicability of the CCIGC model. The capillary columns were the same as the ones used for the experiments at infinite dilution although the length of the columns was reduced as a result of fitting them into the chromatograph. The dimensions are given in table 4.2. The raw data for all of these experiments is given in appendix D2.

5.3.7.1 – High Molecular Weight PMMA/Cyclohexanol

Figure 5.34 shows examples of elution curves obtained at different saturator temperatures, i.e. at different concentrations of solvent in the system at a column temperature of 453.15 K. In all of the elution profiles, the solid line represents the fit from the CCIGC model and the points represent the experimental measurements.
Figure 5.34 – Finite concentration elution profiles for the h-PMMA/cyclohexanol system at 453.15 K. Given are the temperature of the saturator and the weight fraction of solvent.
Also given on these plots are the temperature of the saturator for that particular experiment and the weight fraction of solvent. Given the chosen temperature, the elution profiles are symmetric and the predictions of the model fit the peaks well. Good agreement between the model and the experimental data is observed for measurements at 473.15 K as shown in figure 5.35.

Solvent concentrations in the polymer achieved with this method are limited by the saturator temperature, which always needs to be lower than the column temperature. In addition, the column temperature is limited by the glass transition temperature of the polymer. For these reasons, the entire solvent concentration range cannot normally be measured. It was observed that, as the saturator temperature approached the boiling temperature not only did the system equilibration times increase to several hours but also the saturator temperature stability fell (fluctuations increased to up to ± 0.4 K at high temperatures compared to ± 0 - 0.1 K variations temperatures below the boiling point of cyclohexanol). At 453.15 K, a maximum cyclohexanol concentration of only 9.2 % was achieved and as expected, at the higher temperature of 473.15 K, higher concentrations, up to 28.8 % solvent, were measured.

Presented first of all in figure 5.36 is the functionality of the retention volume, expressed as $V_s/(1-\psi)$, with solvent concentration in the gas phase at the two specified temperatures. As the concentration of solvent in the gas phase increases, the curve becomes increasingly steep. The curves are fitted to a polynomial that is then integrated to yield the area under the curve, as given by equation (5.25). This is then used to calculate the concentration of solvent in the polymer phase, $\psi'$. To obtain a good integral it was necessary to measure enough points at the high cyclohexanol end of the composition range, i.e. at the higher saturator temperatures, not too far from the boiling temperature of cyclohexanol. The only problem with this method of analysis is that, due to the sharp increase in slope of the curves at the higher concentrations, very small variations in the concentration can cause increased errors in the values of $\psi'$ and other derived values. For the infinite dilution case, the retention volume is equal to the product of the volume of the stationary phase and the partition coefficient. The latter is defined as the ratio of solvent concentration in the polymer phase to that in the gas phase and not as the derivative of this, which is the case in finite concentration analysis [given in equation (5.22)]. In actual fact, at low enough concentrations of solvent in the
Figure 5.35 - Finite concentration elution profiles for the h-PMMA/cyclohexanol system at 473.15 K. Given are the temperature of the saturator and the weight fraction of solvent.
polymer phase and as we approach the infinite dilution case, the absorption isotherm becomes linear and overlaps its tangent, which leads to the linear relationship $K = c'/c$. At the higher concentrations and as can be seen from figure 5.37, the absorption isotherm is no longer linear and so the slope is a function of concentration and temperature. The change in the partition coefficient is higher at lower temperatures and higher concentrations.

The values of $\Omega_i$ are given in tables 5.18 and 5.19 together with the temperature in the saturator and the corresponding cyclohexanol vapour pressure, the weight fraction of solvent, the concentrations of solvent in the polymer phase and gas phase, the net retention volume and the activity of the solvent. What can be seen is that $\Omega_i$ is not a strong function of solvent concentration at low concentrations, but decreases sharply at somewhat higher concentrations. The first rows of data in both tables are the results obtained from the independent infinite dilution measurements. We can see that for the measurements at 453.15 K the infinite dilution WFAC is lower that what the finite concentration measurements would give if extrapolated to zero solvent concentration. For the result at 473.15 K it is within experimental error. The experimental run at infinite dilution was repeated after some time at this temperature and a value of $\Omega_i$ was obtained at 7.88 ± 2.2% which would fit with the finite concentration data within the experimental error. A possible explanation for this observation is the effect of temperature of the ordering/disordering of the polymer chains. In taking measurements at infinite dilution, the temperature was raised gradually and the system was left to equilibrate at each of the step-temperature. In the case of the finite experiments, the temperature of the column was set directly to 453.15 K in one-step. This might have had some effect on the polymer chains and their movement. Whilst the experiment was run at this column temperature and at a series of saturator temperatures, the polymer chains had enough time to attain their equilibrium state. This is why the discrepancy is not observed at the next measured column temperature of 473.15 K. Consequently, this could imply that all measurements at the finite concentrations are higher than they

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4 Measurement carried out by H. Betz using the same column and apparatus at The Pennsylvania State University, USA (October 2001).
Figure 5.36 — Retention volume as a function of solvent concentration in the gas phase for the h-PMMA/cyclohexanol system (•) 453.15 K and (▲) 473.15 K.

Figure 5.37 — Absorption isotherms for the h-PMMA/cyclohexanol system (•) 453.15 K and (▲) 473.15 K.
Table 5.18 – Experimental results from IGC at finite concentrations of cyclohexanol in high molecular weight PMMA at 453.15 K.

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<tr>
<th>(w_i)</th>
<th>(T_{\text{sat}}) (K)</th>
<th>(P) (MPa)</th>
<th>(c' \times 10^4) (mol/g polymer)</th>
<th>(c \times 10^5) (mol/cm(^3))</th>
<th>(v) (cm(^3))</th>
<th>(\Omega)</th>
<th>(a_i)</th>
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Table 5.19 – Experimental results from IGC at finite concentrations of cyclohexanol in high molecular weight PMMA at 473.15 K.

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<th>(T_{\text{sat}}) (K)</th>
<th>(P) (MPa)</th>
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<th>(c \times 10^5) (mol/cm(^3))</th>
<th>(v) (cm(^3))</th>
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Figure 5.38 – Weight fraction activity coefficients for the h-PMMA/cyclohexanol system (●) 453.15 K and (▲) 473.15 K.

Figure 5.39 – VLE for the h-PMMA/cyclohexanol system (●) 180°C and (▲) 200°C.
should really be, but unfortunately it was not possible to repeat the experiments and it should be done in the future. In actual fact, similar discrepancies between values at infinite dilution and finite concentrations have been previously observed not only in systems measured using the IGC technique such as PS/toluene at 413.15 and 433.15 K (Tihminlioglu et al., 1997) and poly(vinyl acetate)/2-ethyl hexyl acetate at 333.15 K (Tihminlioglu et al., 1999), but also in the poly(styrene-co-butadiene)/cyclohexane system at 333.15 K studied using gravimetric sorption (Gupta and Prausnitz, 1995).

Plotted in figure 5.38 are the activity coefficients of the solvent as a function of solvent concentration and temperature, and shown in figure 5.39 are the corresponding activities. As is expected the activity coefficients tend to a value of 1 as the weight fraction increases and so does the activity. In terms of temperature dependence, the higher the temperature the lower the activity of the solvent in the polymer and also the activity coefficient. It should be mentioned that the observed downturn in values of the WFAC at low cyclohexanol concentrations, have no significant meaning since they lie within experimental error.

5.3.7.2 — Polystyrene/Cyclohexanol

Measurements for the PS solution were carried out at temperatures of 453.15 K and 493.15 K. Sample elution curves are shown in figures 5.40 and 5.41 respectively. The solid line represents the result from the CCIGC model and the points are the experimental measurements. Figures 5.42 and 5.43 show the dependence of the retention volumes and the absorption isotherms at the two different temperatures on solvent concentration. Similar behaviour to that of the PMMA/cyclohexanol system is observed. The retention volume increases with concentration of solvent in the gas phase and therefore so does the solvent concentration in the polymers phase. Also the slope of the absorption isotherms becomes greater at higher concentrations and at lower temperatures.

For this system, the maximum weight fractions achieved were 13.0 % for the measurements at 180°C and 4.7 % solvent for a column temperature of 493.15 K. The reason for the very small range of solvent at this high temperature is that temperature control became very difficult. Equilibration of the temperature in the
Figure 5.40 - Finite concentration elution profiles for the PS/cyclohexanol system at 453.15 K. Given are the temperature of the saturator and the weight fraction of solvent.
Figure 5.41 – Finite concentration elution profiles for the PS/cyclohexanol system at 493.15 K. Given are the temperature of the saturator and the weight fraction of solvent.
Figure 5.42 — Retention volume as a function of solvent concentration in the gas phase for the polystyrene/cyclohexanol system (•) 453.15 K and (▲) 493.15 K.

Figure 5.43 — Absorption isotherms for the polystyrene/cyclohexanol system (•) 453.15 K and (▲) 493.15 K.
apparatus took an extremely long time and the fluctuations in the temperature readings were up to ± 0.3 K. At these conditions, results were regarded as unreliable. The weight fraction activity coefficients and the activities of the solvents are shown in figures 5.44 and 5.45. Again similar to the PMMA system, there is a decrease in values with temperature and with solvent concentration. Numerical results from the experiments are given in tables 5.20 and 5.21 for temperatures of 453.15 K and 493.15 K respectively. As we can see from the numbers, the infinite dilution measurements at the specified temperatures agree well with the results from the finite concentration experiments. In actual fact two extra measurements were made on this column at infinite dilution before the finite concentrations measurements were started. The $\Omega^*$ values obtained were 5.33 and 5.34. Comparing these values with those obtained from the infinite dilution measurements, $5.35 \pm 0.09$ (reproducibility), the new values are within the experimental error.

5.3.7.3 – Poly(styrene-\(\omega\)-methyl methacrylate)/Cyclohexanol

Lastly, VLE measurements at finite concentrations of cyclohexanol in the PS(40\%)-\(\omega\)-PMMA random copolymer were carried out. Column temperatures were 433.15 K and 453.15 K and sample elution curves are shown in figures 5.46 and 5.47 respectively. The peaks are less symmetric than in the other two systems studied, especially for the measurements at 433.15 K and this is due to the lower temperature. Still, the fit from the CCIGC model is very good and the results of the VLE parameters follow the correct trends and fall within the experimental errors. With the copolymer systems, the maximum solvent concentrations achieved were 24.8 % and 18.7 % for the lower and higher temperatures respectively as given in tables 5.22 and 5.23.
Figure 5.45 - VLE for the polystyrene/cyclohexanol system (○) 453.15 K and (▲) 493.15 K.

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Table 5.20 - Experimental results from IGC at finite concentrations of cyclohexanol in polystyrene at 453.15 K.
Figure 5.46 – Finite concentration elution profiles for the PS (40%)-co-PMMA/cyclohexanol system at 433.15 K. Given are the temperature of the saturator and the weight fraction of solvent.
Figure 5.47 – Finite concentration elution profiles for the PS-co-PMMA/cyclohexanol system at 453.15 K. Given are the temperature of the saturator and the weight fraction of solvent.
### Column temperature, \( T_{\text{column}} = 493.15 \) K

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<th>( V_N ) (cm³)</th>
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<td>5.799x10^4</td>
<td>0.2680</td>
<td>0.0140</td>
<td>2.1115</td>
<td>4.75</td>
<td>0.0013</td>
</tr>
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<td>0.018</td>
<td>79.70</td>
<td>3.797x10^3</td>
<td>1.7782</td>
<td>0.0920</td>
<td>2.1858</td>
<td>4.69</td>
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</tr>
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<td>0.01036</td>
<td>5.0107</td>
<td>0.2510</td>
<td>2.3335</td>
<td>4.56</td>
<td>0.0236</td>
</tr>
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<td>123.00</td>
<td>0.02790</td>
<td>14.8860</td>
<td>0.6768</td>
<td>2.8341</td>
<td>4.18</td>
<td>0.0635</td>
</tr>
<tr>
<td>0.0450</td>
<td>148.60</td>
<td>0.06927</td>
<td>46.6110</td>
<td>1.6065</td>
<td>5.2854</td>
<td>3.51</td>
<td>0.1578</td>
</tr>
<tr>
<td>0.0465</td>
<td>149.50</td>
<td>0.07132</td>
<td>48.43</td>
<td>1.6441</td>
<td>5.4713</td>
<td>3.49</td>
<td>0.1624</td>
</tr>
</tbody>
</table>

**Table 5.21** - Experimental results from IGC at finite concentrations of cyclohexanol in polystyrene at 493.15 K.

### Column temperature, \( T_{\text{column}} = 433.15 \) K

<table>
<thead>
<tr>
<th>( w_i )</th>
<th>( T_{\text{sat}} ) (K)</th>
<th>( P ) (MPa)</th>
<th>( c' \times 10^5 ) (mol/g polymer)</th>
<th>( c \times 10^5 ) (mol/cm³)</th>
<th>( V_N ) (cm³)</th>
<th>( \Omega )</th>
<th>( a_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.4080</td>
<td>5.94</td>
<td>0.0000</td>
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<tr>
<td>0.0246</td>
<td>105.6</td>
<td>0.01354</td>
<td>2.7076</td>
<td>0.0374</td>
<td>4.2670</td>
<td>5.57</td>
<td>0.1370</td>
</tr>
<tr>
<td>0.0426</td>
<td>118.6</td>
<td>0.02344</td>
<td>4.7833</td>
<td>0.0648</td>
<td>4.7867</td>
<td>5.56</td>
<td>0.2372</td>
</tr>
<tr>
<td>0.0602</td>
<td>126.8</td>
<td>0.03228</td>
<td>6.8777</td>
<td>0.0893</td>
<td>5.3376</td>
<td>5.43</td>
<td>0.3266</td>
</tr>
<tr>
<td>0.1083</td>
<td>140.4</td>
<td>0.05270</td>
<td>13.042</td>
<td>0.1467</td>
<td>7.4357</td>
<td>4.93</td>
<td>0.5332</td>
</tr>
<tr>
<td>0.1724</td>
<td>150.3</td>
<td>0.07317</td>
<td>22.386</td>
<td>0.2056</td>
<td>12.414</td>
<td>4.29</td>
<td>0.7404</td>
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<tr>
<td>0.2484</td>
<td>156.2</td>
<td>0.08806</td>
<td>35.502</td>
<td>0.2496</td>
<td>24.990</td>
<td>3.59</td>
<td>0.8910</td>
</tr>
</tbody>
</table>

**Table 5.22** - Experimental results from IGC at finite concentrations of cyclohexanol in random PS(40%)-co-MMA at 433.15 K.
Table 5.23 - Experimental results from IGC at finite concentrations of cyclohexanol in random PS(40%)-α-MMA at 453.15 K.

<table>
<thead>
<tr>
<th>( w_i )</th>
<th>( T_{\text{sat}} ) (K)</th>
<th>( P ) (MPa)</th>
<th>( c \times 10^4 ) (mol/g_{polymer})</th>
<th>( c \times 10^4 ) (mol/cm^3)</th>
<th>( V_i ) (cm^3)</th>
<th>( O_i )</th>
<th>( a_i )</th>
</tr>
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<tr>
<td>0.0000</td>
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<td>-</td>
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<td>-</td>
<td>2.8516</td>
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<td>0.0043</td>
<td>79.0</td>
<td>3.654x10^3</td>
<td>0.4558</td>
<td>0.0096</td>
<td>2.7294</td>
<td>4.93</td>
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</tr>
<tr>
<td>0.0129</td>
<td>101.1</td>
<td>0.01055</td>
<td>1.3871</td>
<td>0.0291</td>
<td>2.9209</td>
<td>4.95</td>
<td>0.0638</td>
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<tr>
<td>0.0477</td>
<td>130.3</td>
<td>0.03679</td>
<td>5.3179</td>
<td>0.0973</td>
<td>4.0136</td>
<td>4.45</td>
<td>0.2124</td>
</tr>
<tr>
<td>0.0844</td>
<td>142.9</td>
<td>0.05738</td>
<td>9.7847</td>
<td>0.1527</td>
<td>5.8064</td>
<td>3.92</td>
<td>0.3312</td>
</tr>
<tr>
<td>0.2484</td>
<td>156.2</td>
<td>0.08806</td>
<td>24.4527</td>
<td>0.2375</td>
<td>17.772</td>
<td>2.71</td>
<td>0.5084</td>
</tr>
</tbody>
</table>

Figure 5.48 - Retention volume as a function of solvent concentration in the gas phase for the PS(40%)-α-MMA/cyclohexanol system (♀) 433.15 K and (▲) 453.15 K.
Figure 5.49—Absorption isotherms for the random PS(40%)–α-MMA/cyclohexanol system (⋆) 433.15 K and (▲) 453.15 K.

Figure 5.50—Weight fraction activity coefficients for the random PS(40%)–α-MMA/cyclohexanol system (⋆) 433.15 K and (▲) 453.15 K.
Figures 5.48-5.51 show the retention volumes, the absorption isotherms, the activity coefficients and the activities of cyclohexanol in the copolymer respectively, as a function of both temperature and cyclohexanol concentration. The same behaviour as in the other two systems is observed. Retention volumes increase with solvent concentration in the polymer and this increase is sharper as the solvent concentration increases, but decreases with temperature. The same is observed with the absorption isotherms. In terms of weight fraction activity coefficients, the values decrease with both increasing temperature and increasing solvent concentration. Also, the temperature dependence does not appear to be very strong and this also holds for the solvent activity. Finally, the infinite dilution weight fraction activity coefficients agree well with the finite concentration data.

5.3.7.4 – Homopolymer vs. Copolymer Solutions

Figures 5.52 and 5.53 show the activity coefficients and activities of cyclohexanol in the three polymers. The comparison has been made using the
Figure 5.52 — Weight fraction activity coefficients of cyclohexanol with PS, PMMA and random PS (40%)-co-MMA at 453.15 K as a function of the solvent concentration.

Figure 5.53 — Activity of cyclohexanol with PS, PMMA and random PS (40%)-co-MMA at 453.15 K as a function of the solvent concentration.
The numerical values are given in table 5.24. The first thing to notice is that the values for the three variables for the copolymer/solvent system do not lie in between those for the two homopolymer/solvent systems. As was discussed before, for this PS-co-PMMA system, intramolecular forces between the molecules play an important role and are probably responsible for the observed behaviour. At the same activity, i.e. at the same pressure, the weight fraction of cyclohexanol in the polymer is greater than in the homopolymers because of the availability of both polar and non-polar sites for the cyclohexanol molecules, in the copolymer. There is a stronger liking between solvent molecules and copolymer molecules.

Finally figure 5.54 shows the effect of increasing the solvent concentration in the polymer on the diffusion coefficients. Due to the glass transition temperature being the most important factor in diffusion of a solvent in a polymer, and as was explained in section 5.3.6.6., cyclohexanol will show diffusion coefficients lying in between those in PS and PMMA, in the random PS-PMMA copolymer, as it has a
Table 5.24 - Experimental results from IGC at finite concentrations of cyclohexanol in PS, PMMA and PS (40%)-co-MMA at 453.15 K.

**PMMA (\(M_w = 996,000\) g/mol) with cyclohexanol**

<table>
<thead>
<tr>
<th>(w_1)</th>
<th>WFAC, (\Omega_t)</th>
<th>(a_t)</th>
<th>(D_p) (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>7.205</td>
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<td>(5.53 \times 10^{-9})</td>
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<tr>
<td>0.0004</td>
<td>8.012</td>
<td>0.0028</td>
<td>(5.84 \times 10^{-9})</td>
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<tr>
<td>0.0007</td>
<td>8.019</td>
<td>0.0052</td>
<td>(5.96 \times 10^{-9})</td>
</tr>
<tr>
<td>0.0015</td>
<td>8.044</td>
<td>0.0124</td>
<td>(5.95 \times 10^{-9})</td>
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<tr>
<td>0.0036</td>
<td>8.108</td>
<td>0.0291</td>
<td>(5.92 \times 10^{-9})</td>
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<td>0.0063</td>
<td>8.184</td>
<td>0.0517</td>
<td>(5.74 \times 10^{-9})</td>
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<td>0.0112</td>
<td>8.189</td>
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<td>0.0368</td>
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<td>(5.99 \times 10^{-9})</td>
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<tr>
<td>0.0682</td>
<td>5.892</td>
<td>0.4019</td>
<td>(6.03 \times 10^{-9})</td>
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<tr>
<td>0.2880</td>
<td>2.005</td>
<td>0.5774</td>
<td>(6.04 \times 10^{-9})</td>
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</table>

**PS (\(M_w = 200,000\) g/mol) with cyclohexanol**

<table>
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<th>(a_t)</th>
<th>(D_p) (cm(^2)/s)</th>
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<td>0.0006</td>
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<td>0.0033</td>
<td>(9.22 \times 10^{-8})</td>
</tr>
<tr>
<td>0.0037</td>
<td>5.803</td>
<td>0.0215</td>
<td>(9.16 \times 10^{-8})</td>
</tr>
<tr>
<td>0.0119</td>
<td>5.647</td>
<td>0.0671</td>
<td>(7.64 \times 10^{-8})</td>
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<td>0.0265</td>
<td>5.360</td>
<td>0.1420</td>
<td>(7.59 \times 10^{-8})</td>
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<tr>
<td>0.0883</td>
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<tr>
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<td>(7.32 \times 10^{-8})</td>
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</table>

**PS(40%)-co-MMA (\(M_w = 125\) kg/mol) with cyclohexanol**

<table>
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<td>0.0043</td>
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<td>0.0211</td>
<td>(2.58 \times 10^{-8})</td>
</tr>
<tr>
<td>0.0129</td>
<td>4.947</td>
<td>0.0638</td>
<td>(2.59 \times 10^{-8})</td>
</tr>
<tr>
<td>0.0477</td>
<td>4.451</td>
<td>0.2124</td>
<td>(2.61 \times 10^{-8})</td>
</tr>
<tr>
<td>0.0844</td>
<td>3.924</td>
<td>0.3312</td>
<td>(2.61 \times 10^{-8})</td>
</tr>
<tr>
<td>0.2484</td>
<td>2.715</td>
<td>0.5084</td>
<td>(2.60 \times 10^{-8})</td>
</tr>
</tbody>
</table>
between the PS $T_g$ and the PMMA $T_g$. This behaviour was also observed in the results at infinite dilution as a function of temperature. It appears that the effect of solvent concentration is not strong on the diffusion coefficients of the solvent although there seems to be slight decrease with increasing mass fraction and a sharp decrease at the very small solvent concentration end. The infinite dilution values are always higher than the finite concentration values. This is more apparent in the PS and the PS-$\alpha$-PMMA systems. This weak dependence on solvent concentration has been reported by Tihminioglu and Danner (1999) for the polyacrylate/ethyl acrylate system and by Iwai et al. (1989) for solutions of polybutadiene in ethyl benzene and $n$-nonane.

5.4 – Summary of Results

The phase behaviour of solutions in cyclohexanol of PS, PMMA and two copolymers of differing structure has been characterised in full. Both LLE and VLE data has been measured, using a thermo-optical apparatus and inverse gas chromatography respectively. The effect of polymer concentration, on the phase behaviour of these systems as well as the differences between the solubility of random and block copolymers, has been studied experimentally.

Measurements were taken successfully in solutions of up to around 25 % polymer by weight in solution with a turbidimeter built for this purpose. In the three systems studied and in the temperature range measured, 290 - 523 K, only upper critical solution behaviour was observed. The shapes of the cloud point curves were found to be very flat especially for the PMMA and the copolymer solutions. In addition, all three systems have cloud-point temperatures that are very close to one another and the cloud point temperatures measured agree well with the results from theta temperatures found in the literature. The effect of molecular weight was studied for the homopolymer solutions and as expected the higher the molecular weight, the higher the UCST. Furthermore, the block copolymer solution phase curve lies in between those for the homopolymer solutions.

The effect of polymer molecular weight on VLE was also investigated. This was done using inverse gas chromatography and the data was analysed with the capillary column IGC model. Two molecular weights of PMMA were used (15
kg/mol and 996 kg/mol) and their VLE behaviour compared at infinite dilution. It has been reported that in most cases, the molecular weight of the polymer does not affect the VLE behaviour greatly and, although it was observed that the partition coefficient does not change significantly, weight fraction activity coefficients (WFAC) at infinite dilution and Flory’s chi parameter show values which are higher for the higher molecular weight polymer, in the temperature range measured (413.15 K to 498.15 K). Although the difference in molecular weights is rather large, the difference in the thermodynamic data might still be considered as significant, however to make any well-founded conclusions, measurements are necessary with more different molecular weight samples. Also, monodisperse samples should be used for the comparison.

In terms of VLE behaviour of cyclohexanol in the copolymer as compared to in its parent polymers, an important finding was made. Due to interactions between the structural units in the PS and PMMA polymers and the cyclohexanol solvent, the thermodynamic properties of the solvent in the random copolymer do not lie in between those for the solvent in PS or in PMMA, as one might initially expect. Cyclohexanol has both a polar and a non-polar end. PS is non-polar but PMMA has a polar group, and so the resulting copolymer will have both types of available sites. Cyclohexanol also has both types of sites and so cyclohexanol molecules will be able to accommodate themselves perfectly well. Moreover, the –OH groups in cyclohexanol will have a tendency to form strong hydrogen bonds with the methyl methacrylate units. This is why the solubility of cyclohexanol was found to be greater in the copolymer than in the corresponding parent homopolymers. This was confirmed by (i) the higher partition coefficients as a function of temperature at infinite dilution, (ii) the lower weight fraction activity coefficients as a function of temperature and (iii) the higher activities in the copolymer at the same solvent concentration.

Different behaviour was observed with the block copolymer. The cloud point curve was measured for PS-\(b\)-PMMA in cyclohexanol and it did lie between those for its homopolymers in the same solvent. In a block copolymer, the “intramolecular repulsion”, i.e. the unfavourable interactions, between unlike bonded PS and PMMA segments in the copolymer molecule, is much reduced as a result of the segregated distribution sequence of the segments in the copolymer. The sequence is of the form \((A)_n-(B)_m\) where \(n\) and \(m\) are very large.
Other observations made on the VLE of these systems, which are common to many polymer solutions, are the decreasing values of the WFAC's and activities of the solvent as a function of increasing temperature and solvent concentration in the polymer, the linear relationship between $\ln K$ and the inverse of temperature and the temperature dependence of Flory's interaction parameter. The range of solvent concentrations in the polymers was a function of the column temperature, the high solvent boiling temperature and the glass transition temperature of the polymers. These in turn affected the resulting elution peaks from the chromatograph and became a limitation. The highest solvent concentration in this work was 28.8% cyclohexanol in the high molecular weight PMMA sample at a column temperature of 180°C.

Finally, from the IGC experiments, information about the diffusion of cyclohexanol in PS, PMMA and a corresponding random copolymer was obtained. Unlike thermodynamic behaviour, the diffusion coefficient (a transport property) of a solvent in a copolymer with respect to that in its parent homopolymers is dependant on the concentration of each homopolymer, i.e. values of $D_p$ do indeed lie in between those for the homopolymers. The systems here studied have confirmed this. Diffusion coefficients in the polymers studied ranged from $1.0 \times 10^{-6} \text{ m}^2/\text{s}$ at the higher temperatures and $1.0 \times 10^{-11} \text{ m}^2/\text{s}$ at the lower temperatures. The possibility of cyclohexanol molecules making their way into the polymer structure is mainly dependant on the empty space (or free volume) available between the polymer chains. Above the glass transition temperature of a polymer, the polymer chains can move around relatively easily so that the solvent molecules can accommodate themselves, but as the temperature is lowered, the movement becomes inhibited until the chains cannot move further and a glass structure is formed. From this it follows that diffusion coefficients should be higher at the higher temperatures and decrease as we lower the temperature. In the case of the systems studied here, the following holds $T_g^{\text{PMMA}} > T_g^{\text{PS-copolymer}} > T_g^{\text{PS}}$ and following the discussion given before, the diffusion coefficients of cyclohexanol in the copolymer should lie in between those in PS and PMMA. This was confirmed experimentally.
Chapter VI

MODELLING PHASE BEHAVIOUR

6.1 – Introduction

This chapter describes the computational methods used to predict both VLE and LLE in the polymer solutions that were investigated experimentally. It describes the implementation and results of the models discussed in Chapter III: the Sanchez-Lacombe (SL) equation of state; and the unified activity coefficient with a free-volume contribution model (UNIFAC-FV). The first section of this chapter outlines the method used to compute behaviour from an equation of state model. It starts by outlining a strategy for solving for density roots of an EoS when this cannot be done analytically, as is the case with the SL equation. It follows with the methods used for solving VLE and LLE problems with such a model. Results are then presented and compared to experimental data. The following sections deal with predictions using the UNIFAC-FV model, both computational aspects and results. All calculations in this work have been carried out with a FORTRAN program, written specifically for this purpose.
6.2 — Strategy for Solving Density Roots of the SL EoS

The term equation of state refers to any expression relating pressure, density, temperature and for a mixture, composition. The SL equation of state is generally written as:

\[
p^\ast + p^\ast + T^\ast \left[ \ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho} \right] = 0 ,
\]

where \( \tilde{\rho} \) is the reduced density \( (\tilde{\rho} = \rho / \rho^\ast) \), \( \tilde{p} \) is the reduced pressure \( (\tilde{p} = p / p^\ast) \), \( \tilde{T} \) is the reduced temperature \( (\tilde{T} = T / T^\ast) \) and \( r \) is the number of lattice sights occupied by the \( r \)-mer. These equation of state parameters are related to the molecular weight \( M \) by:

\[
\frac{RT^\ast \rho^\ast}{P^\ast} = \frac{M}{r},
\]

where \( R \) is the universal gas constant. In general, equation (6.1) has three solutions as illustrated in figure 6.1 (a) where the function \( f(\tilde{\rho}) \), obtained by rearranging the EoS into the following form:

\[
f(\tilde{\rho}) = 1 - \exp \left[ -\left( \tilde{\rho}^2 / \tilde{T} \right) - (1 - 1/r)\tilde{\rho} - (\tilde{p} / \tilde{T}) \right] = \tilde{\rho}
\]

has been plotted against \( \tilde{\rho} \). The solutions at the lowest and the highest values of \( \tilde{\rho} \) correspond to the vapour and the liquid roots of the equation. They correspond to the minima in the Gibbs free energy function given by:

\[
\tilde{\varepsilon} = G/N\rho^\ast = - \tilde{\rho} - \tilde{p} / \tilde{\rho} + \tilde{T} \left[ (1/\tilde{\rho} - 1)\ln(1 - \tilde{\rho}) + (1/r)\tilde{\rho} \right]
\]

whereas the intermediate solution corresponds to a maximum in the function. The three solutions are shown in figure 6.1 (b). The general case where the equation of state has three roots is at temperatures and pressures below their critical values. Shown in figure 6.2 are the isotherms for a pure component. As can be seen, at temperatures \( T < T_c \), there will be three roots for a given pressure, whereas at
Figure 6.1—(a) Schematic of the solutions of the SL equation of state. Solutions at the highest and lowest values of the reduced density correspond to the vapour and liquid phases respectively and occur when the Gibbs free energy function is at its minima. The intermediate solution corresponds to a maximum in the Gibbs function. (b) Schematic of the reduced Gibbs free energy at specified $T$ and $P$ as a function of reduced density.

Figure 6.2—Model isotherms on a $PV$ diagram for a pure fluid.
temperatures $T > T_c$, there is only one root. At the critical isotherm, there will be three roots all equal to the critical volume. The same applies to a mixture of components. Based on these isotherms, the first step in solving for $\bar{\rho}$ is to determine whether the given temperature is below or above the critical temperature, which for the SL equation can be calculated analytically using equation (3.43). If $T > T_c$, there is one root and the appropriate guess would be the critical density, whereas if $T < T_c$, depending on whether $P$ is above or below the maximum or minimum pressures on the isotherm, $P''$ and $P'$ respectively, there will be either a liquid or a vapour root.

At a specified temperature and pressure (and composition if necessary) the solutions to the SL equation of state cannot be obtained analytically and so numerical techniques are necessary, such as the Newton-Raphson iterative method. Assuming an initial guess for $\bar{\rho}$, the functions $f(\bar{\rho})$ and its derivative $f'(\bar{\rho})$ are computed. Using the following expression,

$$\bar{\rho}_{n+1} = \bar{\rho}_n - \frac{f(\bar{\rho}_n)}{f'(\bar{\rho}_n)} = \bar{\rho}_n - \delta$$  \hspace{1cm} (6.5)

where $n$ is the iteration count and $\delta$ is the change in $\bar{\rho}$, a new value of $\bar{\rho}$ is calculated. This new value becomes the new guess in equation (6.5) and calculations are repeated until the value of $\bar{\rho}$ converges to the solution of the equation of state at specified conditions. A similar but more robust technique is Richmond's third order root finder (Plocker and Knapp, 1976). The objective is the same as with Newton's method, to seek a solution for $f(\bar{\rho}) = 0$ iteratively. The expansion of $f(\bar{\rho})$ about an initial value $\tilde{\rho} = \bar{\rho}_0$ is,

$$f(\bar{\rho}_0 + \delta) = f_0 + \delta f'_0 + \frac{1}{2} \delta^2 f''_0 + ...$$  \hspace{1cm} (6.6)

where $\delta$ is a small change in the guessed value $\bar{\rho}_0$, and $f_0$, $f'_0$, and $f''_0$ are the function, its first and second derivatives respectively, all three evaluated at $\bar{\rho}_0$. The Newton-Raphson method considers only the first two terms of this expansion whereas the
Richmond method considers the second derivative term too. Solving the quadratic equation for $\delta$ such that $f(\bar{\rho}_o + \delta) = 0$, first rearranging in terms of $1/\delta$ ($=\Delta$),

$$0 = 2f_o(\Delta^2) + 2f''_o(\Delta) + f''_0$$

and doing some manipulations gives,

$$\delta = \frac{-2f_o f''_o}{f''_o - 2f''_0}.$$  \hspace{1cm} (6.7)

It reduces to the Newton-Raphson equation (6.5) if the second derivative is neglected. This iterative method is faster when in the neighbourhood of the solution and was used in this work to solve the SL equation of state for the reduced density at specified $T$ and $P$. To find the vapour and liquid densities, the dominant density terms are isolated respectively. Looking back at equation (6.1) we can see that at high densities (liquid root), the dominant term will be the $\ln(1 - \bar{\rho})$ term from which $\bar{\rho}$ can be isolated such that:

$$\bar{\rho} = 1 - \exp\left[-\bar{\rho} \left(1 - \frac{1}{r}\right) - \frac{\bar{\rho}^2}{T} - \frac{\bar{\rho}^3}{T^3}\right] = f_{\text{eq}}(\bar{\rho})$$ \hspace{1cm} (6.9)

Richmond's root finder is used to solve $F_{\text{eq}}(\bar{\rho}) = \bar{\rho} - f_{\text{eq}}(\bar{\rho}) = 0$. For low densities (vapour root), the term isolated is the $[1-1/\bar{\rho}]\bar{\rho}$ term such that,

$$\bar{\rho} = \left(\frac{r}{r-1}\right)\left[-\frac{\bar{\rho}^2}{T} - \frac{\bar{\rho}^3}{T^3} - \ln(1 - \bar{\rho})\right] = f_{\text{vap}}(\bar{\rho})$$ \hspace{1cm} (6.10)

and a correct solution can be found by solving $F_{\text{vap}}(\bar{\rho}) = \bar{\rho} - f_{\text{vap}}(\bar{\rho}) = 0$. Table 6.1 gives the functions and derivatives used in solving the SL equation for liquid and vapour roots using this method. For a vapour-like root a reasonable starting guess is the ideal gas vapour reduced density ($= \bar{\rho}_v/T$) and for a liquid-like root, a reasonable good guess is ($a \times \bar{\rho}_v$) where $a$ is a factor multiplying the reduced spinodal density.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour</td>
<td>$f(\bar{p}) = \frac{1}{(1-1/r)} - \frac{\bar{p}^2}{T} - \ln(1 - \bar{p})$</td>
</tr>
<tr>
<td></td>
<td>$F(\bar{p}) = \bar{p} - \frac{1}{(1-1/r)} - \frac{\bar{p}^2}{T} - \ln(1 - \bar{p})$</td>
</tr>
<tr>
<td></td>
<td>$F'(\bar{p}) = 1 - \frac{1}{(1-1/r)} - \frac{2\bar{p}}{T} + \frac{1}{(1-\bar{p})}$</td>
</tr>
<tr>
<td></td>
<td>$F''(\bar{p}) = -\frac{1}{(1-1/r)} - \frac{2}{T} + \frac{1}{(1-\bar{p})^2}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>$f(\bar{p}) = 1 - \exp\left[\frac{-\bar{p}}{T} - \frac{\bar{p}^2}{T} - (1-1/r)\bar{p}\right]$</td>
</tr>
<tr>
<td></td>
<td>$F(\bar{p}) = \bar{p} - 1 + \exp\left[\frac{-\bar{p}}{T} - \frac{\bar{p}^2}{T} - (1-1/r)\bar{p}\right]$</td>
</tr>
<tr>
<td></td>
<td>$F'(\bar{p}) = 1 + \left[-\frac{2\bar{p}}{T} - (1-1/r)\right] \exp\left[\frac{-\bar{p}}{T} - \frac{\bar{p}^2}{T} - (1-1/r)\bar{p}\right]$</td>
</tr>
<tr>
<td></td>
<td>$F''(\bar{p}) = \left[-\frac{2}{T} + \left[-\frac{2\bar{p}}{T} - (1-1/r)\right]^2\right] \exp\left[\frac{-\bar{p}}{T} - \frac{\bar{p}^2}{T} - (1-1/r)\bar{p}\right]$</td>
</tr>
</tbody>
</table>

Table 6.1: Functions and derivatives used in solving the SL equation for liquid and vapour roots using Richmond's 3rd order root finder.
6.3 — Calculating the Vapour Pressure of a Pure Component

In chapter II, the conditions for thermodynamic equilibrium between two coexisting phases were described. For thermodynamic equilibrium between a liquid and a vapour, the fugacity (and equivalently the chemical potential) of a pure component has to be equal in each phase such that,

\[ g(f) = f_{\text{vap}} - f_{\text{liq}} = 0 \]  

(6.11)

where \( f_{\text{vap}} \) and \( f_{\text{liq}} \) are the vapour and liquid fugacities respectively, and \( g(f) \) is the function of fugacity to be solved. At a given temperature \( g(f) \) is a function of pressure and so the vapour pressure of the pure component can be obtained by solving the above using the Newton-Raphson method in the form given below:

\[ P_{\text{eq}} = P_r - \frac{g(P)}{g'(P)} \]  

(6.12)

The fugacity of a pure fluid is calculated from the fugacity coefficient and for the SL equation of state for a pure fluid is calculated using the following expression (derived from equation 2.18):

\[ \ln \phi = -\frac{\bar{T}}{T} + (Z - 1) - r \left[ \frac{1}{\bar{\rho}} \right] \ln \left( 1 - \frac{\bar{\rho}}{r} \right) + \frac{\ln Z}{r} - 1 \]  

(6.13)

6.4 — The Flash Problem

A flash algorithm is a commonly employed method to solve the equilibrium problem and can be applied to vapour-liquid or liquid-liquid equilibrium. Modelling a flash process is probably one of the most important applications of chemical engineering thermodynamics. "A flash process is one in which a stream of known overall composition and flowrate is passed through a throttle, turbine or compressor and into a vessel (flash drum) where liquid and vapour phase are separated before passing through the appropriate outlet." (Assael et al., 1996). The flash process can
occur at different sets of conditions, for example an isothermal flash will take place at
constant temperature and pressure, and an isochoric flash will take place at constant
temperature and volume. Figure 6.3 shows a schematic of an isothermal flash
process. The feed of composition $\xi$ and flowrate $F$ passes through the throttle and
enters the vessel, which is maintained at constant $T$ and $P$, where it phase separates
into vapour (flowrate $F_{\text{vap}}$, composition $\eta$) and liquid (flowrate $F_{\text{liq}}$, composition $\xi$).
The fraction of the overall flowrate in the vapour phase is given $\beta$ and that in the
liquid phase will consequently be $(1-\beta)$.

\[ F_{\text{vap}} = \beta F \]

\[ F_{\text{liq}} = (1-\beta)F \]

\[ x_i \rightarrow y_i, T, P \]

\[ x_i \rightarrow x_i, F_{\text{vap}} = \beta F, F_{\text{liq}} = (1-\beta)F \]

Figure 6.3 — Isothermal flash unit.

A liquid-liquid phase separation at constant temperature and pressure can
also be modelled as an isothermal flash process and this is the treatment used in this
work for the calculation of the coexistence curves of polymer solutions. The flash
calculation yields the compositions of the two coexisting phases as well as the
amount of material that is present in each of the phases formed at a specified
temperature, pressure and overall composition. In this analysis a new variable is
introduced: the distribution ratio $K$ for each component $i$ in the mixture, which is
defined as

\[ K_i = \frac{x_i^{\text{liq}}}{x_i^{\text{vap}}} = \phi_i^{\text{liq}}/\phi_i^{\text{vap}} \]  

(6.14)

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where I and II refer to the two liquid phases in equilibrium and $\phi$ is the fugacity coefficient of component $i$. Expression (6.14) is the equilibrium condition expressed in terms of equality of the fugacities of component $i$ in these phases. Furthermore, $\beta$ needs to be redefined for LLE calculations as the fraction of material in phase I. Performing a material balance on the isothermal flash and using the definition of $K$, the following equation results:

$$z_i = \beta x_i^I + (1-\beta)x_i^II = \left[\beta + K_i(1-\beta)\right]x_i^I$$  \hspace{1cm} (6.15)

Solving for $x_i^I$ and applying the constraint that the mole fractions of all $n$ components in the mixture, in each phase, must add up to 1, the equilibrium condition becomes:

$$f(\beta) = \sum_{i=1}^{n} (x_i^II - x_i^I) = \sum_{i=1}^{n} \frac{z_i(K_i - 1)}{\beta + K_i(1-\beta)} = 0$$  \hspace{1cm} (6.16)

This is the so-called Rachford-Rice formulation of the equilibrium problem. A solution to this function can be found using the method of successive substitutions:

$$\beta_{k+1} = \beta_k + \left[\sum_{i=1}^{n} \frac{z_i(K_i - 1)}{\beta + K_i(1-\beta)}\right]^{-1} \left[\sum_{i=1}^{n} \frac{z_i(K_i - 1)^2}{\left[\beta + K_i(1-\beta)\right]^2}\right]^{-1}$$  \hspace{1cm} (6.17)

where $k$ is the iteration count. In this method, an initial estimate of $\beta$ is assumed and the calculated values of the distribution ratios can be used to obtain a new value of $\beta$. This process is repeated until convergence is achieved to the desired accuracy. The distribution ratios are calculated from the fugacity coefficients, which are in turn a result of the equation of state used. These need to be calculated for each trial value of $\beta$.

6.4.1 – Negative Flash

In solving the flash problem and during the iterative process using equation (6.16), values of $\beta$ outside the range 0 to 1 can be encountered. Values outside this
range might suggest that they are physically unacceptable and a simple remedy is to use $\beta = 0$ for all values of $\beta$ less than zero and $\beta = 1$ for all values greater than one. The function of $\beta$ defined by equation (6.16) decreases monotonically and has the form shown in figure 6.4 (a) where asymptotes occur at values of $\beta = K_i / (K_i - 1)$. Solutions to equation (6.16) are possible between all asymptotes, and only the solution between asymptotes $\beta_{\text{min}} = K_{\text{max}} / (K_{\text{max}} - 1)$ and $\beta_{\text{max}} = K_{\text{min}} / (K_{\text{min}} - 1)$ will yield negative values of the compositions. Figure 6.4 (b) shows a sketch of $\beta$ as a function of $K_i$. $K_{\text{max}}$ will correspond to the pole closest to $\beta = 1$. For $K_{\text{min}}$, if it has a value greater than 1 there will be no solution whereas if $K_{\text{min}} < 1$, the solution will correspond to the pole closest to $\beta = 0$. Furthermore, if all $K_i$’s are greater than one then there will be no solution.

Following this argument there is no reason why values of $\beta$ outside the 0 to 1 range should be considered “incorrect” unless it is outside the range $\beta_{\text{min}}$ to $\beta_{\text{max}}$. An additional property of this method is that it gives (for a binary mixture) the
coexisting compositions at the given temperature and pressure, if the overall composition were such that two phases formed, even if this specified overall composition lay outside the binodals. Moreover, if the phase equilibrium calculation converges to a non-trivial solution with values of $\beta$ smaller than zero or greater than one, the mixture can be assumed to be a stable single phase. Other advantages of allowing these values have been discussed by Whitson and Michelsen (1989). They referred to this implementation as a negative flash calculation, when no value of $\beta$ was discarded during the iterative flash procedure. This was included into the program written for this work.

6.4.2 — Application to Polymer Solutions

Unfortunately, application of the Rachford-Rice algorithm for solving the flash problem for polymer solutions has been found to cause computational problems. Several authors have reported instability of the method and divergence from the solution (Chen et al., 1993; Heidemann and Michelsen, 1995; Koak and Heidemann, 1996) for systems where the deviations from ideal solution behaviour are large, as is the case for polymer/solvent systems. In an isothermal flash problem for a system of $n$ components, there will be $n$ material balances, $n$ equilibrium equations and one consistency equation, i.e. a total of $(2n + 1)$ equations. The form of the equations is shown below:

\[
\begin{align*}
\text{material balances:} & \quad f_{\text{material balances}} = \beta x_i^1 + (1 - \beta)x_i^{11} - x_i = 0 \\
\text{equilibrium equations:} & \quad f_{\text{equilibrium equations}} = K_i x_i^1 - x_i^{11} = 0 \\
\text{consistency equation:} & \quad f_{\text{consistency equation}} = \sum_{i=1}^{n} (x_i^1 - x_i^{11}) = 0
\end{align*}
\]

If the distribution ratios are assumed to be independent of composition then this system of equations can be reduced to a single non-linear equation, equation (6.17) which can be solved using an iterative method for which the step change in $\beta$ is obtained from evaluating the Jacobian matrix. Heidemann and Michelsen (1995)
reported that in polymer solutions, the method of successive substitution becomes unstable because one or more eigenvalues of this matrix is less than \(-1\). An additional computational problem arises because the fugacities and mole fractions obtained for the polymer are extremely small as a result of the large differences in size between solvent and polymer, leading in some cases to the numbers falling below the "underflow" limits of typical computers.

To solve these computational difficulties, several procedures, sometimes system specific, have been used. A relatively simple procedure to overcome oscillatory non-convergence of the solution is by applying a "damping factor" to the computed change in \(K\)'s. The eigenvalues which are less than \(-1\) can therefore be "damped" and made to be higher and even positive, which will lead to convergence of the solution. This method works but may take a very large number of iterations.

Another commonly used procedure is to use a Newton-Raphson approach with truncation. An alternative solution has been proposed (Chen et al. 1993) in which the Jacobian is divided into four smaller matrices, one of which is a diagonal matrix. This approach requires less computational time and is numerically more stable than the original Jacobian because of the reduced dimensionality and the special structure of the sub-matrices.

In this work, a routine obtained from the ISML libraries (FORTRAN 90 Professional edition) called DNEQNF, has been used to solve the system of \((2n + 1)\) non-linear equations presented in equations (6.18) – (6.20). All the systems modelled in this work are binary systems that may separate into at most two phases, so that \(n=\pi\) (where \(\pi\) is the number of phases). The subroutine is used to solve the system of equations for the compositions of polymer and solvent in the coexisting phases at specified temperature pressure and overall composition. Its purpose is to find a zero of the system of non-linear equations using a modified Powell hybrid method. This routine is useful since it calculates the derivatives in the Jacobian numerically, avoiding the derivation of complicated expressions from the SL equation of state. The Jacobian for the binary system is given below:

\[
J = \begin{bmatrix}
(1-\beta) & 0 & \beta & 0 & (x_1^i - x_1^{ii}) \\
0 & (1-\beta) & 0 & \beta & (x_2^i - x_2^{ii}) \\
(k_1 + \partial k_1 / \partial x_1) & (\partial k_1 / \partial x_1) & (k_1 + \partial k_1 / \partial x_1 - 1) & (\partial k_1 / \partial x_1) & 0 \\
(\partial k_2 / \partial x_1) & (k_2 + \partial k_1 / \partial x_1) & (\partial k_2 / \partial x_1) & (k_2 + \partial k_1 / \partial x_1 - 1) & 0 \\
1 & 1 & -1 & -1 & 0
\end{bmatrix}
\]  

(6.21)
The subroutine requires initial population of the $x_{\text{guess}}$ ($x_1^I, x_2^J, x_1^{II}, x_2^{II}, \beta$) vector. Iteratively a solution is found and is returned as $x (x_1^I, x_2^J, x_1^{II}, x_2^{II}, \beta)$. Each time a new iteration occurs, new compositions are returned and the subroutine containing the equation of state expressions is called to calculate the new values of the fugacity coefficients and $K$ factors. The complete algorithm is presented in the next section.

Another important issue in the application of the flash problem to polymer solutions is the choice of composition variables. Up to now, all equations have been presented in terms of mole fractions but given the fact that, due to the large differences in molecular weights between polymer and solvent molecules, the magnitudes of the mole fractions can become very different from each other in the two phases, it might be reasonable to express equations in terms of weight fractions. As can be seen from the general liquid-liquid phase diagrams for these systems (shown in the previous chapters), it is common to have a solvent rich phase where the weight fraction of polymer is almost negligible, and if computations were carried out using mole fractions as the composition variables, one might expect to encounter values which are smaller than the smallest number that can be represented on the computer. Also in polymer/solvent systems, there is a very strong composition dependence of the fugacity coefficients which gives rise to very strong variations in the equilibrium ratios ($K$ factors) with composition. Using very small values of the composition variables will lead to even smaller $K$ factors causing computational difficulties. To avoid the numerical problems associated with very small or very large values of the fugacities, logarithms are used. A change in composition variable to mass fractions could also be used and has been employed to solve multi-phase equilibrium calculations for systems containing polymers (Kosinski and Anderko, 1996), but complicates the equations to be solved. In this work the system of equations was solved using mole fractions and this gave no major problems.

6.4.3 – The Flash Algorithm

Shown in figure 6.5 is the flash algorithm used with the Sanchez-Lacombe equation of state to obtain the coexistence curves of polymer solutions. The algorithm involves the following steps:
Enter $T_1, P, \gamma$.

Assume $x_1^I, x_1^{II}$.

Calculate $\beta$.

Calculate $\phi_I, \phi_{II}$ using the SL equation of state and $K_i$'s.

Solve system of non-linear equations $f_{1\rightarrow 5}$.

Evaluate functions with solution.

Is tolerance on $f_{1\rightarrow 5}$ satisfied?

NO

YES

Output $x_I^I, x_{II}^{II}, \beta$.

Choose next $T_2$.

*Figure 6.5* - Isothermal flash algorithm used for liquid-liquid calculations using the Sanchez-Lacombe equation of state.
1. Specify temperature, pressure and overall composition. Call subroutine LLE_FLASH.

2. Enter initial guesses for the compositions in phase I and phase II.

3. Use mass balance equation (6.17) to calculate $\beta$.

4. Populate the $x_{\text{guess}} (x_1^1, x_2^1, x_1^I, x_2^I, \beta)$ vector.

5. Set maximum number of iterations allowed and the tolerance for the convergence of the iterations.

6. Call subroutine DNEQNF which in turn calls the function FNC which contains the five equations to be solved [The latter will call subroutine EOS which evaluates the logarithm of the fugacity coefficients using the Sanchez-Lacombe model. From these, the corresponding values of $K_i$ are calculated too.] Solve the system of equations and return $x (x_1^1, x_2^1, x_1^I, x_2^I, \beta)$ vector.

7. Evaluate all five functions and check if the tolerance on the functions has been satisfied. If it has then a solution to the flash problem has been found. If not go back to step 6.

Several traps were incorporated into the flash routine, including trapping trivial solutions, trapping for no two-phase solution and trapping for $\beta$ values going to plus or minus infinity. Finally, the stability of the each of the two phases was checked using the stability criterion of the SL equation given in equation (3.47).

In most cases, the phase split was easily found when the initial guess for the polymer weight fractions were 0.2 and 0.04, in the polymer-rich and polymer-lean phases respectively. However, in some instances when the concentration of the polymer in solvent-rich phase was very small (e.g. weight fraction of polymer, $w_{\text{polymer}}=0.05$), the solver became very sensitive to the initial guess. As a result, the calculations either did not converge to a solution or the trivial solution was returned.

All calculations were preformed at a user specified temperature and at the vapour pressure of the solvent. The liquid-liquid equilibrium calculations were then performed in two successive steps. In the first step, a search for a phase split at a specified temperature was performed. In the region where the system is totally miscible, the trivial solution will be returned since it is the only solution to the problem, whereas if immiscibility occurs there will be a non-trivial solution defining two points on the phase diagram. Once a phase split was detected, the second step proceeds where the entire phase diagram is computed starting from the temperature.
where the phase split was located. As the coexistence curve is drawn and the critical solution temperature approached the magnitude of the temperature step (be it an increment or a decrement) was decreased to obtain a more accurate knowledge on what the critical temperature was. This algorithm is applicable for solving liquid-liquid equilibrium problems with two phases and has proved to be applicable to ternary mixtures with two-phase splits, although no in-depth study was been carried out in this work. For multiphase systems, the algorithm will become much more complicated and it is then essential to solve alternatively for stability and a flash problem like that proposed by Michelsen (1982a, b). The phase split calculation would give an estimate of the number, type and approximate compositions of the equilibrium phases and is based on Gibbs' tangent plane analysis and involves finding all the stationary points to a tangent plane distance function in the full composition range. The results from the phase-split calculations would provide good estimates for solving the flash problem.

6.4.4 — Sanchez-Lacombe Equations for Solving the Flash Problem

Expressions for the fugacity coefficients of each component in the binary solution are necessary to solve the flash algorithm. For the Sanchez-Lacombe they are somewhat troublesome to derive and only essential expressions and the final result are given here. The fugacity coefficient \( \phi_i \) of component \( i \) in a mixture at temperature \( T \) and pressure \( P \) is defined as:

\[
\ln \phi_i = -\frac{1}{kT} \int V \left( \frac{\partial P}{\partial N_i}_{T,P,N_j} - \frac{kT}{V} \right) dV - \ln Z
\]

(6.22)

where \( k \) is Boltzmann's constant, \( N \) is number of molecules of component \( i \) in the mixture, \( V \) is the molar volume and \( Z \) is the compressibility factor. The equation of state can be rearranged to obtain an expression for \( P \) (all variables have been defined in chapter III):
\[ P = -\frac{kT}{v^*} \ln(1 - \bar{\rho}) - \frac{kT}{v^*} \left(1 - \frac{1}{r}\right)\bar{\rho} - \frac{\varepsilon^*}{v^*} \bar{\rho}^2 \]  

(6.23)

and the derivative of each of the three terms on the right-hand side of the expression can be taken separately. In doing so, the following expressions are used:

\[ \nu^* = \frac{1}{\nu N} \sum \nu^* \]  

(6.24)

\[ \bar{\rho} = \frac{1}{V} \sum \nu \bar{\rho} \]  

(6.25)

\[ \varepsilon^* = \frac{1}{(\nu N)^2} \sum \sum \nu \nu \varepsilon^* \]  

(6.26)

The following known integral is also used in the derivation:

\[ \int [1 - (a/x)] dx = x \ln[x] - a \ln(x - a) \]  

(6.27)

The final expression for the fugacity coefficient of component \( i \) is:

\[ \ln \phi_i = -\ln Z - \frac{1}{\bar{\rho}} \left( \frac{\nu^*}{\nu} - 1 \right) \ln(1 - \bar{\rho}) + r_i \ln(1 - \bar{\rho}) + \]

\( r_i \left( \frac{\nu^*}{\nu} - 1 \right) + r_i \bar{\rho} \left[ 2 \sum \phi_i \varepsilon^* \left( \frac{\varepsilon^*}{kT} \right) + \left( \frac{\nu^*}{\nu} - 1 \right) \frac{1}{\nu} \right] \]  

(6.28)

where the site fraction is written as \( \phi_i^{\text{site}} \) instead of \( \phi_i \) used in chapter III to differentiate it from the fugacity coefficient. This expression reduces correctly in the case of a pure component ideal gas.
6.4.5 — LLE from an Activity Coefficient Model

Up to this point, the flash algorithm used to calculate coexistence curves in polymer solutions has been described in terms of an equation of state. Of course, the same algorithm can be used with an activity coefficient model. At equilibrium, the activities of all components in a mixture have to be equal in each of the phases. The distribution ratios can therefore be rewritten in terms of mole fractions and activity coefficients $\gamma_i$ as shown:

$$K_i = \frac{x_i^\text{II}}{x_i^\text{I}} = \frac{\gamma_i^\text{I}}{\gamma_i^\text{II}}$$

(6.29)

The algorithm is essentially the same as presented in figure 6.5. The $x\text{guess}$ vector is populated with initial guesses for the compositions in each of the phases and a corresponding value of $\beta$ is calculated using the material. These initial guesses are fed into the non-linear equation solver routine. The activity coefficient model calculates activity coefficients that are used to calculate the distribution ratios. A solution is found and the compositions and fraction of each phase are returned.

6.5 — Solving VLE in Polymer Solutions

Vapour-liquid equilibria in the polymer solutions considered in this work have been studied by considering the activities and activity coefficients of a solvent in a polymer as a function of temperature and composition. These are the variables that have been measured experimentally. Calculations using the Sanchez-Lacombe equation of state or the UNIFAC-FV model are computationally much simpler than in the case of LLE, since analytical expressions can be derived that can be computed directly. In the case of the SL equation, the expression for the logarithm of the activity was given in section 3.5.2 and reads,
\[ \ln a_i = \ln \varphi_i + \left(1 - \frac{r_i}{\varphi_i} \right) + r_i \varphi_i^2 \chi_{12} \]
\[ + r_i \left[ - \frac{\varphi_i + \varphi_{11}}{T_1} + \frac{\varphi_i (\varphi_i - \varphi_{11})}{T_1} + \frac{1}{r_i} \ln \frac{\varphi_i}{\varphi_{11}} + (\varphi_i - 1) \ln (1 - \varphi_i) - (\varphi_i - 1) \ln (1 - \varphi_{11}) \right] \quad (6.30) \]

where subscripts 1 and 2 refer to the solvent and polymer respectively and no subscript represents the mixture property. The reduced density, volume, temperature and pressure have been already defined in chapter III. The \( \chi_{12} \) is the interaction parameter to be fitted to the experimental data and is defined as:

\[ \chi_{12} = \frac{\epsilon_{12}^* + \epsilon_{22}^* - (1 - \delta_{12}) \sqrt{\epsilon_{11}^* \epsilon_{22}^*}}{kT} \quad (6.31) \]

and the volume fraction \( \varphi_i \) is defined as,

\[ \varphi_i = \frac{r_i x_i}{\sum_{i} r_i x_i} = \frac{r_i w_i / M_i}{\sum_{i} r_i w_i / M_i} \quad (6.32) \]

where \( w_i \) and \( M_i \) are the weight fraction and molecular weight of component \( i \) respectively. For polymer solutions it is more convenient to calculate weight fraction activity coefficients \( (\varphi_i) \) and so the expression used for calculating these is:

\[ \ln \varphi_i = \ln \frac{\varphi_i}{\varphi_i} + \left(1 - \frac{r_i}{\varphi_i} \right) + r_i \varphi_i^2 \chi_{12} \]
\[ + r_i \left[ - \frac{\varphi_i + \varphi_{11}}{T_1} + \frac{\varphi_i (\varphi_i - \varphi_{11})}{T_1} + \frac{1}{r_i} \ln \frac{\varphi_i}{\varphi_{11}} + (\varphi_i - 1) \ln (1 - \varphi_i) - (\varphi_i - 1) \ln (1 - \varphi_{11}) \right] \quad (6.33) \]

This is the logarithm of the weight fraction activity coefficients at finite concentrations. In the limit of zero solvent, i.e. at infinite dilution, \( (\varphi_i / \varphi_i) \rightarrow r_i M_i / r_i M_1 \), so that substituting into equation (6.33) gives:
\[
\ln \Omega_i^s = \ln \left( \frac{r_i M_2}{r_2 M_1} \right) + \left( 1 - \frac{r_i}{r} \right) + r_i \phi_i x_{12} \\
+ r_i \left[ -\frac{p + \rho_i}{\bar{T}_i} + \frac{\bar{p}(\bar{v} - \bar{v}_i)}{\bar{T}_i} + \frac{1}{r_i} \ln \frac{\rho}{\rho_i} + (\bar{v} - 1) \ln (1 - \rho) - (\bar{v}_i - 1) \ln (1 - \rho_i) \right]
\]

(6.34)

On the other hand, the UNIFAC-FV model directly provides an expression for the weight fraction activity coefficient as shown,

\[
\ln \Omega_i = \ln \Omega_i^{\text{comb}} + \ln \Omega_i^{\text{res}} + \ln \Omega_i^{\text{f-v}}
\]

and as was described in section 3.7, where all the necessary equations for the calculations are presented, is the summation of three contributions, a combinatorial, a residual and a free-volume contribution. For the specific calculations at infinite dilution two expressions need to be used:

\[
\phi_i = \frac{r_i / M_i}{\sum_{j=1}^{n} r_j w_j / M_j}
\]

and

\[
\theta_i = \frac{\sum_{j=1}^{n} r_j w_j / M_i}{\sum_{j=1}^{n} r_j w_j / M_i}
\]

(6.36)

and they need to be substituted into the expression for the free-volume contribution. All parameters have been previously defined in chapter III. Therefore, direct calculation of the VLE variables is possible. An example calculation is presented in appendix E for the polystyrene/cyclohexanol solution.

### 6.6 – Modelling Polymer Solutions: Input Parameters

The objective of this work is to evaluate the performance of the two different models by comparing their predictions to experimental data. Therefore three systems have been modelled: PS/cyclohexanol, PMMA/cyclohexanol and the copolymer/cyclohexanol. The coexistence curves of three molecular weight solutions of each of the homopolymers were drawn. The results are presented in the next sections.
6.6.1 – Sanchez-Lacombe Parameters

Sanchez-Lacombe parameters for a number of simple pure fluids have been presented by Sanchez and Lacombe (1976) and were obtained by fitting saturated vapour pressures and liquid densities. In the case of pure polymers, these parameters have been determined by a nonlinear least-squares fit to experimental density data (Sanchez and Lacombe, 1977). Unfortunately, no parameters were available in the literature for cyclohexanol and so these were obtained using the method proposed by Gauter and Heidemann (2000). By their methodology the parameters are obtained from the critical temperature, pressure and acentric factor. This is the approach routinely employed with cubic equations of state. Koak and Heidemann (1996) showed that some of the original parameter sets reported in the literature produced significant errors in the vapour pressure and led to an over prediction of the critical temperature, and therefore proposed an alternative method for calculating SL EoS parameters for pure fluids. They rewrote the EoS in terms of three pure component parameters \( r, \nu^* \) and \( \varepsilon \) which denote the number of lattice sites per molecule, the volume of a mole of lattice sites and an energy parameter. These are related to the critical temperature and pressure through the following expressions:

\[
\varepsilon = \frac{RT_c}{2} \left( 1 + \sqrt{r} \right)^2
\]

\[
\nu^* = \frac{RT_c}{P_c} \ln \left( \frac{1 + \sqrt{r}}{\sqrt{r}} \right) - \frac{\sqrt{r} - 1/2}{r}
\]

The \( r \) parameter is obtained from the acentric factor which can be calculated from the vapour pressure at a reduced temperature of 0.7:

\[
\omega = -\log_{10} \left( \frac{P}{P_c} \right)_{T=0.7} - 1
\]

and the relationship between \( r \) and \( \omega \) is well fitted by the following polynomial:

\[
r = 5.1178 + 13.5698\omega + 5.9404\omega^2 - 1.2952\omega^3
\]
For the large number of fluids tested with a range of acentric factors (from 0 to 0.64), calculation of vapour pressures using this parameterisation gave a maximum error of 4% (Gauter and Heidemann, 2000). The resulting parameters for cyclohexanol are given in table 6.2. These parameters give an average error of 2.2% in the liquid densities and 4.1% in the vapour pressures. Figures 6.6 (a) and (b) compare calculated and experimental values.

For the homopolymers, parameters were available in the literature (Sanchez and Lacombe, 1977). Rodgers (1993) fitted PVT data of two random PS-PMMA copolymers of styrene content 20 and 60%. Each of the three parameters could be fitted to a linear function of styrene content in the copolymer and used to calculate the parameters for the specific copolymer contents used in this work. The parameters are presented in table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>$T^*$ (K)</th>
<th>$P^*$ (MPa)</th>
<th>$\rho^*$ ($\text{kg/m}^3$)</th>
<th>$\gamma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanol</td>
<td>552.02</td>
<td>476.85</td>
<td>956.5</td>
<td>10.88</td>
</tr>
<tr>
<td>Polystyrene (atactic)</td>
<td>773.00</td>
<td>366.90</td>
<td>1092.8</td>
<td>---</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>742.00</td>
<td>488.30</td>
<td>1249.8</td>
<td>---</td>
</tr>
<tr>
<td>PS-PMMA copolymer (53.1% MMA)</td>
<td>739.12</td>
<td>450.14</td>
<td>1198.8</td>
<td>---</td>
</tr>
<tr>
<td>PS-PMMA copolymer (58.5% MMA)</td>
<td>743.00</td>
<td>432.40</td>
<td>1195.0</td>
<td>---</td>
</tr>
</tbody>
</table>

(a) For a polymer liquid, $r \rightarrow \infty$.

Table 6.2 – Sanchez-Lacombe equation of state parameters for cyclohexanol, PS, PMMA and PS-PMMA copolymers.

6.6.2 – UNIFAC-FV Parameters

For UNIFAC-FV, the molecular structure of the components is divided into groups and their contributions added together. The contributions are taken from tables found in the literature (High and Danner, 1993; Kontogeorgis et al., 1993). Table 6.3 (a) shows the sub-groups that have been used in the calculations and how many each component molecule (in the case of the polymers a repeat unit) contain. The number of sub-groups constituting a polymer is calculated by
Figure 6.6(a) — Comparison of experimental and calculated liquid densities, using the Koak & Heidemann (1996) approach, for cyclohexanol.

Figure 6.6(b) — Comparison of experimental and calculated vapour pressures, using the Koak & Heidemann (1996) approach, for cyclohexanol.
calculating the number of repeat units for a certain molecular weight polymer. In the case of the copolymers the composition of each constituent polymer is used to evaluate how many repeat units and therefore how many sub-groups there are of polymer A and of polymer B. Also given are the values of the $R_k$ and $Q_k$ parameters, where $k$ refers to the sub-group. The UNIFAC interaction parameters (between sub-groups) are given in table 6.3 (b).

<table>
<thead>
<tr>
<th>Sub-group (#)</th>
<th>Cyclohexanol</th>
<th>PS</th>
<th>PMMA</th>
<th>PS-PMMA copolymer</th>
<th>$R_k$</th>
<th>$Q_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ (1)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.9011</td>
<td>0.848</td>
</tr>
<tr>
<td>CH$_2$ (2)</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>0.6744</td>
<td>0.540</td>
</tr>
<tr>
<td>CH (3)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4469</td>
<td>0.228</td>
</tr>
<tr>
<td>C (4)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.2195</td>
<td>0.000</td>
</tr>
<tr>
<td>ACH (10)</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>0.5313</td>
<td>0.400</td>
</tr>
<tr>
<td>AC-CH (14)</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0.8121</td>
<td>0.348</td>
</tr>
<tr>
<td>OH (15)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5299</td>
<td>0.584</td>
</tr>
<tr>
<td>CH$_3$COO (22)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1.9031</td>
<td>1.728</td>
</tr>
</tbody>
</table>

*Table 6.3(a) – UNIFAC sub-groups and their parameters for cyclohexanol, PS, PMMA and PS-PMMA copolymer molecules.*

<table>
<thead>
<tr>
<th>$a_{jk}$</th>
<th>CH$_2$</th>
<th>ACH</th>
<th>AC-CH$_2$</th>
<th>OH</th>
<th>CCOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$</td>
<td>0.00</td>
<td>61.13</td>
<td>76.50</td>
<td>986.5</td>
<td>232.1</td>
</tr>
<tr>
<td>ACH</td>
<td>-11.12</td>
<td>0.00</td>
<td>167.0</td>
<td>636.1</td>
<td>5.994</td>
</tr>
<tr>
<td>AC-CH$_2$</td>
<td>-69.70</td>
<td>-146.8</td>
<td>0.00</td>
<td>803.2</td>
<td>5688.0</td>
</tr>
<tr>
<td>OH</td>
<td>156.4</td>
<td>89.60</td>
<td>25.82</td>
<td>0.00</td>
<td>101.1</td>
</tr>
<tr>
<td>CCOO</td>
<td>114.8</td>
<td>85.84</td>
<td>-170.0</td>
<td>245.4</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Table 6.3(b) – UNIFAC parameters for the interactions between groups: CH$_2$ encompasses the sub-groups CH$_3$, CH$_2$, CH and C; AC-CH$_2$ encompasses the AC-CH sub-group; CCOO encompasses the CCOO sub-group.*

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6.7 – Performance of the Sanchez-Lacombe EoS

The parameters presented above were used to model cloud-point curves (binodal curves) of the systems measured experimentally as well as to calculate activities and activity coefficients for these systems. In the following section the performance of the Sanchez-Lacombe equation of state for modelling VLE and LLE will be evaluated and discussed. Prior to LLE calculations on the systems studied in this work, two other polymer solutions systems were looked at and these will be presented first. The system polyethylene/n-pentane was used to check for the correct functioning and validity of the computational program. The system polystyrene/cyclohexane was also investigated briefly.

6.7.1 – Modelling Liquid-Liquid Phase Behaviour

6.7.1.1 – Polyethylene/n-Pentane

The liquid-liquid equilibrium of polyethylene/n-pentane solutions has been studied experimentally by Kiran and Zhuang (1992) and compared to predictions made by the Sanchez-Lacombe EoS by Xiong and Kiran (1994, 1995). Four polyethylene solutions of molecular weights $2.15 \times 10^3$, $1.64 \times 10^4$, $1.08 \times 10^5$ and $4.20 \times 10^5$ g/mol were studied. For polyethylene, the characteristic temperature, pressure and density are 521 K (based on solubility data for polyethylene in n-pentane), 359 MPa and 0.895 kg/m$^3$ respectively. For n-pentane, the characteristic temperature, pressure and density are 441 K, 310 MPa and 0.755 kg/m$^3$ respectively. Figure 6.7 shows the performance of the model in predicting the cloud-point curves for these systems at a temperature of 460 K, as a function of pressure. All curves have been calculated using an interaction parameter of value zero. The values of the upper critical solution pressures and critical polyethylene mass fractions obtained from the calculations in this work are compared to those calculated by Xiong and Kiran (1994, 1995) in table 6.4. Results compare well to those from the literature. Compared to the experimental data using a $k_{12}$ equal to zero results from the SL equation only agree for the lower molecular weight polyethylene. For the higher molecular weights $k_{12}$ needs to be fitted to the experimental data and Kiran et al.

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Table 6.4 - Comparison of experimental demixing pressures and critical compositions (Kiran and Zhuang, 1992) and calculated values using the Sanchez-Lacombe EoS for PE/n-pentane solutions of varying molecular weight. Literature values taken from Xiong and Kiran (1994).

<table>
<thead>
<tr>
<th>PE $M_w$ (g/mol)</th>
<th>Exptl.</th>
<th>Calc. (literature)</th>
<th>Calc. (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_c$ (MPa)</td>
<td>$w_{cPE}$</td>
<td>$P_c$ (MPa)</td>
</tr>
<tr>
<td>2,150</td>
<td>4.30</td>
<td>0.100</td>
<td>4.3</td>
</tr>
<tr>
<td>16,400</td>
<td>10.80</td>
<td>0.090</td>
<td>8.6</td>
</tr>
<tr>
<td>108,000</td>
<td>15.00</td>
<td>0.024</td>
<td>10.5</td>
</tr>
<tr>
<td>420,000</td>
<td>16.67</td>
<td>0.023</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Figure 6.7 - Variation of demixing pressures of PE/n-pentane solutions as a function of polymer composition and molecular weight at 460 K. Symbols are experimental data (Kiran and Zhuang, 1992) and solid lines are calculated binodal envelopes using the Sanchez-Lacombe EoS.
(1993) have shown that very good predictions can be obtain by using $k_{12}$ equal to 0.0130, 0.0172 and 0.0175 for the $1.64 \times 10^4$, $1.08 \times 10^5$ and $4.20 \times 10^5$ g/mol polyethylene solutions respectively. No further calculations were performed on this system since it does not constitute the system of interest in this work.

6.7.1.2 — Polystyrene/Cyclohexane

Cloud point curves for the well-characterised system, polystyrene/cyclohexane were calculated using the SL equation of state. As already shown in figure 2.4 (in chapter II), this system exhibits both upper and lower critical solution behaviour. The SL equation was used with characteristic temperature, pressure and density for polystyrene of 735 K, 357 MPa and 1105 kg/m$^3$ respectively (Sanchez and Lacombe, 1977). For cyclohexane the characteristic parameters used were 497K, 383 MPa and 902 kg/m$^3$ (Sanchez and Lacombe, 1976). Figure 6.8 shows the calculated binodal curves for a solution of PS with molecular weight 37,000 g/mol as a function of $k_{12}$, the interaction parameter. The Sanchez-Lacombe equation is capable of predicting both upper and lower critical solution temperatures depending on the interaction parameter. Furthermore, in the region of interaction parameters plotted, it is capable of predicting an hour-glass shaped liquid-liquid phase diagram. For this system the experimental LCST and UCST are 510.9 K and 285.6 K respectively and the corresponding critical PS weight fractions are 0.134 and 0.031 for the LCST and UCST respectively (Saeki et al., 1973). The predicted values using the SL equation are LCST = 437.4 K and UCST = 284.6 K with $k_{12}$ equal to -0.114 and 0.0041 respectively. The LCST deviates from the experimental value by 14.4% and it is the closest value that the model will achieve. In terms of the critical PS weight fractions, that predicted for the LCST is 0.0217 (a deviation of approximately 84 % from the experimental value) and for the UCST is 0.133 which is approximately 330 % higher than the experimental value.

Tables 6.5 (a) and 6.5 (b) present calculated values of the critical solution temperatures and critical polystyrene compositions for polystyrene solutions of differing molecular weights. Results from the SL equation are compared to the experimental data of Saeki et al. (1973). It can be seen that in general the agreement is better between experimental data and SL calculations for the upper critical solution
Figure 6.8 - Calculated binodal curves for the polystyrene (Mw = 37,000 g/mol)/cyclohexane system as a function of $k_{ij}$, the interaction parameter.
<table>
<thead>
<tr>
<th>PS $M_\phi$ (g/mol)</th>
<th>$k_{12}$</th>
<th>Calc. UCST (K)</th>
<th>Exptl. UCST (K)</th>
<th>Calc. $w_{cPS}$</th>
<th>Exptl. $w_{cPS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>37,000</td>
<td>0.00410</td>
<td>284.6</td>
<td>285.6</td>
<td>0.133</td>
<td>0.031</td>
</tr>
<tr>
<td>97,200</td>
<td>0.00341</td>
<td>293.8</td>
<td>293.5</td>
<td>0.082</td>
<td>0.110</td>
</tr>
<tr>
<td>200,000</td>
<td>0.00298</td>
<td>292.8</td>
<td>297.0</td>
<td>0.058</td>
<td>0.095</td>
</tr>
<tr>
<td>400,000</td>
<td>0.00268</td>
<td>290.4</td>
<td>300.3</td>
<td>0.043</td>
<td>0.062</td>
</tr>
<tr>
<td>670,000</td>
<td>0.00252</td>
<td>289.0</td>
<td>301.1</td>
<td>0.033</td>
<td>0.051</td>
</tr>
<tr>
<td>2,700,000</td>
<td>0.00226</td>
<td>287.3</td>
<td>304.2</td>
<td>0.018</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Table 6.5 (a) - Comparison of experimental upper critical solution temperatures and critical compositions (Saeki et al., 1973) and calculated values using the Sanchez-Lacombe EoS for PS/cyclohexane solutions of varying molecular weight. Also given are the fitted $k_{12}$ values.

<table>
<thead>
<tr>
<th>PS $M_\phi$ (g/mol)</th>
<th>$k_{12}$</th>
<th>Calc. LCST (K)</th>
<th>Exptl. LCST (K)</th>
<th>Calc. $w_{cPS}$</th>
<th>Exptl. $w_{cPS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>37,000</td>
<td>-0.1140</td>
<td>437.4</td>
<td>510.9</td>
<td>0.0217</td>
<td>0.136</td>
</tr>
<tr>
<td>97,200</td>
<td>-0.1210</td>
<td>432.0</td>
<td>502.1</td>
<td>0.0130</td>
<td>0.112</td>
</tr>
<tr>
<td>200,000</td>
<td>-0.1240</td>
<td>429.3</td>
<td>496.9</td>
<td>0.0092</td>
<td>0.086</td>
</tr>
<tr>
<td>400,000</td>
<td>-0.1241</td>
<td>427.6</td>
<td>494.7</td>
<td>0.0066</td>
<td>0.061</td>
</tr>
<tr>
<td>670,000</td>
<td>-0.1243</td>
<td>426.7</td>
<td>491.7</td>
<td>0.0053</td>
<td>0.034</td>
</tr>
<tr>
<td>2,700,000</td>
<td>-0.1265</td>
<td>425.2</td>
<td>488.6</td>
<td>0.0030</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Table 6.5 (b) - Comparison of experimental lower critical solution temperatures and critical compositions (Saeki et al., 1973) and calculated values using the Sanchez-Lacombe EoS for PS/cyclohexane solutions of varying molecular weight. Also given are the fitted $k_{12}$ values.
behaviour, although the calculated temperatures are not an increasing function of
molecular weight. Also, there is a slight dependence of the interaction parameter
with polymer molecular weight. For the lower critical solution behaviour the
calculated temperatures are always higher than experimental data and the dependence
on PS molecular weight is smaller than found experimentally. The molecular weight
dependence of the interaction parameter appears to be even smaller than for the
UCST case. In terms of the critical compositions, the SL model does not appear to
be capable of correctly positioning the binodal curves along the polymer
composition axis.

6.7.1.3 — Polystyrene / Cyclohexanol

Shown in figure 6.9 are the calculated binodal curves using the SL equation
of state with the solvent and polymer parameters given in table 6.2. The interaction
parameters have been fitted to best match the position of the experimental points.
As can be seen from the plot, these interaction parameter values give calculated
upper critical solution temperatures which are not in good agreement with the
turbidimetric data. Since an increase or decrease in the value of \( \kappa_{12} \) will shift the
curves up or down, trying to find a value that matches the UCST would shift the
curve downwards losing the fit of the curve to any of the experimental points. As
drawn, the experimental data are well-fitted using the given \( \kappa_{12} \) values but the UCST
and critical PS compositions are very much over predicted. The model predicts a
UCST of 354.9 K at 48.4 % polystyrene of molecular weight 4,215 g/mol, a UCST of
365.8 K at 42.5 % polystyrene of molecular weight 78,800 g/mol and a UCST of
367.8 K at 41.7 % polystyrene of molecular weight 849,000 g/mol in solution with
cyclohexanol. It is also interesting to notice the shape of the calculated binodals.
One would expect binodals for this system to have a UCST tilted towards the
solvent-rich phase and this does not appear to be the case here. Nevertheless, the
model does correctly predict the existence of upper critical solution behaviour and
that the UCST’s increase as a function of increasing polystyrene molecular weight.
Figure 6.9 — Performance of SL model for PS/cyclohexanol solutions as a function of polymer composition and molecular weight. Symbols are experimental data (this work) and solid lines are calculated binodal envelopes.

Figure 6.10 — Performance of SL model for PMMA/cyclohexanol solutions as a function of polymer composition and molecular weight. Symbols are experimental data (this work) and solid lines are calculated binodal envelopes.
6.7.1.4 — Poly(methyl methacrylate)/Cyclohexanol

Binodal curves for the PMMA/cyclohexanol system have been calculated using the SL equation of state parameters given in table 6.2. The curves and data obtained by turbidimetry are shown plotted in figure 6.10. The agreement of the upper critical solution temperatures is much better, after fitting the \( k_{12} \) interaction parameter, than that for the PS/cyclohexanol system. The dependence on molecular weight is also correctly predicted. For a molecular weight of 68,000 g/mol the SL model predicts a UCST of 346.3 K at 7.1\% PMMA. For a molecular weight of 280,000 g/mol the SL model predicts a UCST of 350.6 K at 3.6 \% PMMA and for a molecular weight of 992,200 g/mol, the SL equation of state predicts a UCST of 350.6 K at 2.0 \% PMMA in solution with cyclohexanol.

6.7.1.5 — Poly(styrene-methyl methacrylate) Copolymer/Cyclohexanol

The phase behaviour of only one molecular weight of PS-PMMA copolymer (monodisperse, \( M_w = 125,000 \) g/mol and 53.1 \% PMMA) in solution with cyclohexanol was measured experimentally. The data are plotted in figure 6.11 against the binodal curve obtained using the SL equation with the parameters given in table 6.2 and using a \( k_{12} \) value of 0.01102. The agreement appears to be much better than that for the homopolymers in solution with the same solvent. The experimental UCST is 345.9 K compared with a predicted 345.3 K. Similarly, the critical concentration of copolymer is 9.7 \% experimentally and 13.1 \% from the model. Furthermore, the shape of the curve is as flat as is expected in this type of systems.

6.7.1.6 — Difficulties with LLE Calculations

Obtaining the correct equilibrium compositions was not always trivial, as mentioned previously in section 6.4.3. When the polymer composition in the solvent-rich phase became very small, the solver either diverged from the solution or
Figure 6.11 – Performance of SL model for PS-PMMA/cyclohexanol solutions as a function of polymer composition and molecular weight. Symbols are experimental data (this work) and solid lines are calculated binodal envelopes.

Figure 6.12 – Plot of Gibbs free energy of mixing functions as a function of composition for PS ($M_n = 4,215$ g/mol)/cyclohexanol using the SL EoS at 208.03 K and $k_{12} = 0.01$: (—) $\Delta G_{\text{mix}}$ calculated from analytical expression, (- - -) $(\Delta G_{\text{mix}})'$ calculated from analytical expression and (---) $\Delta G_{\text{mix}}$ calculated from residual properties.
returned the trivial solution. Trial and error can be very tedious and many times unsuccessful, but since the SL model gives an analytical expression for the second derivative of the Gibbs free energy it could be plotted as a function of composition. The points at which the function is equal to zero correspond to the spinodal compositions in each of the liquid phases, if there are indeed two phases present. The spinodals could be used as guesses in the solver although for polymer/solvent systems they are not necessarily close to the sought binodal compositions.

An example where such a problem was encountered is shown for the PS ($M_w = 4,215$ g/mol) and cyclohexanol at 208.0 K and with $k_{12} = 0.02$. A number of initial composition guesses were used and no phase-solution was found by the solver. The easiest way to check if this was indeed true is by finding the spinodal compositions from the analytical expression of the second derivative of the Gibbs free energy of mixing (equation 3.23). It has been plotted against the solvent weight fraction for this system, in figure 6.12 as the dotted line. This revealed that at this temperature there should be a two-phase solution, since the curve crosses the y-axis at zero at the two spinodal compositions. Also plotted, as the solid line, is the Gibbs free energy of mixing which correspondingly should show two minima, at the binodal compositions. Only one is easy to visualise, that in the polymer-rich phase, but nevertheless another minima could between $\nu_{\text{cyclohexanol}} = 0.9-1.0$. According to this analysis the solver should be returning a two-phase solution.

The Gibbs free energy of mixing can also be calculated through an alternative route, from the expression of the residual Gibbs free energy (equation 3.131 in chapter III) as follows:

$$
\Delta G_{\text{mix}} = G^* - \sum x_i G_i^{\text{res}} + kT \sum x_i \ln x_i
$$

(6.41)

This is also plotted in figure 6.12. It is obvious from the plot that the results are numerically different. In this curve there could also be a second minima at high concentrations of solvent which are not necessarily visible either. In order to check if indeed there is a second minima in the curves in a solvent-rich phase, the behaviour of the Gibbs free energy of mixing in the interval of cyclohexanol composition 0.9 to 1.0 is examined closely by looking at the values taking extremely
Figure 6.13 (a) - Change in the Gibbs free energy of mixing as a function of solvent composition for the system PS ($M_w = 4,215$ g/mol)/cyclohexanol, calculated from residual properties for the SL EoS.

Figure 6.13 (b) - Change in the Gibbs free energy of mixing as a function of solvent composition for the system PS ($M_w = 4,215$ g/mol)/cyclohexanol, calculated from the SL model analytical expression.
small steps in the composition. As can be seen from figures 6.13 (a) and (b), calculations using the analytical expression $\Delta G_{\text{mix}}$ give a solution at 0.9995 but if calculated using the residual properties, no two-phase solution is found, which is why the solver returned the trivial solution.

So, the solver was correct in predicting a one-phase solution and proved the inconsistency in the model which was already discussed in section 3.5. The analytical expression of the second derivative of the Gibbs free energy is inconsistent with that for a perfect gas could and is responsible for the incorrect prediction of a two-phase solution. The expressions for the fugacity coefficients derived in section 6.4.4 and used in the solver are consistent with the perfect gas equations and therefore the results returned by the solver, in this case a one-phase solution, were regarded as correct.

6.7.2 — Modelling Vapour-Liquid Phase Behaviour

Activities and weight fraction activity coefficients of cyclohexanol have been calculated using equations (6.30), (6.33) and (6.34) at infinite dilution and at finite concentrations of solvent. The results will be presented in the following section. Initially, the interaction parameter was chosen to be the same as that obtained from the liquid-liquid equilibria calculations but that resulted in over predictions of the activity coefficients for all three systems. Consequently, the effect of changing $k_{12}$ was investigated to best agree with the experimental data from the inverse gas chromatography experiments.

6.7.2.1 — Infinite Dilution

The weight fraction activity coefficients (WFAC's) of cyclohexanol have been calculated using the SL equation and the same interaction parameters obtained from the LLE modelling. The results are plotted in figure 6.14 from which it is clear that these $k_{12}$ values highly over predict the activity coefficients of cyclohexanol in all three polymers. Also, using these parameters result in the behaviour of the copolymer to be somewhere in between that of the homopolymer solutions which is
not the case experimentally. This was to be expected since the copolymer parameters lay in between those of the two pure homopolymer parameters. In addition, the activity coefficients of cyclohexanol in polystyrene are calculated to be higher than those of cyclohexanol in PMMA (also experimentally found to be the opposite). Nevertheless, the decrease of cyclohexanol WFAC's at infinite dilution as a function of increasing temperature is predicted by the SL model. Lacombe and Sanchez (1976) have shown that actually a single temperature independent interaction parameter could be used for simultaneous description of vapour-liquid and liquid-liquid phased behaviour in the system carbon disulphide/acetone which show a UCST at around 230 K and forms an azeotrope at 354 K. This does not seem to be the case here. The model could be used to fit a new VLE $k_{12}$ value to try to improve the prediction. Figure 6.15 shows the experimental WFACs at infinite dilution for all three systems investigated plotted against curves calculated using the SL equation at different values of the interaction parameters. In all three cases in order to get values of the WFAC which are close to the experimental data, $k_{12}$ needs to be negative, implying that the polymer-solvent interactions are stronger than the polymer-
Figure 6.15 — Weight fraction activity coefficients at infinite dilution for (a) PS (Mₐ = 200,000 g/mol), (b) PMMA (Mₐ = 996,000 g/mol) and (c) PS-co-PMMA (Mₐ = 125,000 g/mol)/cyclohexanol solutions. Symbols are the experimental data (this work). Lines are results using the Sanchez-Lacombe equation of state at various interaction parameters.
polymer or solvent-solvent interactions, which is the opposite to what was found with the positive $k_{12}$ values of the LLE calculations. Furthermore, at these negative $k_{12}$ values, the dependence of the weight fraction activity coefficients on temperature is not correctly modelled. As $k_{12}$ decreases, WFAC's start increasing with temperature. Nevertheless, negative values of the interaction parameter might be correct for the PMMA/cyclohexanol and the copolymer/cyclohexanol systems since hydrogen bonding is expected to be present, thus increasing the strength of polymer-solvent interactions over the pure component interactions. The Sanchez-Lacombe equation which has combining rules which assume random mixing may be thought as an inappropriate tool for modelling mixtures that exhibit specific interactions such as hydrogen bonding, and this is confirmed by these results.

6.7.2.2 — Finite Concentrations of Solvent

Similar conclusions can be drawn from comparing SL calculations for weight fraction activity coefficients of cyclohexanol at finite concentrations in the solution. Figure 6.16 shows the weight fraction activity coefficients at 453.15 K as a function of cyclohexanol content in solution. The weight fraction coefficients in all three systems are over predicted and opposite to experimental findings the WFAC of cyclohexanol in PS is modelled to be higher than that in PMMA. Also, the curve for the copolymer lies in between those of the homopolymer solutions.

As a function of temperature, experimental results show that the weight fraction activity coefficient falls significantly with increasing temperature and so does the activity. The Sanchez-Lacombe fails to predict this as shown with an example in figures 6.17 and 6.18, for the PMMA/cyclohexanol system. As can be seen, the curves at 453.15 K and at 473.15 K overlap each other. Although not presented, exactly the same behaviour is observed in the PS and PS/PMMA copolymer systems.

It was shown for the infinite dilution case that changing the values of the interaction parameters, making them negative, slightly improved the agreement between the model and the experimental data. The effect of varying $k_{12}$ on the weight fraction coefficients and activities of cyclohexanol in the PS-co-PMMA solution is shown in figures 6.19 - 6.22. The agreement is highly improved if $k_{12}$ is set to -0.0110 for modelling both the activities and activity coefficients as a function
Figure 6.16 – Composition dependence of cyclohexanol WFAC's in PS, PMMA and PS (40%)-co-PMMA at 453.15 K. Symbols are experimental data (this work) and solid lines are calculated using SL equation of state with LLE fitted $k_{12}$ parameters.

Figure 6.17 – Composition dependence of cyclohexanol WFAC's in PMMA ($M_w = 996$ kg/mol) at 453.15 K and 473.15 K. Symbols are experimental data (this work) and solid lines are calculated using SL equation of state with LLE fitted $k_{12}$ parameters ($0.00725$).
of composition at 433.15 K, but this interaction parameter value is not good for results 453.15 K. Therefore, not only does it appear that the SL model requires different interaction parameters for VLE and LLE calculations, but also it might be necessary to make it temperature dependent which will introduce one more parameter.

6.8 – Performance of UNIFAC-FV

A similar analysis has been performed using this model to test its capability in modelling both VLE and LLE of polymer solutions. The group parameters were presented in section 6.6.2 and the equations were presented in chapter III. Comparison of UNIFAC-FV predictions of cyclohexanol activity coefficients at infinite dilution and at finite concentrations with data obtained from IGC will be presented first, for all three systems. Predictions for liquid-liquid phase behaviour will follow.
Figure 6.19 – Composition dependence of the WFAC of cyclohexanol in PS-co-PMMA ($M_n = 125$ kg/mol) at 433.15 K. Symbols are experimental data (this work) and solid lines are calculated using SL equation of state.

Figure 6.20 – Composition dependence of the WFAC of cyclohexanol in PS-co-PMMA ($M_n = 125$ kg/mol) at 453.15 K. Symbols are experimental data (this work) and solid lines are calculated using SL equation of state.
Figure 6.21 – Composition dependence of the activities of cyclohexanol in PS-ω-PMMA ($M_w = 125$ kg/mol) at 433.15 K. Symbols are experimental data (this work) and solid lines are calculated using SL equation of state.

Figure 6.22 – Composition dependence of the activities of cyclohexanol in PS-ω-PMMA ($M_w = 125$ kg/mol) at 453.15 K. Symbols are experimental data (this work) and solid lines are calculated using SL equation of state.
6.8.1 — Modelling Vapour-Liquid Phase Behaviour

6.8.1.1 — Infinite Dilution

Figure 6.23 shows the predicted WFAC’s of cyclohexanol at infinite dilution in the three polymer solutions. For all three, the predictions are better than those obtained from the Sanchez-Lacombe equation of state. The PMMA/cyclohexanol systems is the system which is best predicted with an average deviation of around 8% in the WFAC at infinite dilution. The PS/cyclohexanol solution is the worst with an average deviation of around 80%. The dependence of WFAC with increasing temperature is predicted correctly, but the relationship between VLE behaviour in the three systems is not. UNIFAC-FV predicts that the behaviour of the copolymer in solution lies in between that of its constituent homopolymer solutions in the same solvent. In addition, it incorrectly predicts that the results for the PMMA/cyclohexanol system should be higher than those for the PS/cyclohexanol solution.
6.8.1.2 — Finite Concentrations of Solvent

Figures 6.24 and 6.25 show the predictions of the weight fraction activity coefficients and activities of cyclohexanol using the UNIFAC-FV model, at finite concentrations of solvent and at 453.15 K. This model under predicts the weight fraction activity coefficients of cyclohexanol in the PMMA solution but over predicts them for the other two systems. In addition, the predicted dependence on temperature is very small compared to that measured experimentally for the three systems. An example is shown in figures 6.26 and 6.27 for the PS/cyclohexanol system. For all systems though, UNIFAC-FV correctly predicts that the activities and activity coefficients increase as a function of decreasing temperature at the same concentration of solvent and polymer in the solution.

6.8.1.3 — UNIFAC and UNIFAC-FV

To apply the UNIFAC group contribution method to polymer solutions, Oishi and Prausnitz (1978) recognised the need for an additional term into the formulation for the activity of the solvent, a free-volume term that would account for size differences between polymer and solvent. This improvement with the addition of this extra term is shown in Figure 6.28. The system PS ($M_w = 200,000$ g.mol$^{-1}$)/cyclohexanol is considered. Figure 6.28 compares the predictions of the original UNIFAC model (without the free volume) and the newer UNIFAC-FV model to the experimental measurements obtained using the IGC technique. As shown, both models over predict the values for the weight fraction activity coefficients of cyclohexanol but UNIFAC-FV improves the predictions greatly. The same improvement is observed for the dependence of the weight fraction activity coefficients of cyclohexanol on the composition of the solution, as shown in figure 6.29, at a temperature of 453.15 K. Both models over predict the results but UNIFAC-FV is closer to the experimental values.
Figure 6.24 — Composition dependence of cyclohexanol UNIFAC's in PS, PMMA and PS (40%)-co-PMMA at 453.15 K. Symbols are experimental data (this work) and solid lines are calculated using UNIFAC-FV.

Figure 6.25 — Composition dependence of the activity of cyclohexanol in PS, PMMA and PS (40%)-co-PMMA at 453.15 K. Symbols are experimental data (this work) and solid lines are calculated using UNIFAC-FV.
Figure 6.26 – Composition dependence of the WFAC of cyclohexanol in PS \((M_v = 200,000 \text{ g/mol})\) at 453.15 K and 493.15 K. Symbols are experimental data (this work) and solid lines are calculated using UNIFAC-FV.

Figure 6.27 – Composition dependence of the activity of cyclohexanol in PS \((M_v = 200,000 \text{ g/mol})\) at 453.15 K and 493.15 K. Symbols are experimental data (this work) and solid lines are calculated using UNIFAC-FV.
6.8.2 – Modelling Liquid-Liquid Phase Behaviour

UNIFAC-FV was used to predict the liquid-liquid phase splits in the three systems. Unfortunately, it became somewhat difficult at times to find a solution because of the small polymer activities encountered (for example \( a_2 = 1\times10^{-10} \)) and also because of the large activity differences between polymer and solvent. In many cases, the trivial solutions were returned and graphical checks were necessary to ensure that there was no 2-phase solution to the problem (as described in section 6.7.1.6). Unfortunately, it was found that UNIFAC-FV fails to predict a phase-split for the systems PMMA/cyclohexanol or PS-co-PMMA/cyclohexanol but it does for the PS/cyclohexanol solutions. Given the failure in these cases, the capability of the original UNIFAC model was tested too. The predictions of these models are presented in what follows.

6.8.2.1 – Polystyrene/Cyclohexanol

Figure 6.30 shows the predictions using the original UNIFAC for three solutions of cyclohexanol and PS of three different molecular weights, 4215 g/mol, 78800 g/mol and 849000 g/mol. Although the values of the cloud-point temperatures are highly over predicted (maximum deviation is around 160%), the binodal curve dependence on the molecular weight of the polymer is correctly predicted. Figure 6.31 shows the results using UNIFAC-FV. The solid points are the experimental data from turbidimetric measurements and the crosses and lines are the values obtained using UNIFAC-FV. The crosses have been included to show what temperature calculations did work. As we approached the top of the binodal curves, which turn very flat, no solution was obtained. Thus we conclude that the model does not work close to the critical solution temperature. It is difficult to guess where the upper critical solution temperature will lie but it appears as if the PS (\( M_w = 78,800 \) g/mol)/cyclohexanol systems is in good agreement whereas the UCST for the higher molecular weight PS solution is greatly over predicted.
Figure 6.28 – Temperature dependence of the weight fraction activity coefficient of cyclohexanol in PS ($M_w = 200,000$ g/mol). Symbols are experimental data (this work). Solid line are calculated values using the original UNIFAC, dashed line are calculated values with UNIFAC-FV.

Figure 6.29 – Composition dependence of the weight fraction activity coefficient of cyclohexanol in PS ($M_w = 200,000$ g/mol) at $453.15$ K. Symbols are experimental data (this work). Solid line are calculated values using the original UNIFAC, dashed line are calculated values with UNIFAC-FV.
Figure 6.30 – Liquid-liquid phase diagram for PS/cyclohexanol solutions as a function of PS molecular weight. Symbols are turbidimetry experimental data (this work). Solid lines represent calculated values using the original UNIFAC model.

Figure 6.31 – Liquid-liquid phase diagram for PS/cyclohexanol solutions as a function of PS molecular weight. Symbols are turbidimetry experimental data (this work). Solid lines join the crosses which are calculated values using the UNIFAC-FV model.
6.8.2.2 — Poly(methyl methacrylate)/Cyclohexanol

As already pointed out, UNIFAC-FV failed to find a 2-phase solution for all three molecular weights of PMMA in solution with cyclohexanol. On the other hand, binodal curves could be calculated with the original UNIFAC model and are plotted against the measured cloud point temperatures and compositions in figure 6.32. UNIFAC over predicts the UCST's for all three solutions, although the difference deviation is much smaller (maximum deviation, for the highest molecular weight solution is around 40%) than in the PS/cyclohexanol case. The model correctly predicts the molecular weight dependence of the binodal curves.

6.8.2.2 — Poly(styrene-co-methyl methacrylate)/Cyclohexanol

The binodal curve for the PS-PMMA copolymer solution in cyclohexanol could not be predicted by the UNIFAC-FV model either. However, UNIFAC does find a phase-split although the UCST is around 34% higher than measured from turbidimetry. The phase diagram is shown in figure 6.33.

6.8.3 — Calculations Using UNIFAC-FV

A possible reason for the inability of UNIFAC-FV in calculating liquid-liquid equilibrium in polymer solutions as compared with the original UNIFAC model, could be the effect of the pure component molar volumes. The sensitivity of the model to the volume has been recognised as being of great importance (Pappa et al., 1999; Lindvig et al., 2002). Lindvig et al. (2002) have recently found that UNIFAC-FV is significantly more sensitive to the volume values than for example the entropic-FV model (another activity coefficient model) and they found that for very dense polymers it may be even impossible to carry out a calculation with UNIFAC-FV. This will happen if the hard-core volume exceeds the actual volume (the hard-core volume is proportional to the van der Waals volume where the proportionality constant has a value of 1.28). The calculation of binodal curves involves in many cases, coverage of a large range of temperatures and unfortunately UNIFAC-FV has
Figure 6.32 – Liquid-liquid phase diagram for PMMA/cyclohexanol solutions as a function of PMMA molecular weight. Symbols are turbidimetry experimental data (this work). Solid lines are calculated values using the original UNIFAC model.

Figure 6.33 – Liquid-liquid phase diagram for PS-MMA copolymer \( (M_w = 58,500 \text{ g/mol}) \)/cyclohexanol solution. Symbols are turbidimetry experimental data (this work). Solid lines are calculated values using the original UNIFAC model.
a free-volume contribution in the model which requires knowledge of pure component molar volumes as a function of temperature, which have to be supplied externally. When experimental values are not available, these volumes need to be estimated in some way. Different authors have chosen different methods to estimate volumes if data is not available, the two most commonly used are the more recent GCVOL method (Elbro et al., 1991) which is a group-contribution method. Another simpler group-contribution method is that proposed by van Krevelen (1990). For the calculations in this work, cyclohexanol experimental densities were available in the range 323.15 – 473.15 K (Novak et al., 1960; Steel et al., 1997) but polymer densities were obtained from the fitted Tait equations (Rodgers, 1993). They are valid in general from 383.15 – 453.15 K (see section 5.3.3 for details) and although they are fitted to experimental data, there will be some uncertainty in the results.

A second reason was recognised by Lindvig et al. (2002). They have also found that for polyacrylates where there is a CHCOO group in the contributions, results were not that good and could be improved by splitting this group into a CH and a COO group. Finally, the effect of the value of the ε parameter, the external degree of freedom parameter also present in the free-volume term could have a significant effect on the results. For solvents it is usually taken to be 1.1 and Oishi and Prausnitz (1978) stated that the value should be higher than that for polymer molecules but did not specify a value. Different authors have proposed different methods and that used here was the same as used by Belfiore et al. (1988) based on Flory’s equation of state definition (see section 3.178). Changing the calculation method here might indeed change the behaviour of the model.

None of these effects have been looked at in this work and are proposed for further study and understanding the failure of this model in predicting the systems here studied.

6.9 – Conclusions

In this chapter the computational aspects involved in modelling polymer solution phase behaviour have been discussed. An algorithm has been described and difficulties encountered for the calculations in these systems presented. Three
polymer solutions have been modelled using two thermodynamic approaches, the Sanchez-Lacombe equation of state and the UNIFAC-FV activity coefficient model. The solutions modelled contained PMMA, PS and their copolymer in a common solvent cyclohexanol.

In terms of liquid-liquid phase behaviour, the Sanchez-Lacombe equation predicts an upper critical solution phase-split in all three systems and the UCST can be fitted to best agree with experimental results by changing the value of the interaction parameter. Unfortunately, the composition of the solution at which this takes place does not agree with the experimental data in any of the systems. The shape of the calculated binodal curves is less flat than measured for the two homopolymer/solvent systems. In both cases the SL equation predicts the correct molecular weight dependence for the binodal curves. For the copolymer/cyclohexanol solution the agreement in both UCST and shape of the binodal curve is much better. It was found that the binodal curves are rather sensitive to the value of the interaction parameter, which for the three systems studied is small and positive. The UNIFAC-FV model on the other hand, is only capable of predicting a two-phase solution for the PS/cyclohexanol case and even for this system it fails to compute when approaching the upper critical solution temperature. In comparison, the original version of UNIFAC which does not contain the free-volume term, added to account for the size differences between polymer and solvent molecules, does predict phase-splits in all three systems although the UCST is highly over predicted. Possible reasons for the poor behaviour of the UNIFAC-FV model are the uncertainty introduced in the variables of the free volume term, namely the molar volume of the pure components at the specified temperature and the value of the external degree of freedom parameter for the polymers. The model has actually been found to be very sensitive to values of the molar volumes of the pure components by other authors. The failure to predict a phase-split in the PMMA and copolymer systems might be associated with using the CHCOO group contributions instead of dividing it into a CH and a COO group. No further investigation was carried out though to make any valid conclusions. Finally, like the SL equation, the original UNIFAC predicts the correct dependence of the binodal curves on polymer molecular weight, i.e. in systems that exhibit upper critical solution behaviour, the UCST increases with increasing molecular weight, tending towards a specific temperature at zero polymer concentration, referred to as the theta temperature.
In terms of activity coefficients and activities of cyclohexanol, both models appear to over predict the experimental data both at infinite dilution and at finite concentrations of solvent. In general UNIFAC-FV agrees better with the measurements from the inverse gas chromatography experiments, as expected since it is an activity coefficient model. The SL fails to predict comparable temperature dependence to the results at finite concentrations of solvent, whereas the UNIFAC-FV model does. Also, improvement of calculated values from the SL equation can be achieved by changing the value of the interaction parameter, although this means making it negative which is the opposite to what was found with the liquid-liquid phase diagrams. Finally, neither model can predict the fact that the random copolymer solution activities are not in between the two homopolymer/solvent systems as was found experimentally. In the case of the SL equation of state it is expected since the parameters used for the copolymer were calculated from a linear dependence on homopolymer content. To differentiate between structural influences on thermodynamic behaviour, a model that distinguishes between the structures of the polymers in solution is required. Furthermore, cyclohexanol is a polar molecular that has specific interactions which neither model has incorporated into their equations. It is not surprising therefore that the agreement between calculated phase behaviour and experimental phase behaviour is not perfect. Given this, the performance of both models was found to be satisfactory and as was to be expected, the equation of state model performs better in modelling liquid-liquid phase behaviour whereas the group-contribution model performs better predicting vapour-liquid phase behaviour.
CONCLUSIONS

This work resulted from the need for understanding better how polymer molecules behave in the presence of a low-molecular weight solvent and for developing thermodynamic models that are able to describe accurately their behaviour. In doing this, three aims were pursued:

(1) To obtain experimental data on liquid-liquid and vapour-liquid equilibrium on various polymer/solvent systems.
(2) To develop a suitable computational algorithm to solve thermodynamic models and generate LLE and VLE predictions.
(3) To compare experimental and computational results and in this way test the validity and applicability of the thermodynamic models.

To achieve these goals, two common polymers, polystyrene and poly(methyl methacrylate), were chosen together with a common solvent, cyclohexanol. In addition, two of the copolymers, a block and a random copolymer, were investigated in the same solvent, allowing us to test further the capability of the thermodynamics models for such systems. The models investigated were the Sanchez-Lacombe equation of state and the UNIFAC-free volume activity coefficient model.
A turbidimeter was constructed to measure cloud-point temperatures of monodisperse polymers in solution at the solvent vapour pressure, as a function of composition. Operation was limited to 523 K and 30 MPa, and the maximum polymer content achieved by weight was 25% due to volume limitations. Upper critical solution behaviour was observed in all three systems and the UCST's were very close to each other (which agree well with the literature). Cloud-point curves appear to be very flat in shape especially for the PMMA and PS-co-PMMA systems. Three molecular weights of the homopolymers were investigated and the expected dependence resulted, i.e. UCST increases with increasing polymer molecular weight. The block copolymer curve lies in between those for the homopolymers of the same molecular weight as expected. This type of copolymer can be considered as nearly a mixture of PS and PMMA chains since the units are well segregated: the chain structure being -(PS)_m-(PMMA)_n- with m and n very large. Hence the behaviour of the resulting polymer will lie somewhere in between that of its constituent homopolymers, and is to be expected to be a function of the composition of each of these in the copolymer. The observed behaviour is correctly predicted by the SL equation of state, almost certainly due to the fact that the copolymer pure component equation of state parameters were calculated from the homopolymer parameters and the composition of the copolymer. This model correctly predicts the existence of a UCST behaviour in all three polymer solutions as well as the molecular weight dependence of the cloud-point curves. The binary interaction parameter was fitted to successfully predict the UCST's of all systems however not the critical compositions. In addition, the shape of the predicted curves is not as flat as found experimentally, except for the copolymer/solvent system. In general, it was found that the model results for LLE are extremely sensitive to the value of the binary interaction parameter, \( k_{12} \). For example, in the PMMA \( (M_w = 68 \text{ kg/mol}) / \text{cyclohexanol} \) system, a change of \( k_{12} \) from 0.0085 to 0.0090 leads to a change from hour-glass behaviour to UCST behaviour, and even more extreme, is the case of the PS \( (M_w = 37 \text{ kg/mol}) / \text{cyclohexane} \) system, where changing \( k_{12} \) from a value of 0.0045 to 0.0041 results in a similar change of behaviour and a change of \( k_{12} \) from 0.00000 to -0.00001 leads to a change from UCST to LCST. This shows the ill-conditioned nature of the problem: a small error in the input parameters will result in a large error in the results.
The UNIFAC-FV model is unable to predict any phase-split in the PMMA or copolymer systems, and even for the PS solution the UCST appears to be significantly higher than the experimental value given that it fails to compute as the critical temperature is approached. UNIFAC-FV is a modification of the original UNIFAC model and has an additional free-volume contribution which accounts for the differences in size between polymer and solvent molecules. With this term come added variables which lead to inaccuracies. First an accurate knowledge of the specific volumes of the polymer and solvent as a function of temperature and pressure are necessary and, secondly, the correct calculation of the external degrees of freedom parameter is required. Unfortunately, there is as yet no consensus amongst the research community on one formulation of this parameter and it is a topic which requires closer examination. The addition of these two inaccuracies is confirmed by the fact that the original version of UNIFAC is capable of predicting a phase-split in all three systems although the critical temperatures are highly over predicted.

In terms of VLE, partition coefficients were measured using an inverse gas chromatography set-up at the Pennsylvania State University, USA. Measurements were taken at infinite dilution and at finite concentrations of solvent using the elution on a plateau technique. Capillary columns were used and the data analysis using the capillary column IGC model originally developed by Macris (1979). From this, weight fraction activity coefficients as well as information of the diffusion of the solvent in the polymers were extracted from the measured data. The model is limited to measurements at temperatures above the glass transition temperature of the polymers as highly asymmetric peaks arise at lower temperatures. The model could be improved by including terms accounting with the behaviour at these lower temperatures. In the measured temperature range, 383.15-493.15K, the activity coefficients of cyclohexanol in all three polymers decreases as a function of increasing temperature, as in many common polymers. The solubility of cyclohexanol in PMMA is greater than PS as a result of the strong hydrogen bonding between molecules, and furthermore the solubility in the random copolymer is greater than in either two constituent polymers. This can be attributed to the even stronger interactions between copolymer and solvent molecules. Since PMMA has a polar end, PS has a non-polar end and cyclohexanol has both types of sites, solvent molecules can easily accommodate themselves in between the polymer chains. In
addition, the interactions between the ester group in the PMMA units will form strong hydrogen bonds with the alcohol group in the cyclohexanol. The same enhanced solubility was observed at finite concentrations. The maximum achieved concentration of solvent in the polymer was ca. 30% and was limited by the high boiling point of the solvent and the column temperature (affected by the glass transition temperature limitation for the analysis of the elution peaks). Weight fraction activity coefficients at a specified temperature decreased with increasing solvent content in the polymer. Two very different molecular weights of PMMA, 15kg/mol and 996 kg/mol were investigated to check for any effect of molecular weight on the VLE results. Although the difference in activity coefficients can be considered as significant, a more in depth study should be performed.

These results were compared to results from both models. Both models over predict the activity coefficients although UNIFAC-FV agrees better, as expected since it is an activity coefficient model. In addition it predicts the correct temperature dependence which is not achieved by the SL equation. In order for the SL to get close to the experimental data, binary interaction parameters need to be re-fitted and this generates negative values which is the opposite to that found for the LLE fittings. Finally, neither model is capable of predicting the enhanced solubility of cyclohexanol in the random copolymer. In the case of the SL equation it is expected following the calculation method for the pure copolymer equation of state parameters. To differentiate the effect of structural differences on thermodynamic behaviour, a model able to use information about these structural differences is required. Moreover, as already mentioned, cyclohexanol and PMMA molecules interact very strongly as a consequence of the hydrogen bonds, and neither of the two models tested include any such contribution in their equations. This recognised, neither model performs too poorly.

In addition to the thermodynamic information on these systems, the model used for analysis the data form the inverse gas chromatography also provided us with information about the diffusion of cyclohexanol in the homopolymers versus the copolymer. Unlike thermodynamic behaviour, the diffusion coefficient of any copolymer, being a block or a random one, generally depends on the concentration of the constituent homopolymers, since the glass transition temperature for a copolymer generally falls in between those of the parent polymers. The diffusion of a solvent in a polymer, i.e. the possibility of cyclohexanol molecules making their way
into the polymer structure depends mainly on the available empty space or free volume, between the polymer chains. Above the glass transition temperature polymer molecules can move relatively easily so that the solvent molecules can accommodate themselves. But as the temperature is lowered, the movement becomes inhibited, until the chains cannot move further due to the "freezing" of their motion when a glass is formed. In this work, $T_g^\text{PMMA} > T_g^\text{PS-co-PMMA} > T_g^\text{PS}$ and so the diffusion coefficients of the cyclohexanol in PS-co-PMMA will lie in between those of the homopolymers. This has been confirmed experimentally.

As can be seen from this work, although there are very successful and convenient methods for determining liquid-liquid and vapour-liquid equilibrium behaviour of these long-chain molecules in solution experimentally, there is still no reliable and accurate thermodynamic model which can describe such observed behaviour in these complex systems. The Sanchez-Lacombe equation of state like other equations that contain binary interaction parameters, requires fitting of these to binary system experimental data. Since this requires experimental work, it contradicts the purpose of using a thermodynamic model. Furthermore, the model presents significant computational challenges owing to the complexity of the systems studied and the model itself. For instance, even solving for density roots is not straightforward. In this work, some computational difficulties have been addressed. It has been shown that a flash calculation procedure can be used to solve the phase behaviour problem, by simultaneously solving the material balances, the equilibrium equations and the composition constraint. On the other hand, UNIFAC-FV, being a predictive model, might appear to be more attractive since it only requires knowledge of the chemical structure of the polymer and solvent molecules and has no added complications associated with fitting binary interaction parameters. Unfortunately, although it is successful predicting VLE behaviour, it has been shown in this work to be poor at predicting LLE behaviour. Improvements on equations of state have been applied such as including temperature and/or composition dependencies in the binary interaction parameters, leading in many cases to better agreement with experimental data but increasing the number of parameters to be fitted. For UNIFAC-FV a closer look at the parameters that might be bringing in some errors is needed. In addition the treatment of the ester group in the PMMA repeat units should be investigated. Maybe the group should not be treated as single $-\text{COOCH}_3$, but as two separate group contributions, one from the $-\text{CH}_3$ group and another from
the –COO group. In terms of structural considerations, an alternative route to calculating the pure component equation of state parameters should be considered that will incorporate the structure of the molecules in some way. Alternatively, a more structure-based equation such as those based on hard-sphere formulations might prove to be more appropriate.

There are many thermodynamic models in the literature for modelling/predicting the phase behaviour in complex systems, but there are many more possible polymer/solvent combinations. Even the models that work for some systems require experimental data to determine the parameters and are not therefore fully predictive for binary mixtures. Thus we are forced to the pessimistic conclusion that no existing model has truly predictive capabilities for the class of systems investigated in this work.
BIBLIOGRAPHY


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Van Krevelen D. W., Properties of polymers. Their correlation with chemical structure; their numerical estimation and prediction from additive group contributions, Elsevier Scientific, Amsterdam (1992).


Appendix A

DERIVATION OF SANCHEZ-LACOMBE EQUATION OF STATE

A – The Sanchez-Lacombe Equation of State

An expression for the Gibbs free energy at specified temperature and pressure for the Sanchez-Lacombe equation of state can be obtained by deriving expressions for the entropy, energy and volume of the system and using the following equation:

\[ G = U + PV - TS \] (A.1)

A.1 – Entropy of mixing

A lattice such as that shown in figure A1.1 is used to count the number of configurations \( \Omega \) available to a system of \( N_1 r_1 \)-mers, \( N_2 r_2 \)-mers, ..., \( N_k r_k \)-mers and \( N_0 \) empty sites (holes), where an \( r \)-mer is defined as a molecule that occupies \( r \) sites on a lattice of co-ordination number \( z \). The number of configurations available in
the system is approximately given by Guggenheim-Huggins-Miller (Guggenheim, 1952; Sanchez and Lacombe, 1976) as:

\[ \Omega = \prod_{i=1}^{k} \delta_i^{N_i} \frac{N_i!}{N_0!N_1!N_2!...N_k!} \left( \frac{N_q}{N_i!} \right)^{1/2} \]  \hspace{1cm} (A.2)

where \( N_i \) is the total number of lattice sites and is given by,

\[ N_t = N_0 + \sum_{i=1}^{k} r_i N_i = N_0 + rN \]  \hspace{1cm} (A.3)

and the other terms are defined as follows,

\[ N_q = N_0 + \sum_{i=1}^{k} q_i N_i = N_0 + qN \]  \hspace{1cm} (A.4)

\[ \left( \frac{z}{2} \right)^N_q = \left( \frac{z}{2} - 1 \right) N_t + \sum_{i=1}^{k} N_i + N_0 \]  \hspace{1cm} (A.5)
\[ r = \sum_{i=1}^{k} \frac{r_i N_i}{\sum_{i=1}^{k} N_i} = \sum_{i=1}^{k} x_i r_i \]  
\hspace{1cm} (A.6)

\[ q = \sum_{i=1}^{k} x_i q_i \]  
\hspace{1cm} (A.7)

\[ q,z = r,(z - 2) + 2 \]  
\hspace{1cm} (A.8)

The vacancy fraction \( f_0 \) is defined as:

\[ f_0 = \frac{N_0}{N_0 + rN} = 1 - \tilde{\rho} \]  
\hspace{1cm} (A.9)

where \( \tilde{\rho} \) is the fraction of sites occupied by all molecules defined as:

\[ \tilde{\rho} = \frac{1}{\tilde{\nu}} = \frac{rN}{N_0 + rN} \]  
\hspace{1cm} (A.10)

Similarly, the fraction of sites occupied by molecules of type \( i, f_i \) is defined as:

\[ f_i = \frac{r_i N_i}{N_0 + rN} = \phi_i \tilde{\rho} \]  
\hspace{1cm} (A.11)

where \( \phi_i \) is the site fraction in the absence of vacancies defined as:

\[ \phi_i = \frac{r_i N_i}{rN} \]  
\hspace{1cm} (A.12)

Using Stirling's approximation in the form \( N! \equiv (N/e)^N \) and equation (A.5) combined with equation (A.2) yields the following expression for the total number of configurations, \( \Omega \).
\[
\Omega = \left( \frac{1}{f_0} \right)^{N_0} \prod_{i=1}^{k} \left( \frac{\delta r_i}{f_i} \right)^{N_i} \left( \frac{N_\Delta}{N_r} \right)^{\frac{\theta}{2}}
\]

\(N_\Delta\) and \(N_r\) can be expressed in a more convenient manner by introducing a parameter \(\theta\), defined as the fraction of mer-mer bonds per molecule that are chemical bonds. If \(\chi\) becomes very large then this fraction \(\theta\) becomes negligible.

\[
N_q = rN \left[ \frac{1}{\bar{\rho}} - \left( 1 - \frac{q}{r} \right) \right] = rN(\bar{\nu} - \theta)
\]

\[
\frac{N_\Delta}{N_r} = 1 - \theta \bar{\rho}
\]

\[
\theta = 1 - \frac{q}{r}
\]

Taking the term containing \(N_q\) and \(N_r\) in equation (A.13) and rearranging gives the following expressions:

\[
\left( \frac{N_q}{N_r} \right)^{\frac{\theta}{2}} = \exp \left[ \frac{N(r-1)(1-\theta \bar{\rho})}{\bar{\rho} \theta} \ln(1-\theta \bar{\rho}) \right]
\]

\[
\Omega = (1-\bar{\rho})^{-N_\Delta} \bar{\rho}^{-N} \prod_{i=1}^{k} \left( \frac{\delta r_i}{\phi_i} \right)^{N_i} \exp \left[ \frac{N(r-1)(1-\theta \bar{\rho})}{\bar{\rho} \theta} \ln(1-\theta \bar{\rho}) \right]
\]

Introducing a new variable \(\omega_i\) defined as:

\[
\omega_i = \frac{\delta r_i}{e^{\sigma-1}}
\]

and rearranging gives a final expression for the total number of configurations: 306
\[ \Omega = (1 - \bar{\rho})^{-N_c} \bar{\rho}^{-N} \prod_{i=1}^{k} \left( \frac{\omega_i}{\phi_i} \right)^N_i \exp \left\{ N(r - 1) \left[ 1 + \frac{(1 - \bar{\rho}) \ln(1 - \bar{\rho})}{\bar{\rho}} \right] \right\} \]  

(A.20)

Also expressing the term in brackets in the exponential part of equation (A.20) as a polynomial, an expression can be derived for the large \( z \) approximation where \( \theta \to 0 \).

In the case where there are no vacancies, i.e. \( \bar{\rho} \to 1 \), the result is referred to as "Flory's approximation":

\[ \Omega = (1 - \bar{\rho})^{-N_c} \bar{\rho}^{-N} \prod_{i=1}^{k} \left( \frac{\omega_i}{\phi_i} \right)^N_i \]  

(A.21)

Finally, the entropy of the system is given by Boltzmann's equation \( S = k \ln \Omega \) and therefore for the large \( z \) approximation,

\[ \frac{-S}{k} = rN \left[ (\bar{\nu} - 1) \ln(1 - \bar{\rho}) + \frac{1}{r} \ln \bar{\rho} + \sum_{i=1}^{k} \left( \frac{\phi_i}{r_i} \right) \ln \left( \frac{\omega_i}{\phi_i} \right) \right] \]  

(A.22)

This is the expression for the entropy of mixing for the system.

A.2 – Enthalpy of Mixing

According to Sanchez and Lacombe, the energy of the lattice only depends on the nearest neighbour interactions. In general it can be written as (attraction energy),

\[ U = -\left( \frac{z}{2} \right) N \sum_{i=1}^{k} \sum_{j=1}^{k} \rho_{ij} \epsilon_{ij} \]  

(A.23)

where \( \epsilon_{ij} \) is the pair interaction energy between components \( i \) and \( j \) and \( \rho_{ij} \) is the pair probability of an \((ij)\) pair in the system. The model being described here contains only holes and mers so that the only non-zero pair interaction energy is the one from
the non-bonded mer-mer. Assuming random mixing of holes and molecules, the mean-field value of \( p_x \) is then given by:

\[
\begin{align*}
    p_x &= \frac{(q_i N_i)(q_j N_j)}{N_q N_r} \\
    \text{(A.24)}
\end{align*}
\]

Substituting this into equation (A.23) and using some of the previous definitions, the following expression for the lattice energy can be derived:

\[
U = -rN\sum_{i=1}^{k} \sum_{j=1}^{k} \frac{\phi_i \phi_j}{1 - 6}\varepsilon_{y}^{-} \\
\text{(A.25)}
\]

where,

\[
\varepsilon_{y}^{*} = \frac{z}{2} \left( \frac{q_i}{r_i} \right) \left( \frac{q_j}{r_j} \right) \varepsilon_{y} \\
\text{(A.26)}
\]

As already mentioned, for the large \( z \) approximation \( \theta \to 0 \) and equation (A.26) becomes,

\[
U = -rN\sum_{i=1}^{k} \sum_{j=1}^{k} \phi_i \phi_j \varepsilon_{y}^{*} = -rN\bar{\rho}\varepsilon^{*} \\
\text{(A.27)}
\]

where,

\[
\varepsilon^{*} = \sum_{i=1}^{k} \sum_{j=1}^{k} \phi_i \phi_j \varepsilon_{y}^{*} = \sum_{i=1}^{k} \phi_i \varepsilon_{y}^{*} - \sum_{i=1}^{k} \sum_{j=1}^{k} \phi_i \phi_j kT\chi_{y} \\
\text{(A.28)}
\]

\[
kT\chi_{y} = \varepsilon_{y}^{*} - 2\varepsilon_{y}^{*} \\
\text{(A.29)}
\]

If all the \( k \) lattice fluids are mixed together, then the net change in energy upon mixing will be given by:
\[ \Delta U = rN \left[ \tilde{\rho} \sum_{i=1}^{k} \sum_{j=1}^{\frac{1}{\phi}} \phi_i \phi_j kT \chi_{ij} - \sum_{i=1}^{k} \phi_i (\tilde{\rho} - \tilde{\rho}_i) \varepsilon_{ij}^* \right] \]  

(A.30)

where \( \tilde{\rho} \) and \( \tilde{\rho}_i \) represent the fraction of sites occupied by all molecules and molecules of type \( i \) respectively. Finally, an expression is derived for the volume of mixing needs to be derived. The volume associated with a mer is \( \nu^* \). In the absence of holes, the volume occupied by the \( i \)th lattice fluid is \( N\nu^*_i \). In the case were holes exist the volume becomes \( N\nu^*_i \). Hence in a mixed lattice containing \( k \) lattice fluids the volume becomes:

\[ \sum_{i=1}^{k} N_i \nu^*_i \]  

(A.31)

The expression above has been derived assuming additivity of the close-packed volumes, i.e. such that the average mer volume \( \nu^* \) is given by

\[ \nu^* = \sum_{i=1}^{k} \phi_i \nu^*_i \]  

(A.32)

Thus the total volume of a lattice fluid \( V \) and the net volume change upon mixing \( \Delta V \) can be written as:

\[ V = N_i \nu^* = \nu^* \]  

(A.33)

\[ \Delta V = rN \left( \nu^* - \sum_{i=1}^{k} \phi_i \nu^*_i \right) \]  

(A.34)

A.3 – Chemical Potential

Equations (A.22), (A.30) and (A.34) can be substituted into the expression for the Gibbs free energy of mixing, equation (A.1), to give:
\[ G = rN\left\{ -\rho e^* + P\nu^* + kT\left[ (\nu - 1)\ln(1 - \rho) + \frac{1}{r}\ln \rho + \sum_{i=1}^{k} \left( \frac{\phi_i}{\omega_i} \right) \ln \left( \frac{\phi_i}{\omega_i} \right) \right] \right\} \] (A.35)

From this, an expression for the chemical potential for component \( i \) in the mixture can be obtained by simply differentiating the Gibbs free energy with respect to \( N_i \). It is more convenient to handle the expression as \( g \) defined as \( G/rN \) making the derivation simpler,

\[ \mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T,P,N_{\neq i}} = r_i \left[ g + \left( \frac{\partial g}{\partial \phi_i} \right)_{T,P,N_{\neq i}} - \sum_{j=1}^{k} \phi_j \left( \frac{\partial g}{\partial \phi_j} \right)_{T,P,N_{\neq j}} \right] \] (A.36)

so that:

\[ \frac{\mu_i}{RT} = \ln \frac{\phi_i}{\omega_i} + \left( 1 - \frac{r_i}{r} \right) + r_i \nu_0 \left[ \sum_{j=1}^{k} \phi_j \chi_{ij} - \sum_{j=1}^{k} \sum_{i} \phi_i \phi_j \chi_{ij} \right] \] (A.37)

\[ + r_i \left[ -\frac{\rho}{T_i} + \frac{P\nu}{T_i} + \frac{1}{r_i} \ln \rho + (\nu - 1)\ln(1 - \rho) \right] \]

where \( \tilde{T} \) and \( \tilde{P} \) are the reduced temperature and pressure respectively given as:

\[ \tilde{T} = \frac{T}{T^*} = \frac{kT^*}{\varepsilon} \] (A.38)

\[ \tilde{P} = \frac{P}{P^*} = \frac{PV^*}{\varepsilon} \] (A.39)

For thermodynamic equilibrium, the Gibbs free energy has to be at a minimum with respect to all possible changes at given temperature and pressure, which yields the Sanchez and Lacombe equation of state:

\[ \tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) + \left( 1 - \frac{1}{r} \right) \tilde{\rho} \right] = 0 \] (A.40)
This equation has three characteristic parameters which define every pure component, $T$, $P$, and $\rho^*$, and they are related to each other and to the size parameter $r$ and the molecular weight $M$ by the following expression:

$$ r = \frac{M}{\rho^* v^*} = \frac{M P^*}{\rho^* k T^*} \quad (A.41) $$

This expression is valid for pure fluid components as well as for mixtures of components. Tables with values of the characteristic parameters for both simple fluids and polymers can be found in the literature (Sanchez and Panayiotou, 1994). They have been determined experimentally from measurements of thermodynamic properties. For simple fluids they used saturated vapour pressures and for polymers they carried out a simple non-linear least-squares fitting with experimental liquid densities. Once the parameters are known, as with any EoS, it can be used to derive other thermodynamic properties. Examples include the thermal expansion coefficient $\alpha$ and the thermal compressibility coefficient $\beta$,

$$ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\left( \frac{\partial \ln \rho^*}{\partial T} \right)_p = \frac{1}{T} \left[ \frac{\frac{1}{\tilde{T}_p} \left( \frac{1}{\tilde{v} - 1} + \frac{1}{r} \right) - 2}{\frac{1 + \tilde{P}^2}{\tilde{T}_p} \left( \frac{1}{\tilde{v} - 1} + \frac{1}{r} \right) - 2} \right] \quad (A.42) $$

$$ \beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\left( \frac{\partial \ln \rho^*}{\partial P} \right)_T = \frac{1}{P} \left[ \frac{\tilde{P}^2}{\tilde{T}_p} \left( \frac{1}{\tilde{v} - 1} + \frac{1}{r} \right) - 2 \right] \quad (A.43) $$

Likewise, these properties can be measured and also used to determine the EoS parameters.
Appendix B

TURBIDIMETER SPECIFICATIONS

B1 – Optical Fibres, Photodiodes, Photodetectors

Given below are the specifications obtained from Farnell UK on the light source components used in the turbidimeter.

B1.1 – Fibre Optic

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cable type</td>
<td>3.2 mm reinforced</td>
</tr>
<tr>
<td>Connector type</td>
<td>Polished FSMA</td>
</tr>
<tr>
<td>Numerical aperture</td>
<td>0.37</td>
</tr>
<tr>
<td>Fibre attenuation</td>
<td>6dB/km at 850 nm</td>
</tr>
<tr>
<td>Bandwidth (typical)</td>
<td>10 MHz</td>
</tr>
<tr>
<td>Minimum recommended bend radius</td>
<td>50 mm</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>-20 °C to 80 °C</td>
</tr>
</tbody>
</table>

Table B.1 – Fibre optic specifications
**B1.2 — SMA Emitter**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Launch power (typ. At 50 mA dc)</td>
<td>60 μW into a 200/250 μm fibre</td>
</tr>
<tr>
<td>Peak emission wavelength</td>
<td>660 nm at 20 mA dc</td>
</tr>
<tr>
<td>Response time</td>
<td>70 ns (typical)</td>
</tr>
<tr>
<td>Forward voltage drop</td>
<td>1.6 V</td>
</tr>
<tr>
<td>Reverse voltage (max.)</td>
<td>5 V</td>
</tr>
<tr>
<td>Forward current (max.)</td>
<td>50 mA</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>-20 °C to 70 °C</td>
</tr>
</tbody>
</table>

*Table B.2 — SMA emitter specifications*

**B1.3 — SMA Detector**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Responsivity (typ. at 850 nm)</td>
<td>0.6 A/W</td>
</tr>
<tr>
<td>Dark current (typ. at 5V)</td>
<td>1 nA</td>
</tr>
<tr>
<td>Capacitance (typ. at 5V)</td>
<td>3.5 pF</td>
</tr>
<tr>
<td>Response time</td>
<td>2 ns typ., 4 ns. max.</td>
</tr>
<tr>
<td>Reverse voltage (max.)</td>
<td>30 V</td>
</tr>
<tr>
<td>Power dissipation</td>
<td>100 mV</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>-40 °C to 80 °C</td>
</tr>
</tbody>
</table>

*Table B.3 — SMA detector specifications*

**B2 — Calculation for LED arrangement**

For the SMA emitters used, a maximum current of 50 mA can be passed through each diode. The simple circuit is shown in figure B.1 where R is the unknown resistance, I is the current through the circuit, \( V_R \) is the voltage across the resistance and \( V_D \) the forward voltage drop across the diode equal to 1.6V. From \( V \)
\[ R = \frac{(V - V_0)}{I} \]

where \( V \) is the total voltage. So for a voltage of 9 V, the required resistance is 148 Ω which gives a current of 49.3 mA.

**Figure B.1 — LED circuit**

**B3 — Stability of Light Emission/Detection Set-up in Turbidimeter**

The background noise in each channel was recorded during five minutes. DC Voltages have been plotted in figure B.2 as a function of time.

**B4 — Stirring Mechanism for Turbidimetry Apparatus**

Figure B.4 shows a closer view of the assembled turbidimeter set-up.
B5 — Calibration of Platinum Resistance Thermometers (PRT’s)\(^1\)

Two PRT’s were used in the turbidimetry apparatus, one for controlling the temperature in the cell block and the other for recording the measured temperatures on the data acquisition box. Previous to used, they were calibrated against the ice-point of water and a standard (PRT, four lead, air filled platinum capsule, serial number B249) obtained from the National Physical Laboratory UK, taking the following steps:

1. **Resistance at the ice-point of water**

The uncalibrated thermometers were placed in a glass tube filled with dodecane, which is liquid at 0 °C, inside a dewar vessel filled with a mixture of distilled water ice and distilled water. This ice/water mixture was stirred continuously to maintain a constant temperature throughout the vessel. The resistances of the thermometers were measured using a HP data acquisition box during half an hour. Essentially measurements were stopped if for 10 mins the

---

\(^1\) In the calibration procedure here described, all equations unless stated otherwise, are taken from the NPL Certificate of Calibration (1990) for the PRT standard used, serial number B249.
resistance values were constant. Experimental data and the average value of the resistance and the standard deviation are given in table B.4 where IP refers to the ice-point and TP refers to the triple point.

The resistance at the ice-point of water was also measured for the standard. An in-house set-up for this purpose consisted of a resistance bridge between a calibrated 25 Ω block and the standard in the ice-point cell. With the bridge resistance ratio \( \alpha \) between the resistance of the standard and the resistance of the 25 Ω block was measured. The calibration equation of the block is:

\[
R(T) = R(20\,^\circ C)[1.0 - 9.8 \times 10^{-8}(T - 20)^2]
\]  

(B.1)

where \( R(T) \) is the resistance at temperature \( T(\circ C) \) and \( R(20\,^\circ C) \) is the resistance at 20 °C equal to 24.99988 Ω. Therefore the resistance of the standard at 0 °C is given by,

\[
R_{\text{standard}}(0\,^\circ C) = \alpha \times R_{\text{standard}}(T_{\text{ambient}})
\]  

(B.2)

Although the data were measured at the ice-point, the standard was calibrated in terms of the International Temperature Scale of 1990 (ITS90) which uses the triple point of water as the reference state, i.e. 0.01 °C. Consequently, the measurements at the ice point of water made here were changed to the equivalent triple point of water using the following relationship:

\[
R(0.01\,^\circ C) = R(0\,^\circ C) \times 0.999960
\]  

(B.3)

Experimental values are given in table B.5 for PRT 1 and table B.6 for PRT2. The resistances at the triple point of water are 100.03978 Ω for PRT1, 95.12357 Ω for PRT 2 and 24.74638 Ω for the standard.

2. ** Resistances at temperature in the range –20 °C to 160 °C

Resistances for both PRT’s were measured in a temperature controlled bath at –20 °C, 40 °C, 80 °C, 120 °C and 160 °C. The resistances of the standard
<table>
<thead>
<tr>
<th>Time, t (s)</th>
<th>R (ohms)</th>
<th>Time, t (s)</th>
<th>R (ohms)</th>
<th>Ratio, R/R₀</th>
<th>R at IP, Exp. (ohms)</th>
<th>R at IP, Calc. (ohms)</th>
<th>R at TP, calc. (ohms)</th>
<th>R at TP, diff (millions)</th>
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</thead>
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<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
<td>1.000</td>
<td>26.0137770</td>
<td>26.9135235</td>
<td>21.83625</td>
<td>2167.9252</td>
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<td>1.00</td>
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</tbody>
</table>

Table D4.1 – Experimental and calculated resistances as a function of time for PRT 1, PRT 2 and PRT Standard at the ice point (IP) and triple points (TP) of water.
Table B.5 - Resistances, resistance ratios and calibration constants above and below 0 °C for PRT 1. Note that $\Delta = \left[ (W_{W-\text{ref}}) - (W_{W-\text{Ref}}) \right]$. [Table containing data analysis results for PRT 1 resistances and related constants.]
| Table B.6 – Resistances, resistance ratios and calibration constants above and below 0°C for PRT 2. Note that $\Delta = [W^2 - W^2_{ref} - a(W-1)]$. |
| PRT Standard Resistance Ω (ohms) | W   | W ref | Term D₀ | Term D₁ | Term D₂ | Term D₃ | Term D₄ | Term D₅ | Term D₆ |
|----------------------------------|-----|-------|---------|---------|---------|---------|---------|---------|---------|-------|
| 22.73365283                      | 0.918648776 | 0.918612594  | 0.183324722 | 0.23130266 | 0.192658615 | 0.168415626 | 0.121087572 | 0.06354753 | 0.009756867 |
| 28.71509                         | 1.160353388 | 1.160266542  | -439.932854  | -426.2516771 | 30.67905512 | -5.488540163 | 1.935818188 | -0.00310001 | -0.520060218 |
| 32.5750833                      | 1.316358388 | 1.316183651  | -439.932854  | -381.3382308 | 24.55446482 | -3.929973178 | 1.240056727 | -0.00177658 | -0.266636201 |
| 36.28955333                     | 1.466131901 | 1.466170829  | -439.932854  | -338.1329591 | 19.305666 | -2.739813868 | 0.76657113 | -0.0009738 | -0.129593154 |
| 40.011775                        | 1.616849083 | 1.616494083  | -439.932854  | -294.8308774 | 14.6776223 | -1.816257376 | 0.443090075 | -0.00049079 | -0.056950143 |

<table>
<thead>
<tr>
<th>Term D₇</th>
<th>Term D₈</th>
<th>Term D₉</th>
<th>Term D₁₀</th>
<th>Term D₁₁</th>
<th>Term D₁₂</th>
<th>Term D₁₃</th>
<th>Term D₁₄</th>
<th>Term D₁₅</th>
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<td>-0.024222387</td>
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<td>-0.03905672</td>
<td>0.050587499</td>
<td>0.078947156</td>
<td>-0.017860668</td>
<td>-0.053527137</td>
<td>0.000742555</td>
<td>0.014077349</td>
<td>-8.1592</td>
</tr>
<tr>
<td>0.001880439</td>
<td>0.083986961</td>
<td>-0.019430072</td>
<td>0.034464013</td>
<td>-0.007133007</td>
<td>0.013169919</td>
<td>-0.002416947</td>
<td>0.006959389</td>
<td>-0.00704103</td>
<td>40.2843</td>
</tr>
<tr>
<td>0.042143712</td>
<td>0.034464013</td>
<td>-0.007133007</td>
<td>0.013169919</td>
<td>-0.002416947</td>
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<tr>
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<td>0.013169919</td>
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<td>0.006959389</td>
<td>-0.00704103</td>
<td>0.00742555</td>
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<td>-8.1592</td>
<td>40.2843</td>
<td>119.0017</td>
</tr>
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<td>0.004400143</td>
<td>-0.00704103</td>
<td>0.00742555</td>
<td>0.014077349</td>
<td>-8.1592</td>
<td>40.2843</td>
<td>89.1908</td>
<td>119.0017</td>
<td>158.3490</td>
</tr>
</tbody>
</table>

Table B.7 – Data for the calculation of the temperature using equations from the NPL ITS90 Report for the PRT Standard.
Table B.8 — Data for the calculation of the temperature using equations from the NPL ITS90 Report for PRT 1.
### Table B.9 - Data for the calculation of the temperature using equations from the NPL ITS90 Report for PRT 2.

<table>
<thead>
<tr>
<th>Term D₁</th>
<th>Term D₂</th>
<th>Term D₃</th>
<th>Term D₄</th>
<th>Term D₅</th>
<th>Term D₆</th>
<th>Term D₇</th>
<th>Term D₈</th>
<th>Term D₉</th>
<th>Term D₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.214485418</td>
<td>0.192963234</td>
<td>0.1683815216</td>
<td>0.121470787</td>
<td>0.063799021</td>
<td>0.008903221</td>
<td>-0.021356698</td>
<td>-0.05198313</td>
<td>0.05198313</td>
<td>0.05090969</td>
</tr>
<tr>
<td>-26.762921</td>
<td>-30.41294236</td>
<td>-5.4189298869</td>
<td>-1.935046847</td>
<td>-0.003409467</td>
<td>-0.001774341</td>
<td>-0.26621333</td>
<td>0.003198453</td>
<td>0.01321897</td>
<td>-0.000971685</td>
</tr>
<tr>
<td>-181.3421935</td>
<td>-214.5209169</td>
<td>-1.297003409</td>
<td>1.133807298</td>
<td>0.001774341</td>
<td>-0.26621333</td>
<td>-0.26621333</td>
<td>0.01321897</td>
<td>0.01321897</td>
<td>-0.000971685</td>
</tr>
<tr>
<td>-3379.788828</td>
<td>-406.54807607</td>
<td>-2.73607204</td>
<td>0.765170688</td>
<td>-0.000971581</td>
<td>-0.12923925</td>
<td>-0.12923925</td>
<td>0.006928702</td>
<td>0.006928702</td>
<td>-0.000971685</td>
</tr>
<tr>
<td>-294.6480852</td>
<td>14.65910162</td>
<td>-1.812820514</td>
<td>0.441972571</td>
<td>-0.00489245</td>
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<td>-0.05673488</td>
<td>0.006928702</td>
<td>0.006928702</td>
<td>-0.000971685</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Term D₁₊</th>
<th>Term D₁₃</th>
<th>Term D₁₅</th>
<th>Term D₁₇</th>
<th>Term D₁₉</th>
<th>Temperature (°C)</th>
<th>(Tₛ-Tₐ)/Tₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.079636148</td>
<td>-0.01803078</td>
<td>-0.054079655</td>
<td>0.000750812</td>
<td>0.014243146</td>
<td>-49.9621965</td>
<td>-0.182012676</td>
</tr>
<tr>
<td>-14.06720223</td>
<td>0.47820223</td>
<td>0.345949899</td>
<td>0.145975855</td>
<td>0.15556845</td>
<td>0.107374542</td>
<td>0.107374542</td>
</tr>
</tbody>
</table>

Note: Values are rounded for clarity.
were also measured using a resistance bridge and recorded as resistance ratios, but this time the reference is a calibrated block of 50 Ω whose calibration equation is:

\[ R(T) = R(20°F) \left[ 1.0 + 4.4 \times 10^{-6} (T - 20) - 0.523 \times 10^{-8} (T - 20)^2 \right] \]  \hspace{1cm} (B.4)

where \( R(20°F) \) is equal to 49.99959 Ω. Measurements of all three thermometers were taken every 10 minutes during an hour. Results are given in table B.7 for the standard, in table B.8 for PRT 1 and in table B.9 for PRT 2.

3. Calculation of calibration constants

Another resistance ratio of \( W_i(T) \) at temperature \( T \) is defined as:

\[ W_i(T) = \frac{R(T)}{R(0.01°F)} \]  \hspace{1cm} (B.5)

where \( i \) represents the PRT in question. This equation was used to calculate the values of \( W_i(T) \) for each PRT at each measured temperatures, including those for the standard, \( W_{\text{standard}}(T) \). Next, reference resistance ratios were calculated using the following equations depending on the temperature, if above or below 0 °C:

Above 0 °C:

\[ W_{\text{standard}} - W_{\text{ref}} = -5.367715 \times 10^{-4} (W - 1) + 4.920607 \times 10^{-5} (W - 1)^2 \]  \hspace{1cm} (B.6)

and below 0 °C:

\[ W_{\text{standard}} - W_{\text{ref}} = -4.446268 \times 10^{-4} (W - 1) + 1.64029 \times 10^{-6} (W - 1) \ln W \]  \hspace{1cm} (B.7)

The next step was to compare the two PRT's with the standard and so substituting the calculated values of \( W_{\text{standard,ref}}(T), W_i(T), \) the following two equations result:

Above 0 °C:

\[ W_i - W_{\text{ref}} = a(W - 1) + \nu (W - 1)^2 \]  \hspace{1cm} (B.8)
and below 0 °C:

\[ W_i - W_{r1} = a(W - 1) \]  (B.9)

and a least squares method, the values of \(a\) and \(b\) can be calculated. The Microsoft Excel regression analysis tool was used for the fitting. The method of least squares is based on minimising the function \(q\) given by,

\[ q = \sum_{i=1}^{n} (y_i - p(x_i))^2 \]  (B.10)

where \(i = 1, \ldots n\) where \(n\) is the number of points used for the fit and \(p(x_i)\) is a function of the form

\[ p(x_i) = a_0 + a x_i + b x_i^2 \]  (B.11)

In the case of the calibration, for temperature both below and above 0 °C, \(a_0 = 0\).

The results of the regression are summarised in table B.10.

<table>
<thead>
<tr>
<th>Temperatures above 0 °C</th>
<th>Temperatures below 0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>PRT 1</td>
<td>-1.8076 (\times 10^{-2})</td>
</tr>
<tr>
<td>PRT 2</td>
<td>-1.9875 (\times 10^{-2})</td>
</tr>
</tbody>
</table>

*Table B.10 – Calibration constants for platinum resistance thermometers in the turbidimeter, where PRT 1 is connected the controller and PRT2 is used to record the temperature in the cell block.*

4. **Calculation of temperatures**

The temperature was measured using the calibrated PRT as a resistance. From the measurement, knowledge of the resistance of the PRT at the triple point of water \(R (0.01^\circ C)\) and using equation (B.5), the value of \(W\) was calculated. Then
the appropriate equation (B.8) or (B.9) was used to calculate $W_{\text{ref}}$ ($T$). Finally, depending on the value of $W$, the temperature was calculated using one of the two following equations:

Above 0 °C
($T$ accurate to ± 0.00013°C)

$$T({}^\circ \text{C}) = D_0 + \sum_{i=1}^{9} D_i \left[ \frac{(W_{\text{ref}} - 2.64)}{1.64} \right]^i$$  \hfill (B.12)

Below 0 °C
($T$ accurate to ± 0.0001 °K)

$$T({}^\circ \text{K}) = B_0 + \sum_{i=1}^{15} B_i \left[ \frac{(W_{\text{ref}}^{1/6} - 0.65)}{0.35} \right]^i$$  \hfill (B.13)

where $D_i$ and $B_i$ are constants for the equations and the values are given in table B.11.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$D_i$</th>
<th>$B_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>439.932854</td>
<td>0.183324722</td>
</tr>
<tr>
<td>1</td>
<td>472.418020</td>
<td>0.240975303</td>
</tr>
<tr>
<td>2</td>
<td>37.684494</td>
<td>0.209108771</td>
</tr>
<tr>
<td>3</td>
<td>7.472018</td>
<td>0.190439972</td>
</tr>
<tr>
<td>4</td>
<td>2.920828</td>
<td>0.142648498</td>
</tr>
<tr>
<td>5</td>
<td>0.005185</td>
<td>0.077993465</td>
</tr>
<tr>
<td>6</td>
<td>-0.963864</td>
<td>0.012475611</td>
</tr>
<tr>
<td>7</td>
<td>-0.188732</td>
<td>-0.032267127</td>
</tr>
<tr>
<td>8</td>
<td>0.191203</td>
<td>-0.075291522</td>
</tr>
<tr>
<td>9</td>
<td>0.049025</td>
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<tr>
<td>10</td>
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<tr>
<td>11</td>
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<td>12</td>
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<tr>
<td>13</td>
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<td>-0.075291522</td>
</tr>
<tr>
<td>14</td>
<td>0.001317696</td>
<td>-0.056470670</td>
</tr>
<tr>
<td>15</td>
<td>0.026025526</td>
<td>0.012475611</td>
</tr>
</tbody>
</table>

*Table B.11 – Constants for the calculation of temperatures from calibrated platinum resistance thermometers in the ITS90 as given in the NPL Certificate of Calibration report (1990).*
Appendix C

INVERSE GAS CHROMATOGRAPHY ADDITIONAL INFORMATION

C1 – General Procedure for Capillary Column Manufacture

The procedure given here for the preparation of capillary columns for experiments using the IGC technique involving polymer solutions is based on the static coating technique. The following steps should be carried out:

1. Make a solution of the polymer in chloroform or dichloromethane of a concentration that will yield the desired polymer film thickness on the walls of the capillary column according to the following equation:

   \[ C = \frac{4 \pi \rho}{D} \]  

   (C.1)

   where \( C \) is the polymer solution concentration \((g/cm^3)\), \( \tau \) is the polymer thickness \((cm)\), \( \rho \) is the density of the polymer \((g/cm^3)\) and \( D \) is the inner

---

1 Written with the permission of CSPSS at the Fenske Laboratory, The Pennsylvania State University, PA, USA.
diameter of the capillary column (cm). Stir the solution using a magnetic stirrer and sonicate it during approximately 20 minutes.

2. Obtain the desired length of the fused silica glass capillary column according to the equation:

\[ L = \pi DN \]  \hspace{1cm} (C.2)

where \( L \) is the length of the capillary column (cm), \( D \) is the average diameter of each round of the capillary column and \( N \) is the number of rounds. Leave about ~1.5 feet on each side of the capillary column to work with later.

3. Place the column in a temperature controlled water bath and tape it down the side of the vacuum apparatus.

4. Burn off approximately two inches of coating from the column and wipe it off with a wet paper towel leaving a clear, spotless end. Also, using a special cutter, cut a small piece of column on both ends to ensure that there are no jagged edges.

5. Take a clean syringe and after making sure that the piston can moves up and down with little friction, fill it with approximately 10 ml of polymer solution. Tilt the syringe so that air can escape and push the piston down the syringe to remove all air bubbles before filling the column with the polymer solution.

6. Connect the column to the syringe using Swagelok fittings and ferrules. Turn on the syringe pump and fill the column completely with the polymer solution, but keep the syringe pump running for an extra minute or two to flush the column of any possible contaminants. After this, turn off the syringe pump and disconnect the column from the syringe.

7. Put any excess polymer solution back into the original container and clean the syringe completely (this might require more solvent to dissolve any remains of polymer in it).

8. Leave about 20 cm$^3$ of air in the syringe and reconnect it to the column. Push on the piston until the air/solution phase line is under the water bath.

9. Prepare a short, open container with glue that will allow it to be sucked up easily. Then wipe the end of the column with a dry paper towel so that it has a smooth finish and gently push on the piston so that a small bubble is left on the end of the column and then thrust the column into the glue.
10. Use the syringe to suck up the glue approximately one inch into the column (phase line should still be under the water bath). Depending on the type of glue used, do the following:
   a. If a UV light curing glue is used, cure the glue for approximately five minutes.
   b. If a double epoxy glue is used, just allow it to sit for five minutes, after which time push on the piston to check if the glue moves. If this is the case, allow it to cure for another five minutes or alternatively cut the end off, suck more glue in and try again.

11. In all cases, once the glue is completely cured, detach the column from the syringe and reattach it to the vacuum system. Close all the valves and turn on the vacuum pump.

12. Set the desired vacuum pressure and slowly open the valve that the column is connected to. This will cause the air/solution phase line to move slightly to the vacuum side, although if it continues to move in that direction, it means that the glue plug has not been correctly made. If this is the case, close the valve and detach the column from the apparatus. Cut the plug off, reconnect the column to the syringe and push the phase line under the water bath. Repeat steps 10 and 11.

13. If on the other hand the plug has been correctly made, the air/solution phase line should start moving away from the vacuum side slowly at about 1 cm/min. This indicates that the solvent is being evaporated from the solution. Evacuation can take anywhere from 24 to over 72 hours depending on the polymer solution used.

14. Once the evacuation is complete, cut of the glue plug while the vacuum pump is still on so that the air will go through the column, sweeping away any residual solvent. Suck air through for about 10 minutes and then turn off the vacuum pump.

15. Finally detach the column from the apparatus and cut the column on the side where the original phase line was and on the side where the column was out of the bath (glue side) to a smooth finish.
C2 — Expression for WFAC at Infinite Dilution from IGC Data

In gas chromatographic experiments retention volumes are measured and the net retention can be calculated as the difference between the retention volume of the solvent in question and the gas hold-up:

\[ V_N = V_R - V_G \]  

(C.3)

The basic independent variable is not the retention volume but the specific retention volume \( V'_k \) which at zero temperature is defined as,

\[ V'_k = \frac{V'_k}{273.15} = \frac{V'_k}{273.15} \]

where subscript 2 refers to the polymer stationary phase, \( m, n \) and \( M \) refer to the weight, number of moles and molecular weight of the component. At infinite dilution for an ideal gas, the following equation holds:

\[ y_r P = \frac{n_2 R T}{V'} \]

(C.5)

where \( y_r \) is the mole fraction activity coefficient of the solvent at infinite dilution, \( P_1 \) is the vapour pressure of the solvent, \( x_1 \) is the mole fraction of the solvent and \( R \) is the gas constant. Substituting for \( V'_N / n_{2i} \) in equation (C.5) gives,

\[ \left( \frac{P_1}{x_1} \right)^* = \frac{273.15 R}{V'_k M_2} \]

(C.6)

To correct for non-ideal gas behaviour, the fugacity coefficient needs to be introduced such that:
The fugacity coefficient of the solvent in the carrier gas can be calculated by using the virial equation truncated after the second virial coefficient:

$$\ln \phi_i = \left( \frac{2}{\sum y_j B_{ij} - B_{mix}} \right) \frac{P}{RT}$$ \hspace{1cm} (C.8)

Where $y_j$ is the mole fraction of component $j$ in the vapour phase and $B_{mix}$ is the second virial coefficient of the mixture defined as:

$$B_{mix} = \sum_i \sum_j y_i y_j B_{ij}$$ \hspace{1cm} (C.9)

Since the polymer has extremely low volatility therefore setting $y_2$ to a value of zero then,

$$\ln \phi_i = \frac{P}{RT} \left[ 2(y_1 B_{11} + y_3 B_{13}) - (y_1^2 B_{11} + y_1 y_3 B_{13} + y_3^2 B_{33}) \right]$$ \hspace{1cm} (C.10)

where component 3 refers to the carrier gas which being inert has no interaction with either component 1 or 2 and so $B_{13} = 0$ and $B_{33} = 0$. Furthermore, at infinite dilution $y_i \rightarrow 0$ and hence the expression for $\ln \phi_i \rightarrow 0$, meaning that $\phi_i \rightarrow 1$. Substituting this into equation (C.7) gives,

$$\left( \frac{f_i}{x_i} \right) = \left( \frac{P_i}{x_i} \right) = \frac{273.15R}{V_g M_2}$$ \hspace{1cm} (C.11)

Also, the activity coefficient is related to the fugacity and the fugacity coefficient by:

$$\gamma_i = \left( \frac{f_i}{x_i \phi_i} \right)$$ \hspace{1cm} (C.12)
where $f_i^0$ is the fugacity of the pure solvent at zero reference pressure and the system temperature defined as:

$$f_i^0 = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left( \int_0^{V_i^{\text{sat}}} \frac{V_i^{\text{sat}}}{RT} dP - P_i^{\text{sat}} \frac{P_i^{\text{sat}}}{RT} \right)$$

(C.13)

where $\phi_i^{\text{sat}}$ is the fugacity coefficient of the solvent at the saturation pressure, $V_i$ is the molar volume of liquid solvent at saturation and $B_{1i}$ is the second virial coefficient of the pure solvent. Therefore using equations (C.11), (C.12) and (C.13) and rearranging gives the following expression for the mole fraction activity coefficient at infinite dilution at system temperature $T$:

$$
\gamma_i^\infty = \frac{RT}{V_i^{\text{sat}} M_2} \frac{1}{P_i^{\text{sat}}} \exp \left[ \frac{P_i^{\text{sat}} (V_i - B_{1i})}{RT} \right]
$$

(C.14)

When dealing with systems containing polymers it is common practice to calculate the weight fraction activity coefficient (WFAC) of the pure solvent at infinite dilution $\Omega_i^\infty$, rather than the mole fraction activity coefficient. These two quantities are related through the following equation:

$$
\Omega_i^\infty = \frac{\gamma_i^\infty}{w_i}
$$

(C.15)

where $w_i$ is the weight fraction of the solvent. From this and the definitions of mole and weight fractions and knowing that at infinite dilution there is nearly no solvent such that $m_i \to 0$, the following derivation gives a simple relationship between the two activity coefficients.

$$
\frac{x_i}{w_i} = \frac{n_i}{n_i + n_2} = \frac{n_i (m_1 + m_2)}{m_1 (n_1 + n_2)} = \frac{n_i (m_1 + m_2)}{M_1 (m_1 + m_2)} = \frac{m_1 + m_2}{m_1 + m_2 M_1} \frac{M_2}{M}
$$

(C.16)
\[ \Omega_i^\infty = \frac{\gamma_i^* M_i}{M_1} \]  

(C.17)

Using equation (C.15) the expression for the WFAC is,

\[
\Omega_i^\infty = \frac{RT}{V_g^0 M_i} \frac{1}{P_i^{\text{sw}}} \exp \left[ \frac{P_i^{\text{sw}} (V_i - B_{1i})}{RT} \right] 
\]

(C.18)

and

\[
\ln \Omega_i^\infty = \ln \left[ \frac{RT}{V_g^0 M_i} \frac{1}{P_i^{\text{sw}}} \right] - \left[ \frac{P_i^{\text{sw}} (B_{1i} - V_i)}{RT} \right] 
\]

(C.19)
Appendix D

INVERSE GAS CHROMATOGRAPHY RAW DATA

D1 – Experiments at Infinite Dilution

In the following set of tables, methane marker times (\(t_m \pm 0.005\) min) are given as well as all the parameters and data obtained from the CCIGC model. Table D.1 shows data for the low molecular weight PMMA/cyclohexanol system, table D.2 shows data for the high molecular weight PMMA/cyclohexanol system, table D.3 shows data for the PS/cyclohexanol system and finally table D.4 shows data for the random PS-\(\omega\)-PMMA/cyclohexanol system. The data obtained using the CCIGC that are given in these tables are the mobile phase velocity \(u\), the three model parameters \(\alpha, \beta\) and \(\Gamma\), and the partition coefficient \(K\) and diffusion coefficient \(D_r\). All the data in this section correspond to measurements taken at infinite dilution.

D2 – Experiments at Finite Concentrations

In tables D.5 – D.10, the parameters and data obtained from the CCIGC model is given as well as the values for the intermediate variables used in the calculation of the partition coefficients and solvent weight fractions of solvent in the
polymer using the elution on a plateau technique. All the definitions of the parameters as well as the equations used to calculate them are given in Chapter V. Tables marked (a) give the results from the CCIGC model and tables marked (b) give the parameters used for the finite concentration results. Presented in this order are: the data file name, the temperature of the saturator (°C), the vapour pressure of cyclohexanol in atm (calculated), the pressure drop across the system (psig), the velocity of the carrier gas (cm/s), the $\alpha$, $\beta$ and $\Gamma$ parameters, the diffusion coefficient (cm$^2$/s), the mole fraction of solvent in the carrier gas calculated from the saturated vapour pressure at the temperature in the saturator, the retention time of the solvent (min), the retention time of the marker gas (min), the value of the parameter $k$, the compressibility and the gas non-ideality correction factors, the true mole fraction of solvent in the carrier gas, the retention volume (cm$^3$), the concentration of solvent in the gas phase (mol/cm$^3$) and in the polymer phase (mol/g of polymer), the partition coefficient, the weight fraction of solvent in the system and finally, the activity coefficient and activity of the solvent.
<table>
<thead>
<tr>
<th>Column temperature $T_{col}$ (°C)</th>
<th>File name</th>
<th>Carrier gas retention time $\alpha$ (min)</th>
<th>Carrier gas velocity $u$ (cm/s)</th>
<th>Partition coefficient $K$</th>
<th>Diffusion coefficient $D_p$ (cm²/s)</th>
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Notes: $\alpha$, $\beta$, $\Gamma$, $K$, $D_p$ are the partition coefficient,relative velocity,partition coefficient, partition coefficient, and diffusion coefficient, respectively.
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<th>PMMA 96</th>
<th>PMMA 74</th>
<th>PMMA 77</th>
<th>PMMA 80</th>
<th>PMMA 197</th>
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Table D.1 - Results from IGC experiments and data analysis for PMMA (M_w = 15,000g/mol) with cyclohexanol at infinite dilution.
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<th>Carrier gas velocity $u$ (cm/s)</th>
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<th>$\beta$</th>
<th>$\Gamma$</th>
<th>Partition coefficient $K$</th>
<th>Diffusion coefficient $D_p$ (cm$^2$/s)</th>
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<td>$1.48 \times 10^{-10}$</td>
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Table D.2 – Results from IGC experiments and data analysis for PMMA (M_w = 990,000 g/mol) with cyclohexanol at infinite dilution
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<th>Carrier gas velocity $u$ (cm/s)</th>
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<th>$\beta$</th>
<th>$\Gamma$</th>
<th>Partition coefficient $K$</th>
<th>Diffusion coefficient $D_r$ (cm²/s)</th>
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*Table D.3 – Results from IGC experiments and data analysis for PS (M<sub>e</sub> = 200,000g/mol) with cyclohexanol at infinite dilution*
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<th>Column temperature $T_{col}$ (°C)</th>
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<th>Carrier gas retention time $t_M$ (min)</th>
<th>Carrier gas velocity $u$ (cm/s)</th>
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<th>$\beta$</th>
<th>$\Gamma$</th>
<th>Partition coefficient $K$</th>
<th>Diffusion coefficient $D_p$ (cm²/s)</th>
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Table D.4 – Results from IGC experiments and data analysis for PS (40%-$\alpha$-MMA ($M_w = 100,000 - 150,000$ g/mol) with cyclohexanol at infinite dilution

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1 Variation of temperature during the experiment
Table D.5 (a) - Results from CCIGC model at specified conditions for PMMA ($M_n = 996,000$ g/mol) with cyclohexanol at 180°C.
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Table D.5 (b) – Parameters used in elution on a plateau analysis at finite concentration measurements for PMMA (\( M_w = 996,000g/mol \)) with cyclohexanol at 180°C.

\(^2\) The equation used for the integral is \( V_N/(1-\psi) = 2.0132 \cdot (1.7780 \times 10^9)e^{-2.1738 \times 10^9}e^2 + (1.0701 \times 10^9)e^3 - (1.0311 \times 10^9)e^4 + (2.9691 \times 10^9)e^5 \)
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3 Variation of temperature during the experiment
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<td>PAHF292</td>
<td>PAHF295</td>
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<td>0.25 ± 0.05</td>
<td>13.27</td>
<td>3.8356</td>
<td>0.0302</td>
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<td>3.00 x 10^-8</td>
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<tr>
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<td>0.0324</td>
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Table D.6 (a) - Results from CCIGC model at specified conditions for PNINIA (Mₜ = 996,000g/mol) with cyclohexanol at 200°C.
<table>
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<tr>
<th>$\lambda$</th>
<th>$n$</th>
<th>$M_1$</th>
<th>$k$</th>
<th>$j$</th>
<th>$a$</th>
<th>$\psi$</th>
<th>$V_0$</th>
<th>$c$</th>
<th>$c'$</th>
<th>$K$</th>
<th>$m$</th>
<th>$a$</th>
<th>$\Omega$</th>
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<tbody>
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<td>$4.035 \times 10^{-3}$</td>
<td>2.339</td>
<td>1.540</td>
<td>0.5189</td>
<td>0.996606</td>
<td>0.9479</td>
<td>3.812 $\times 10^{-3}$</td>
<td>1.4749</td>
<td>1.0389 $\times 10^{-3}$</td>
<td>2.5012 $\times 10^{-6}$</td>
<td>21.63</td>
<td>0.0002</td>
<td>0.0015</td>
<td>6.4460</td>
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<td>1.517</td>
<td>0.5402</td>
<td>0.996610</td>
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<td>5.3803 $\times 10^{-7}$</td>
<td>1.3995 $\times 10^{-5}$</td>
<td>21.70</td>
<td>0.0012</td>
<td>0.0075</td>
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<td>0.9492</td>
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<td>7.1428 $\times 10^{-7}$</td>
<td>1.7276 $\times 10^{-5}$</td>
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<td>0.0100</td>
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<td>1.622</td>
<td>0.5417</td>
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<td>1.6361</td>
<td>1.6979 $\times 10^{-6}$</td>
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<td>2.5803 $\times 10^{-6}$</td>
<td>6.3610 $\times 10^{-5}$</td>
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<td>0.0360</td>
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Table D.6 (b) — Parameters used in elution on a plateau analysis at finite concentration measurements for PMMA ($M_e = 996,000$ g/mol) with cyclohexanol at 200°C.

*The equation used for the integral is $V_\psi/(1-\psi) = 1.5736 + (2.0503 \times 10^3)c + (6.6841 \times 10^9)c^2 - (6.5326 \times 10^{14})c^4 + (3.8207 \times 10^{10})c^6$. 


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<tr>
<th>$T_{an} \pm \Delta T_{an}$</th>
<th>File name</th>
<th>$P_1^{\text{eff}}$</th>
<th>$\Delta P$</th>
<th>$\nu$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\Gamma$</th>
<th>$D_p$</th>
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<td>0.0369</td>
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<td>$7.80 \times 10^{8}$</td>
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<td>$7.52 \times 10^{8}$</td>
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5 Variation of temperature during the experiment
Table D.7 (a) – Results from CCIGC model at specified conditions for PS (\(M_w = 200,000\text{g/mol}\)) with cyclohexanol at 180°C.

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<td>(1.8 \pm 0.1)</td>
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<tr>
<td>(14.59)</td>
<td>(1.5349)</td>
<td>(0.0407)</td>
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<td>(7.14 \times 10^8)</td>
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<td>(2.85 \times 10^{-5})</td>
<td>(7.28 \times 10^8)</td>
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<tr>
<td>(15.24)</td>
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<td>(0.0411)</td>
<td>(2.74 \times 10^{-5})</td>
<td>(7.38 \times 10^8)</td>
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<tr>
<td>(14.98)</td>
<td>(1.4001)</td>
<td>(0.0400)</td>
<td>(2.79 \times 10^{-5})</td>
<td>(7.51 \times 10^8)</td>
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Table D.7 (b) – Parameters used in elution on a plateau analysis at finite concentration measurements for PS (\(M_w = 200,000\text{g/mol}\)) with cyclohexanol at 180°C.

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<th>(\theta_s)</th>
<th>(\theta_M)</th>
<th>(k)</th>
<th>(j)</th>
<th>(\alpha)</th>
<th>(\psi)</th>
<th>(V_N^e)</th>
<th>(c)</th>
<th>(c')</th>
<th>(K)</th>
<th>(m_1)</th>
<th>(m_2)</th>
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<td>(5.685 \times 10^{-4})</td>
<td>(3.150)</td>
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<td>(0.9388)</td>
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<td>(5.6058 \times 10^{-6})</td>
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<td>(3.664 \times 10^{-2})</td>
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<td>(9.8521 \times 10^{-7})</td>
<td>(3.6527 \times 10^{-5})</td>
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<td>(65.04)</td>
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The equation used for the integral is \(V_N^e/(1-\psi) = 4.0645 + (8.9066 \times 10^9)e^{-(2.3772 \times 10^9)e^2} + (2.0624 \times 10^{11})e^3 + (7.9470 \times 10^{19})e^4\)
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<td>5.37 x 10⁻⁷</td>
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<td>2.6206</td>
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<td>4.72 x 10⁻⁷</td>
</tr>
<tr>
<td>123.00 ± 0.3</td>
<td>PSF102</td>
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<td>10.85</td>
<td>2.6575</td>
<td>0.0045</td>
<td>4.47 x 10⁻⁵</td>
<td>4.82 x 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>PSF105</td>
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<td>10.86</td>
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<td>0.0049</td>
<td>4.46 x 10⁻⁵</td>
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<tr>
<td></td>
<td>PSF108</td>
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<td></td>
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<td>0.0048</td>
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<td>4.52 x 10⁻⁷</td>
</tr>
<tr>
<td>148.60</td>
<td>PSF115</td>
<td>6.837 x 10⁻¹</td>
<td>0.9 ± 0.1</td>
<td>19.09</td>
<td>2.6587</td>
<td>0.0047</td>
<td>4.32 x 10⁻⁵</td>
<td>4.78 x 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>PSF118</td>
<td></td>
<td></td>
<td>19.21</td>
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<td>0.0050</td>
<td>4.31 x 10⁻⁵</td>
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<td>149.50 ± 0.2</td>
<td>PSF121</td>
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<td>19.27</td>
<td>2.6344</td>
<td>0.0050</td>
<td>4.30 x 10⁻⁵</td>
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Table D.8(a) – Results from CCIGC model at specified conditions for PS ($M_w = 200,000\text{g/mol}$) with cyclohexanol at 220°C.

* Variation of temperature during the experiment
<table>
<thead>
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<th>$a_M$</th>
<th>$k$</th>
<th>$j$</th>
<th>$a$</th>
<th>$\psi$</th>
<th>$V_N^a$</th>
<th>$c$</th>
<th>$c'$</th>
<th>$K$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$\Omega$</th>
</tr>
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<tbody>
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<td>5.685 x 10^{-3}</td>
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<td>1.919</td>
<td>0.7550</td>
<td>0.9554</td>
<td>5.413</td>
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<td>1.404 x 10^3</td>
<td>2.6801</td>
<td>19.77</td>
<td>0.0003</td>
<td>0.0013</td>
<td>4.7500</td>
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</tr>
<tr>
<td>3.722 x 10^{-2}</td>
<td>3.771</td>
<td>2.145</td>
<td>0.7579</td>
<td>0.9568</td>
<td>3.549</td>
<td>2.1858</td>
<td>9.1957 x 10^7</td>
<td>1.7782</td>
<td>20.04</td>
<td>0.0018</td>
<td>0.0086</td>
<td>4.6947</td>
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</tr>
<tr>
<td>1.016 x 10^{-1}</td>
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<td>2.041</td>
<td>0.7574</td>
<td>0.9597</td>
<td>9.716</td>
<td>2.3335</td>
<td>2.5103 x 10^6</td>
<td>5.0107</td>
<td>20.68</td>
<td>0.0052</td>
<td>0.0236</td>
<td>4.5624</td>
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<tr>
<td>2.735 x 10^{-1}</td>
<td>3.531</td>
<td>2.017</td>
<td>0.7502</td>
<td>0.9674</td>
<td>2.637</td>
<td>2.8341</td>
<td>6.7676 x 10^6</td>
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<td>0.0152</td>
<td>0.0635</td>
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<tr>
<td>6.442 x 10^{-1}</td>
<td>3.419</td>
<td>1.953</td>
<td>0.7512</td>
<td>0.9831</td>
<td>6.149</td>
<td>5.2855</td>
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<td>4.6611</td>
<td>29.29</td>
<td>0.0450</td>
<td>0.1578</td>
<td>3.5058</td>
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<tr>
<td>6.590 x 10^{-1}</td>
<td>3.413</td>
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<td>0.7550</td>
<td>0.9836</td>
<td>6.273</td>
<td>5.4713</td>
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<td>4.8432</td>
<td>29.64</td>
<td>0.0465</td>
<td>0.1624</td>
<td>3.4905</td>
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</table>

Table D.8 (b) – Parameters used in elution on a plateau analysis at finite concentration measurements for PS ($M_w = 200,000$ g/mol) with cyclohexanol at 220°C.

---

*The equation used for the integral is $V_N/(1-\psi) = 2.1138 + (6.4024 \times 10^9)c + (1.3231 \times 10^{10})c^2 + (1.8123 \times 10^{11})c^3 + (1.3176 \times 10^{12})c^4 + (2.3677 \times 10^{14})c^5$*
<table>
<thead>
<tr>
<th>$T_{mt} \pm \Delta T_{mt}$</th>
<th>File name</th>
<th>$P_1^{\text{emp}}$</th>
<th>$\Delta P$</th>
<th>$\nu$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\Gamma$</th>
<th>$D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>105.60 ± 0.2</td>
<td>COPF89</td>
<td>$1.336 \times 10^{-1}$</td>
<td>0.1</td>
<td>19.99</td>
<td>1.2143</td>
<td>0.3000</td>
<td>$2.13 \times 10^{-5}$</td>
<td>$5.04 \times 10^{-9}$</td>
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<tr>
<td></td>
<td>COPF92</td>
<td></td>
<td></td>
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<td>$5.10 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>COPF95</td>
<td></td>
<td></td>
<td>20.03</td>
<td>1.2126</td>
<td>0.2979</td>
<td>$2.13 \times 10^{-5}$</td>
<td>$5.08 \times 10^{-9}$</td>
</tr>
<tr>
<td>118.60 ± 0.3</td>
<td>COPF100</td>
<td>$2.314 \times 10^{-1}$</td>
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<td>20.07</td>
<td>1.2126</td>
<td>0.2967</td>
<td>$2.13 \times 10^{-5}$</td>
<td>$5.11 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>COPF103</td>
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<td></td>
<td>20.13</td>
<td>1.2087</td>
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<td>$5.24 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>COPF106</td>
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<td></td>
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<td>1.1961</td>
<td>0.2970</td>
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<td>$5.16 \times 10^{-9}$</td>
</tr>
<tr>
<td>126.80 ± 0.2</td>
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<td>$3.186 \times 10^{-1}$</td>
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<td>20.20</td>
<td>1.2097</td>
<td>0.2962</td>
<td>$2.11 \times 10^{-5}$</td>
<td>$5.16 \times 10^{-9}$</td>
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<tr>
<td></td>
<td>COPF114</td>
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</tr>
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<td>140.40 ± 0.3</td>
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<tr>
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<tr>
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<td>$4.96 \times 10^{-9}$</td>
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<tr>
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<td>1.2143</td>
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<td>$2.08 \times 10^{-5}$</td>
<td>$5.05 \times 10^{-9}$</td>
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<tr>
<td></td>
<td>COPF47</td>
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<td></td>
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<td>1.2134</td>
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<td>$5.03 \times 10^{-9}$</td>
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<tr>
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<td></td>
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<td>1.2130</td>
<td>0.3056</td>
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<td>$5.07 \times 10^{-9}$</td>
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<tr>
<td></td>
<td>COPF54</td>
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<td>1.2068</td>
<td>0.3034</td>
<td>$2.08 \times 10^{-5}$</td>
<td>$5.10 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

*Variation of temperature during the experiment*
Table D.9 (a) - Results from CCIGC model at specified conditions for random PS (40%)-co-MMA ($M_w = 100-150$ kg/mol) with cyclohexanol at 160°C.

| COPF59 | COPF62 | COPF65 | COPF68 | COPF71 | $156.20 \pm 0.4$ | $8.691 \times 10^{-1}$ | 0.1 | 20.51 | 20.52 | 20.56 | 20.51 | 20.40 | 1.2157 | 1.2100 | 1.2041 | 1.2149 | 1.2181 | 0.3011 | 0.3084 | 0.3079 | 0.3071 | 0.3083 | $2.08 \times 10^{-5}$ | $2.08 \times 10^{-5}$ | $2.08 \times 10^{-5}$ | $2.08 \times 10^{-5}$ | $2.09 \times 10^{-5}$ | $5.15 \times 10^{-9}$ | $5.03 \times 10^{-9}$ | $5.05 \times 10^{-9}$ | $5.05 \times 10^{-9}$ | $5.00 \times 10^{-9}$ |

Table D.9 (b) - Parameters used in elution on a plateau analysis at finite concentration measurements for random PS (40%)-co-MMA ($M_w = 100-150$ kg/mol) with cyclohexanol at 160°C.

<table>
<thead>
<tr>
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<th>$\beta_5$</th>
<th>$\alpha_i$</th>
<th>$K$</th>
<th>$j$</th>
<th>$a$</th>
<th>$\psi$</th>
<th>$V_n^{10}$</th>
<th>$c$</th>
<th>$c'$</th>
<th>$K$</th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\Omega$</th>
</tr>
</thead>
<tbody>
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<td>1.327 x $10^{-1}$</td>
<td>2.440</td>
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<td>1.4611</td>
<td>0.996609</td>
<td>0.9363</td>
<td>1.239 x $10^{-1}$</td>
<td>4.2670</td>
<td>3.7361 x $10^{-6}$</td>
<td>2.7076 x $10^{-4}$</td>
<td>67.34</td>
<td>0.0246</td>
<td>0.1370</td>
<td>5.5745</td>
</tr>
<tr>
<td>2.298 x $10^{-1}$</td>
<td>2.427</td>
<td>0.984</td>
<td>1.4666</td>
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<td>0.9440</td>
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<td>4.7867</td>
<td>6.4762 x $10^{-4}$</td>
<td>4.7833 x $10^{-4}$</td>
<td>68.63</td>
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<td>0.2372</td>
<td>5.5655</td>
</tr>
<tr>
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<td>5.3376</td>
<td>8.9325 x $10^{-4}$</td>
<td>6.8777 x $10^{-4}$</td>
<td>71.55</td>
<td>0.0602</td>
<td>0.3266</td>
<td>5.4289</td>
</tr>
<tr>
<td>5.166 x $10^{-1}$</td>
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<td>2.2386 x $10^{-3}$</td>
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Equation used for the integral is $V_n/(1-\psi) = 4.4046-(1.2654\times10^{10})c+(1.8607\times10^{10})c^2+(3.0721\times10^{10})c^3-(3.3157\times10^{10})c^4+(9.6063\times10^{10})c^5$. 

The equation used for the integral is $V_n/(1-\psi) = 4.4046-(1.2654\times10^{10})c+(1.8607\times10^{10})c^2+(3.0721\times10^{10})c^3-(3.3157\times10^{10})c^4+(9.6063\times10^{10})c^5$. 

The equation used for the integral is $V_n/(1-\psi) = 4.4046-(1.2654\times10^{10})c+(1.8607\times10^{10})c^2+(3.0721\times10^{10})c^3-(3.3157\times10^{10})c^4+(9.6063\times10^{10})c^5$.
<table>
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<th>$\Delta P$</th>
<th>$u$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\Gamma$</th>
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<td>16.69</td>
<td>1.8825</td>
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<td>2.77 x 10^{-5}</td>
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</tr>
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<td>COPF184</td>
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<td>16.73</td>
<td>1.8827</td>
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<td>2.76 x 10^{-5}</td>
<td>2.59 x 10^{8}</td>
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<td>1.8808</td>
<td>0.0477</td>
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<td>2.65 x 10^{8}</td>
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<td>2.59 x 10^{8}</td>
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<tr>
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<td>17.36</td>
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<td>0.0505</td>
<td>2.66 x 10^{-5}</td>
<td>2.60 x 10^{8}</td>
</tr>
<tr>
<td></td>
<td>COPF154</td>
<td></td>
<td></td>
<td>17.42</td>
<td>1.9666</td>
<td>0.0518</td>
<td>2.65 x 10^{-5}</td>
<td>2.54 x 10^{8}</td>
</tr>
<tr>
<td></td>
<td>COPF157</td>
<td></td>
<td></td>
<td>17.40</td>
<td>1.8874</td>
<td>0.0493</td>
<td>2.65 x 10^{-5}</td>
<td>2.67 x 10^{8}</td>
</tr>
</tbody>
</table>

Table D.10 (a) – Results from CCIGC model at specified conditions for random PS (40%)-co-MMA ($M_w = 100-150$ kg/mol) with cyclohexanol at 180°C.

\[ V_{ariation of temperature during the experiment] \]
<table>
<thead>
<tr>
<th>$y_0$</th>
<th>$e_0$</th>
<th>$\Delta_M$</th>
<th>$k$</th>
<th>$j$</th>
<th>$a$</th>
<th>$\psi$</th>
<th>$V_N^{12}$</th>
<th>$c$</th>
<th>$c'$</th>
<th>$K$</th>
<th>$m_1$</th>
<th>$\alpha_1$</th>
<th>$\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.583 x 10^{-2}</td>
<td>2.410</td>
<td>1.187</td>
<td>1.0309</td>
<td>0.996606</td>
<td>0.9406</td>
<td>3.359 x 10^{-2}</td>
<td>2.7294</td>
<td>9.6332 x 10^{-7}</td>
<td>4.5584 x 10^{-5}</td>
<td>44.51</td>
<td>0.0043</td>
<td>0.0211</td>
<td>4.9345</td>
</tr>
<tr>
<td>1.084 x 10^{-1}</td>
<td>2.396</td>
<td>1.183</td>
<td>1.0251</td>
<td>0.996608</td>
<td>0.9451</td>
<td>1.021 x 10^{-1}</td>
<td>2.9209</td>
<td>2.9145 x 10^{-6}</td>
<td>1.3871 x 10^{-4}</td>
<td>44.77</td>
<td>0.0129</td>
<td>0.0638</td>
<td>4.9474</td>
</tr>
<tr>
<td>3.606 x 10^{-1}</td>
<td>2.321</td>
<td>1.145</td>
<td>1.0271</td>
<td>0.996620</td>
<td>0.9605</td>
<td>3.452 x 10^{-1}</td>
<td>4.0136</td>
<td>9.7343 x 10^{-1}</td>
<td>5.3179 x 10^{-4}</td>
<td>51.39</td>
<td>0.0477</td>
<td>0.2124</td>
<td>4.4513</td>
</tr>
<tr>
<td>5.624 x 10^{-1}</td>
<td>2.315</td>
<td>1.139</td>
<td>1.0317</td>
<td>0.996639</td>
<td>0.9729</td>
<td>5.454 x 10^{-1}</td>
<td>5.8064</td>
<td>1.5270 x 10^{-5}</td>
<td>9.7847 x 10^{-4}</td>
<td>60.27</td>
<td>0.0844</td>
<td>0.3312</td>
<td>3.9244</td>
</tr>
<tr>
<td>8.632 x 10^{-1}</td>
<td>2.306</td>
<td>1.141</td>
<td>1.0216</td>
<td>0.996684</td>
<td>0.9914</td>
<td>8.529 x 10^{-1}</td>
<td>17.772</td>
<td>2.3752 x 10^{-5}</td>
<td>2.4453 x 10^{-3}</td>
<td>96.84</td>
<td>0.1872</td>
<td>0.5084</td>
<td>2.7149</td>
</tr>
</tbody>
</table>

Table D.10 (b) – Parameters used in elution on a plateau analysis at finite concentration measurements for random PS (40%)-co-MMA ($M_w = 100$-150 kg/mol) with cyclohexanol at 160°C.

\[ \text{The equation used for the integral is } V_N/(1-\psi) = 2.8222 - (8.1059 \times 10^4)c + (4.6289 \times 10^6)c^2 - (3.9287 \times 10^1)c^3 + (1.3637 \times 10^2)c^4 \]
Appendix E

CALCULATING ACTIVITY COEFFICIENTS USING UNIFAC-FREE VOLUME

Calculation of the weight fraction activity coefficient of cyclohexanol in polystyrene (M_r = 200,000 g/mol) with a weight fraction of 0.5 at 453.15 K.

Specific volume of cyclohexanol (453.15 K) \( v_1 = 1.2510 \times 10^{-3} \text{ m}^3/\text{kg} \)

Specific volume of polystyrene (453.15 K) \( v_2 = 1.0185 \times 10^{-3} \text{ m}^3/\text{kg} \)

Molecular weight of cyclohexanol \( M_c = 100.161 \text{ g/mol} \)

Mass of styrene repeat unit \( M_{styrene} = 104.153 \text{ g/mol} \)

No. of repeat units \( N_{repeat} \approx 1920 \)

Figure E.1 — Molecular structure of cyclohexanol (component 1, l.h.s.) and the styrene repeat unit (component 2, r.h.s.). Included are the UNIFAC-FV constituent groups.
The structures of cyclohexanol and the styrene repeat unit are shown in figure E.1 with their associated UNIFAC groups. The groups present in the molecules are summarised in the table below, together with the group area and volume parameters, \( R_k \) and \( Q_k \) respectively (High and Danner, 1993):

<table>
<thead>
<tr>
<th>Sub-group (#)</th>
<th>(1) Cyclohexanol</th>
<th>(2) PS repeat unit</th>
<th>( R_k )</th>
<th>( Q_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2) (2)</td>
<td>5</td>
<td>1</td>
<td>0.6744</td>
<td>0.540</td>
</tr>
<tr>
<td>CH (3)</td>
<td>1</td>
<td>0</td>
<td>0.4469</td>
<td>0.228</td>
</tr>
<tr>
<td>ACH (10)</td>
<td>0</td>
<td>5</td>
<td>0.5313</td>
<td>0.400</td>
</tr>
<tr>
<td>AC-CH (14)</td>
<td>0</td>
<td>1</td>
<td>0.8121</td>
<td>0.348</td>
</tr>
<tr>
<td>OH (15)</td>
<td>1</td>
<td>0</td>
<td>0.5299</td>
<td>0.584</td>
</tr>
</tbody>
</table>

*Table E.1 - UNIFAC sub-groups and their parameters for cyclohexanol and the polystyrene repeat unit.*

The UNIFAC interaction parameters, \( a_{ij} \), between these sub-groups (High and Danner, 1993) are given below, where the sub-groups are now classified into main groups I\{CH\(_2\), CH\}, II\{ACH\}, III\{AC-CH\(_2\)\} and IV\{OH\}:

\[
\begin{align*}
\text{I} & : a_{11}, a_{111}, a_{1111}, a_{111v}, a_{11v}, a_{1v}, a_{1v1}, a_{1v11} \\
\text{II} & : a_{22}, a_{222}, a_{2222}, a_{222v}, a_{22v}, a_{2v}, a_{2v2}, a_{2v22} \\
\text{III} & : a_{33}, a_{333}, a_{3333}, a_{333v}, a_{33v}, a_{3v}, a_{3v3}, a_{3v33} \\
\text{IV} & : a_{44}, a_{444}, a_{4444}, a_{444v}, a_{44v}, a_{4v}, a_{4v4}, a_{4v44} \\
\end{align*}
\]

So the volume and area parameters, \( r_i \) and \( q_i \), for each component \( i \) are calculated as follows:

\[
r_i = \sum_{k=1}^{4} \nu_{i,k} R_k \quad \text{(E.1)}
\]

\[
r_1 = 5(0.6744) + 1(0.4469) + 1(0.5299) = 4.3488 \\
r_2 = 1920 \times [1(0.6744) + 5(0.5313) + 1(0.8121)] = 7954.56
\]

Similarly,

\[
q_i = \sum_{k=1}^{4} \nu_{i,k} Q_k \quad \text{(E.2)}
\]
\[ q_1 = 5(0.540) + 1(0.228) + 1(0.584) = 3.512 \]
\[ q_2 = 1920 \times [1(0.540) + 5(0.4) + 1(0.348)] = 5544.96 \]

Calculate the \( l_i \) parameter:

\[ l_i = 5(r_i - q_i) - (r_i - 1) \quad \text{(E.3)} \]
\[ l_1 = 5(4.3488 - 3.512) - (4.3488 - 1) = 0.8352 \]
\[ l_2 = 5(7954.56 - 5544.96) - (7954.56 - 1) = 4094.44 \]

Calculate the molecular volume fraction \( \phi \):

\[ \phi_i = \frac{r_i w_i / M_i}{r_i w_i / M_i + r_j w_j / M_j} \quad \text{(E.4)} \]
\[ \phi_1 = \frac{4.3488 \times 0.5/100.161}{(4.3488 \times 0.5/100.161) + (7954.56 \times 0.5/200000)} = 0.5219 \]
\[ \phi_2 = \frac{7954.56 \times 0.5/200000}{(4.3488 \times 0.5/100.161) + (7954.56 \times 0.5/200000)} = 0.4781 \]

Calculate the molecular area fraction \( \theta \):

\[ \theta_i = \frac{q_i w_i / M_i}{q_i w_i / M_i + q_j w_j / M_j} \quad \text{(E.5)} \]
\[ \theta_1 = \frac{3.512 \times 0.5/100.161}{(3.512 \times 0.5/100.161) + (5544.96 \times 0.5/200000)} = 0.5584 \]
\[ \theta_2 = \frac{5544.96 \times 0.5/200000}{(3.512 \times 0.5/100.161) + (5544.96 \times 0.5/200000)} = 0.4416 \]

So the combinatorial contribution, \( \ln \Omega_i^{\text{comb}} \), is 0.5591 calculated as follows:

\[ \ln \Omega_i^{\text{comb}} = \ln \frac{\phi_i}{w_i} + 5q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i M_i}{w_i} \sum_{j=1}^{3} \frac{w_j}{M_j} \quad \text{(E.6)} \]
\[
\ln \mathcal{Q}_i^{\text{comb}} = \ln \frac{0.5219}{0.5} + 5 \times 3.5121 \ln \frac{0.5584}{0.5219} + 0.8352
\]
\[
- \frac{0.5219 \times 100.161}{0.5} \left[ 0.8352 \times \frac{0.5}{100.161} + 4094.44 \times \frac{0.5}{200000} \right] = 0.5591
\]

Now, calculate the group mole fraction, \( X_m \), for each group \( m \) in the solution:

\[
X_m = \frac{\sum_j v_{ij} w_j / M_i}{\sum_j w_j / M_i \sum_p v_{ip}^{(j)}}
\]  
(E.7)

Subgp. (2) \( X_2 = \frac{(5 \times 0.5 / 100.161) + (1920 \times 1 \times 0.5 / 200000)}{[0.5(5+1+1)/100.161] + [0.5 \times 1920(1+5+1)/200000]} = 0.4342
\]

Subgp. (3) \( X_3 = \frac{(1 \times 0.5 / 100.161) + (1920 \times 0 \times 0.5 / 200000)}{[0.5(5+1+1)/100.161] + [0.5 \times 1920(1+5+1)/200000]} = 0.0728
\]

Subgp. (10) \( X_{10} = \frac{(0 \times 0.5 / 100.161) + (1920 \times 5 \times 0.5 / 200000)}{[0.5(5+1+1)/100.161] + [0.5 \times 1920(1+5+1)/200000]} = 0.3501
\]

Subgp. (14) \( X_{14} = \frac{(0 \times 0.5 / 100.161) + (1920 \times 1 \times 0.5 / 200000)}{[0.5(5+1+1)/100.161] + [0.5 \times 1920(1+5+1)/200000]} = 0.0701
\]

Subgp. (15) \( X_{15} = \frac{(1 \times 0.5 / 100.161) + (1920 \times 0 \times 0.5 / 200000)}{[0.5(5+1+1)/100.161] + [0.5 \times 1920(1+5+1)/200000]} = 0.0728
\]

Calculate the group surface area fraction, \( \Theta_m \), for each group \( m \) in the solution:

\[
\Theta_m = \frac{Q_m X_m}{\sum_p Q_p X_p}
\]  
(E.8)

\[
\sum_p Q_p X_p = [0.54 \times 0.4342] + [0.228 \times 0.0728] + [0.4 \times 0.3501] + [0.348 \times 0.0701] + [0.584 \times 0.0728] = 0.4580
\]
Subgp. (2) \[ \Theta_2 = \frac{0.54 \times 0.4342}{0.4580} = 0.5119 \]
Subgp. (3) \[ \Theta_3 = \frac{0.228 \times 0.0728}{0.4580} = 0.0362 \]
Subgp. (10) \[ \Theta_{10} = \frac{0.4 \times 0.3501}{0.4580} = 0.3058 \]
Subgp. (14) \[ \Theta_{14} = \frac{0.348 \times 0.0701}{0.4580} = 0.0533 \]
Subgp. (15) \[ \Theta_{15} = \frac{0.584 \times 0.0728}{0.4580} = 0.0928 \]

Now, calculate the group interaction parameter function \( \psi_{\text{mmt}} \) for each main group,

\[ \psi_{\text{mmt}} = \exp(-a_{\text{mmt}}/T) \] \hspace{1cm} (E.9)

\[ \begin{align*}
\psi_{1,1} &= 1.00 \\
\psi_{1,II} &= 0.8738 \\
\psi_{1,III} &= 0.8447 \\
\psi_{1,IV} &= 0.1134 \\
\psi_{II,1} &= 1.0248 \\
\psi_{II,II} &= 1.00 \\
\psi_{II,III} &= 0.6917 \\
\psi_{II,IV} &= 0.2457 \\
\psi_{III,1} &= 1.1663 \\
\psi_{III,II} &= 1.3826 \\
\psi_{III,III} &= 1.00 \\
\psi_{III,IV} &= 0.1699 \\
\psi_{IV,1} &= 0.7081 \\
\psi_{IV,II} &= 0.8206 \\
\psi_{IV,III} &= 0.9446 \\
\psi_{IV,IV} &= 1.00
\end{align*} \]

the residual activity coefficient of sub-group \( k, \Gamma_k \):

\[ \ln \Gamma_k = \frac{Q_k}{1 - \ln \left( \sum_m \theta_m \psi_{m,k} \right) - \sum_m \frac{\theta_m \psi_{m,k}}{\sum_{m'} \theta_{m'} \psi_{m',k}}} \] \hspace{1cm} (E.10)

\[ \begin{align*}
k = 2, \quad & \sum_m \theta_m \psi_{m2} = 0.5119(1.00) + 0.0362(1.00) + 0.3058(1.0248) \\
& + 0.0533(1.1663) + 0.0928(0.7081) = 0.9894 \\
k = 3, \quad & \sum_m \theta_m \psi_{m3} = 0.5119(1.00) + 0.0362(1.00) + 0.3058(1.0248) \\
& + 0.0533(1.1663) + 0.0928(0.7081) = 0.9894 \\
k = 10, \quad & \sum_m \theta_m \psi_{m10} = 0.5119(0.8738) + 0.0362(0.8738) + 0.3058(1.00) \\
& + 0.0533(1.3826) + 0.0928(0.8206) = 0.9346
\]
\[ k = 14, \quad \sum_{m}^{\theta} \psi_{m14} = 0.5119(0.8447) + 0.0362(0.8447) + 0.3058(0.6917) + 0.0533(1.00) + 0.0928(0.9446) = 0.8155 \]

\[ k = 15, \quad \sum_{m}^{\theta} \psi_{m15} = 0.5119(0.1134) + 0.0362(0.1134) + 0.3058(0.2457) + 0.0533(1.00) + 0.0928(1.00) = 0.2391 \]

\[ k = 2, \quad \sum_{p}^{\theta} \psi_{pk} = (0.5119(0.100)/0.9894) + (0.0362(0.100)/0.9894) \]
\[ + [0.3058(0.8738)/0.9346] + [0.0533(0.8447)/0.8155] + [0.0928(0.1134)/0.2391] = 0.9391 \]

\[ k = 3, \quad \sum_{p}^{\theta} \psi_{pk} = (0.5119(0.1048)/0.9894) + (0.0362(0.1048)/0.9894) \]
\[ + [0.3058(0.9346)/0.9346] + [0.0533(0.6917)/0.8155] + [0.0928(0.1699)/0.2391] = 1.0483 \]

\[ k = 10, \quad \sum_{p}^{\theta} \psi_{pk} = (0.5119(1.1663)/0.9894) + (0.0362(1.1663)/0.9894) \]
\[ + (0.3058(1.3826)/0.9346) + (0.0533(1.00)/0.8155) + (0.0928(0.2457)/0.2391) = 1.2298 \]

\[ k = 14, \quad \sum_{p}^{\theta} \psi_{pk} = (0.5119(0.7081)/0.9894) + (0.0362(0.7081)/0.9894) \]
\[ + (0.3058(0.8206)/0.9346) + (0.0533(0.9446)/0.8155) + (0.0928(1.00)/0.2391) = 1.1106 \]

\[ k = 2, \quad \ln \Gamma_2 = 0.54[1 - \ln(0.9894) - 0.9391] = 0.0271 \]

\[ k = 3, \quad \ln \Gamma_3 = 0.228[1 - \ln(0.9894) - 0.9391] = 0.0163 \]

\[ k = 10, \quad \ln \Gamma_{10} = 0.4[1 - \ln(0.9346) - 1.0483] = 7.735 \times 10^{-3} \]

\[ k = 14, \quad \ln \Gamma_{14} = 0.3484[1 - \ln(0.8155) - 1.2298] = -9.005 \times 10^{-3} \]

\[ k = 15, \quad \ln \Gamma_{15} = 0.584[1 - \ln(0.2391) - 1.1106] = 0.7710 \]

Next, a reference solution is considered containing only the solvent component and the same calculations as before performed. Therefore the residual contribution, \( \ln \Omega^{\text{res}} \), is \(-8.0011 \times 10^{-3}\) calculated as follows:
\[ \ln \Omega_i^\text{ex} = \sum_k v_k^{1/3} [\ln \Gamma_k - \ln \Gamma_k^\text{RIP}] \]  

(E.11)

\[
\ln \Omega_i^\text{ex} = 5(0.0271-0.0547) + 1(0.0163-0.0231) + 1(0.7710-0.6342) = -8.0011 \times 10^{-3}
\]

Lastly, calculate the free-volume contribution. First calculate the reduced volumes of both solvent and polymer,

\[
\bar{\nu}_i = \frac{\nu_i M_i}{0.01517 \times 1.28 \times r_i}
\]

(E.12)

\[
\bar{\nu}_1 = \frac{0.001251 \times 100.161}{0.01517 \times 1.28 \times 4.3488} = 1.4839
\]

\[
\bar{\nu}_2 = \frac{0.0010185 \times 200000}{0.01517 \times 1.28 \times 7954.56} = 1.3188
\]

Then the reduced volume of the mixture:

\[
\bar{\nu}_\text{mix} = \frac{\sum_i \nu_i w_i}{0.01517 \times 1.28 \sum_i \frac{\nu_i w_i}{M_i}}
\]

(E.13)

\[
\bar{\nu}_\text{mix} = \frac{(0.001251 \times 0.5) + (0.0010185 \times 0.5)}{0.01517 \times 1.28 \times [(4.3488 \times 0.5 / 100.161) + (7954.56 \times 0.5 / 200000)]} = 1.4049
\]

Therefore the free-volume contribution, \( \ln \Omega_i^F \), is 0.02133 calculated as follows:

\[
\ln \Omega_i^F = 3c_i \ln \left[ \frac{\bar{\nu}_i^{1/3}}{(\bar{\nu}_i^{1/3})} \right] - c_i \left[ \left( \frac{\bar{\nu}_i}{\bar{\nu}_\text{mix}} - 1 \right) \left( 1 - \frac{1}{\bar{\nu}_i^{1/3}} \right) \right]^{-1}
\]

(E.14)

\[
\ln \Omega_i^F = 3 \times 1.1 \ln \left[ \frac{1.4839}{1.4049} \right] - 1.1 \left[ \frac{1.4839}{1.4049} - 1 \right] \left( 1 - \frac{1}{1.4839^{1/3}} \right) = 0.02133
\]

Finally,

\[
\ln \Omega_i = \ln \Omega_i^\text{comb} + \ln \Omega_i^\text{ex} + \ln \Omega_i^F = 0.5591 - 8.0011 \times 10^{-3} + 0.02133 = 0.5726
\]

(E.15)