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Abstract

Research into the thermodynamic behaviour of copolymer blends has been stimulated by the increasing number of applications in which these materials can be used. In this work, it was intended to characterise the thermodynamics of mixtures of two industrial copolymers and to review the experimental techniques and theoretical analyses currently used in this field.

The copolymers used were poly(ethylene-co-vinyl acetate), with $\bar{M}_n = 3290$, and poly(tetradecyl fumarate-co-vinyl acetate), with $\bar{M}_n = 10400$. The thermodynamics of these mixtures was studied using Differential Scanning Calorimetry, Inverse Phase Gas Chromatography, Solvent Vapour Sorption, Heats of Mixing Calorimetry and Phase Contrast Optical Microscopy. The results of these experiments were interpreted using Flory-Huggins Lattice fluid theory and Flory-Prigogine equation of state theory. Additionally, the results of the calorimetry and chromatography experiments were used to predict the theoretical phase boundary with the intention of comparing the phase boundaries determined experimentally with those predicted theoretically. Unfortunately this comparison could not be made because none of the techniques listed above located a miscibility limit between 303 and 393K. Although some of the experimental results are in conflict, it has been concluded that these materials are immiscible in all proportions in this temperature range. The theoretically simulated spinodal condition occurs between 5 and 50K and is of little practical use in the absence of its experimental equivalent and its extreme temperature.

The free energy change which occurs on mixing these copolymers is dominated by the entropic contribution and the equation of state was concluded to be inadequate to interpret this type of behaviour. It is believed that this is the first work which uses experimental data and a partition function to calculate directly a phase boundary without the inclusion of a fixing parameter.
Thermodynamics of Polymer Mixtures

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April 1991

Submitted for the Degree of Doctor of Philosophy of the University of Durham

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from it should be acknowledged.

10 FEB 1992
To The Angel - Heaven can wait
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"Ooh, I get by with a little help from my friends"
"You play, you win, you play, you lose, you play"

- Jeanette Winterton, The Passion
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Chapter 1  Introduction

The last four decades have seen significant research into the occurrence and characterisation of mutually soluble polymeric species. This effort was initiated and has been sustained by both academic interest and the many commercial applications where either an averaging of pure polymer properties or a useful combination of different properties has been sought.

Until the 1960s very few polymer pairs were known to be miscible and, conceptually, polymer miscibility was always considered to be unusual since high molecular weight materials have a negligibly small entropic contribution to mixing energetics and consequently a small, unfavourable enthalpic contribution would preclude miscibility. The majority of the early polymer blends were found to be miscible because of some strong specific interaction between components in different chains, e.g. hydrogen bonding, which dominated the free energy change on mixing. However, a wide range of materials has been studied and a host of compatible pairs identified\(^{(1)}\), including poly(vinylchloride) with poly(acrylates)\(^{(2)}\), vinyl acetate copolymers\(^{(3)}\) and butadiene-acrylonitrile copolymers\(^{(4)}\), all of which have found applications as additives in the industrial manufacture of PVC, and polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) which form a strong engineering plastic which is sold under copyright as 'Noryl'\(^{(5)}\). There are essentially three methods of preparing miscible polymer blends,

(a) mechanical mixing,

(b) mixing in a common solvent, and

(c) \textit{in situ} polymerisation.

Although physically mixing two polymers is the simplest and most widely utilised method of producing blends in industry it has several inherent disadvantages. Firstly, polymeric materials often have relatively low thermal stability and the lengthy periods, at elevated temperatures, necessary for the inter-diffusion of viscous polymers often cause degradation of the product. Secondly, efficient mixing can be extremely difficult and when this is not achieved the resulting blend often contains regions of heterogeneous polymer and degraded material, caused by prolonged exposure to excessive temperatures in the reactor. Dissolution and mixing of polymers in a common solvent is the preferred academic method as it is suitable for small-scale preparations and generally forms more homogeneous mixtures since the viscosity and mobility problems of physically contacting the polymers are avoided.
However, this is not necessarily true, since the introduction of a common solvent results in a ternary system which has its own miscibility limits and subsequent evaporation of the solvent may cause the entire system to become thermodynamically unstable and completely phase separate, e.g. polystyrene and poly(vinyl methyl ether) form two-phase systems when cast from chlorinated solvents but homogeneous blends when cast from toluene. Finally, in situ polymerisation involves reacting a monomer in the presence of another polymer. This technique is particularly attractive in industrial processes because it can be used to fabricate both engineering plastics, which are essentially insoluble, and base polymers which have poor thermal stability and/or a high glass-transition temperature. It has also found favour as an alternative to existing large scale commodity processes which generate enormous solvent effluents. However, this approach does not guarantee a miscible blend since two-phase regions can exist within the polymer/polymer/monomer phase diagram, and frequently this approach involves a series of reaction steps which are designed to maintain the composition within the miscibility window.

Owing to the limited number of monomeric species which can be polymerised, and the processing difficulties which arise while attempting to manufacture miscible polymer blends, significant interest has developed in copolymers, i.e. species which are formed from more than one monomer. Copolymers have a distinct advantage over homopolymer blends because the monomers are part of the same molecular chain, and hence their intimate contact is guaranteed. Although these materials often display the complementary properties desired in the corresponding polymer blend, they have also been found to have completely unique properties, e.g. synthetic rubber is commonly prepared as a terpolymer comprising butadiene for elasticity, styrene for rigidity and acrylonitrile for solvent resistance. In this material the polystyrene molecules are segregated spatially and form supporting cross-linked structures which can be thermally decomposed. This reversibility may lead to a synthetic alternative to natural rubber which would be capable of being recycled. Copolymers have also found applications as 'compatibilisers', where an AB copolymer can be used to solubilise a mixture of A and B bulk polymers in a similar manner to the way that a soap molecule behaves at the oil/water interface. They have also found applications as crystal structure modifiers where the incorporation of a minute quantity of a copolymer contaminant disrupts the order of the crystallising bulk polymer chains.
Some confusion is evident when the terms compatibility and miscibility are used with reference to polymer systems. The academic literature describes a mixture which behaves as a single phase as being compatible, whereas the same term is frequently used in an industrial context to describe materials, capable of being processed, which are heterogeneous and phase separated. Similarly, many commercially available materials which are described as being miscible actually are micro-phase separated dispersions. To eliminate this confusion, miscibility is most clearly defined on a thermodynamic basis where the essential, unambiguous criterion for its existence is a negative and favourable free energy of mixing. The original theories of polymer-polymer thermodynamics were derived from liquid-liquid and polymer-solvent theories$^{(6,7,8,9,10)}$ and Flory’s lattice theory$^{(11)}$. The latter remains the most successful of the simple approaches and retains many of the original features of the small molecule theories. More recently, an equation of state approach has been developed which links all of the state parameters, and hence physical characteristics, of a polymer or a mixture of polymers, by a single partition function. This type of theory is generally agreed to provide a more accurate description of blend behaviour but its application requires a considerable data input which in some cases appears to outweigh its advantages. However, both of these types of theory include a term which characterises the energetic interaction between two heterospecies and, by the numerical value or sign of this term, gives an indication of whether these materials are likely to be miscible. This term is generally defined as the interaction parameter. A host of analytical techniques has been applied, or developed, to determine the value of these interaction parameters for a wide range of polymer mixtures.

The simplest method of measuring the enthalpic interaction of two fluids is to measure their heat of mixing. The main advantage of this type of experiment are that the operation is being measured directly and only the enthalpic contribution to the free energy of mixing is detected. The theoretical and experimental simplicity of this measurement should provide data which are both accurate and absolute. Unfortunately, it is almost impossible to determine the heat of mixing of polymeric materials owing to their physical state, and consequently the existing heat of mixing studies on polymer blends have used either a common solvent as a third component and extracted the polymer-polymer contribution using a Hess's law$^{(12)}$ type calculation, or they have used low molecular weight analogues and attempted to modify these values for the high molecular weight case$^{(13,14)}$. Not surprisingly, neither approach has been particularly successful as the enthalpy of mixing of macromolecular species tends to be small, and consequently the errors in a
Hess's law calculation are significant, and the corrections to oligomeric determinations are extremely crude. Another classical and simple technique which has been applied to polymer systems is solvent vapour sorption\(^{(15)}\) which comprises exposing a homopolymer or blend to solvent vapour and measuring the uptake as a function of solvent vapour pressure. As with heats-of-mixing experiments, this technique also has the advantage of providing absolute thermodynamic information and does not require the polymer phase to be either mobile or volatile. The main disadvantage of SVS is that it is a static equilibrium method and consequently a measurement can only be taken once the solvent has diffused into the bulk polymer structure and an absorption equilibrium has been established. This can take a period of days or even weeks and during this period complete control of temperature and vapour pressure are required. The polymer-polymer interaction is calculated from SVS data by measuring each homopolymer-solvent response, the blend-solvent response and then extracting the difference algebraically and defining this as the polymer-polymer contribution. This method of analysis is also used in inverse phase gas chromatography which involves eluting a volatile solvent of known physical characteristics over a polymeric stationary phase, the inverse situation to conventional gas chromatography. This technique was first reported in 1969\(^{(16)}\) and stimulated considerable interest as it appeared to be a rapid, cheap and reliable method of studying the thermodynamics of polymer-solvent and polymer-polymer systems. However, this initial optimism soon waned when it became clear that the polymer-polymer interaction parameters which were derived from IGC measurements exhibited a clear dependence on the nature of the solvent probe. Much of the subsequent research into the application of IGC to polymer blends has been devoted to characterising this solvent dependence but a definitive solution has not yet been found and this remains an inherent weakness.

If one of the components of a polymer blend is amorphous while the other is crystalline at any particular temperature, the depression of the crystalline component's melting point can be used to evaluate an interaction parameter\(^{(11,17)}\) and the most convenient techniques to follow this effect are differential scanning calorimetry and turbidity measurements. Although this approach is appealing theoretically it has been found to be difficult in practice owing to heterogeneity and diffusion limitation on sample heating and supercooling in reverse. Another technique which can be used to evaluate polymer-polymer interaction parameters is intrinsic viscosity measurements, which have been used for some time to determine the interaction parameters of dilute polymer-solvent-non-solvent systems, but some work has also been
carried out to examine its suitability to polymer blends\textsuperscript{(18)}. The scattering of radiation, \textit{i.e.} X-rays and light, has also been widely used to characterise the thermodynamics of polymer blends but since this area is so large, and the techniques were not applicable in this work, it was felt that further discussion was outwith the scope of this study.

The equation of state theory can also be used to evaluate interaction parameters by fitting theoretical spinodal functions to experimental data, using $Q$, the entropic correction factor, as the adjustable parameter\textsuperscript{(19)}. This approach assumes that the free energy of mixing can be represented by an enthalpic component, which is constant for any polymer pair, and an entropic correction factor. The value of the enthalpic component dictates the position of the spinodal and small adjustments are then made to $Q$ in order to improve the fit. However, as $Q$ has no physical significance, and was incorporated into the equation of state model to improve the original predictions, this arbitrary fitting procedure is difficult to justify since it assumes that the adopted partition function upon which the EOS is based represents exactly the thermodynamic mixing of polymer molecules and any poor correlation between theoretical and experimental results can be ascribed to entropic effects which are not accounted for by the model.

The intentions behind this current work were to characterise the mixing of two copolymers on the basis that they were homopolymers and examine the applicability and accuracy of the homopolymer models to this system. This study was to include determination of the free energy polymer-polymer interaction parameter from an indirect technique, \textit{e.g.} IGC or SVS, determination of the enthalpic interaction parameter from heats of mixing experiments and then, for the first time, directly calculating the value of $Q$. From this information the phase boundary can be simulated. It was then hoped to measure the experimental phase boundary using phase contrast optical microscopy or differential scanning calorimetry and compare these results to the simulated condition.
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Chapter 2  Theories of Polymer Miscibility

2.0  Introduction

Solution thermodynamics\(^{(1)}\) forms the basis for many of the theories of polymer-polymer miscibility. These theories normally involve modelling the mixture and interpreting its behaviour with statistical techniques. The difference in many of the theories lies in either the nature and sophistication of the initial model, or the statistical mechanics with which it is interpreted. This chapter aims to describe and discuss the salient features and areas of application of some of the more widely used theories without explicitly deriving them from first principles since these procedures are well documented elsewhere.

The equilibrium properties of a material can be fully characterised by a knowledge of the Gibbs free energy, \(G\), as a function of the independent state variables, \(e.g.\) temperature, \(T\), pressure, \(P\), and composition. The change in this function must be negative for a potential mixing process, \(i.e.\) \(\Delta G_{\text{mix}} < 0\), and this is a necessary, although not sufficient, criterion for miscibility.

For the process,

\[
(Molecule)_1 + (Molecule)_2 \rightarrow (Molecule)_{12}
\]

this change is defined as,

\[
\Delta G_{\text{mix}} = G_{12} - (n_1 G_i^0 + n_2 G_j^0)
\]  \hspace{1cm} (2.1)

where,

\(G_{12}\) = Gibbs free energy of mixture, \(J\)

\(n_i\) = number of moles of component 'i', mol

\(G_i^0\) = molar Gibbs function of pure component 'i' at the temperature and pressure of the system, \(J\)

This study has used both classical Flory\(^{(2-6)}\) - Huggins\(^{(5-8)}\) - Chang\(^{(6)}\) - Miller\(^{(10-12)}\) theory, which is based on a lattice model, and Prigogine\(^{(13,14)}\) - Flory\(^{(15,17)}\) theory, which uses an arbitrary partition function to interpret the changes in the Gibbs free energy in terms of an equation of state, and their relative merits are considered. The discussion of Prigogine-Flory theory concentrates on the concepts involved rather than the mathematical treatment as a full description of how to apply this theory is detailed in chapter 8.
2.1 Flory-Huggins-Chang-Miller Theory (FHCM)

Flory-Huggins-Chang-Miller theory considers $\Delta G_{\text{mix}}$ as the sum of enthalpic and entropic contributions and develops these terms independently, *i.e.* from the classical expansion,

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$  \hspace{1cm} (2.2)

where, $\Delta H_{\text{mix}}$ = change in enthalpy of the system on mixing, J mol$^{-1}$

$\Delta S_{\text{mix}}$ = change in entropy of the system on mixing, J mol$^{-1}$ K$^{-1}$

$T$ = absolute temperature, K

The fundamentals of this approach will be derived initially for small molecules and then developed for polymers.

The Enthalpic Contribution, ($\Delta H_{\text{mix}}$)

Intermolecular forces between uncharged molecules decrease rapidly as the separation distance increases and thus this model considers the effect of mixing only on neighbouring molecules. The enthalpic change, defined as the heat of mixing, $\Delta H_{\text{mix}}$, is considered to originate from the difference in contact energy between like and unlike molecules, *e.g.* for a system comprising species 1 and 2,

$$W = 0.5 \left| (E_{11} + E_{22} - 2E_{12}) \right|$$  \hspace{1cm} (2.3)

where

$W$ = change in contact energy for the formation of a molecule of '12', J

$E_{ij}$ = contact energy between species 'i' and 'j', J

If a single arrangement of molecules on the lattice is specified, in which there are $N_c$ unlike contacts, the heat of formation, $\Delta H_{\text{conformation} 1}$, of this particular configuration, from the pure components is,

$$\Delta H_{\text{conformation} 1} = N_c W$$  \hspace{1cm} (2.4)
An average value of \( N_c \) is now required to represent random mixing in the solution. This term is the product of the number of contact sites available and the probability that neighbouring molecules are different,

\[
N_c = z n_1 p_{12}
\]  

(2.5)

where

\[
\begin{align*}
 z &= \text{the coordination number of the lattice} \\
n_1 &= \text{the number of molecules of 'species 1'} \\
p_{12} &= \text{the probability that the neighbour of a molecule of component 1 is a molecule of component 2}
\end{align*}
\]

This probability term is difficult to evaluate since the frequency of different contacts is governed by Boltzmann factors. Instead it is replaced with the probability, \( p_2 \), that any molecule in the solution is of component 2 irrespective of its position. If it is assumed that the arrangement of the molecules on the lattice is completely random, this probability is equal to the mole fraction of component 2,

\[
p_{12} = p_2 = N_2 / (N_1 + N_2) = x_2
\]  

(2.6)

where

\[
\begin{align*}
 N_i &= \text{the number of molecules of species 'i'} \\
x_i &= \text{mole fraction of 'i'}
\end{align*}
\]

and hence,

\[
\Delta H_{\text{conformation 1}} = \frac{z W N_1 N_2}{N_1 + N_2} = z W N_{AV} n_1 x_2 \equiv \Delta H_{\text{mix}}
\]  

(2.7)

where

\[
\begin{align*}
 n_i &= \text{number of moles of 'i'} \\
 N_{AV} &= \text{Avogadro's number, } 6.023 \times 10^{23} \text{ mol}^{-1}
\end{align*}
\]

The product \( z W N_{AV} \) represents the enthalpy change that occurs when 1 mole of pure A is infinitely diluted in a solution of B, or vice versa. This theory then simplifies the situation by introducing the 'interaction parameter', \( \chi_{12} \),

\[
\chi_{12} \equiv \frac{z W N_{AV}}{RT} \equiv \frac{z W}{kT}
\]  

(2.8)
where
\[ R = \text{General gas constant, } 8.31441 \text{ J mol}^{-1}\text{K}^{-1} \]
\[ k = \text{Boltzmann constant, } 1.38066 \times 10^{-23} \text{ JK}^{-1} \]
and therefore
\[ \Delta H_{\text{mix}} = zW N_A n_1 x_2 = RT n_1 x_2 x_{12} \] (2.9)

This dimensionless quantity, \( x_{12} \), incorporates the difference in energy that a molecule possesses when it is surrounded by molecules of another species, compared to that of the pure state. \( x_{12} \) can be either positive or negative and theoretically is inversely proportional to temperature. It should be noted that none of the original parameters of the hypothetical lattice is retained in this final expression as they have been incorporated into the \( x_{12} \) parameter.

This predicted independence was supported by the work of Longuet-Higgins\(^{(18)}\) who derived the same expression, starting from the free energy of mixing, and derived on a classical basis.

The Entropic Contribution, (\( \Delta S_{\text{mix}} \))

Using statistical mechanics, the entropy of any system can be subdivided conceptually into several components:

(a) external degrees of freedom, e.g. translational movement
(b) internal degrees of freedom, e.g. vibration and rotation
(c) intermolecular interactions, and
(d) configurational entropy

Configurational entropy, \( S_{\text{conf}} \), plays a significant role in the thermodynamics of polymer chains, because of the numerous orientations that these molecules can adopt, and Flory-Huggins-Chang-Miller theory assumes that it is the only significant entropic effect that occurs during mixing of polymers, i.e. \( \Delta S_{\text{mix}} \equiv S_{\text{conf}} \). This can be calculated from the Boltzmann relation,
\[ S_{\text{conf}} = k \ln C \] (2.10)

where \( C \) = the number of different molecular arrangements compatible with the same macroscopic state of the system.
The relationship above implies total randomness and thus C can be equated to
the total number of configurations that \( N_1 \) molecules of substance 1 can
assume upon a lattice comprising molecules of 1 and 2 arranged over \( N_1 + N_2 \)
locations.

From this concept \( C \) can be redefined as,

\[
C = \frac{(N_1 + N_2)!}{(N_1!N_2!)}
\]  \hspace{1cm} (2.11)

From which (2.10) becomes,

\[
S_{\text{conf}} = k \ln \left( \frac{(N_1 + N_2)!}{(N_1!N_2!)} \right)
\]  \hspace{1cm} (2.12)

If the factorial terms are simplified by Stirling’s approximation,

\[
i.e. \quad \ln (N!) = N \ln (N) - N,
\]

Equation 2.10 becomes,

\[
S_{\text{conf}} = -k \left( N_1 \ln \left( \frac{N_1}{(N_1 + N_2)} \right) \right) + N_2 \ln \left( \frac{N_2}{(N_1 + N_2)} \right)
\]  \hspace{1cm} (2.13a)

This can now be re-expressed in terms of moles and mole fractions,

\[
i.e. \quad R = kN_{av} \quad \text{and} \quad \frac{N_i}{(N_1 + N_2)} = x_i,
\]

then

\[
S_{\text{conf}} = -R \left( n_1 \ln (x_1) + n_2 \ln (x_2) \right)
\]  \hspace{1cm} (2.13b)

From the assumption stated earlier, that this term represents the only
contribution to entropic change during mixing,

\[
\Delta S_{\text{mix}} = -R \left( n_1 \ln (x_1) + n_2 \ln (x_2) \right)
\]  \hspace{1cm} (2.13c)

This is the general form of the entropic contribution to the mixing from FHCM
theory. If equations 2.9 and 2.13c are substituted into equation 2.2, an
expression for the free energy change is obtained,

\[
\Delta G_{\text{mix}} = n_1 x_2 x_{12} RT - \left( -RT \left( n_1 \ln (x_1) + n_2 \ln (x_2) \right) \right)
\]

or,

\[
\frac{\Delta G_{\text{mix}}}{RT} = n_1 x_2 x_{12} + n_1 \ln (x_1) + n_2 \ln (x_2)
\]  \hspace{1cm} (2.14a)

or

\[
\Delta G_{\text{mix}} = RT \left( n_1 \ln (x_1) + n_2 \ln (x_2) + n_1 x_2 x_{12} \right)
\]  \hspace{1cm} (2.14b)

This is the classical FHCM expression for the free energy of mixing of small
molecules which, in turn, requires to be modified to represent the mixing of
polymeric species.
In order to place both solvent molecules and macromolecules on the same lattice it is necessary to subdivide the polymer chains into segments, each of which have the same volume as a solvent molecule. If the ratio of the molar volumes of the polymer, subscript 2, and solvent, subscript 1, is defined as \(f\), the number of sites available on the lattice is now \(N_1 + fN_2\) and these must accommodate \(N_1\) molecules of solvent and \(N_2\) macromolecules. In this system the configurational entropy is equal to the number of different arrangements in which these species can coexist in the lattice. In this case the calculation is more complex than for a small molecule, since each segment of the macromolecule is not discrete. The optimum solution to this problem is again obtained by the use of probabilities. In the small molecule derivation, it was assumed that the probability of a specific neighbouring cell already being occupied was equal to that of any other cell already being occupied, which is also equal to the number of cells occupied at any given time in the lattice filling process. For simplicity this assumption is also applied to macromolecular systems. It is adequate for highly concentrated polymer solutions and polymer blends, but renders the theory useless for dilute solutions where the local density of the polymeric segments may be high even though the overall concentration may be approaching infinite dilution. Since the polymer dimension which is now of interest is the volume of the segment, which is equivalent to the volume of each cell in the lattice, the mole fractions used in equation 2.14b are replaced by volume fractions, \(\phi_i\):

\[
\Delta G_{\text{mix}} = RT \left\{ n_1 \ln(\phi_1) + n_2 \ln(\phi_2) + n_1 n_2 \chi_{12} \right\}
\]

(2.14c)

where \(\phi_1 = 1 - \phi_2 = n_1 / (n_1 + f n_2)\) and \(\phi_2 = f n_2 / (n_1 + f n_2)\).

This is the classical FHCM theory expression for the free energy change on mixing polymeric species. Since the enthalpic and entropic contributions have been developed separately they will now be examined separately to investigate their predicted individual effects on this free energy change.

The influence of the enthalpic component

From equation 2.3, \(i.e.\)

\[
W = 0.5 \left| (E_{11} + E_{22} - 2E_{12}) \right|
\]

the enthalpy change on mixing non-polar materials will unfavourable since \(E_{12}\) is equivalent to the geometric mean, \(i.e.\ E_{12} = (E_{11}E_{22})^{0.5}\), which is smaller than the arithmetic mean, \(i.e.\ 0.5(E_{11} + E_{22})\).
The influence of the entropic component

From equation 2.13c it is apparent that the magnitude of the entropic change is highly dependent on the molecular weight of the materials being mixed. As the molecular weight of the components increases, the number of moles decreases, (for a constant mass of mixture), hence as \( M \to \infty \) then \( n_i \to 0 \) and hence \( \Delta S_{mix} \to 0 \). In polymeric systems the component molecular weights are usually high and consequently the entropic effect is assumed to be extremely small.

In view of these two predictions it is not surprising that very few polymers are miscible. Three exceptions exist to this general condition.

(a) If the molecular weights of the components are relatively small, the negative entropic contribution may dominate the enthalpic effect and produce a favourable free energy.

(b) If the polymer pair are chemically and physically very similar the heat of mixing is likely to be very small and again the miscibility will be determined by the favourable entropic contribution.

(c) The enthalpy of mixing for species with specific interactions, e.g. hydrogen bond, is significantly negative, which dominates the \( \Delta G_{mix} \) term.

To examine the temperature dependence of the free energy change, it is convenient to replace the interaction parameter, \( \chi_{12} \), with the interaction energy density characteristic of the polymer pair, \( B \), defined as,

\[
B = \chi_{12} RT/V_1
\]  

where,

\[
V_1 = \text{the molar volume of component 1, cm}^3\text{mol}^{-1}
\]

If equation 2.15 is substituted into equation 2.9, we have,

\[
\Delta H_{mix} = B n_1 V_1 \phi_2
\]  

and consequently (2.14) becomes,

\[
\Delta G_{mix} = RT \left[ n_1 \ln (\phi_2) + n_2 \ln (\phi_{12}) \right] + B n_1 V_1 \phi_2 \]  

\[\begin{align*}
\{\text{Entropic}\} & \quad \{\text{Enthalpic}\}
\end{align*}\]

In this form the effect of temperature is apparent. The favourable entropic component is directly dependent on absolute temperature and thus becomes increasingly large as \( T \) increases. Conversely, the enthalpic component is
independent of temperature and constant for a specific polymer pair, thus \( \Delta G_{\text{mix}} \) has the same temperature dependence as the entropic component and becomes increasingly negative and favourable as the temperature is increased. This gives rise to the limits of miscibility and a phase diagram as shown in Figure (2.1). This type of phase behaviour, called Upper Critical Solution Temperature, (UCST), is typical of blends which have low molecular weight constituents. At \( T_\gamma \), Figure (2.1), the polymers are miscible in all proportions and the second derivative of the free energy with respect to composition is always positive,

\[
\frac{d^2(\Delta G_{\text{mix}})}{d\phi_b^2} > 0
\]  

(2.16)

This is the essential criterion for miscibility. At \( T_\gamma \) all compositions between \( \phi_a \) and \( \phi_b \) can phase separate to reduce the overall energy. This produces two discrete phases whose compositions are \( \phi_a \) and \( \phi_b \) and which have equal free energy/composition first derivatives,

\[
\frac{d(\Delta G_{\text{mix}})_{\phi_a}}{d\phi_a} = \frac{d(\Delta G_{\text{mix}})_{\phi_b}}{d\phi_b}
\]  

(2.17)

The maximum temperature at which miscibility occurs in monodisperse polymers is \( T_\gamma \). At \( T_\gamma \) the critical point is given by,

\[
\frac{d^2(\Delta G_{\text{mix}})_{\phi_a}}{d\phi_a^2} = \frac{d^3(\Delta G_{\text{mix}})_{\phi_a}}{d\phi_a^3} = 0
\]  

(2.17)

Between \( \phi_a \) and \( \phi_b \) and between \( \phi_{a'} \) and \( \phi_{b'} \) a region of metastability occurs since any small fluctuation in composition produces an increase in the free energy, which prevents phase separation. In this region phase separation can only proceed via a mechanism of nucleation and growth. This mechanism involves the growth of phases which have constant composition and consequently results in an irregular pattern of separation. Between compositions \( \phi_b \) and \( \phi_b' \) a small fluctuation in composition causes a lowering of the free energy and phase separation occurs by spinodal decomposition. The mechanism of spinodal decomposition involves the growth of a preferred concentration fluctuation which causes a continuous change in the composition of the phases. In the early stages of spinodal decomposition the spacing of the phases remains constant while the composition varies.
IDEALISED PHASE DIAGRAM SHOWING
UCST BEHAVIOUR

Figure 2.1
The spinodal condition is given by,

$$\frac{d^2(\Delta G_{\text{mix}})}{d\phi^2} = 0 \quad (2.19)$$

and the line satisfying this condition and connecting all points of composition \(\phi_b\) is the spinodal. This function has the physical significance of being the systems limit of stability to small concentration fluctuations.

The line connecting points at various temperatures at composition \(\phi_a\) satisfying equation 2.17 is the binodal which represents the limit of two phase coexistence. However, the majority of polymeric systems exhibit a Lower Critical Solution Temperature, (LCST), type behaviour rather than an UCST and the resulting phase diagram is the inverted parabola of Figure 2.1. Simple Flory-Huggins-Chang-Miller theory cannot predict LCST behaviour unless the interaction parameter is redefined as the sum of both enthalpic and entropic contributions,

\[ i.e., \ B = B_H - TB_S \quad (2.20) \]

This equation treats the interaction energy density characteristic as a temperature dependent free energy term, and can be directly compared to equation 2.2. LCST behaviour is thought to arise for several reasons.

(a) The true free energy change contains a contribution from the volume change on mixing, and this becomes increasingly unfavourable as temperature increases. Simple FHCM theory assumes that the lattice is always completely filled and consequently there is no volume change on mixing.

(b) If the miscibility of the polymer pair arises from specific interaction, this can lead to a strong dependence of the heat of mixing on temperature.

(c) If the mixing in the blend is not truly random, e.g. specific interactions causing some degree of ordering, unfavourable entropic contributions may arise, and a temperature dependence other than that described in equation 2.20 may exist.

These conditions all demonstrate a different inadequacy of the lattice model. To avoid the assumptions necessary for the FHCM theory, and to prevent the thermodynamic treatment of polymer blends becoming a series of ad hoc additions to simple lattice theory, it was recognised that another model was required.
It was perceived that this new theory must provide the entropy and enthalpy change on mixing in addition to the relationship between pressure, volume and temperature of the system. These parameters are often described as the state variables and consequently these theories have become known as the equation of state theories. There exists a number of different approaches but they all rely on Prigogine's original hypothesis that a polymer can be adequately described by a partition function.

2.2 Prigogine-Flory: (EOS or Equation of State theory)\(^{(13-17, 19-26)}\)

The central quantity in statistical thermodynamics is the canonical partition function, \(Q\). This parameter arises from quantum theory and contains the systems thermodynamic information. All of the thermodynamic functions can be derived from this quantity via the Helmholtz function, \(A\),

\[
e.g. \quad A = -kT \ln(Q) \tag{2.21a}\]

The Helmholtz function for solids and liquids at low pressures is approximately equal to the Gibbs function, \(i.e.\)

\[
G = A = -kT \ln(Q) \tag{2.21b}\]

and,

\[
U = \left\{ \frac{\partial(A/T)}{\partial(1/T)} \right\}_v \tag{2.22a}\]

where,

\(U = \) internal energy of the system, \(J\)

However, in non-gaseous systems, the internal energy - which is the time average molecular energy - can be approximated to the enthalpy, \(H\),

\[
H = U = \left\{ \frac{\partial(A/T)}{\partial(1/T)} \right\}_v \tag{2.22b}\]

The entropy of the system, \(S\), is given by
\[ S = \left( \frac{\partial A}{\partial T} \right)_V \] (2.23)

and the pressure by

\[ P = -\left( \frac{\partial A}{\partial V} \right)_T \] (2.24)

The EOS theories generally abandon the lattice model, although some useful features are retained, and instead aim to model statistically the movements of macromolecules. This theory rests upon three important assumptions.

1. The internal degrees of freedom of a molecule do not change during mixing and do not contribute to the mixing process, and consequently can be neglected. However, because the contributions which enable sections of the molecule to move from one volume to another are closely associated to the entropy, they must be included. If each section of the molecule is considered independently it has 3 external degrees of intermolecular motion. However, because of the constraints of the chain, the number of degrees of freedom are reduced and this is represented in the model by introducing \( c \), the coefficient of segmental constraint. The intermolecular motion is thus \( 3c \), \( 0 < c < 1 \).

2. All molecules can be subdivided into segments of arbitrary but equal size. There are \( r \) segments per molecule and the volume required for each segment under normal conditions is \( v \). However, it is also assumed that these segments have an orientation which occupies a minimum volume, below which they cannot be compressed, \textit{i.e.} a hard core. The volume required to accommodate a segment under this condition is described as the core volume, \( v^* \). This criterion was intended to enable the theory to cope with mixtures comprising components of greatly differing size, \textit{e.g.} high homopolymer-solvent systems.

3. The partition function of a pure liquid is postulated as,

\[ Z = Z_{\text{comb}} \left( g \left( v^{1/3} - v^{*1/3} \right) \right)^{3Nrc} \text{Exp} \left( -E/kT \right) \] (2.25)
where,

\[ N = \text{the number of molecules in the system} \]

\[ g = \text{a geometric factor} \]

\[ E = \text{the intermolecular energy of the liquid} \]

\[ Z_{\text{comb}} = \text{a factor representing the number of ways of arranging the molecules in the liquid; this term has been derived from the lattice model and can be equated to } S_{\text{conf}}, \text{ eqn (2.10), by} \]

\[ Z_{\text{comb}} = \text{Exp}(S_{\text{conf}}/k) \tag{2.26} \]

\( v^{1/3} \) is the linear space in which the segment can move and \( v^{*1/3} \) is the characteristic linear dimension, of the segment, hence \( (v^{1/3} - v^{*1/3}) \) is the free volume in which the segment can move. Like Lattice theory, the intermolecular energy of the liquid, \( E \), is based on the concept of contact energies and can be subdivided into energetic and geometric contributions,

\[ E = -Nrs_\eta /2v \tag{2.27} \]

where,

\[ \eta = \text{contact energy parameter}, \]

\[ s = \text{number of contact sites per segment, and} \]

\[ -s_\eta/2v = \text{intermolecular energy per segment.} \]

If expressions (2.25) and (2.27) are substituted for the respective terms in equation 2.21a,

\[ A = -kT\left\{ \text{Ln}(Z_{\text{comb}}) + 3Nrc \text{Ln}(g(v^{1/3} - v^{*1/3})) \right\} - Nrs/2v \tag{2.28} \]

The volume of the system is \( V = Nrv \), thus equation 2.24 becomes,

\[ P = ckTv^{-2/3}(v^{1/3} - v^{*1/3}) - s_\eta/2v^2 \tag{2.29} \]

These expressions are of little practical use since they contain the arbitrary parameters \( s, \eta \) and \( c \). These parameters are removed by defining the characteristic pressure, \( P^* \), and temperature, \( T^* \), such that

\[ P^* = s_\eta/2v^{*2} \tag{2.30} \]

\[ T^* = s/2v^*ck \tag{2.31} \]
$P^*$ and $T^*$ are related to the physical parameters by the 'reduced state parameters',

\[
\text{Reduced pressure } = \tilde{P} = P/P^* \tag{2.32}
\]
\[
\text{Reduced volume } = \tilde{\nu} = \nu/\nu^* \tag{2.33}
\]
\[
\text{Reduced temperature } = \tilde{T} = T/T^* \tag{2.34}
\]

Prigogine-Flory theory postulates that the equation of state for pure liquids is,

\[
\tilde{P}\tilde{\nu} = \left(\frac{\tilde{\nu}^{4/3}}{\tilde{\nu}^{4/3} - 1} - 1\right) \tag{2.35}
\]

However, at ambient pressures the product comprising the left hand side of the equation is insignificant and thus equation 2.35 reduces to,

\[
\tilde{T} = \frac{\tilde{\nu}^{4/3}}{\tilde{\nu}^{4/3} - 1} \tag{2.36}
\]

To solve this equation it is necessary to know the values of $P^*$, $T^*$ and $\tilde{\nu}$. The best estimations of these parameters are obtained when the equation of state is fitted to pure component PVT data when available. A less satisfactory procedure involves calculating these parameters from other characteristic properties, e.g. using the thermal expansion coefficient to obtain $\tilde{\nu}$ and the thermal pressure coefficient $\gamma$ to obtain $P^*$.

(1) The thermal expansion coefficient $\alpha$

The thermal expansivity, or expansion coefficient, is defined as,

\[
\alpha \equiv \frac{1}{\nu} \left( \frac{\partial \nu}{\partial T} \right)_{p,n} \tag{2.37}
\]

and the reduced volume can be calculated from,

\[
\tilde{\nu} = \left( 1 + \frac{\alpha T}{3(1 + \alpha T)} \right) \tag{2.38}
\]

The thermal expansion coefficient is normally calculated from density data measured as a function of temperature.
(2) The thermal pressure coefficient, $\gamma$

The thermal pressure coefficient, defined as,

$$\gamma = \left( \frac{\partial P}{\partial T} \right)_V$$

(2.39)

can be used to calculate the hard core pressure characteristic as follows,

$$P^* = \gamma T V^2$$

(2.40)

The thermal pressure coefficient is not often known and hence is estimated from the Hildebrand solubility parameter, $\delta$, using,

$$\gamma \approx \frac{\delta^2}{T}$$

(2.41)

(3) The reduced temperature can be calculated from equation (2.36) by introducing the value of the reduced volume calculated from equation (2.38).

With this information the equation of state can be solved. If the equation is solved by using the approximate expressions the results have been found to be in only approximate agreement with experiment. The main fault of the treatment is that the characteristic temperature, $T^*$, which although defined constant, increases as the data measurement temperature increases.

The main advantage of the theory is in its application to mixtures. To enable this theory to be applied to mixtures two further assumptions are required.

(1) The core volumes of the components are additive, and the specification of the dimensions of a segment remains arbitrary. It is convenient to choose segments of equal size such that,

$$v_1^* = v_2^* = v^*$$

(2.42)

(2) The intermolecular energy of the mixture only depends on the surface area of contact between these segments, as intermolecular attractions are short range relative to the molecular diameter of most liquids.

On the basis of this extended model, some of the previous expressions require to be redefined. The number of external degrees of intermolecular motion is now the appropriate sum over all the components, e.g. for a binary mixture,

$$3 N_r c = 3 (N_1 r_1 c_1 + N_2 r_2 c_2)$$

(2.43)
The intermolecular energy also requires to be altered to include heterogeneous contacts and this is done using the contact energy parameter $\eta_{ij}$ and the surface fraction $\theta_i$, defined by equations 2.46a and 2.46b. Contacts between identical molecules are designated by $\eta_{11}$ and $\eta_{22}$ while a contact between differing molecules is designated by $\eta_{12}$. Equation 2.27 becomes,

$$E = -(N_1 r_1 s_1 \eta_{11} + N_2 r_2 s_2 \eta_{22} + 2N_1 r_1 s_1 \theta_1 \eta_{12})/2\nu$$  \hspace{1cm} (2.44a)

or

$$E/(N_1 r_1 + N_2 r_2) = P^* \nu^*/\nu$$  \hspace{1cm} (2.44b)

(from equation 2.30, $P^* = s\eta/2\nu^2$)

The volume fractions are redefined using the hard core volume of the components, $\phi_i^*$,

$$\phi_i^* \equiv 1 - \phi_2^* \equiv N_i r_i/(N_1 r_1 + N_2 r_2)$$  \hspace{1cm} (2.45a)

or,

$$\phi_i^* \equiv w_i V_i^*/(w_1 V_1^* + w_2 V_2^*)$$  \hspace{1cm} (2.45b)

where,

$$w_i = \text{weight fraction of component 'i'}$$

$$V_i^* = \text{molar hard core volume of component 'i'}$$

Hard core volume fractions are more useful than normal volume fractions because they are, by definition, independent of temperature, pressure and any volume changes that may occur during mixing. Since the characteristic dimension is now a segment and the intermolecular energy is dependent on the surface area of this quantity, it is convenient to introduce the surface fraction, $\theta$,

$$\theta_i \equiv 1 - \theta_2 \equiv N_i r_i s_i/(N_1 r_1 s_1 + N_2 r_2 s_2)$$  \hspace{1cm} (2.46a)

or,

$$\theta_i \equiv \frac{(s_2/s_1) \phi_i^*}{(s_2/s_1) \phi_1^* + \phi_2^*}$$  \hspace{1cm} (2.46b)

where, $s_2/s_1 = \text{surface area per unit volume ratio}$
With these modifications the mixture can again be described by the equations of state as defined by (2.35) and (2.36). The hard core parameters, $P^*$ and $T^*$, now describe the properties of the mixture and can be related to the pure component data as follows,

\[
P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}
\]

(2.47)

\[
T^* = \frac{\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}}{\phi_1 P_1^*/T_1^* + \phi_2 P_2^*/T_2^*}
\]

(2.48)

where,

\[
X_{12} = \text{an interaction term which reflects the difference in energies of the homo/heterogeneous contacts and is comparable with the zW term in equation (2.8)}.
\]

and $X_{12}$ is defined as,

\[
X_{12} \equiv (\eta_{11} + \eta_{22} - 2 \eta_{12} (s_1/2v^2))
\]

(2.49)

The change in enthalpy, \textit{i.e.} excess enthalpy, on mixing is equal to the energy change on mixing at low pressure,

\[
\Delta H_{\text{mix}} = E_{12} - (E_{11} + E_{22})
\]

(2.50)

From equation (2.44b), this equation can be defined in terms of the hard core and reduced parameters,

\[
\Delta H_{\text{mix}} = (N_1 r_1 + N_2 r_2) v^* \left\{ \phi_1 P_1^{*}/\tilde{\nu}_1 + \phi_2 P_2^{*}/\tilde{\nu}_2 - P^{*}/\tilde{\nu} \right\}
\]

(2.51)

and substitution of $P^*$ from (2.47) gives,

\[
\Delta H_{\text{mix}} = (N_1 r_1 + N_2 r_2) v^* \left\{ \phi_1 P_1^{*} (1/\tilde{\nu}_1 - 1/\tilde{\nu}) + \phi_2 P_2^{*} (1/\tilde{\nu}_2 - 1/\tilde{\nu}) \right\}
\]

(2.52a)

\[
+ \phi_1 \theta_2 X_{12} / \tilde{\nu}
\]

\[
\Delta H_{\text{mix}} = v^* \left\{ N_1 r_1 \phi_2 X_{12} / \tilde{\nu} - N_1 r_1 P_1^{*} (1/\tilde{\nu} - 1/\tilde{\nu}_1) - N_2 r_2 P_2^{*} (1/\tilde{\nu} - 1/\tilde{\nu}_2) \right\}
\]

(2.52b)

\[
\Delta H_{\text{mix}} = n_1 v^* \left\{ \phi_2 X_{12} / \tilde{\nu}_1 + P_1^{*} (1/\tilde{\nu} - 1/\tilde{\nu}_1) - (\phi_2^{*}/\phi_1) P_2^{*} (1/\tilde{\nu} - 1/\tilde{\nu}_2) \right\}
\]

(2.52c)
The first term inside the braces in equation 2.52c corresponds to the contact enthalpy term in FHCM theory, i.e. equation 2.9. The two remaining contributions, called the equation of state terms, are still significant even if \( X_{12} = 0 \), i.e. there is no difference in the chemical nature of the components, as the magnitude of their contribution is determined by the reduced volume of the mixture. From equation 2.38 it is apparent that the reduced volume is a function of the thermal expansion coefficient and consequently a significant excess enthalpy may still occur on mixing materials which have a small degree of interaction but very different thermal expansivities.

The entropy of mixing can be obtained from the partial derivative in equation 2.23,

\[
\Delta S_{\text{mix}} - \Delta S_{\text{comb}} = 3(N_1 r_1 + N_2 r_2) \nu^* \left( \frac{\phi_1^* P_1^*}{T_1^*} \ln \left( \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_1^{1/3} - 1} \right) + \frac{\phi_2^* P_2^*}{T_2^*} \ln \left( \frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}_2^{1/3} - 1} \right) \right)
\]

\[
\Delta S_{\text{mix}} - \Delta S_{\text{comb}} = 3n_1 \nu_1^* \left( \frac{P_1^*}{T_1^*} \ln \left( \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_1^{1/3} - 1} \right) + \frac{\phi_2^* P_2^*}{\phi_1^* P_1^*} \ln \left( \frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}_2^{1/3} - 1} \right) \right)
\]

(2.53a)

(2.53b)

For macromolecular solutions the FHCM entropy of mixing, equation 2.13, is equated to \( \Delta S_{\text{comb}} \) and the difference \( \Delta S_{\text{mix}} - \Delta S_{\text{comb}} \) is called the residual entropy of mixing \( \Delta S^8 \).

A general expression for the free energy of mixing can now be constructed,

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T (\Delta S_{\text{comb}} + \Delta S^8)
\]

(2.54)

and,

\[
\Delta G_{\text{mix}} = RT \left( n_1 \ln(\phi_1^*) + n_2 \ln(\phi_2^*) + n_1 \phi_1^* (\chi_{1H}^* + \chi_{1G}^*) \right)
\]

(2.55)

where,

\[
\chi_{1H}^* = \frac{\nu_1^*}{RT} \left( \frac{\phi_2^* X_{12} \tilde{v}_1^{1/3} - \frac{P_1^*}{\phi_2^*} (\tilde{v}_2^{1/3} - \tilde{v}_1^{1/3}) - \frac{P_2^*}{\phi_1^*} (\tilde{v}_1^{1/3} - \tilde{v}_2^{1/3})}{\phi_2^*} \right)
\]

(2.56)

and
\[
\chi_s^* = \frac{3V_i^*}{R} \left( \frac{P_1^*}{T_1^*\phi_2^*} \ln \left( \frac{\tilde{\nu}_1^{1/3} - 1}{\tilde{\nu}_1^{1/3} - 1} \right) + \frac{P_2^*}{T_2^*\phi_1^*} \ln \left( \frac{\tilde{\nu}_2^{1/3} - 1}{\tilde{\nu}_2^{1/3} - 1} \right) \right)
\] (2.57)

These two terms are the enthalpic and entropic interaction coefficients which give some indication of which thermodynamic effect is dominant in any mixing process.

When applied on a qualitative basis, this form of the Prigogine-Flory theory had some success in explaining the behaviour of many systems but its quantitative success was only moderate and significant variation was observed in the theoretically constant quantities, e.g. \(v^*, P^*\) and \(T^*\). An improvement in its quantitative performance was achieved by adding a correction term to the enthalpic exchange parameter. In this term, \(Q_{12}T\tilde{\nu}_1, Q_{12}\) is an adjustable parameter characterising excess entropic effects. This additional parameter has no physical meaning and consequently many derived relationships are no longer directly related to the original model.

The Phase Diagram

McMaster\(^{(27)}\) considered both internal and external degrees of freedom in addition to polydispersity while developing a generalised form of this relationship which simulated both the binodal and spinodal curves of a hypothetical polymer mixture. From this he showed that it was possible to predict both UCST and LCST behaviour both individually and simultaneously. McMaster, and Walsh and Rostami\(^{(28)}\), have examined the influence of a variety of the parameters on the miscibility limits of hypothetical mixtures. Their conclusions can be summarised as follows.

(a) The largest range of miscibility, with respect to temperature is found when the components have similar thermal expansion coefficients. This is equivalent to having similar values of \(\tilde{\nu}\) and \(T^*\).

(b) Variations in \(\gamma\) have less effect on miscibility than changes in \(\alpha\). High values of \(\gamma\) reduce the range of miscibility and a difference in the thermal pressure between components affects the shape of the limits and the position of the minimum.
(c) If the molecular weight of the components is increased the mixture will become less miscible, as also predicted from FHCM theory.

(d) As $X_{12}$ becomes increasingly positive the mixture becomes less miscible while conversely as it becomes more negative the mixture becomes more miscible.

(e) The value of the surface area to volume ratio, $s_2/s_1$, is only significant for large values of either $Q_{12}$ or $X_{12}$. Under these circumstances, the miscibility limit is skewed by an amount proportional to the deviation of $s_2/s_1$ from unity.

(f) A negative value of $Q_{12}$ makes the mixture less miscible.

This theory has also been used to simulate the phase diagrams of real polymer mixtures\textsuperscript{(29–33)} using $Q_{12}$ as an adjustable parameter. This work has simulated the phase diagram of the EVA/FVA mixture using calculated values of both $X_{12}$ and $Q_{12}$ and this is described and discussed in chapter 8.

Other free volume approaches, such as the ‘lattice-fluid’ theory of Sanchez and Lacombe\textsuperscript{(34)} and the equation of state theory of Simha and Somcynski\textsuperscript{(35)}, are based on the lattice model and all or part of the free volume arises from vacancies on the lattice unlike Prigogine-Flory theory where the free volume arises from an overall increase in molecular separations. These theories may prove to be valuable, because their description of the pure component properties is superior but to date their main application has been to polymer solutions.

2.3 Summary

In this chapter two quite different approaches to the thermodynamics of polymer mixtures have been discussed. The FHCM lattice theory, which has been the basis of much research for the last forty years, has been shown to be inadequate for understanding and predicting many of the phenomena routinely observed in polymer blends. The equation of state treatment is seen to be an improvement on the lattice model, although the necessary introduction of the adjustable $Q_{12}$ parameter is an indication that the initial model is inadequate. It should also be apparent that the latter theory requires substantially more information about both the pure components and the mixture than the FHCM theory, and consequently the choice of which approach to use should be based on a balance between the relative input required and the information obtained.
2.4 REFERENCES


Chapter 3 General Experimental Work

This chapter describes experimental work which gave ambiguous results or which is subsidiary to another part of the project. Included are the initial characterisation of the materials, their density-temperature functions and a DSC study of their blends. Each series of experiments has been reported as a brief introduction, description, list of results and discussion. The final section reviews the value of all the information obtained.

3.0 Characterisation of materials

Three copolymers have been used in this work,

(a) poly(ethylene-vinyl acetate) or EVA

(b) poly(tetradecyl/hexadecyl fumarate-vinyl acetate) or $C_{14/16}$ FVA

(c) poly(tetradecyl fumarate-vinyl acetate) or $C_{14}$ FVA (or simply FVA).

EVA was a random copolymer which was prepared industrially by a free radical process in a mixed solvent of cyclohexane and oligomeric poly(iso-butylene). It was necessary to anneal the polymer at 353K under vacuum for 12 hours to remove the residual processing solvents and any water or air which had been absorbed. The polymer was analysed elementally to determine the structure of the statistical repeat unit, i.e. the ratio of ethylene to vinyl acetate in the polymer.

The polymer was a viscous, opaque liquid which became less turbid when it was heated. Provisional experiments in a test tube showed that the sample became transparent when it was heated to approximately 323-328K. It was unclear whether this was the final melt of any crystallinity present resulting from long sequences of polyethylene in the statistical composition or if the copolymer did not exist as a single homogeneous phase at ambient temperature owing to the disperse nature of its composition.

This effect was investigated

(a) thermally: using differential scanning calorimetry, (3.4), and

(b) optically: by

(i) a laser/photo-multiplier tube arrangement, (3.5), and

(ii) a microscope fitted with a hot stage, (7.0).
The FVA samples were also prepared industrially by a free radical process and had an alternating structure of (fumarate-vinyl acetate). The C\textsubscript{14/16} FVA was a yellowish wax which began to melt at approximately 300K: the C\textsubscript{14} FVA was a viscous yellow liquid at room temperature. The behaviour of the EVA/C\textsubscript{14/16} FVA blend was of prime industrial interest and was studied initially. Unfortunately the ratio of tetradecyl to hexadecyl substitution in the fumarate was unknown and this blend was eventually discarded in favour of the simpler EVA/C\textsubscript{14} FVA mixture.

3.1 Elemental Analysis of EVA

Duplicate EVA samples were analysed for carbon, hydrogen and, by difference, oxygen. The results were as follows:-

<table>
<thead>
<tr>
<th>Mass Fraction</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA1</td>
<td>0.749</td>
<td>0.127</td>
<td>0.124</td>
</tr>
<tr>
<td>EVA2</td>
<td>0.750</td>
<td>0.129</td>
<td>0.121</td>
</tr>
</tbody>
</table>

From these results the average structure was determined by a mass balance calculation as that given in Figure 3.1. This structure contains six ethylene units per vinyl acetate and although it represents only the statistical average of the composition distribution it has been used as the unit structure for this work.

The general structure of the FVA samples is given in Figure 3.2, where \( R = C\textsubscript{14}H_{29} \) or \( C\textsubscript{16}H_{33} \).
Figure 3.1: Macro structure of EVA

where $R = C_{14}H_{29}$ or $C_{16}H_{33}$

Figure 3.2: Macro structure of $C_{14}$FVA
3.2 Gel Permeation Chromatography (GPC)

The GPC measurements were performed by Exxon Chemicals using polystyrene as the calibrant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA1</td>
<td>3290</td>
<td>9704</td>
<td>2.948</td>
</tr>
<tr>
<td>$C_{14}$FVA</td>
<td>10400</td>
<td>28543</td>
<td>2.756</td>
</tr>
</tbody>
</table>

3.3 Density Measurements

These measurements were undertaken to determine the densities and the thermal expansion coefficients of EVA and $C_{14}$FVA from which were derived many of the pure component parameters needed for an Equation of State analysis (Chapter 8).

Additionally it was hoped that the optically observed apparent phase change that EVA exhibits (section 3.0) might result in a discontinuity in the relationship between density and temperature.

The density measurements were carried out using an Anton Paar KGDMA60 densitometer with a DMA602 external cell (\(^{i}\)). This apparatus comprises a vibrating U-tube whose frequency of oscillation alters when filled with different fluids. This change is converted into an absolute value by calibrating the apparatus with materials of known density. The temperature of the cell was controlled by the circulation of heated water from a Townson and Mercer bath, but the range of the study was restricted by the operational limits of the sample tube.

3.3.1 Experimental Procedure

The experimental procedure involved equilibrating the water bath at the desired temperature and ensuring that a stable temperature, ($\pm 0.01$K), was observed for a minimum of 30 minutes. The cell was calibrated with doubly distilled water and dry air before and after each density measurement and the calibration constant calculated from the expression below,

$$K = \frac{(\rho_w - \rho_a)}{(T_w - T_a)}$$  \hspace{1cm} (3.1)
where,

\[ K = \text{calibration constant} \]

\[ \rho_w = \text{density of water}^{(2)}, \text{g cm}^{-3} \]

\[ \rho_a = \text{density of air}^{(2)}, \text{g cm}^{-3} \]

\[ T_w = \text{period of oscillation measured for water, s} \]

\[ T_a = \text{period of oscillation measured for air, s} \]

A sample of approximately 4g was injected into the cell but because of the viscosity of these materials, the standard practice was to heat the mixture under vacuum at 353K for a minimum of 12 hours and inject the samples hot.

A reading was taken when the frequency of oscillation was constant. Each measurement was repeated several times and a mean value calculated. The sample density was then evaluated from the following equation:-

\[ \rho = \rho_w - K(T_w - T_s) \quad (3.2) \]

where,

\[ \rho = \text{density of sample, g cm}^{-3} \]

\[ T_s = \text{period of oscillation for sample, s} \]
3.3.2 Density - Temperature Results:

Table 3.3

The relationship between temperature, composition and density (g cm\(^{-3}\)) for mixtures of EVA and \(C_{14}\) FVA

<table>
<thead>
<tr>
<th>Mass Fraction EVA</th>
<th>Temperature / K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303</td>
</tr>
<tr>
<td>0.0000 (FVA)</td>
<td>0.95001</td>
</tr>
<tr>
<td>0.1181</td>
<td>0.94935</td>
</tr>
<tr>
<td>0.2426</td>
<td>0.94877</td>
</tr>
<tr>
<td>0.3620</td>
<td>0.94780</td>
</tr>
<tr>
<td>0.4836</td>
<td>0.94755</td>
</tr>
<tr>
<td>0.6940</td>
<td>0.94582</td>
</tr>
<tr>
<td>0.8013</td>
<td>0.94528</td>
</tr>
<tr>
<td>0.9060</td>
<td>0.94466</td>
</tr>
<tr>
<td>1.0000 (EVA)</td>
<td>0.94416</td>
</tr>
</tbody>
</table>

These results are shown graphically in Figure 3.3.

A least-squares fit was performed on these data and the results were found to be essentially linear with respect to composition and temperature thus the coefficients of the composition-density fit could be linearised with the temperature-density function reducing these data to the following expression,

\[ \frac{1}{\rho} = v = (b_0 + b_1T) + (c_0 + c_1T + c_2T^2)w \]  

(3.3)

where,

\[ v = \text{specific volume, cm}^3\text{g}^{-1} \]

\[ T = \text{temperature, degrees Celsius} \]

\[ w = \text{mass fraction of EVA} \]
with

\[
\begin{align*}
  b_0 &= 1.029764 \quad \text{cm}^3 \text{ g}^{-1} \\
  b_1 &= 7.582750 \times 10^{-4} \quad \text{cm}^3 \text{ g}^{-1} \text{ K}^{-1} \\
  c_0 &= 2.255139 \times 10^{-3} \quad \text{cm}^3 \text{ g}^{-1} \\
  c_1 &= 1.484851 \times 10^{-4} \quad \text{cm}^3 \text{ g}^{-1} \text{ K}^{-1} \\
  c_2 &= 3.291172 \times 10^{-11} \quad \text{cm}^3 \text{ g}^{-1} \text{ K}^{-2}
\end{align*}
\]

\(b_0, b_1, c_0, c_1\) and \(c_2\) were evaluated from the least-squares calculations.

3.3.3 Discussion

It was assumed that no further phase changes, or other processes which were likely to radically alter the density, would occur, and thus the density-temperature-composition function could be extrapolated linearly to 393K for the inverse phase gas chromatography (Section 4.0) and vapour sorption (Section 6.0) analyses. No change in the EVA density was observed at around 325K, where the optically observed phase change had been detected, suggesting that whatever its origin, it had no effect on the density of the bulk material.

The linearity of these functions describes a system which demonstrated an additive change in volume when the components were mixed. This is an unusual effect since species which demonstrate electron-donor-acceptor interactions often display a volume contraction when mixed\(^{13}\), whereas the majority of normal liquids expand, (these effects arising from whether the intermolecular interactions of the mixture are greater or less than those of the pure components, respectively). The physical significance of this apparent volume additivity is that, either the intermolecular forces of each pure copolymer are essentially equal, or that these materials do not truly mix on a molecular level. Since neither of these materials were likely to have strong or specific intermolecular forces, e.g. dipole-dipole or hydrogen bonding, and that miscibility was likely to arise from the cohesion of alkyl groups, it was assumed that mixing did occur and that it was additive.
3.4 Differential Scanning Calorimetry, (DSC)

3.4.1 Introduction

All materials store energy in the form of thermal movement and this quantity changes with the state of the material. This is reflected by the heat capacity of the material and its magnitude is dependent on the number of modes of thermal movement that are available. Consequently, the heat capacity of glassy and crystalline polymers is small because of the morphological restrictions and larger for viscoelastic materials.

This change is defined as the glass transition temperature, \( T_g \). Numerous other morphological changes and state transitions are accompanied by a heat flux into or out of the system, \( e.g. \) melting, crystallisation, vaporisation, polymerisation and decomposition. Differential scanning calorimetry measures this flux by measuring the amount of thermal energy required to increase the temperature of a sample by \( \Delta T \) over that required by a reference, \( e.g. \) an empty sample vessel. A temperature sensor provides feedback control to electrical heaters which ensures that a constant rate of temperature change is maintained in both the sample and the reference. The electrical supply to the heaters is measured precisely and, after correction, provides a record of the heat capacity of the sample as a function of temperature. The technique has two distinct applications in polymer science,

(a) the determination of the miscibility limits of the blend, and,

(b) the quantitative evaluation of the Flory-Huggins interaction parameter.

3.4.2 Theoretical

3.4.2.1 Miscibility limits

Although the exact nature of the glass transition is still in some dispute the following definition is adequate for this work:-
"For every amorphous polymer there exists a narrow temperature region in which it changes from a viscous or rubbery condition at temperatures above this region, to a hard and relatively brittle one below it. This transformation is equivalent to the solidification of a liquid to a glass; it is not a phase transition. Not only do hardness and brittleness undergo rapid changes in the vicinity of the glass transition temperature, \( T_g \), but other properties such as the thermal expansion coefficient, the heat capacity, and the dielectric constant (in the case of a polar polymer) also change markedly over an interval of a few degrees. \( T_g \) is regarded variously as the brittle temperature, the critical temperature for the glassy state, or the second-order transition temperature, although as mentioned above no phase transition is involved and reference to a transition may therefore be misleading."

- P. J. Flory

Immiscible mixtures of polymeric materials retain the individual \( T_g \) values of the homopolymers: miscible polymer blends which behave as a single homogeneous phase have a single glass transition temperature, commonly between the \( T_g \) values of the pure components. The miscibility limits of a blend can be found by annealing various compositions at an arbitrary temperature then quenching the sample in liquid nitrogen and running a thermogram. This process freezes the blend in its equilibrium state at the temperature at which it was annealed, and the number of \( T_g \) values observed in the thermogram indicates whether it was homogeneous or heterogeneous at that temperature. By varying this temperature the limits of miscibility can be found.

3.4.2.2 The Flory - Huggins Interaction Parameter, \( \chi'_{23} \)

When crystals of one component are in equilibrium with a mixed amorphous phase, the melting point will be lower than when the equilibrium is with a pure amorphous phase of the same component comprising the crystals. This depression of melting point can be used to measure the Flory-Huggins interaction parameter of the mixture using the expression derived by Flory,

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_2} \frac{V_0}{V_1} (\phi_3 - \chi'_{23} \phi_3^2)
\]  

(3.4)
where, subscript 2 refers to a repeat unit of crystalline polymer, and subscript 3 to the diluent, \textit{i.e.} amorphous polymer.

\[ T_m = \text{equilibrium melting temperature, K} \]
\[ T^0_m = \text{equilibrium melting temperature of the pure crystalline polymer, K} \]
\[ \Delta H_2 = \text{heat of fusion per repeating unit, J} \]
\[ \phi_i = \text{volume fraction of species 'i'} \]
\[ R = \text{universal gas constant,}\ (8.3144 \text{ J mol}^{-1} \text{K}^{-1}) \]
\[ V_i = \text{molar volume of species 'i' m}^3\text{ mol}^{-1} \]

The interaction parameter can be obtained from the slope of a plot of

\[ \frac{1}{\phi_3} \left( \frac{1}{T_m} - \frac{1}{T^0_m} \right) \text{ versus } \phi_3 \]

A significant amount of work has subsequently been done to refine this technique both experimentally and theoretically\(^{5-10}\).

3.4.3 Apparatus and Materials

The thermograms were recorded on a DuPont 9900 DSC apparatus, which could be fitted with a mechanical cooling head. It was calibrated regularly on a single point basis with Indium. The polymers were annealed at 353K in a vacuum oven for 12 hours and stored in a desiccator containing silica.

It should be noted that all of the DSC work was carried out on the EVA - C\(_{14/16}\) FVA blend.
3.4.4 Experimental Procedures and Results

3.4.4.1 Miscibility

Typically 10mg of each mixture of interest was annealed at a series of temperatures between 298 and 353K for 10 minutes. Several pretreatments were tried in an attempt to improve the reproducibility of the data and these are discussed in section 3.4.6. Thereafter, a thermogram was obtained at a scanning rate of 10 K min\(^{-1}\) for the temperature range 133 - 373K. The number of \(T_g\) values identified was recorded and the process repeated until the limits of miscibility were obtained. The phase diagram was established by repeating this procedure for the entire composition range.

Table 3.4

<table>
<thead>
<tr>
<th>Mass Fr. EVA</th>
<th>No. (T_g) vals</th>
<th>(T_{\text{anneal}}/\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.066</td>
<td>2</td>
<td>333.6</td>
</tr>
<tr>
<td>0.066</td>
<td>1</td>
<td>340.0</td>
</tr>
<tr>
<td>0.174</td>
<td>2</td>
<td>325.5</td>
</tr>
<tr>
<td>0.174</td>
<td>1</td>
<td>328.1</td>
</tr>
<tr>
<td>0.360</td>
<td>2</td>
<td>313.8</td>
</tr>
<tr>
<td>0.360</td>
<td>1</td>
<td>319.1</td>
</tr>
<tr>
<td>0.512</td>
<td>2</td>
<td>311.5</td>
</tr>
<tr>
<td>0.512</td>
<td>1</td>
<td>318.8</td>
</tr>
<tr>
<td>0.623</td>
<td>2</td>
<td>310.8</td>
</tr>
<tr>
<td>0.623</td>
<td>1</td>
<td>316.1</td>
</tr>
<tr>
<td>0.781</td>
<td>2</td>
<td>309.2</td>
</tr>
<tr>
<td>0.781</td>
<td>1</td>
<td>313.4</td>
</tr>
<tr>
<td>0.954</td>
<td>2</td>
<td>313.0</td>
</tr>
<tr>
<td>0.954</td>
<td>1</td>
<td>317.9</td>
</tr>
</tbody>
</table>

If the limiting points for each composition are plotted the phase diagram is obtained, Figure 3.4
Phase Diagram of EVA/FVA Mixture as determined by DSC

Mass Fraction EVA

0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 1.00

300.00 310.00 320.00 330.00 340.00

Temp

X / Temp

- Upper Limit
- Lower Limit

Figure 3.4
The phase diagram obtained from the $T_g$ analysis, Figure 3.3, suggests that this copolymer pair is miscible in all proportions up to $\sim 308\text{K}$ at which they undergo lower critical solution temperature type behaviour, (LCST), and phase separate. These results are discussed more fully in section 3.4.6.

3.4.4.2 Melting Point Depression

All of the results were obtained at a scanning rate of $10\text{K min}^{-1}$ in the range $223 - 353\text{K}$ and each experiment comprised both a heating and cooling cycle. Approximately $10\text{mg}$ of material were annealed at $353\text{K}$ for 10 minutes to ensure that it was amorphous and in thermal equilibrium before scanning to $223\text{K}$, where it was maintained for 10 minutes before the cycle was completed. $C_{14/10} \text{FVA}$ melts at $\sim 302\text{K}$ and this was the endotherm which was followed: EVA was defined as the amorphous phase.

Melting Point Depression Results

Table 3.5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Frn.EVA</th>
<th>Melting Point / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0000</td>
<td>303.30</td>
</tr>
<tr>
<td>2</td>
<td>0.0843</td>
<td>301.99</td>
</tr>
<tr>
<td>3</td>
<td>0.2094</td>
<td>301.43</td>
</tr>
<tr>
<td>4</td>
<td>0.2287</td>
<td>302.49</td>
</tr>
<tr>
<td>5</td>
<td>0.2422</td>
<td>303.11</td>
</tr>
<tr>
<td>6</td>
<td>0.3062</td>
<td>300.98</td>
</tr>
<tr>
<td>7</td>
<td>0.3389</td>
<td>301.18</td>
</tr>
<tr>
<td>8</td>
<td>0.4541</td>
<td>303.09</td>
</tr>
<tr>
<td>9</td>
<td>0.5305</td>
<td>300.45</td>
</tr>
<tr>
<td>10</td>
<td>0.6275</td>
<td>301.19</td>
</tr>
<tr>
<td>11</td>
<td>0.7003</td>
<td>301.47</td>
</tr>
<tr>
<td>12</td>
<td>0.8471</td>
<td>300.12</td>
</tr>
</tbody>
</table>
From the data in table 3.5 it can be seen that there is virtually no depression in the melting point of $C_{14/16}$ FVA when it is mixed with EVA.

3.4.6 Discussion

The applicability of DSC to this system was in some doubt owing to the complexity and non-reproducibility of the thermograms obtained. In an attempt to improve and simplify these signals a variety of pretreatments was investigated, these included,

(1) Heating approximately 1g of the materials to 393K, in the bulk state, and then sealing into DSC cells.

(2) Dissolving the polymers in chloroform and re-precipitating from methanol.

(3) Applying (1) to the re-precipitated polymers.

(4) Quenching the 'canned' samples by crash-cooling within the DSC.

(6) Physically plunging the cans into liquid nitrogen and placing these in the DSC at ~ 133K.

All these procedures had significant effects on the thermograms obtained and consequently it was concluded that a consistent pretreatment was required to ensure comparable results. Additional variation of the thermal histories was carried out and the following protocol was finally established:-

(1) Heat the samples to 393K in the bulk.

(2) 'Can' at room temperature.

(3) Ramp at 20K min$^{-1}$ to 393K and maintain isothermally for 10 minutes.

(4) Cool to the temperature of annealing and hold for 10 minutes.

(5) Crash-cool within the DSC, (include maximum rate), to 133K.

(6) Heat at 10K min$^{-1}$ to 373K.

Even when this convoluted procedure was used the degree of reproducibility was not particularly good and the resulting traces were still difficult to interpret. Figures 3.5 and 3.6 are typical results and their salient features are described below.
Comment: DRIED IN VAC-OVEN, TINNED, GLASS-OVEN, PLUNGED IN N2
From Figure 3.4

<table>
<thead>
<tr>
<th>Temperature Range / K</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>148 to 158</td>
<td>$T_g$</td>
</tr>
<tr>
<td>223 to 263</td>
<td>This effect is non-reproducible and its origin is unknown.</td>
</tr>
<tr>
<td>268 to 278</td>
<td>This sharp endotherm is produced by the melting of ice which has</td>
</tr>
<tr>
<td></td>
<td>accumulated either in the sample vessel or in the DSC cell</td>
</tr>
</tbody>
</table>

From Figure 3.5

<table>
<thead>
<tr>
<th>Temperature Range / K</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>153 to 163</td>
<td>Unknown non-reproducible effect</td>
</tr>
<tr>
<td>248 to 263</td>
<td>$T_g$</td>
</tr>
<tr>
<td>293 to 303</td>
<td>Sharp endotherm of the FVA melt</td>
</tr>
</tbody>
</table>

It should be noted that the EVA signal, (excluding the ice peak), shows a variation of only $\sim 0.25\text{ W}\text{ g}^{-1}$ over the temperature range 100 to 373K while the C$_{14/16}$ FVA sample is only slightly more responsive at $\sim 1.0\text{ W}\text{ g}^{-1}$; the data listed in Table 3.2 show a variation of $\pm 20\text{ K}$ in the identified position of the respective $T_g$ values. The interpretation of such small and fickle effects is consequently difficult. Additionally, both copolymers have a discontinuity in the range -125 to -110 °C that resembles a glass transition, (although this effect is not always observed in C$_{14/16}$ FVA). Since the whole construction of the phase diagram is based on the reliable identification of the $T_g$ values in the blend, it is apparent that this may not have been done and consequently the validity of the phase diagram is questionable.
This diagram shows lower critical solution temperature type behaviour which is common amongst polymeric materials, and is characteristic of exothermic mixing and associated entropy effects. A Flory-Huggins interaction parameter can qualitatively be assumed to have a negative or small positive value below ~ 308K, where the blend is miscible at all compositions. This parameter then becomes more positive as the temperature is increased and phase separation occurs. From the melting point data it appears that no depression occurs despite the apparent miscibility.

The variation in melting point observed, (± 3K), was considered to be within the experimental error. In view of the data and the accepted restrictions of this type of analysis, e.g. the dependence of the results on the heating/cooling rates, the effects of diffusion limitation, supercooling and non-homogeneity within the sample, it was felt that the evaluation of a $\chi$ parameter would be pointless. The data suggest that no interaction exists between EVA and C_{14/10}FVA and thus the polymer-polymer interaction parameter would be unfavourable and positive. This leads to a discrepancy with the qualitative conclusions reached from the $T_g$ work. However, the melting point depression results may also be misleading since Flory's original derivation requires one of the materials to be completely amorphous, i.e. EVA. The turbid nature of the EVA may have resulted from some crystallinity in the material.

As a result of the ambiguous nature of these experiments, and the close proximity of the estimated phase limit to the unidentified transition in EVA at 325K, it was decided to investigate this effect further using laser turbidimetry, and to use alternative techniques to obtain more information about the phase diagram of this blend.

3.5 Laser Turbidimetry

This experiment was done to obtain an accurate temperature profile of the EVA sample between 313 and 338K. Approximately 1.5g of EVA was charged to an optical cell immersed in a bath of xylene. A spectra physics 124B Helium/Neon laser was directed through this cell and the 90° scattering intensity measured with a photon-multiplier tube connected to a Malvern K7025 photo-correlator, Figure 3.7. The xylene bath was set to a series of temperatures and numerous determinations made of the intensity, from which the arithmetic mean and standard deviation were calculated.
Figure 3.7: Schematic Diagram of Turbidimetry Apparatus
This apparatus could not be used for studying blends because the beam only collided with a very small area of the vertically mounted sample and since blends were observed to separate into two distinct layers when left at ~ 353K for 12 hours\(^{(11)}\), this prohibited any further work as shown in Figure 3.8.

3.5.1 Turbidimetry Results

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>Arbitrary Intensity</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.2</td>
<td>14133</td>
<td>959</td>
</tr>
<tr>
<td>315.9</td>
<td>13223</td>
<td>866</td>
</tr>
<tr>
<td>319.1</td>
<td>11887</td>
<td>766</td>
</tr>
<tr>
<td>323.2</td>
<td>9762</td>
<td>597</td>
</tr>
<tr>
<td>324.6</td>
<td>8418</td>
<td>506</td>
</tr>
<tr>
<td>325.6</td>
<td>8170</td>
<td>482</td>
</tr>
<tr>
<td>326.0</td>
<td>6626</td>
<td>467</td>
</tr>
<tr>
<td>326.1</td>
<td>8827</td>
<td>533</td>
</tr>
<tr>
<td>326.5</td>
<td>5128</td>
<td>421</td>
</tr>
<tr>
<td>326.9</td>
<td>3199</td>
<td>456</td>
</tr>
<tr>
<td>327.7</td>
<td>2752</td>
<td>403</td>
</tr>
<tr>
<td>328.2</td>
<td>3299</td>
<td>459</td>
</tr>
<tr>
<td>329.1</td>
<td>1853</td>
<td>226</td>
</tr>
<tr>
<td>330.2</td>
<td>1208</td>
<td>176</td>
</tr>
<tr>
<td>331.4</td>
<td>975</td>
<td>144</td>
</tr>
<tr>
<td>332.4</td>
<td>757</td>
<td>126</td>
</tr>
<tr>
<td>333.2</td>
<td>344</td>
<td>39</td>
</tr>
<tr>
<td>338.2</td>
<td>90</td>
<td>19</td>
</tr>
</tbody>
</table>

These results show that the intensity of the scattered light decreases evenly between 313 and 326K and then falls dramatically between 326 and 329K before reaching a minimum at approximately 333K. This suggests that the clarification of the sample starts below 326K though this effect is not
Optical Cell containing Sample

Figure 3.8: Schematic Diagram of Turbidimetry Sample Cell
apparent to the naked eye. These results are expressed graphically in Figure 3.9.

3.6 General Discussion

The initial characterisation showed that both of these materials comprised long alkyl sequences and ester groups. If the macro structures are considered, (Figs. 3.1 and 3.2), it appears likely that any interaction between these species was likely to arise between substituted alkyl groups of the fumarate and the backbone of EVA, rather than between the ester linkages which are substantially protected. Any intermolecular interaction which existed between the alkyl chains was likely to be weak and thus difficult to measure. The volume additivity observed from the density measurements, and the insignificant depression of the $C_{14}$FVA melting point as determined by DSC, support this simple hypothesis. The GPC data show that both of these copolymers are polydisperse and of low molecular weight, the degree of polymerisation being 13 and 17 for EVA and $C_{14}$FVA respectively. Additionally, the EVA sample underwent some type of transition which the turbidimetry measurements showed as starting at temperatures of less than 313K and continuing towards a maximum at about 325-327K. No corresponding effect was seen with DSC. These factors complicated this work since many of the thermodynamic models and theories assume a monodisperse system of infinitely high molecular weight, and all further experiments had to be carried out above 353K to ensure that the EVA was in a stable state. These factors together with the non-reproducibility of the $T_s$ data were considered to be sufficient evidence to doubt the value of the phase diagram as obtained in section 3.4.

Other experimental and theoretical techniques, which were used in an attempt to characterise this problematic blend, are described in subsequent chapters of this thesis.
90 Degree Scattering Intensity Profile of EVA

Figure 3.9
3.7 REFERENCES

(1) Anton Paar KG (Densiometer) Instruction manual.


(12) Private communication from EXXON Chemicals.
Chapter 4  Inverse Phase Gas Chromatography

4.1  Introduction

The technique of Inverse Phase Gas Chromatography, (IGC), was first devised approximately twenty years ago\(^{(1)}\) and was so-called because it uses the properties of an known volatile phase to examine the properties of an unknown stationary phase. This has particular application in polymer science because the vapour pressure of most polymers is effectively zero at practical temperatures, making conventional Gas Liquid Chromatography, (GC), unsuitable. IGC involves depositing the polymer onto an inert chromatographic support which forms the stationary phase in a GC column. A small quantity of volatile probe is vaporised and passed through this column and the time required to elute this probe gives a measure of the polymer-solute interaction. IGC has been used to study a variety of physico-chemical parameters\(^{(2-4)}\) which can all be derived from this elution time. This technique measures the total free energy of interaction and consequently includes combinatorial and residual interactions in addition to any residual entropy contributions. Although it serves as an inexpensive, rapid and simple method which yields reproducible qualitative and relative information, \textit{i.e.} between individual experiments, the quantitative reliability has often been found lacking, owing to the intrinsic but unpredictable surface adsorption and diffusion of the solvent probe in the stationary phase.

4.2  Theoretical

The time between injection of the probe on to the column and its elution peak maximum is defined as the elution time, \(\Delta t\). In common with most dynamic techniques, \(\Delta t\) is normally converted to a more flexible parameter which normalises for many of the experimental conditions, \textit{e.g.} the inlet pressure and volumetric flow rate of the carrier gas, and the mass of polymer on the support. The preferred parameter is the elution volume\(^{(5)}\), \(V_r\), defined as,

\[
V_r = 1.5 F \Delta t \left( \frac{(P_{\text{inlet}}/P_{\text{outlet}})^2 - 1}{(P_{\text{inlet}}/P_{\text{outlet}})^3 - 1} \right) \left( \frac{273.16}{T_r} \right)
\]  
(4.1)
where,

\[ F = \text{Carrier gas volumetric flow rate, cm}^3\text{ s}^{-1} \]

\[ T_r = \text{Temperature at which data were recorded, K} \]

\[ P_{\text{inlet}} = \text{Carrier gas pressure at inlet, mmHg} \]

\[ P_{\text{outlet}} = \text{Carrier gas pressure at outlet, mmHg} \]

However, this term contains contributions from both the void volume of the column, \( V_o \), and the retention volume of the chromatographic support, \( V_s \). The void volume is a characteristic of the column which is determined by passing a sample of inert, non-interacting gas, usually methane, through the column and recording its elution time. This value is then assumed to be the minimum time required to pass an unretentive species through a particular column. However, this procedure has been found to introduce a significant systematic error since the retention volume of methane is often of a similar magnitude to that of many of the solvent probes. To avoid this error Munk \textit{et al.} \(^{(6)}\) suggested eluting a series of hydrocarbons and extrapolating the natural logarithm of their elution volumes to zero carbon number. The exponent of this value represents the elution volume of a true unretentive species. This current work used \( \text{CH}_4 \), and \( \text{C}_5\text{H}_{12} \) to \( \text{C}_8\text{H}_{18} \), and observed a linear relationship between \( \text{Ln} (V_r) \) and carbon number for all of the columns employed. It has also been reported\(^{(10)}\) that the chromatographic support can make a substantial contribution to the elution time. This effect can be removed by duplicating each experiment on an uncoated column and subtracting this contribution from the retention volume of the probe.

If both of these effects are removed, then

\[ V_s = V_r - V_o - V_s \] \hspace{1cm} (4.2)

where,

\[ V_o = \text{column void volume, cm}^3 \]

\[ V_s = \text{retention volume of support, cm}^3 \]

The support retention volume can be further reduced as it contains a contribution from the void volume of the blank column, \( V_{o(\text{Blank})} \), i.e.,

\[ V_s = V_{r(\text{Blank})} - V_{o(\text{Blank})} \] \hspace{1cm} (4.3)

If equations (4.2) and (4.3) are combined, and the result normalised for the mass of polymer on the stationary phase, \( w \), equation (4.4) is obtained,
\[
V_{gc} = \left( V_r - V_v - \left( V_{r(Blank)} - V_{v(Blank)} \right) \right) / w \tag{4.4}
\]

where,

- \( V_{gc} \) = corrected net retention volume, cm\(^3\)g\(^{-1}\)
- \( V_r \) = elution volume of solvent on coated column, cm\(^3\)
- \( V_v \) = void volume of the coated column, cm\(^3\)
- \( V_{r(Blank)} \) = elution volume of solvent on blank column, cm\(^3\)
- \( V_{v(Blank)} \) = void volume of blank column, cm\(^3\)
- \( w \) = mass of polymer on coated column, g

It should be noted that these corrections are made as retention volumes rather than elution times because the experimental conditions often differ. The corrected net retention volume is the experimental parameter which is used in the following thermodynamic treatment. In this chapter the results are considered only in terms of Flory-Huggins-Miller-Chang theory: a full equation of state analysis is included in Chapter 8.

Calculation of Flory-Huggins-Chang-Miller Interaction Parameters

Since IGC measures the free energy of interaction the interaction parameters are denoted as \( \tilde{\chi} \) as opposed to \( \chi \) which has been used elsewhere in this thesis to denote interaction parameters based solely on the enthalpic mixing contribution. The first interaction to be considered is that between the infinitely dilute solvent probe and the bulk polymeric stationary phase, \( \tilde{\chi}_{II} \),

\[
\tilde{\chi}_{II} = \ln \left( \frac{RTv_1}{V_{gc} V_1 P_1^o} \right) - \left( 1 - \frac{V_1}{M_n v_1} \right) - \frac{P_1^o}{RT} \left( B_{II} - V_1 \right) \tag{4.5}
\]

where,
\[ \bar{M}_n = \text{number average molecular weight of polymer, g mol}^{-1} \]

\[ R = \text{Universal Gas Constant, cm}^3\text{atm K}^{-1} \text{mol}^{-1} \]

\[ T = \text{operating temperature, K} \]

\[ V_1 = \text{molar volume of solvent at T, cm}^3 \text{mol}^{-1} \]

\[ p_1^o = \text{saturated vapour pressure of solvent at T, atm} \]

\[ v_i = \text{specific volume of polymer at T, cm}^3 \text{g}^{-1} \]

\[ B_{11} = \text{second virial coefficient of solvent vapour phase at T, cm}^3 \text{mol}^{-1} \]

Note: The subscripts used here denote the following quantities

1 - solvent  
2 - EVA  
3 - C_{14} FVA,

From equation 4.5 the two solvent-polymer interaction parameters, \( \tilde{x}_{12} \) and \( \tilde{x}_{13} \), together with the solvent-polymer-polymer interaction parameter, \( \tilde{x}_{1,23} \), can be stated explicitly as,

\[ \tilde{x}_{12} = \ln \left( \frac{RTv_2}{V_{gc} V_1 p_1^o} \right) - \left( 1 - \frac{V_1}{Mn_2v_2} \right) \frac{p_1^o}{RT} \left( B_{11} - V_1 \right) \] (4.5a)

\[ \tilde{x}_{13} = \ln \left( \frac{RTv_3}{V_{gc} V_1 p_1^o} \right) - \left( 1 - \frac{V_1}{Mn_3v_3} \right) \frac{p_1^o}{RT} \left( B_{11} - V_1 \right) \] (4.5b)

\[ \tilde{x}_{1,23} = \ln \left( \frac{RT(w_2v_2 + w_3v_3)}{V_{gc,23} V_1 p_1^o} \right) - \left( 1 - \frac{V_1}{Mn_2v_2} \right) \phi_2 
- \left( 1 - \frac{V_1}{Mn_3v_3} \right) \phi_3 \frac{p_1^o}{RT} \left( B_{11} - V_1 \right) \] (4.5c)

The polymer-polymer interaction parameter, \( \tilde{x}_{23} \), can be evaluated from the three equations above by considering the solvent effect to be additive,
\[
\tilde{x}_{23} = \frac{1}{\phi_2\phi_3} \left( \phi_2 \tilde{x}_{12} + \phi_3 \tilde{x}_{13} - \tilde{x}_{4,23} \right) \tag{4.6}
\]

If the common factors are removed from the individual interaction parameters in equation 4.6,

\[
\tilde{x}_{23} = \frac{V_2}{V_1} \left( \frac{1}{\phi_2\phi_3} \ln \left( \frac{V_{gc,23}}{w_2V_2 + w_3V_3} \right) - \phi_2 \ln \left( \frac{V_{gc,2}/V_1}{V_{gc,2}/V_2} \right) - \phi_3 \ln \left( \frac{V_{gc,3}/V_1}{V_{gc,3}/V_3} \right) \right)
\tag{4.7}
\]

where,

\[\tilde{x}_{23} = \text{true polymer-polymer interaction parameter.}\]
\[V_2 = \text{molar volume of polymer, cm}^3 \text{ mol}^{-1}\]
\[\phi_i = \text{volume fraction of component 'i'}\]
\[w_i = \text{weight fraction of component 'i' in blend}\]

(the subscripts on the corrected retention volumes denote which column was used to derive the data)

An alternative definition of interaction parameter, \(\tilde{x}_{23}'\), is sometimes used, namely,

\[
\tilde{x}_{23}' = \tilde{x}_{23}(V_1/V_2) \tag{4.8}
\]

This form is favoured because the molar volumes of both the solvent and the polymer need not be known. Another definition arises defined by removing the molar volume of the solvent from equation 4.8.

\[
\tilde{x}_{23,\text{app}} = \tilde{x}_{23}/V_2 \tag{4.9}
\]

This was introduced to remove the intrinsic solvent effects from IGC data by normalising the interaction parameter for the molar volume of the probe used. However, it has been found to be a scaling factor rather than a correlation.
Another definition involves the interaction energy density characteristic of the polymer-polymer pair, $B_{23}$

$$B_{23} = \tilde{\chi}_{23}^{*} \frac{RT}{V_1} \quad (4.10)$$

These definitions of interaction parameter are related, i.e.

$$\tilde{\chi}_{23} = \tilde{\chi}_{23}^{*} \left(\frac{V_2}{V_1}\right) = \tilde{\chi}_{23}^{app} V_2 = B_{23} V_2 / RT$$

and the final choice is usually made on the basis of the information available about the polymer and the probe. Munk et al.\(^{(8)}\) reported an empirical correlation between the $B_{23}$ values obtained for blends of poly(ε-caprolactone) and poly(epichlorohydrin), and the Hildebrand solubility parameters of the eluents. It was originally hoped that this function could be used to predict and/or remove the obvious solvent dependence in the data. The same procedure was also attempted in this work but no correlation was apparent and consequently the results of this work have been presented in terms of $\tilde{\chi}_{23}^{*}$.

4.3 Apparatus and Materials

A PYE Unicam G.C.D. chromatograph equipped with flame ionisation detector, (FID), was adapted to perform the IGC measurements in this work,\(^{(9)}\) Fig.(4.1). Oxygen-free-nitrogen, (OFN), was used as the carrier gas which was supplied to the system through a 3-way valve, allowing the flow to be directed either to a mercury manometer, (A), which determined the inlet pressure, or to a pair of needle valves, (B), which accurately controlled the volumetric flow rate to the column. Approximately $0.5 \mu L$ of solvent was injected through a silicon rubber septum into section (C) which was maintained at 523K. As the solvent was vaporised it became entrained in the entering OFN stream and was propelled through the column as a molecular plug.

An additional 3-way valve was inserted at the exit of the column to allow the stream to be directed either to a pair of 100 cm$^3$ bubble flowmeters, (F), or the FID, (E) : two independent flowmeters were used to reduce the time required to determine the flow rate and to ensure the reproducibility of the measurement. The electrical output from the GC control unit, (G), was sent simultaneously to a chart recorder, (H), and an Atari personal computer, (K).

This arrangement provided both accurate information on the shape of the elution profile and the time at which the elution maxima occurred. The output to the Atari was processed initially by an amplifier, (I), which optimised the gain of the signal, and was then fed to a 8-bit Analog-Digital converter\(^{(10)}\), (J).
Figure 4.1

Schematic diagram of IGC apparatus

A: MANOMETER
B: NEEDLE VALVES
C: INJECTION PORT
D: COLUMN
E: FLAME IONIZATION DETECTOR
F: BUBBLE FLOWMETER
G: S.C. CONTROL UNIT
H: CHART RECORDER
I: A-D CONVERTER
J: I/A P.C.
An Atari 1040 ST, (K), was chosen for this task as it has an internal clock which could be accessed to provide sampling intervals down to 0.01s. Previous workers\(^8\) used a sampling interval of 0.5 s and obtained the elution-peak maximum by fitting a quadratic to the data. This quadratic was then differentiated and set equal to zero; the maximum was found by solving the resulting equation. This method assumes that the profile is entirely symmetrical which is frequently not the case as may be seen from Fig.4.2. Using a sampling interval of 0.01 s eliminates the need for such an assumption. The data acquisition software was developed for this apparatus using GFA Basic (version 3.2). The data was then stored as a series of values between 0 and 256 on floppy disk, and was immediately available for further manipulation e.g. graphical representation, integration of the area under the peak or estimation of the baseline stability. Additionally, a series of programs was written in Pascal and Modula2 to reduce the data and to calculate the relevant physico-chemical parameters.

4.4 Experimental Procedure

The stationary phase which was packed into the columns comprised the polymeric material, at typically 7\% loading, which had been deposited onto approximately 15 g of the chromatographic support from a suitably volatile solvent using the method suggested by Al-Saigh and Munk\(^{11}\): 30/80 mesh PTFE\(^{12}\) (which had been re-sieved, acid washed and treated with dichloromethyl-siloxane) was used as the support. The coated material was drawn into glass columns\(^{13}\) of dimensions 2 m x 4 mm (i.d.) by an aspirator pump and left under vacuum until no further compression of the support could be detected. Approximately 0.05 cm\(^3\) of 1 mm diameter beads were then inserted on top of the packing at the inlet to the column, to aid solvent vaporisation and distribution, and the column was then placed in the G.C. oven and conditioned for 24 hours at 100 K above the nominal operating temperature.

The solvent probes were of AnalAR grade and were used as supplied, as any contaminants were effectively separated on the column. At hourly intervals during experimentation the inlet pressure and volumetric flow rate were recorded to ensure that the carrier gas stream remained constant. It was found that over any 12 hour period the variation in these conditions lay within the resolution of the measuring devices. Similarly, the temperature of the GC oven was independently measured with a platinum resistance thermometer and was found to remain virtually constant over periods of up to 6 weeks although a 0.2 K variation was found within the oven.
IGC Elution Curve of Dichloromethane at 353K on an FVA Column

Figure 4.2
The carrier gas flow rate was measured a minimum of 5 times on each occasion, and a mean value recorded. Once these parameters had been measured the elution times of the solvents could be studied. Each solvent was injected a minimum of 5 times and a mean value recorded. Elution times for different solvents varied from a minimum of 30 seconds to a maximum of 6 minutes. The reproducibility for any given solvent was typically 1%.

One disadvantage of sampling at an interval of 0.01s was that enormous quantities of irrelevant data could be accumulated with slowly eluting solvents. To eliminate this, the data acquisition program examined a predetermined number of consecutive samples which were required to increase by a given percentage before data logging began, (both of these parameters were variable and were set at the start of each run). The program then sampled the GC output for a specified duration and recorded the time at which the maximum signal was recorded. At the end of each run the data were transferred from RAM to a floppy disc and the process repeated.

4.5 Results

A sample calculation has been included to illustrate the calculation of interaction parameters from the IGC data.

4.5.1 Sample calculation and estimation of errors.

At each stage of the calculation an error has been estimated so that the significance of each term and its associated error can be examined, and to assist in estimating a total error for the interaction parameters. Owing to the limited number of results, a standard deviation analysis was not attempted and instead a simple best/worst case treatment has been used.

The specimen calculation uses the results for chloroform with the 0.3589 (wt/wt) EVA column at 373K; this was a random choice. This calculation illustrates the evaluation of the terms required for the processing of the IGC data which ultimately gives a value of $\bar{x}_{1,23}$
(1) Carrier gas volumetric flow rate.

<table>
<thead>
<tr>
<th>Start / cm</th>
<th>Stop / cm</th>
<th>Total / cm</th>
<th>Time / s</th>
<th>Flow / cm³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>68</td>
<td>30</td>
<td>88.39</td>
<td>0.3394</td>
</tr>
<tr>
<td>64</td>
<td>34</td>
<td>30</td>
<td>87.82</td>
<td>0.3416</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>30</td>
<td>88.38</td>
<td>0.3394</td>
</tr>
</tbody>
</table>

Mean = 0.3401 cm³ s⁻¹

Error: (+ve value = 0.3416, -ve value = 0.3394 cm³ s⁻¹)

(2) Inlet and outlet carrier gas pressures

The inlet pressure was measured using a 2m manometer which was attached to a millimetre calibrated scale. The associated error in reading this scale was approximately 0.5 mmHg. The inlet pressure was always measured at equilibrium. Hence in this case only a single point was ever recorded.

Inlet Pressure = 2327.0 ± 0.5 mmHg

Error: (+ve value = 2327.5, -ve value = 2326.5 mmHg)

The outlet pressure was always taken as the atmospheric condition, measured on a mercury barometer fitted with a Vernier scale. The error in reading this scale was 0.1 mmHg, thus,

Outlet Pressure = 760 ± 0.1 mmHg

Error: (+ve value = 760.1, -ve value = 759.9 mmHg)
(3) Elution Times

These data were recorded at an interval of 0.01 s between points

<table>
<thead>
<tr>
<th>Run</th>
<th>Elution time / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>164.17</td>
</tr>
<tr>
<td>2</td>
<td>164.59</td>
</tr>
<tr>
<td>3</td>
<td>164.07</td>
</tr>
<tr>
<td>4</td>
<td>164.33</td>
</tr>
<tr>
<td>5</td>
<td>164.21</td>
</tr>
</tbody>
</table>

Mean = 164.27 cm³ s⁻¹ (standard deviation 0.18)

Error: (+ve value = 164.45, -ve value = 164.09 cm³ s⁻¹)

This value now requires to be converted into an elution volume which normalises the result for the conditions of the experiment, using equation 4.1,

\[ V_r = 1.5 F \Delta t \left( \frac{(P_{inlet}/P_{outlet})^2 - 1}{(P_{inlet}/P_{outlet})^3 - 1} \right) \left( \frac{273.16}{T_r} \right) \]

substituting,

\[ V_r = 1.5 \times 0.3401 \times (164.27) \left( \frac{(2327/760)^2 - 1}{(2327/760)^3 - 1} \right) \left( \frac{273.16}{373.16} \right) \]

\[ V_r = 18.544 \text{ cm}^3 \]

Error: (+ve value = 18.657, -ve value = 18.489 cm³)

To simplify the error calculation, the difference between the +ve value and the mean value has been assumed to represent the typical error associated with measuring a retention volume. If this is expressed as a percentage of the mean value, i.e.

\[ \text{Difference} = 18.657 - 18.544 = 0.1126 \text{ or } 0.6\% \text{ (expressed as a %age)} \]
It is now assumed that this magnitude of error is present in all retention volume measurements and the high/low values quoted for the following values represent 0.6% of the mean values given. This retention volume now requires to be corrected for the contributions from the PTFE support and the void volume in accordance with equation 4.4.

(3a) PTFE Contribution

The elution time of chloroform on a blank column was determined as,

$$\Delta t = 46.52 \text{s}$$

under the following experimental conditions

$$P_i = 2302 \text{ mmHg} : P_o = 760 \text{ mmHg} : F = 0.2606 \text{ cm}^3\text{s}^{-1}$$

which gives a gross retention volume of,

$$V_{r(\text{blank})} = 5.549 \text{ cm}^3$$

However, this term includes the blank column void volume contribution which was evaluated by the extrapolation process described below, as 1.487 cm$^3$, i.e.

$$V_v = V_{r(\text{blank})} - V_{v(\text{blank})}$$

$$= 5.549 - 1.487 = 4.062 \text{ cm}^3$$

Error: (+ve value = 4.086, -ve value = 4.038 cm$^3$)

(3b) Column void volume

The void volume of each column was determined by eluting methane, pentane, hexane, heptane and octane, at each temperature, and extrapolating the natural logarithm of their retention volume, as a function of carbon number, to give an intercept with the y-axis, and thus an estimate of the retention volume of a hypothetically non-interacting solvent probe.
Under the same conditions that are quoted above for the support contribution, the following elution times were measured,

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Carbon No.</th>
<th>( \Delta t / s )</th>
<th>( \ln(\Delta t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>30.71</td>
<td>3.43</td>
</tr>
<tr>
<td>Pentane</td>
<td>5</td>
<td>57.85</td>
<td>4.06</td>
</tr>
<tr>
<td>Hexane</td>
<td>6</td>
<td>90.78</td>
<td>4.51</td>
</tr>
<tr>
<td>Heptane</td>
<td>7</td>
<td>161.03</td>
<td>5.08</td>
</tr>
<tr>
<td>Octane</td>
<td>8</td>
<td>304.73</td>
<td>5.72</td>
</tr>
</tbody>
</table>

The following values of slope and intercept were obtained from a linear least-squares fit for this data:

Intercept = 1.23, Slope = 0.56 with a correlation coefficient of 0.9971

Thus for a carbon number of 1, \( \ln(\Delta t) \) was recalculated as 1.79; hence the void elution time was estimated as \( \exp(1.79) \) or 5.96 s

\[
\text{Void Volume} = V_v = 1.015 \text{ cm}^3
\]

Error: (+ve value = 1.021, -ve value = 1.009 cm\(^3\))

If the non-polymer contributions are now removed from \( V_r \) and the result normalised for the weight of material on the column, the net retention volume can be obtained from equation 4.2,

\[
V_g = (V_r - V_v - V_d)/w
\]

where, \( w = 0.9996\) g

Error: (+ve value = 0.99965, -ve value = 0.99955 g)

\[
V_{gc} = (18.544 - 4.062 - 1.015) / 0.9996 = 13.472 \text{ cm}^3 \text{ g}^{-1}
\]

Error: (+ve value = 13.5561, -ve value = 13.3907 cm\(^3\) g\(^{-1}\))

This value is the retention volume arising from only the polymer-polymer -solvent interaction.
Equation 4.5 requires the estimation of a number of physical properties of both the polymer and the solvent. The methods that were used to calculate or measure these parameters are listed below:

\[ \tilde{\chi}_{ii} = \ln \left( \frac{RTV_i}{V_g \frac{1}{V_1} P_i^\circ} \right) - \left( 1 - \frac{V_1}{M_i \gamma_i} \right) - \frac{P_i^\circ}{RT} \left( B_{ii} - V_i \right) \]  

(4.5)

solvent properties: \( V_i, P_i^\circ \) and \( B_{ii} \)

polymer properties: \( v_{23} \) and \( M_{23} \)

Solvent Properties

(a) molar volumes of solvents: \( V_i \)

These were calculated from an abbreviated form of the Gunn and Yamada expression\(^{14}\),

\[ V = V_{Ref} \frac{V_r^{(0)} (T_r) \left( 1 - \omega g (T_r) \right)}{V_{r,Ref}^{(0)} \left( 1 - \omega g (T_{r,Ref}) \right)} \]  

(4.11)

where,

\[ T \] = temperature for which the molar volume is required, K

\[ T_c \] = critical temperature of the solvent, K

\[ T_r \] = reduced temperature, \( T/T_c \)

\[ T_{Ref} \] = reference temperature, K

\[ T_{r,Ref} \] = reduced reference temperature, \( T_{Ref}/T_c \)

\[ V_{Ref} \] = molar volume of material at \( T_{Ref} \), cm\(^3\) mol\(^{-1}\)

\[ \omega \] = Pitzer and Curl acentric factor
\( V_r^{(0)} \) and \( g \) are empirical functions of reduced temperature, such that

For \( 0.2 \leq T_r \leq 0.8 \)

\[
V_r^{(0)} = 0.33593 - 0.33953 T_r + 1.51941 T_r^2 \\
- 2.02512 T_r^3 + 1.11422 T_r^4
\]  \hspace{1cm} (4.12)

and for \( 0.2 \leq T_r \leq 1.0 \)

\[
g = 0.29607 - 0.09045 T_r - 0.04842 T_r^2
\]  \hspace{1cm} (4.13)

For the sample data \( V_i \) was calculated from the Gunn and Yamada correlation as 89.8 \( \text{cm}^3 \text{mol}^{-1} \).

This method is recommended as one of the most accurate available for calculating the molar volume of a saturated liquid. It is said to be applicable for non-polar and slightly polar compounds although acetonitrile and alcohols have also been fitted. Another recommended correlation is a modified version of the Rackett equation \(^{(15)} \) which replaces the critical compressibility factor, \( Z_{cr} \), with an empirical constant characteristic of the compound under study, \( Z_{Ra} \).

\[
V = \frac{RT_c}{P_c} \exp \left\{ (1 - T_r) \sqrt{\gamma} \ln (Z_{Ra}) \right\}
\]  \hspace{1cm} (4.14)

where,

\[
P_c = \text{critical pressure of the solvent, and}
\]

\[
Z_{Ra} = 0.29056 - 0.08775 \omega
\]  \hspace{1cm} (4.15)

For the sample data, the calculated specific volume using the Rackett equation was 89.9 \( \text{cm}^3 \text{mol}^{-1} \).

Both methods were used, where empirical data was available, to ensure reproducibility and although very little difference was observed between the results the modified Rackett equation was used preferentially. The error associated with this calculation is reported to be smaller than 1\%, and this was taken as the worst possible case, \textit{i.e.}

\textbf{Error: (}+ve value = 90.8, -ve value = 89.0 \( \text{cm}^3 \text{mol}^{-1} \)\textbf{)}
(b) Saturated vapour pressure, $P_1^o$

$P_1^o$ was calculated preferentially from the Wagner equation\(^{(14)}\), where data were available,

$$P_1^o = \exp\left(\frac{w_1 \tau + w_2 \tau^{1.5} + w_3 \tau^3 + w_4 \tau^6}{T_r}\right)$$  \hspace{1cm} (4.16)

where $\tau = 1.0 - T_r$ and $w_i$ are the Wagner coefficients from Reid, Prausnitz and Polling\(^{(14)}\),

or from the Antoine equation\(^{(14)}\),

$$P_1^o = \exp\left(A_0 - A_1/(T + A_2)\right)$$  \hspace{1cm} (4.17)

where, $A_i$ are the Antoine coefficients from Reid, Prausnitz and Polling\(^{(14)}\).

For chloroform at 373.16 K, the Wagner equation gave a vapour pressure of 2325 mmHg. Although the error in the calculated vapour pressure will vary for different solvents, Reid, Prausnitz and Polling include a specimen calculation for acetone where the typical error does not exceed 0.2%. It was concluded that errors in vapour pressure calculations could be neglected when compared with other sources of error.

(c) Second virial coefficient of the solvent in the vapour phase: $B_{11}$

Gaseous second virial coefficients can be calculated either from the integration of theoretical expressions, which relate intermolecular energy to the distance of molecular separation, or by employing corresponding-states relations to experimental data. The latter approach is usually favoured owing to the limited information on the energetic relationships of molecules. This work has employed two techniques to estimate the vapour phase virial coefficients of the solvent probes from the collected data of Dymond and Smith\(^{(15)}\). The Tsonopoulos\(^{(14)}\) correlation is a modified version of the Pitzer and Curl expansion,

$$\frac{B_{11}P_c}{RT_c} = f^{(0)} + \omega f^{(1)}$$  \hspace{1cm} (4.18)

where, $f^{(0)} = 0.1445 - 0.330/T_r - 0.1385/T_r^2$ - $0.0121/T_r^3 - 0.000607/T_r^4$  \hspace{1cm} (4.19)

and $f^{(1)} = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^4$  \hspace{1cm} (4.20)

for the data in the specimen calculation, $B_{11}$ is $-663$ cm$^3$ mol$^{-1}$. 
Where possible it is preferable to use experimental results for \( B_i \), and to permit this least-squares techniques were employed to derive a relationship between the reduced second virial coefficient, \( B_i \), and a function of reduced temperature (MacDonald\(^ {17}\)). The function chosen makes use of the fact that a plot of \( \ln(x)/x \) versus \( x \) has a very similar shape to a plot of \( B_i \) versus \( T_i \); thus a plot of \( B_i \) versus \( \ln(T_i)/T_i \) is substantially linear and hence a least-squares quadratic gives a very good fit over the temperature range of immediate interest.

This method gave a value of -675 cm\(^3\)mol\(^{-1}\) for the second virial coefficient.

The error is dependent on the quality of the experimental data which varies from solvent to solvent but for the specimen calculation it is convenient to use Dymond and Smith’s estimate of \( \pm \) 30 cm\(^3\)mol\(^{-1}\).

**Error**: (+ve value = -705, -ve value = -645 cm\(^3\)mol\(^{-1}\))

**Polymer Characteristics**

(a) **Specific Weights of Polymers :** \( v_2 \) and \( v_3 \)

These values were extrapolated from the least-squares fit of the data relating the reciprocal of density to temperature and composition for each material, section 3.3, thus

\[
v_{EVA,373K} = 1.1227 \text{ cm}^3\text{g}^{-1}
\]

\[
v_{FVA,373K} = 1.1056 \text{ cm}^3\text{g}^{-1}
\]

The errors associated with these measurements were considered to be insignificant in relation to the other errors and consequently it has been neglected.

(b) **Number average molecular weight of the polymer phase:** \( \bar{M}_n \) and \( \bar{M}_n \)

The number average molecular weights were obtained from the GPC measurements described in section 3.2. It is difficult to estimate the accuracy of the GPC measurements since the Mark-Houwink parameters were not known for either polymer and the calibrant was polystyrene, which is unrepresentative of poly(alkyl) materials.
For the purpose of testing the significance of this term in the final answer it has been estimated liberally as 20%, i.e.

\[ \bar{Mn}_{EVA} = 3290 \text{ g mol}^{-1} \text{ and } \bar{Mn}_{FVA} = 10400 \text{ g mol}^{-1} \]

Error\(_{EVA}\) : (+ve value = 3948, -ve value = 2632 g mol\(^{-1}\))

Error\(_{FVA}\) : (+ve value = 12480, -ve value = 8320 g mol\(^{-1}\))

If the values calculated from all of the expressions above are now substituted into the equation 4.5c,

\[
\bar{x}_{1,23} = \ln \left( \frac{RT(w_2y_2 + w_3y_3)}{V_{g,c,23} V_1 P_1^{0}} \right) - \left( 1 - \frac{V_1}{Mn_2y_2} \right) \phi_2 \\
- \left( 1 - \frac{V_1}{Mn_3y_3} \right) \phi_3 - \frac{P_1^{0}}{RT} \left( B_{v1} - V_1 \right)
\]

\[ w_2y_2 + w_3y_3 = (0.3588)(1.1227) + (0.6412)(1.1056) = 1.1117 \]

\[ \text{term 1} = \ln \left( \frac{83.144)(273.16)(1.1117)}{13.472)(89.9)(2325/750)} \right) \]

\[ \text{term 1} = 1.9058 \]

\[ \text{term 2} = \left( 1.0 - \frac{89.9}{3290}(1.1227) \right)(0.3588) \]

\[ \text{term 2} = 0.3501 \]

\[ \text{term 3} = \left( 1.0 - \frac{89.9}{10400}(1.1056) \right)(0.6412) \]

\[ \text{term 3} = 0.6362 \]

\[ \text{term 4} = \frac{2325/750}{83.144)(373.16)} \left( -675 - 89.9 \right) \]

\[ \text{term 4} = -0.0764 \]

\[ \bar{x}_{1,23} = 1.9055 - 0.6326 - 0.3536 - (-0.0764) \]

\[ \bar{x}_{1,23} = 0.9960 \]
This calculation was repeated for chloroform on the pure EVA and C_{14} FVA columns to evaluate $\tilde{x}_{12}$ and $\tilde{x}_{13}$ respectively.

$$\tilde{x}_{12} = 1.057$$

$$\tilde{x}_{13} = 1.069$$

These three values can now be used to calculate the polymer-polymer interaction parameter in equation 4.6, *i.e.*

$$\tilde{x}_{23} = \frac{1}{\phi_2 \phi_3} \left( \phi_2 \tilde{x}_{12} + \phi_3 \tilde{x}_{13} - \tilde{x}_{1.23} \right) \quad (4.6)$$

$$\begin{align*}
\text{term1} & = (0.3588)(1.057) = 0.3793 \\
\text{term2} & = (0.6412)(1.069) = 0.6854 \\
\tilde{x}_{23} & = (0.3793 + 0.6852 - 0.9957)/(0.3588)/(0.6412) \\
& = 0.2999
\end{align*}$$

Alternatively, the net retention volumes of the three experiments can be used directly in equation 4.7 which yields,

$$\tilde{x}_{23} = 0.2972$$

The discrepancy between the values of $\tilde{x}_{23}$ as calculated from equations 4.6 and 4.7 can be attributed to the different method of calculation.
4.5.2 Tabulated Results

Table 4.1
Polymer-solvent interaction parameters at 353K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tilde{x}_{13}$</th>
<th>$\tilde{x}_{12}$</th>
<th>$\Delta \tilde{x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>1.7156</td>
<td>1.8708</td>
<td>0.1552</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.5361</td>
<td>1.7963</td>
<td>0.2602</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.2541</td>
<td>1.5804</td>
<td>0.3263</td>
</tr>
<tr>
<td>Octane</td>
<td>1.3074</td>
<td>1.6320</td>
<td>0.3246</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.4880</td>
<td>3.4908</td>
<td>0.0028</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>2.5467</td>
<td>2.5287</td>
<td>0.0180</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.2106</td>
<td>2.3111</td>
<td>0.1005</td>
</tr>
<tr>
<td>Methylene ketone</td>
<td>1.8528</td>
<td>1.9495</td>
<td>0.0967</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>2.0115</td>
<td>2.1549</td>
<td>0.1434</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>2.5140</td>
<td>2.5817</td>
<td>0.0677</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>1.2237</td>
<td>1.2796</td>
<td>0.0559</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.7962</td>
<td>0.8461</td>
<td>0.0499</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>1.1198</td>
<td>1.3096</td>
<td>0.1898</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.1927</td>
<td>1.2983</td>
<td>0.1056</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.1038</td>
<td>1.2283</td>
<td>0.1245</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.2690</td>
<td>1.5692</td>
<td>0.3002</td>
</tr>
</tbody>
</table>

Mean: 0.1428

Standard Deviation: 0.1062
| Solvent                  | $\tilde{x}_{13}$ | $\tilde{x}_{12}$ | $|\Delta \tilde{x}|$ |
|-------------------------|------------------|------------------|------------------|
| Pentane                 | 2.0067           | 2.5196           | 0.5129           |
| Hexane                  | 1.6421           | 2.0567           | 0.4146           |
| Heptane                 | 1.4121           | 1.7131           | 0.3010           |
| Octane                  | 1.3889           | 1.7487           | 0.3598           |
| Methanol                | 4.1420           | 4.0805           | 0.0615           |
| Isopropyl alcohol       | 2.7015           | 2.6436           | 0.0579           |
| Acetone                 | 2.5519           | 2.6258           | 0.0738           |
| Methyl ethylketone      | 2.0512           | 2.1226           | 0.0714           |
| Methyl Acetate          | 2.3642           | 2.3653           | 0.0011           |
| Ethyl Acetate           | 2.5087           | 2.5661           | 0.0574           |
| Dichloromethane         | 1.5225           | 1.5515           | 0.0290           |
| Chloroform              | 1.0687           | 1.0568           | 0.0119           |
| Carbon Tetrachloride    | 1.3165           | 1.4471           | 0.1306           |
| Benzene                 | 1.3145           | 1.4695           | 0.1550           |
| Toluene                 | 1.2189           | 1.3595           | 0.1406           |
| Cyclohexane             | 1.4484           | 1.6663           | 0.2179           |

Mean: 0.1459

Standard Deviation: 0.1667
Table 4.3
Polymer-solvent interaction parameters at 393K

| Solvent            | $\tilde{x}_{13}$ | $\tilde{x}_{12}$ | $|\Delta\tilde{x}|$ |
|--------------------|------------------|------------------|-------------------|
| Pentane            | 2.3689           | 3.4446           | 1.0757            |
| Hexane             | 1.8190           | 2.2782           | 0.4592            |
| Heptane            | 1.5399           | 1.8471           | 0.3072            |
| Octane             | 1.4889           | 1.7709           | 0.2820            |
| Methanol           | 7.3473           | 6.8630           | 0.4843            |
| Isopropyl alcohol  | 2.8418           | 2.7749           | 0.0669            |
| Acetone            | 2.9218           | 2.9627           | 0.0409            |
| Methyl ethylketone | 2.1646           | 2.2186           | 0.0540            |
| Methyl Acetate     | 2.6963           | 2.7535           | 0.0572            |
| Ethyl Acetate      | 2.4985           | 2.5754           | 0.0769            |
| Dichloromethane    | 1.7300           | 1.8012           | 0.0712            |
| Chloroform         | 1.2208           | 1.2290           | 0.0082            |
| Carbon Tetrachloride| 1.4032          | 1.5754           | 0.1722            |
| Benzene            | 1.3978           | 1.5584           | 0.1606            |
| Toluene            | 1.2556           | 1.4092           | 0.1536            |
| Cyclohexane        | 1.5094           | 1.7774           | 0.2680            |

Mean                                      0.2169

Standard Deviation                        0.2595
Table 4.4

$\bar{\chi}_{23}^*$ versus wt. fraction EVA in the mixture at 353K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wt. Fraction EVA in the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0904</td>
</tr>
<tr>
<td>C_5H_{12}</td>
<td>-2.0049</td>
</tr>
<tr>
<td>C_6H_{14}</td>
<td>-2.1632</td>
</tr>
<tr>
<td>C_7H_{16}</td>
<td>-2.4872</td>
</tr>
<tr>
<td>C_8H_{18}</td>
<td>-2.6731</td>
</tr>
<tr>
<td>CH_3OH</td>
<td>-2.6796</td>
</tr>
<tr>
<td>C_3H_2OH</td>
<td>-2.1632</td>
</tr>
<tr>
<td>C_3H_6O</td>
<td>-0.2194</td>
</tr>
<tr>
<td>C_4H_8O</td>
<td>-0.1580</td>
</tr>
<tr>
<td>C_3H_4O_2</td>
<td>-2.7010</td>
</tr>
<tr>
<td>C_4H_6O_2</td>
<td>0.3554</td>
</tr>
<tr>
<td>CH_2Cl_2</td>
<td>-0.2539</td>
</tr>
<tr>
<td>CHCl_3</td>
<td>-0.5703</td>
</tr>
<tr>
<td>CCl_4</td>
<td>-0.4438</td>
</tr>
<tr>
<td>C_6H_6</td>
<td>0.7243</td>
</tr>
<tr>
<td>C_7H_8</td>
<td>0.6616</td>
</tr>
<tr>
<td>C_8H_12</td>
<td>-0.2563</td>
</tr>
</tbody>
</table>

Mean  | -0.9973  | -1.1071  | 0.6001  | 0.8600  | 0.5351  | 0.3508  | -0.4527 |
S.Dev | 1.2621   | 0.6763   | 0.3273  | 0.1300  | 0.1441  | 0.1385  | 0.6261  |
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wt. Fraction EVA in the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0904</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>-1.8144</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>-0.7363</td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>-0.2244</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>-0.4871</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>-0.6407</td>
</tr>
<tr>
<td>C₄H₂OH</td>
<td>0.2999</td>
</tr>
<tr>
<td>C₃H₆O</td>
<td>-0.6545</td>
</tr>
<tr>
<td>C₄H₈O</td>
<td>0.2023</td>
</tr>
<tr>
<td>C₃H₆O₂</td>
<td>-0.3208</td>
</tr>
<tr>
<td>C₅H₈O₂</td>
<td>-0.0237</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>-0.7293</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0.5848</td>
</tr>
<tr>
<td>CCl₄</td>
<td>0.5772</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>0.1107</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>0.6655</td>
</tr>
<tr>
<td>C₈H₁₂</td>
<td>0.6358</td>
</tr>
</tbody>
</table>

Mean   | -0.1639 | 0.5269 | 0.4103 | 0.3004 | 0.8172 | 1.0369 |
S.Dev  | 0.6652  | 0.1216 | 0.0960 | 0.1180 | 0.2701 | 0.2350 |
Table 4.6

$x_{12}$ versus wt. fraction EVA in the mixture at 393K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wt. Fraction EVA in the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0904</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>-2.4971</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>-0.9706</td>
</tr>
<tr>
<td>C₆H₁₆</td>
<td>-0.0048</td>
</tr>
<tr>
<td>C₆H₁₈</td>
<td>0.2779</td>
</tr>
<tr>
<td>CH₂OH</td>
<td></td>
</tr>
<tr>
<td>C₃H₇OH</td>
<td>0.0850</td>
</tr>
<tr>
<td>C₃H₆O</td>
<td>0.1484</td>
</tr>
<tr>
<td>C₄H₈O</td>
<td>0.7448</td>
</tr>
<tr>
<td>C₅H₆O₂</td>
<td>0.2899</td>
</tr>
<tr>
<td>C₄H₈O₂</td>
<td>0.6007</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>0.5154</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0.8401</td>
</tr>
<tr>
<td>CCl₄</td>
<td>0.8032</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>0.7156</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>0.8326</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>0.8443</td>
</tr>
</tbody>
</table>

Mean 0.4088 0.3236 0.5805 0.6653 0.8082 1.0014
S.Dev 0.4814 0.2392 0.1223 0.0813 0.3366 0.1770
4.6 Discussion

The preparative technique and experimental apparatus employed in this study produced highly consistent net retention volumes. These volumes were found to be independent of the carrier gas flowrate and thus these flowrates did not require extrapolation to zero, as required by some authors. The net retention volumes were also found to be independent of the volume of solvent injected in the range 0.2 - 0.8 μL. Small volumes of solvent were used to ensure essentially symmetrical elution peaks and to satisfy the infinite dilution condition of equation 4.5. The elution peaks were generally symmetrical around the maxima, with the exception of methanol at 393K, confirming the infinite dilution condition and the attainment of equilibrium between the vapour and stationary phase. However, a truly Gaussian distribution was seldom seen as the tails of the elution peak were generally asymmetric. An investigation of this effect was not attempted. The reproducibility of the $V_{sc}$ values was also examined by preparing two columns from a single batch of stationary phase, and, under a variety of experimental conditions, were found to yield values within a 1% error. From these experiments it was concluded that the measured results were extremely reliable. This conclusion is particularly relevant when the obvious solvent dependence of the $x_{i3}$ values is considered. Most data obtained from IGC experiments show some solvent dependence and considerable effort has been made to understand and correlate what is, without doubt, the greatest disadvantage of this technique. The origin of these effects has been the focus of some attention, with some workers arguing that the variation in values between solvents lies within their experimental error and are thus artifacts, while others maintain that the effects are real and can be related to either some physical attribute of the probe or to a limitation of the theoretical treatment.

Munk et al. reported that a correlation could be made between the $B_{23}$ values obtained from a blend of poly(ε-caprolactone) and poly(epichlorohydrin) and the Hildebrand solubility parameters of the probe species. In view of this apparent relationship they argued that the true $B_{23}$ value of the blend would only be obtained if its solubility parameter, as estimated by Guillet's method, was equal to that of the solvent. This study re-analysed Munk's data both by rescaling the results, and recalculating the solubility parameter using Price's method. Both procedures were found to distort the proposed correlation. The data obtained here were also treated in this manner but no correlation was observed. This study also attempted to correlate the variation in both the $x_{i3}$ and $B_{23}$ values with other physical characteristics of the solvent probes,
e.g. (a) molar volume,
(b) second virial coefficient of the vapour phase,
(c) boiling point,
(d) saturated vapour pressure, and
(e) molecular weight.

None of the physical attributes mentioned above was found to influence the interaction parameters in any systematic manner. The $\Delta \bar{\chi}$ effect (30–32) has also been reported to have a significant effect on the thermodynamics of ternary mixtures. $\Delta \bar{\chi}$ is calculated from,

$$\Delta \bar{\chi} = \left| \tilde{x}_{12} - \tilde{x}_{13} \right|$$  (4.21)

This parameter arises from the idea that the compatibility of polymers in solution is dependent both on the polymer-polymer interaction and the difference between the interactions of the homopolymers and the solvent. The similarity between the $\tilde{x}_{12}$ and $\tilde{x}_{13}$ values obtained from the EVA and C$_{14}$ FVA experiments shows that the $\Delta \bar{\chi}$ effect is not significant in this case.

It has also been suggested that hydrogen bonding, or some other preferential specific interactions, between the probe and, either one or both, of the polymers may cause short-range ordering or non-random mixing in the ternary solution (33,34) giving rise to these effects. Galin and Rapprech (35) suggested that the solvent dependence of $\tilde{x}_{23}$ may be a consequence of non-molecular mixing, which supports Olabisi's concept that polymeric blends are at best micro-heterogeneous (22).

Another widely reported source of the solvent dependence of $\tilde{x}_{23}$ was the limited ability of Flory-Huggins theory to account for all the polymer-probe interactions in a ternary system (11,36). Prolongo et al (37) argue that a true interaction parameter can never be obtained from this theory because the residual chemical potential of the probe in the ternary system is approximated to the sum of binary contributions. Instead they have applied an equation of state treatment, which does not rely on this approximation, and concluded that the solvent dependence arises from the assumption that the Gibbs mixing function for the polymer-polymer-solvent system is additive with respect to the binary contributions and thus true interaction parameters are only obtained from experiments where $\Delta \bar{\chi}$ is either zero or constant.
Another potentially fruitful approach may utilise moment analyses to interpret the elution peak obtained from IGC. The shape and position of this peak is known to depend on the column characteristics and the dynamic processes which occur, e.g. the diffusion of the probe into the stationary phase, the partitioning of the probe between the phases, the void volume of the column and the adsorption of the probe on the surface of the polymer and the support. This technique has always had theoretical appeal as it potentially would provide a wealth of information but in practice it has found relatively little favour owing to the large experimental errors generated in the measurement of the moments. Some improvements to the technique have been published recently and more information is promised.

It is now apparent that these solvent effects cannot be removed easily and that a full study of the processes involved in IGC, from both a chromatographic and a theoretical perspective, would be beneficial. Within this context, the results obtained in this study are discussed below.

The polymer-solvent interaction values are considered first, then the polymer-polymer results, which have been considered at each temperature separately and the overall implications and temperature dependences are discussed at the end.

### 4.6.1 Polymer-Solvent Interaction Parameters

The arithmetic means of $\tilde{x}_{12}$ and $\tilde{x}_{13}$ for all of the solvents at 353K, 373K and 393K are given in Table 4.7. Although these mean values have no physical significance they have been calculated and included to show the general trends in polymer-solvent behaviour.

#### Table 4.7

Mean value of polymer-solvent interaction parameter

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>$\tilde{x}_{13}$</th>
<th>s dev</th>
<th>$\tilde{x}_{12}$</th>
<th>s dev</th>
<th>$\Delta \tilde{x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>1.6964</td>
<td>0.6854</td>
<td>1.8392</td>
<td>0.6384</td>
<td>0.1428</td>
</tr>
<tr>
<td>373</td>
<td>1.9162</td>
<td>0.7689</td>
<td>2.0620</td>
<td>0.7141</td>
<td>0.1459</td>
</tr>
<tr>
<td>393</td>
<td>1.8920</td>
<td>0.5889</td>
<td>2.0380</td>
<td>0.5355</td>
<td>0.2169</td>
</tr>
</tbody>
</table>

All of the mean values are small and positive, and show a small positive increase as the temperature is increased. Although these results reflect the
bulk properties of the polymers at infinitely dilute solvent, their magnitude gives some indication of the solubility of the copolymers in the bulk solvent, e.g. at 353K octane ($\tilde{\chi}_{13} = 1.2898$) is a known solvent for FVA whereas MEK ($\tilde{\chi}_{13} = 1.8098$) is a known non-solvent. The polymer-solvent interaction parameters for FVA are generally smaller, suggesting that it is the more soluble in this range of solvents, particularly in the hydrocarbons. This may result from an interaction between the hydrocarbons and the pendant alkyl groups of FVA. These data show that both polymers behave similarly to a wide variety of other molecules and are consequently chemically similar, and thus liable to be miscible. Additionally, the $\Delta\tilde{\chi}$ effect is small and unlikely to dominate the thermodynamics of blends of these materials.

4.6.2 Polymer-Polymer Interaction Parameters

From the data in Table 4.8 it is apparent that the polymer-polymer interaction parameter varies significantly with blend composition and temperature. Results are not quoted for the 0.8033 (wt/wt) EVA column at either 373 or 393K because it was damaged prior to completion of the experimental programme.

Table 4.8

Mean values of $\tilde{\chi}_{13}'$ vs composition at 353, 373 and 393K

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>Wt. Fr. EVA in the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0904</td>
</tr>
<tr>
<td>353</td>
<td>-0.9973</td>
</tr>
<tr>
<td>373</td>
<td>-0.1639</td>
</tr>
<tr>
<td>393</td>
<td>0.4088</td>
</tr>
</tbody>
</table>

4.6.2.1 353K : The means and standard deviations of these results are shown in Figure 4.3. At EVA weight fractions below 0.2906 the $\tilde{\chi}_{13}'$ values are generally negative, suggesting that FVA rich blends interact favourably in these compositions, at this temperature, and consequently may be miscible. However, as the proportion of EVA is increased the interaction parameter becomes increasingly positive, reaching a maximum at about a weight fraction of 0.35 EVA.
The polymer-polymer interaction parameter

as a function of wt fraction EVA: 353K

Figure 4.3
If the blend composition is re-expressed in mole fractions, the change from negative to positive occurs between 0.44 and 0.50 mol fraction EVA, reflecting that the maximum unfavourable interaction occurs when the concentration of each copolymer's repeat unit is approximately equal. The value of $\tilde{x}_{23}$ then decreases with increasing EVA concentration and ultimately, between 0.75 and 0.80 (wt/wt) EVA, becomes negative again. These results show that at 353K, mixtures of EVA and FVA are miscible at the extremes of composition. However, the standard deviation amongst the $\tilde{x}_{23}$ values is also largest at these compositions and this arises partially from the intrinsic error in measuring a small effect, but predominantly from the strong solvent dependence of the measured retention volume, e.g. isopropyl alcohol on the 0.0904 (wt/wt) EVA column. (This particular datum was not included in the calculation of either the arithmetic mean or the standard deviation since it bears no relation to any other value and was assumed to be erroneous). The hydrocarbons, methanol and methyl acetate all yield $\tilde{x}_{23}$ values which are particularly negative. This may indicate that the hydrocarbons are interacting with the pendant C$_{14}$ chains, while the methanol and methyl acetate are interacting with the vinyl acetate groups of the FVA. From the macrostructure of FVA, given in Figure 3.10, the hydrocarbon-alkyl interaction seems plausible. However the vinyl acetate groups are highly protected and the opportunity for hydrogen bonding with the solvent is severely hindered unless the FVA assumes a non-bulk orientation when it is deposited on the column. At low EVA concentrations the value of $\tilde{x}_{1(23)}$ would be expected to approximate to that for $\tilde{x}_{12}$, e.g. for 0.0904 (wt/wt) EVA; these values are compared in Table 4.9.
Table 4.9
Comparison of polymer-solvent and (polymer-polymer)-solvent interaction parameters at 353 K for low EVA concentrations

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tilde{\chi}_{13}$</th>
<th>$\tilde{\chi}_{12}$</th>
<th>$\tilde{\chi}_{1(23)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>1.7156</td>
<td>1.8708</td>
<td>1.5023</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.5361</td>
<td>1.7963</td>
<td>1.4587</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.2541</td>
<td>1.5804</td>
<td>1.1519</td>
</tr>
<tr>
<td>Octane</td>
<td>1.3074</td>
<td>1.6320</td>
<td>1.2337</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.4880</td>
<td>3.4908</td>
<td>3.2971</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>2.5467</td>
<td>2.5287</td>
<td>2.3339</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.2106</td>
<td>2.3111</td>
<td>2.0487</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>1.8528</td>
<td>1.9495</td>
<td>1.6874</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>2.0115</td>
<td>2.1549</td>
<td>1.8444</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>2.5140</td>
<td>2.5817</td>
<td>2.2821</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>1.2237</td>
<td>1.2796</td>
<td>1.0919</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.7962</td>
<td>0.8461</td>
<td>0.6631</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>1.1198</td>
<td>1.3096</td>
<td>1.0081</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.1927</td>
<td>1.2983</td>
<td>1.0432</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.1038</td>
<td>1.2283</td>
<td>0.9568</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.2690</td>
<td>1.5692</td>
<td>1.1822</td>
</tr>
</tbody>
</table>

From the data shown above it is obvious that the value of $\tilde{\chi}_{1(23)}$ does not approximate $\tilde{\chi}_{13}$ at low EVA concentrations and thus it can be concluded that at a concentration of approximately 10% (wt/wt) EVA still has a significant effect. However, the values of $\tilde{\chi}_{1(23)}$ do not appear to resemble either of the corresponding polymer-solvent results hence the small concentration of EVA must be assumed to be affecting either the morphology or the orientation of the major FVA phase. This conclusion is discussed more fully at the end of this chapter.
4.6.2.2 373K: The mean values and standard deviations of these results are shown in Figure 4.3

At 373K, small negative interaction parameters are still observed at very low EVA concentration, *i.e.* 0.0904 (wt/wt). However, their mean value at this composition is -0.1639 which is not sufficiently negative to guarantee miscibility. As the fraction of EVA in the mixture is increased the mean interaction value becomes more positive reaching its maximum value of 1.0369 at approximately 0.75 (wt/wt) EVA. The variation with composition is not as pronounced as that observed at 373K. These results show that blends of EVA and FVA of any composition are unlikely to be miscible at this temperature.

4.6.2.3 393K: The mean values and standard deviations of these results are shown in Figure 4.4

All the interaction parameters measured at 393K are positive and are generally larger than those at 353 and 373K. The values vary from 0.3260 to 0.9485 and show a general increase as the EVA fraction in the mixture increases. It should be noted that no results were obtained for methanol with mixtures containing less than 0.3589 (wt/wt) EVA because extremely asymmetric elution peaks were obtained and a reliable maximum could not be identified. The other methanol measurements give unlikely values of \( \tilde{\chi}_{23} \), and as a consequence, have been removed from the calculations for the mean and standard deviation.

4.6.3 General Discussion

The polymer-solvent interaction parameters measured by IGC are generally small and positive, and decrease as temperature increases. The \( \Delta \tilde{\chi} \) effect is also small, *i.e.* the degree of interaction between each homopolymer and a specific solvent is approximately equal, and thus the apparent miscibility of this blend is unlikely to be controlled by the respective polymer-solvent interactions. The polymer-polymer interaction parameters were also found to be generally small and positive, showing that no strong interaction exists between the copolymers, and were observed generally to increase with temperature. Since \( \tilde{\chi}_{23} \) is a measure of the change in free energy during mixing and becomes more unfavourable as the temperature is increased, it can be concluded that miscibility is more likely to occur at temperatures below 353K. However, at 353K, negative values of \( \tilde{\chi}_{23} \) were obtained for FVA rich blends which suggests miscibility under these conditions.
The polymer-polymer interaction parameter
as a function of wt fraction EVA: 373K

Figure 4.4
The microscopy experiments detailed in chapter 7 show that this predicted miscibility does not occur and the discrepancy has been assumed to be a consequence of the incompatibility of the mixture, and the respective domain sizes at these particular compositions and temperature. Equations 4.5a to 4.5c are rigorously applicable only to homogeneous systems and thus it can be argued that the results quoted earlier are of no relevance if the EVA/FVA mixture is immiscible. However, incompatible systems have been studied before using IGC\(^{21,35,42-46}\), and extremely unrealistic values of \(x_{23}\) were usually obtained when the experiment was unsuitable.

From these reports the question of IGC's applicability to any specific problem appears to be self-evident since Zhikaun and Walsh\(^{47}\) stated, in a study of chlorinated poly(ethylene)/poly(butyl-acrylate), that the specific net retention volumes of immiscible blends, \(V_{gc(23)}\), are merely the sum of the composition weighted values of the pure components, i.e.,

\[
V_{gc(23)} = w_2 V_{gc,2} + w_3 V_{gc,3} \tag{4.21}
\]

If these reports are correct then provisional experiments on any proposed, but unsuitable system, would yield results which would either satisfy equation 4.21 or be obviously incorrect. If the net retention volumes of the data used for the sample calculation in this work are considered, (i.e. chloroform at 373K on the 0.3589 (wt/wt) EVA column),

\[
V_{gc(23)} \text{ measured} = 13.472 \text{ cm}^3 \text{ g}^{-1}
\]

and \(V_{gc,2} = 12.380 \text{ cm}^3 \text{ g}^{-1}\) and \(V_{gc,3} = 12.934 \text{ cm}^3 \text{ g}^{-1}\)

hence, \(V_{gc(23)} = (1.0 - 0.3589)(12.380) + (0.3589)(12.934)\)

\[
V_{gc(23)} \text{ calculated} = 12.579 \text{ cm}^3 \text{ g}^{-1}
\]
If this calculation is repeated across the composition range of the blend, for the same solvent at the same temperature, the following results are obtained,

Table 4.10

Comparison of experimental blend net retention volumes
and those calculated from equation 4.21

<table>
<thead>
<tr>
<th>Vₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉ.enterprise</th>
<th>Wt. Fr. EVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm³ g⁻¹</td>
<td></td>
</tr>
<tr>
<td>measured</td>
<td>13.050</td>
</tr>
<tr>
<td>calculated</td>
<td>12.430</td>
</tr>
<tr>
<td></td>
<td>0.2516</td>
</tr>
</tbody>
</table>

It is apparent from these data that although the EVA/FVA mixture is incompatible at 373K, the net specific volumes of the blend are not simply the sums of the weighted means of the pure components, as predicted by reference (47), but do reflect some attribute of the mixture. The composition dependence of the net specific retention volumes quoted above is unclear although Dipaola-Baranyi et al (29) reported a similarly inexplicable effect in a PS_{(oligomeric)} - PBMA system, particularly at PBMA rich compositions. Some understanding of the composition dependence of $\bar{\chi}_{23}$, which has been found in some low molecular weight systems, may be obtained from the work of Galin et al (39). These workers confirmed the basic incompatibility of poly(styrene)/poly(dimethyl-siloxane) using IGC with low molecular weight block copolymers of varying composition, (for which small positive $\bar{\chi}_{23}$ values were obtained), and then found that if the molecular weight of the samples was increased, a negative value of $\bar{\chi}_{23}$ was finally obtained for this incompatible mixture. From these data Galin concluded that IGC was only suitable for either homogeneous or highly dispersed micro-phase separated block copolymers and not for incompatible blends which separate into macro domains. If the morphology of the EVA/FVA mixture is neither homogeneous nor micro-phase separated at low EVA concentrations around 353K, this hypothesis may explain the negative values of $\bar{\chi}_{23}$ which were obtained.
4.7 REFERENCES

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Chapter 5  Heats of Mixing

5.1 Introduction

The determination of the heat of mixing, $\Delta H_{mix}$, of a binary system yields invaluable thermodynamic information since such data allow the general free energy of mixing term to be divided into enthalpic and entropic contributions. Unfortunately, the direct determination of this effect in polymer systems is often prohibited by the physical state and high viscosity of the materials or the restrictive operating temperatures of the calorimetric apparatus. Several attempts have been made to circumvent these problems, e.g. by determining the heats of mixing in the presence of a common solvent and extracting the polymer-polymer contribution using Hess’s Law \(^{(1)}\), or by using low molecular weight analogues, i.e. unit structure models, or oligomers, and normalising the results with respect to the interacting segments of the actual polymers \(^{(2,3)}\). Neither of these approaches has proven to be particularly reliable because significant errors have been reported and their origin is unclear. The heat of mixing measurements reported here are for the copolymers themselves, which was possible due to their low molecular weight and viscosity, and thus the use of the indirect methods described above was avoided.

5.2 Theoretical

5.2.1 Flory - Huggins Theory

Flory-Huggins theory relates the heat of mixing of two components to their interaction parameter with the following expression \(^{(4)}\),

$$\Delta H_{mix} = kT \chi_{12} n_1 \phi_2$$

(5.1a)

where,

$\chi_{12} = \text{Flory-Huggins binary Interaction Parameter}$

$n_1 = \text{number of molecules of solvent}$

$k = \text{the Boltzmann constant, (1.380662} \times 10^{-23} \text{J K}^{-1})$

$T = \text{absolute temperature, K}$

$\phi_2 = \text{volume fraction of solute}$

This expression was originally derived for polymer solutions but it can be expressed for polymer blends as,
\[ \Delta H_{\text{mix}} = kT \chi_{23} n_2 \phi_3 \] 

(5.1b)

thus,

\[ \chi_{23} = \frac{\Delta H_{\text{mix}}}{k T n_2 \phi_3} \] 

(5.1c)

Using this expression the enthalpic polymer-polymer interaction parameters were calculated for each value of \( \Delta H_{\text{mix}} \) measured.

5.2.2 Flory's Equation of State

In the equation of state theory of Prigogine-Flory\(^{(5-9)}\), the residual free energy of mixing is given by,

\[ G_M^R = \Delta H_M - T \Delta S_M^R - rN V^* Q_{23} \theta_3 \phi_2 \] 

(5.2)

where,

\[ \Delta H_M = rN V^* \left[ \phi_2 P_2^*(v_2^{-1} - v^{-1}) + \phi_3 P_3^*(v_3^{-1} - v^{-1}) + \phi_2 \theta_3 X_{23}/\nu \right] \] 

(5.3)

This interaction parameter, \( X_{23} \), includes only the enthalpic contribution of the mixing process. Theoretically it represents the enthalpic interaction between the unit structures of the components being mixed. Consequently \( X_{23} \) should be constant for any polymer pair at a specific temperature and also independent of blend composition. It is commonly evaluated by fitting equation 5.3 to experimental heat of mixing data.

5.3 Materials

The EVA copolymer and \( C_{14}FVA \) copolymer were both annealed in a vacuum oven at 393K for 24 hours.

5.4 Apparatus

The heats of mixing were determined using a NBS batch-type calorimeter\(^{(10)}\), which measures the heat flux that occurs when two materials are mixed, using a series of thermo-electric cells. A significant period of time was spent modifying this apparatus from the description in reference\(^{(10)}\) because it was found that the original cell design, Figure 5.1, was inadequate in that it allowed leakage of both material and heat. It was apparent that the use of steel bolts with an aluminium press was unsuitable as continued usage
distorted and damaged the aluminium, thus causing the seal between the cell body and the PTFE end caps to fail, (points A & B). Additionally, after inversion, the mixing process occurred at A which aggravated the leakage. Another problem was the observed dependence of the baseline on the position of the sample cell, Figure 5.2. Although this effect was always present its magnitude varied thus preventing simple subtraction during data reduction. The variation in baseline was greatest when the loading channels of the inner and outer jackets were exactly aligned, i.e. at 0 degrees. It was concluded that the baseline drift was caused by heat loss through these channels owing to poor insulation and an excessive dead volume within the inner jacket arising from the design of the cell, region C in Figure 5.1. Consequently the cell was redesigned, Figure 5.3, to fill the inner jacket completely, and carefully machined steel and PTFE components were employed to ensure the seal. Additionally, by introducing the PTFE sample holder into the aluminium body horizontally, the mixing process now occurred in a less vulnerable section of the cell. PTFE blocks were introduced all round the cell body to improve insulation and ensure that any heat flux that occurred during mixing was directed through the walls which were in contact with the Peltier cells. Finally an aluminium block, machined to be a 'push-fit', was inserted behind the sample cell which effectively insulated the loading channel. Using this new system no material leakage was ever detected and the baseline was found to be independent of the position of the cell. Diagrams showing a cross-sectional view of the calorimeter together with a full schematic representation of the complete apparatus are given in Figures 5.4a and 5.4b respectively.
1: STEEL BOLTS
2: ALUMINIUM BRACES
3: PTFE END CAP
4: ALUMINIUM SHELL
5: BAFFLES
6: PTFE SAMPLE HOLDER

FIGURE 5.1: CHONGS ORIGINAL CELL DESIGN
5.5 Experimental Procedure

The temperature of the calorimeter was set using a potentiometer on the heating unit: the choice of setting being read from a calibration chart: the apparatus took approximately 48 hours to equilibrate at the selected temperature. Equilibrium was known to have been achieved when a constant reading was observed on the decade resistance bridge. The precise temperature of the instrument was then calculated from another calibration chart which correlated the settings of the resistance bridge with temperature.

Approximately 0.5g of each component was then carefully weighed, to six significant figures, and charged to the individual compartments of the PTFE sample holder. This was placed inside the aluminium shell which then was sealed with the 2 machined PTFE end plates. Finally this was enclosed in the steel and PTFE bracing system and heated in an oven mounted on the front of the calorimeter, which was maintained at approximately the temperature of the instrument. After typically 1 hour the sample cell was inserted into the central block of the calorimeter followed by the aluminium block to seal the inner chamber of the apparatus. The temperature difference between these components and the calorimeter caused a heat flux which was detected by the thermo-electric cells which resulted in a deflection on the strip chart recorder. When this signal had stabilised the sample cell was considered to be in equilibrium with the calorimeter. The magnitude of the output from the thermo-electric modules was controlled by an amplifier on the integrator unit.

The detection of thermal equilibrium is essential for this type of measurement. Consequently the sensitivity of the amplifier was always increased beyond that normally required for the determination of the heat of mixing. When equilibrium had been attained, commonly 18-24 hours, and a steady baseline recorded, the amplifier was reset to the gain desired for the mixing measurement and the chart recorder and digital integrator reset to their zero values. The shaft of the central block was then rotated through 180 degrees, to mix the samples. The shaft was then attached to a motor-driven arm which moved slowly backwards and forwards through 90 degrees to agitate the mixture. Periodically the cell was inverted and this process repeated until the output returned to the baseline value.

The output from the Peltier cells was recorded on a digital integrator and converted to a heat of mixing value from the electrical calibration data.
Dependency of Calorimeter Baseline on Angle of Central Block Rotation

Figure 5.2
FIGURE 5.3: EXPLODED VIEW OF THE IMPROVED CELL DESIGN

1: STEEL BOLTS
2: PTFE COMPONENTS
3: ALUMINIUM SHELL
4: STEEL COMPONENTS
5: PTFE SAMPLE HOLDER
6: HANDLING ROD
7: BAFFLES
FIG. 5.4a
MICROCALORIMETER-END VIEW CROSS SECTION
FIGURE 5.4b: SCHEMATIC DIAGRAM OF THE CALORIMETER APPARATUS
5.6 Results

Heats of mixing measurements and electrical calibrations were obtained at 348.7 and 359.3K for the EVA/C$_{18}$FVA blend.

Estimation of Errors

A full analysis of the accuracy and sensitivity of the calorimeter was not possible due to the limited time available on the instrument. However, since the apparatus was rebuilt to a standard higher than that quoted by Chong, it was assumed that the performance would be at least comparable. Chong and Rostami (11) both quote the thermal stability as ± 0.001K over a 3 hour period, and the accuracy as ± 0.002 J g$^{-1}$ as determined by an acid-base reaction. The reproducibility of the results was investigated by running approximately duplicate samples 48 hours apart. The results were as follows,

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Wt Fr EVA</th>
<th>$\Delta H_{mix}/10^{-2}$ J g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4752</td>
<td>10.077</td>
</tr>
<tr>
<td>2</td>
<td>0.4786</td>
<td>10.047</td>
</tr>
</tbody>
</table>

These data show that the reproducibility was very high and that the error associated with each reading was less than 0.0001 J g$^{-1}$

Electrical Calibration

The sample cell used to calibrate the calorimeter was similar to the cell described earlier, except that it contained a 147.4 $\Omega$ (±0.02 %) Muirhead wire-wound resistor immersed in a 50% (wt/wt) mixture of the system being studied. Since the calibration cell is not inverted, a small hole was created at the top of the PTFE seal through which the contacts of the resistor were fed. These were connected to a 0.02% Current Calibrator. It was found that the mains switch on this unit caused a detectable spike in the response of the thermo-electric cells and was consequently fitted with an additional switch across the output terminals. A variable current was applied to the resistor over a range of time periods, measured by stop watch, and the response recorded.
From this information it was possible to evaluate a calibration function as follows;

\[ E = I^2 R t \]  \hspace{1cm} (5.4)

where

\[ E = \text{energy, } J \]
\[ I = \text{current, } A \]
\[ R = \text{resistance, } \Omega \]
\[ t = \text{time, } s \]

When the analogue output of the cell, as determined by the integrator, is plotted against the calculated electrical energy supplied, a linear relationship is obtained. From this function the relative response of the calorimeter can be converted into an absolute measure of the enthalpy change within the system. Theoretically, the total heat of mixing, \( q \), is proportional to the area \( A \) \( (cm^2) \) bounded by the peak and the baseline,

\[ q = FA \]  \hspace{1cm} (5.5)

where, \[ F = \text{calibration constant, } J \text{ cm}^{-2}. \]

A plot of \( q \) versus \( A \) should be linear and pass through the origin. The slope, \( F \), is a function of the thermal conductivity and heat capacity of the material being examined and must be determined for every mixture at every temperature of interest.
Table 5.1

Electrical Calibration at 348.7K

<table>
<thead>
<tr>
<th>Run</th>
<th>( E/J \times 10^{-2} )</th>
<th>Integrator Counts/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.65</td>
<td>4226</td>
</tr>
<tr>
<td>2</td>
<td>5.41</td>
<td>6772</td>
</tr>
<tr>
<td>3</td>
<td>7.22</td>
<td>10833</td>
</tr>
<tr>
<td>4</td>
<td>9.53</td>
<td>15047</td>
</tr>
<tr>
<td>5</td>
<td>12.30</td>
<td>19934</td>
</tr>
<tr>
<td>6</td>
<td>14.89</td>
<td>26339</td>
</tr>
<tr>
<td>7</td>
<td>15.76</td>
<td>27769</td>
</tr>
</tbody>
</table>

The intercept (a) and slope (b) were obtained by least-squares techniques.

\[ a = -3511.5 \quad b = 1970 \quad r = 0.9986 \]

Table 5.2

Electrical Calibration at 359.3K

<table>
<thead>
<tr>
<th>Run</th>
<th>( E/J \times 10^{-2} )</th>
<th>Integrator Counts/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.69</td>
<td>4481</td>
</tr>
<tr>
<td>2</td>
<td>7.44</td>
<td>11260</td>
</tr>
<tr>
<td>3</td>
<td>9.43</td>
<td>15400</td>
</tr>
<tr>
<td>4</td>
<td>10.65</td>
<td>18201</td>
</tr>
<tr>
<td>5</td>
<td>12.18</td>
<td>21278</td>
</tr>
</tbody>
</table>

Again, from least-squares,

\[ a = -3118.4 \quad b = 1987 \quad r = 0.9990 \]
These calibration data are shown graphically in Figure 5.5

The slopes of these relationships correspond to the calibration constants of the calorimeter for this blend at these temperatures. These data show that the minimum energy detection limit of the apparatus is approximately 1.6 to 1.8×10⁻² J for this temperature range and an amplifier gain equivalent to 300 µV.

Least-squares techniques were applied to some of Chong’s data and the following limits found,

(a) polystyrene (1010)-polybutadiene (960) at 70.1 °C,(10, p87),

\[ \text{fsd} = 100 \mu V \quad \text{minimum detection limit} = 2.3 \times 10^{-3} J \]

(b) distilled water at 30.0 °C,(10, p83),

\[ \text{fsd} = 1 mV \quad \text{minimum detection limit} = 4.6 \times 10^{-2} J \]

It is apparent that the minimum detection limit of the apparatus was not changed significantly by either the new design of sample cell or the replacement of the original thermo-electric modules. However, Chong recommends that the following equilibrium times be used for the respective amplifier settings,

<table>
<thead>
<tr>
<th>Amplifier Setting</th>
<th>Equivalent FSD / mV</th>
<th>Equil. Time / h</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>G</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>H</td>
<td>0.03</td>
<td>&gt; 12.0</td>
</tr>
</tbody>
</table>

The time required to reach equilibrium with the rebuilt calorimeter at setting G was always more than 12 hours. This order of magnitude increase was attributed to poor temperature control of the pre-heating oven, and the increased heat capacity of the sample cell and aluminium insulating block. It is unknown whether this also reflected an increase in the sensitivity of the instrument as the limited time available for experiment prohibited calibration with standard acid-base neutralisations.
Table 5.3
Heat of Mixing data at 348.7K

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt.Fr. EVA</th>
<th>Int/10</th>
<th>Total Mass/g</th>
<th>Int/10 g</th>
<th>$\Delta H_{\text{mix}}/10^{-2}\text{J g}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1193</td>
<td>5973</td>
<td>1.4991</td>
<td>3984</td>
<td>3.804</td>
</tr>
<tr>
<td>2</td>
<td>0.2432</td>
<td>15616</td>
<td>1.4728</td>
<td>10603</td>
<td>7.162</td>
</tr>
<tr>
<td>3</td>
<td>0.2987</td>
<td>21360</td>
<td>1.5006</td>
<td>14234</td>
<td>9.005</td>
</tr>
<tr>
<td>4</td>
<td>0.3610</td>
<td>26085</td>
<td>1.5018</td>
<td>17369</td>
<td>10.596</td>
</tr>
<tr>
<td>5</td>
<td>0.4752</td>
<td>24534</td>
<td>1.5014</td>
<td>16341</td>
<td>10.077</td>
</tr>
<tr>
<td>6</td>
<td>0.4786</td>
<td>24477</td>
<td>1.5029</td>
<td>16287</td>
<td>10.047</td>
</tr>
<tr>
<td>7</td>
<td>0.6353</td>
<td>23263</td>
<td>1.5303</td>
<td>15202</td>
<td>9.496</td>
</tr>
<tr>
<td>8</td>
<td>0.8333</td>
<td>4358</td>
<td>1.5003</td>
<td>2905</td>
<td>3.257</td>
</tr>
</tbody>
</table>

Table 5.4
Heat of Mixing data at 359.3K

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt.Fr. EVA</th>
<th>Int/10</th>
<th>Total Mass/g</th>
<th>Int/10 g</th>
<th>$\Delta H_{\text{mix}}/10^{-2}\text{J g}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2991</td>
<td>13956</td>
<td>1.4977</td>
<td>9318</td>
<td>5.390</td>
</tr>
<tr>
<td>2</td>
<td>0.3613</td>
<td>18295</td>
<td>1.5011</td>
<td>12188</td>
<td>7.703</td>
</tr>
<tr>
<td>3</td>
<td>0.4786</td>
<td>13956</td>
<td>1.4977</td>
<td>9318</td>
<td>6.259</td>
</tr>
</tbody>
</table>

These results are shown in Figure 5.6
Flory-Huggins Analysis

Definition: subscript 2 = C_{14}FVA, 3 = EVA

From Equation (5.1c) the polymer-polymer interaction parameters were evaluated at both 348.7K, Table 5.5, and 359.3K, Table 5.6,

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt Fr EVA</th>
<th>ΔH_m / 10^{-2} J g^{-1}</th>
<th>(\phi_3)</th>
<th>n_2</th>
<th>(\chi_{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1193</td>
<td>3.804</td>
<td>0.1206</td>
<td>5.100</td>
<td>1.285</td>
</tr>
<tr>
<td>2</td>
<td>0.2432</td>
<td>7.162</td>
<td>0.2454</td>
<td>4.382</td>
<td>1.384</td>
</tr>
<tr>
<td>3</td>
<td>0.2987</td>
<td>9.005</td>
<td>0.2987</td>
<td>4.061</td>
<td>1.529</td>
</tr>
<tr>
<td>4</td>
<td>0.3610</td>
<td>10.596</td>
<td>0.3610</td>
<td>3.700</td>
<td>1.635</td>
</tr>
<tr>
<td>5</td>
<td>0.4752</td>
<td>10.077</td>
<td>0.4752</td>
<td>3.039</td>
<td>1.369</td>
</tr>
<tr>
<td>6</td>
<td>0.4786</td>
<td>10.047</td>
<td>0.4786</td>
<td>3.019</td>
<td>1.374</td>
</tr>
<tr>
<td>7</td>
<td>0.6353</td>
<td>9.496</td>
<td>0.6353</td>
<td>2.112</td>
<td>1.464</td>
</tr>
<tr>
<td>8</td>
<td>0.8333</td>
<td>3.257</td>
<td>0.8333</td>
<td>9.653</td>
<td>0.084</td>
</tr>
</tbody>
</table>

Taking the density values at 348.7K as,

\[ \rho_{EVA} = 0.90836 \text{ g cm}^{-3} \quad \rho_{FVA} = 0.91947 \text{ g cm}^{-3} \] (Chapter 3.3)

Table 5.6

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt Fr EVA</th>
<th>ΔH_m / 10^{-2} J g^{-1}</th>
<th>(\phi_3)</th>
<th>n_2</th>
<th>(\chi_{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2991</td>
<td>5.390</td>
<td>0.3020</td>
<td>4.059</td>
<td>0.866</td>
</tr>
<tr>
<td>2</td>
<td>0.3613</td>
<td>7.703</td>
<td>0.3644</td>
<td>3.698</td>
<td>1.152</td>
</tr>
<tr>
<td>3</td>
<td>0.4786</td>
<td>6.259</td>
<td>0.4820</td>
<td>3.019</td>
<td>0.867</td>
</tr>
</tbody>
</table>
Taking the density values at 359.3K as

\[ \rho_{EVA} = 0.90000 \text{ g cm}^{-3} \quad \rho_{FVA} = 0.91235 \text{ g cm}^{-3} \] (Section 3.3)

These results are shown in Figure 5.7,

The free energy of mixing was calculated from the classical Flory-Huggins relation,

\[ \Delta G_{mix} = RT(\ln n_2 \phi_2 + \ln n_3 \phi_3 + n_2 \phi_2 \chi_{23}) \quad (5.6) \]

The many refinements which have been made to this expression have not been included here because it is intended to demonstrate the difference in the results obtained from a simple lattice theory and those from a simple partition theory, i.e. from the Flory-Huggins and the Equation of State theories respectively.

Table 5.7
Free Energy of Mixing at 348.7K

<table>
<thead>
<tr>
<th>Run</th>
<th>(n_2/10^{19})</th>
<th>(\phi_2)</th>
<th>(n_3/10^{19})</th>
<th>(\phi_3)</th>
<th>(\chi_{23})</th>
<th>(\Delta G_{mix})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.100</td>
<td>0.8794</td>
<td>2.184</td>
<td>0.1206</td>
<td>1.285</td>
<td>-0.216</td>
</tr>
<tr>
<td>2</td>
<td>4.382</td>
<td>0.7546</td>
<td>4.452</td>
<td>0.2454</td>
<td>1.384</td>
<td>-0.289</td>
</tr>
<tr>
<td>3</td>
<td>4.061</td>
<td>0.6988</td>
<td>5.467</td>
<td>0.3012</td>
<td>1.529</td>
<td>-0.296</td>
</tr>
<tr>
<td>4</td>
<td>3.700</td>
<td>0.6362</td>
<td>6.608</td>
<td>0.3638</td>
<td>1.635</td>
<td>-0.296</td>
</tr>
<tr>
<td>5</td>
<td>3.039</td>
<td>0.4970</td>
<td>8.698</td>
<td>0.5030</td>
<td>1.396</td>
<td>-0.287</td>
</tr>
<tr>
<td>6</td>
<td>3.019</td>
<td>0.4969</td>
<td>8.760</td>
<td>0.5031</td>
<td>1.374</td>
<td>-0.291</td>
</tr>
<tr>
<td>7</td>
<td>2.112</td>
<td>0.3619</td>
<td>11.629</td>
<td>0.6381</td>
<td>1.464</td>
<td>-0.260</td>
</tr>
<tr>
<td>8</td>
<td>0.965</td>
<td>0.1650</td>
<td>15.253</td>
<td>0.8350</td>
<td>0.840</td>
<td>-0.184</td>
</tr>
</tbody>
</table>
ENTHALPIC POLYMER-POLYMER INTERACTION PARAMETER
AND CHANGE IN FREE ENERGY ON MIXING AT 348.7K

![Graph showing Mole Fraction EVA vs. Polymer-Polymer Interaction Parameter and Change in Free Energy on Mixing at 348.7K.](image)

Filled Circles - Free Energy Change on Mixing
Empty Circles - Interaction Parameter

Figure 5.7
Table 5.8
Free Energy of Mixing at 359.3K

<table>
<thead>
<tr>
<th>Run</th>
<th>n_2/10^{19}</th>
<th>\phi_2</th>
<th>n_3/10^{19}</th>
<th>\phi_3</th>
<th>\chi_{23}</th>
<th>\Delta G_{mix}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.059</td>
<td>0.6980</td>
<td>5.475</td>
<td>0.3020</td>
<td>0.866</td>
<td>-0.345</td>
</tr>
<tr>
<td>2</td>
<td>3.698</td>
<td>0.6356</td>
<td>6.613</td>
<td>0.3644</td>
<td>1.152</td>
<td>-0.337</td>
</tr>
<tr>
<td>3</td>
<td>3.019</td>
<td>0.5180</td>
<td>8.760</td>
<td>0.4820</td>
<td>0.087</td>
<td>-0.353</td>
</tr>
</tbody>
</table>

These results form the lower section of Figure 5.7.

5.7 Discussion

Lattice theory assumes that configurational entropy, \( S_{conf} \), is the only contribution to the entropy change on mixing and thus \( S_{conf} = \Delta S_{mix} \). This term is often small for long chain molecules because the number of possible configurations that the chains can adopt on the lattice is small. Consequently, the miscibility of the majority of polymer blends, which do not show specific interactions, is controlled by the enthalpic contribution.

All the heat of mixing values obtained for EVA/C_{14} FVA were small and endothermic, ranging from approximately 3.3 \times 10^{-2} to 10.6 \times 10^{-2} J g^{-1}. Although a positive \( \Delta H_{mix} \) is unfavourable to the mixing process it does not preclude it, and it is the change in free energy that occurs during this process that must be considered.

The Flory-Huggins interaction parameters, which are derived on a purely enthalpic basis, are all positive and unfavourable, suggesting that the blend, if miscible at all, is likely to exhibit upper critical solution temperature behaviour. The calculated free energy of mixing values are however all negative, and consequently favourable, suggesting that this blend is miscible in all compositions in this temperature range. The discrepancy between these results can be attributed to the influence of the combinatorial entropy term. This is not unreasonable since both EVA and C_{14} FVA are of low molecular weight and the value of \( S_{conf} \) is likely to be relatively large since the chains can
adopt a greater number of lattice configurations. Interpretation of the results obtained from Flory-Huggins theory suggests that this blend is likely to have undergone UCST type behaviour somewhere below 348.7K while it remains miscible between this temperature and 359.3K, *i.e.* as shown in Figure 5.8. Additionally, it has been found that the thermodynamics of this blend are dominated by the entropic contribution.

The interaction parameters obtained from the EOS model are also small and positive but again they represent only the enthalpic component. A more extensive analysis of these results is presented in Chapter 8.
5.8 REFERENCES


Chapter 6  Solvent Vapour Sorption

6.1  Introduction

Solvent vapour sorption, SVS, has been used for some decades to study the interactions of polymer mixtures. It involves exposing a polymeric sample under high vacuum to solvent vapour and measuring the equilibrium adsorption in terms of increased sample mass and respective solvent vapour pressure. In the context of polymer blends this technique shares a theoretical basis with IGC as it uses another species to quantify indirectly the interactions of interest. However, SVS has the advantage of being a static technique, and once equilibrium has been attained, in principle, it should be free of the surface adsorption and diffusion limitations inherent in IGC. Another advantage of SVS is that it comprises a true ternary system and provides information at a variety of solvent concentrations, as opposed to IGC which normally assumes the probe species to be at infinite dilution. The main disadvantage of the technique is the length of time required to achieve vapour adsorption equilibrium as each measurement can take up to a week. SVS and IGC have often been assumed to be synergistic and several workers have applied both techniques to the same system(1-6) with mixed conclusions. It was intended in this work to duplicate the IGC experiments to provide additional information about the EVA-C\textsubscript{14} FVA interaction, and to consider both the relative merits and the agreement between the methods, but as a consequence of both technical and time constraints this was not possible. Instead a limited range of experiments was carried out and these results and those of their IGC analogues are reported and discussed.

6.2  Theoretical

The thermodynamic parameter which is commonly evaluated from SVS measurements is the the activity of the solvent, $a_1$. In a binary system, \textit{i.e.} solvent-homopolymer, this parameter is defined as,

\[
\ln (a_1) = \ln \left( \frac{P}{P^0} \right) + \frac{B_{11}(P - P^0)}{RT}
\]  

(6.1)

where,

- $P$ = measured vapour pressure of the solvent, atm.
- $P^0$ = saturated vapour pressure of the solvent at $T$, atm.
- $B_{11}$ = second virial coefficient of the solvent at $T$, cm\textsuperscript{3} mol\textsuperscript{-1}
- $T$ = operating temperature, K
The activity coefficient can be related to the Flory-Huggins-Miller-Chang, (FHMC), interaction parameter, $x_{ij}$, by,

$$\ln(a_i) = \ln(\phi_i) + (1 - r_i/r_2)\phi_2 + x_{12}\phi_2^2$$  \hspace{1cm} (6.2)

$$\phi_i = \text{volume fraction of component } i$$

$$x_{12} = \text{solvent - polymer interaction parameter}$$

$$r_i = \text{the number of segments per molecule}$$

Subscript 1 refers to the solvent, subscript 2 to the polymer. In the case of the solvent molecule, $r$ is normally assumed to be unity as the solvent molecule is often approximately equal in size to a single segment unit.

If this approach is now extended to a ternary system consisting of solvent '1', and polymers '2' and '3', equation 6.2 becomes,

$$\ln(a_i) = \ln(\phi_i) + (1 - r_i/r_2)\phi_2 + (1 - r_1/r_3)\phi_3$$

$$+ (x_{12}\phi_2 + x_{13}\phi_3)(1 - \phi_1) - x_{23}\phi_2\phi_1$$  \hspace{1cm} (6.3)

where,  \hspace{1cm} $x_{23} = x_{23}(r_1/r_2)$  \hspace{1cm} (6.4)

However, equation 6.3 can only be used in the limiting case of $\phi_1 \to 0$, since both the homopolymer-solvent interaction parameters depend on the composition of the polymer blend which usually is unknown. To overcome this, the activity of the solvent in a ternary system is redefined as,

$$\ln(a_i) = \ln(\phi_i) + (1 - r_i/r_{23})\phi_{23} + x_{123}\phi_{23}^2$$  \hspace{1cm} (6.5)

where,

$$\ln(a_i) = \ln(\phi_i) + (1 - r_i/r_{23})\phi_2 + x_{12}\phi_2^2$$

$$x_{123} = [(x_{12}\phi_{12} + x_{13}\phi_{13})(1 - \phi_1) - x_{23}\phi_{12}\phi_{13}/\phi_{23}]$$  \hspace{1cm} (6.6)

By considering the polymer phase as a single entity, this definition avoids the need to calculate the individual homopolymer-solvent interaction values and reduces the ternary system to a binary, equation 6.5 becoming analogous to equation 6.2. The combined mixture parameters, i.e. $r_{23}$ and $\phi_{23}$, are calculated from the weighted averages of the individual contributions at zero solvent concentration,

$$r_{23} = x_{p2}r_2 + x_{p3}r_3$$  \hspace{1cm} (6.7)

and,
\[ \phi_{23} = \phi_2 + \phi_3 = 1 - \phi_1 \]  

(6.8)

where,

\[ x_{pi} = \text{mole fraction of polymer component i at zero solvent concentration} \]

The volume fraction is most representative when the components have similar molar volumes and thus the polymer chain is subdivided into a number of segments which are approximately equivalent in size to a solvent molecule,

\[ \phi_i = \frac{m_i v_{pi}^*}{\Sigma m_i v_{pi}^*} \]

\[ = \frac{x_i}{\Sigma x_i} \]

(6.9)

where,

\[ v_{pi}^* = \text{characteristic specific volume of component 'i', cm}^3\text{g}^{-1} \]

\[ \text{(i.e. the specific volume of the defined segment)} \]

\[ x_i = \text{mole fraction of component 'i' in the ternary mixture} \]

If (6.5) is now equated to the measured experimental quantities, via (6.2), and rearranged for \( x_{1,23} \),

\[ x_{1,23} = \frac{1}{(\phi_{23})^2 \left\{ \ln \left( \frac{P}{P^0} \right) + B_{11}(P - P^0)/RT - \ln(\phi_1) - (1 - r_1/r_{23}) \phi_{23} \right\} } \]

from equations 6.7 and 6.8 and substituting \( r_1 = 1 \) gives,

\[ x_{1,23} = \frac{1}{(\phi_{23})^2 \left\{ \ln \left( \frac{P}{P^0} \right) + B_{11}(P - P^0)/RT - \ln(\phi_1) ight\} + \left\{ 1/(x_{p2} r_2 + x_{p3} r_3) - 1 \right\} (\phi_2 + \phi_3) } \]

(6.10)

Thus, this approach simplifies the ternary by treating it as a pair of binary systems, i.e. the polymer-polymer system and the combined polymer-solvent system, and assumes volume additivity.

The true polymer-polymer interaction parameter, \( \chi_{23} \), is calculated from the polymer-polymer-solvent interaction parameters at zero solvent content, \( \chi_{1,23}^\infty \), using equation 6.11(7),

\[ \chi_{23} = (\chi_{12}^\infty \phi_2^\infty + \chi_{13}^\infty \phi_3^\infty - \chi_{1,23}^\infty)/(\phi_2^\infty \phi_3^\infty) \]

(6.11)

where,

\[ \phi_i^\infty = \text{volume fraction of component 'i' in the polymer blend} \]
The values of $\chi^\infty$ are obtained by linear extrapolation of the $\chi_{1j}^{l}$ vs. $\phi_j$ relationship to $\phi_j = 1$. This procedure introduces the possibility of a significant error since the results may not be linear and the selection of data for this fitting procedure is arbitrary.

6.3 Materials

Samples of both the EVA copolymer and the $C_{14}$ FVA copolymer were stored at 393K under vacuum for the duration of these experiments. As the blends were prepared in the open atmosphere at ambient temperature, they were returned to a vacuum oven for 2 hours before being left under vacuum in the SVS rig overnight. This process served to remove excess air/moisture and to evenly distribute the molten sample within the glass holder.

6.4 Apparatus

The apparatus which was used in these experiments was designed and constructed as part of this experimental programme and is represented schematically in Figure 6.1. The components are listed below:-

6.4.1 The Isothermal Envelope

The apparatus was enclosed in a wooden box, (dimensions 2m x 1m x 1m), which was constructed of plywood of 3 cm thickness. The front of the box was hinged to allow access, and double glazed with 4mm MAKROLOM to permit optical measurements. The interior was insulated with 16cm thick pads of fire retardant material.

6.4.2 The Vacuum System

The pump system comprised an Edwards E2M2 two-stage rotary pump and an Edwards (Type 53) diffusion pump. The latter was connected to the glassware via a flange joint with a neoprene 'O' ring. The glassware was fabricated from 12mm o.d. tubing and Young's greaseless taps were employed throughout. Another neoprene 'O' ring was used as a seal between the glass stopper and hook, (from which the quartz spring and sample basket were suspended), and the remaining glassware.
6.4.3 The Heating System and Temperature Control

A pair of platinum resistance thermometers were mounted on either side of the sample holder in the vacuum line, one of which served as the probe for a Digitron 3754 thermometer unit, while the other acted as the sensor for a CAL 9000 temperature control unit. This unit controlled a pair of 300W infrared lamps, mounted on the roof of the box, which provided the control energy. The bulk of the heat was supplied by a Bibby halogen hotplate, which was situated at the bottom of the box, and a 400W Electrothermal heating tape which was loosely wrapped around the internal support framework. The air was circulated by a 7cm, 240V a.c. fan. This arrangement controlled the temperature of the box to ±0.05K.

6.4.4 The Optical Measurements

The mercury levels in the manometer and the displacement of the sample basket were monitored using a cathetometer (The Precision Tool & Instrument Co., Model 2005). This instrument was mounted on a stand whose height was 1.5m with a 1m Vernier scale giving an accuracy of ±5×10⁻³ mm.

6.5 Experimental Procedure

Before absorption experiments could be performed the relationship between the extension of the quartz spring and the suspended mass had to be determined for each operating temperature. This involved the careful weighing of a series of aluminium foil weights, (typically from 140 to 180 mg), inserting each into the evacuated apparatus and recording the resulting extension. These results were then fitted by linear least-squares procedure to give calibration data for that particular spring at that temperature. Each polymer sample was placed in a glass basket and roughly weighed to ensure that it was within the calibration range. The basket was then suspended from the silica spring and the assembly inserted into the apparatus which was then evacuated by rotary pump for approximately 2 hours followed by overnight evacuation by a diffusion pump. Once the system had equilibrated the resulting spring extension was recorded relative to a reference rod, which hung in the middle of the spring coil, and the equivalent mass evaluated from the calibration function. This mass was then used as the initial mass in the subsequent calculations. The apparatus was then separated into the vapour pressure measurement section and the absorption section by closing tap 4, and left for approximately 4 hours until thermal stability was regained. The solvent reservoir was then opened at tap 7 and the rate of addition was monitored from the increase in vapour pressure on the manometer. After the required
volume of solvent had been added, the vapour pressure and the displacement of
the sample basket were noted every 2 hours until no change in their positions
were detected and it was assumed that equilibrium had been established.
Using the same polymer mixture, this procedure was repeated with a range of
solvent concentrations.

6.6 Results

A sample calculation has been included to demonstrate explicitly how the SVS
data were analysed, and to show the sensitivity of the final results to the
precision of the original measurements. The sample data are for Blend 2,
_i.e._ with 41.3% (wt/wt) EVA in the EVA/C_{14}FVA mixture, at 313K.

6.6.1 Sample Calculation

(a) Saturated Vapour Pressure, \(P^0\)

As described in section 4.5.1, \(P^0\) was calculated from the Wagner
equation\(^{(8)}\),

\[
P^0_i = \text{Exp} \left[ (w_i t + w_2 t^{1.5} + w_3 t^2 + w_4 t^6) / T_r \right]
\]

where,

\[ t = 1.0 - T_r \] and

\[ w_i = \text{Wagner coefficients from Reid, Prausnitz and Polling}^{(8)} \]

and the Antoine equation\(^{(8)}\),

\[
P^0_i = \text{Exp} \left[ A_0 - A_1 / (T + A_2) \right]
\]

where,

\[ A_i = \text{Antoine coefficients from reference (8)} \]

A selection of the \(P^0_i\) values at the SVS operating temperatures,
which have been estimated by both of these methods is included in
Table 6.1 for reference.
Table 6.1

The saturated vapour pressures of Hexane, $P_1^0$

<table>
<thead>
<tr>
<th>T/K</th>
<th>$P_1^0$ / mmHg</th>
<th>$P_1^0$ / mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Antoine)</td>
<td>(Wagner)</td>
</tr>
<tr>
<td>312.8</td>
<td>273.3</td>
<td>274.7</td>
</tr>
<tr>
<td>312.9</td>
<td>276.4</td>
<td>275.8</td>
</tr>
<tr>
<td>313.0</td>
<td>277.4</td>
<td>276.8</td>
</tr>
<tr>
<td>313.1</td>
<td>278.5</td>
<td>277.9</td>
</tr>
<tr>
<td>313.2</td>
<td>279.6</td>
<td>279.0</td>
</tr>
<tr>
<td>352.7</td>
<td>1053.2</td>
<td>1050.7</td>
</tr>
<tr>
<td>352.8</td>
<td>1056.3</td>
<td>1053.8</td>
</tr>
<tr>
<td>352.9</td>
<td>1059.4</td>
<td>1056.9</td>
</tr>
<tr>
<td>353.0</td>
<td>1062.4</td>
<td>1059.9</td>
</tr>
<tr>
<td>353.1</td>
<td>1065.5</td>
<td>1063.0</td>
</tr>
<tr>
<td>353.2</td>
<td>1068.7</td>
<td>1066.1</td>
</tr>
<tr>
<td>353.3</td>
<td>1071.8</td>
<td>1069.2</td>
</tr>
<tr>
<td>353.4</td>
<td>1074.9</td>
<td>1072.4</td>
</tr>
<tr>
<td>353.5</td>
<td>1078.0</td>
<td>1075.5</td>
</tr>
<tr>
<td>353.6</td>
<td>1081.2</td>
<td>1078.6</td>
</tr>
<tr>
<td>353.7</td>
<td>1084.3</td>
<td>1081.7</td>
</tr>
<tr>
<td>353.8</td>
<td>1087.5</td>
<td>1084.9</td>
</tr>
<tr>
<td>353.9</td>
<td>1090.6</td>
<td>1088.0</td>
</tr>
</tbody>
</table>

From the Wagner expression the saturated vapour pressure of hexane at 313K is estimated as 276.8 mmHg. The relative error in this value is considered to be insignificant.
Table 6.2
Reproducibility of extension measurements

<table>
<thead>
<tr>
<th>Run</th>
<th>Reference Point/cm</th>
<th>Basket/cm</th>
<th>Extension / cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.839</td>
<td>9.640</td>
<td>4.199</td>
</tr>
<tr>
<td>2</td>
<td>13.849</td>
<td>9.654</td>
<td>4.195</td>
</tr>
<tr>
<td>3</td>
<td>13.852</td>
<td>9.644</td>
<td>4.208</td>
</tr>
<tr>
<td>4</td>
<td>13.852</td>
<td>9.634</td>
<td>4.218</td>
</tr>
<tr>
<td>5</td>
<td>13.849</td>
<td>9.647</td>
<td>4.202</td>
</tr>
<tr>
<td>Mean</td>
<td>13.848</td>
<td>9.644</td>
<td>4.204</td>
</tr>
</tbody>
</table>

Standard Deviation of extension = \(8.02 \times 10^{-3}\)

hence, mean extension = \(4.204 \pm 0.008\) cm

The total range of extension values is 8.108 cm to 3.982 cm for this experiment, thus the standard deviation of the measurement when expressed as a percentage of the total range is,

\[
\text{Error} = \frac{0.008}{(8.108 - 3.982)} = 0.2\%
\]

From equation 6.1 the activity of the hexane is given by,

\[
\ln(a_1) = \ln\left(\frac{P}{P_0}\right) + \left[B_{11}(P - P_0)/RT\right] = \ln\left(\frac{4.278}{27.68}\right)
+ (-1619.8)(4.278 - 27.68)/(82.057313) = -1.867 + 1.476 = -0.391
\]
Substituting this value into (6.10) gives:

$$x'_{1,23} = 1/(\phi_{23})^2 \left\{ \ln \left( \frac{P}{P^o} \right) + B_{11}(P - P^o)/RT - \ln (\phi_1) \right. \right.$$  
$$\left. + \left[ 1/(x_{p2}r_2 + x_{p3}r_3) - 1 \right] (\phi_2 + \phi_3) \right\} \quad (6.10)$$

The values of $r$ are constant for each polymer sample and are calculated from the number average molecular weight of the polymer, as determined by GPC, divided by the unit structure molecular weight,

$$r_i = M_n / \text{Unit Structure Molecular Weight}$$

hence,

$$r_2 \text{ (EVA)} = 3290 / 254.4 = 12.9 \text{ segments}$$

$$r_3 \text{ (C}_{14}\text{FVA)} = 10400 / 594.8 = 17.5 \text{ segments}$$

If the binary system of polymers is considered, the mole fractions, $(x_{pi})$, of the components are,

mass EVA = 59.5mg

hence moles of EVA = $59.5/3290 \times 10^3 = 1.81 \times 10^{-5}$ moles

mass of C$_{14}$FVA = 84.7mg

hence moles of C$_{14}$FVA = $84.7 / 10400 \times 10^3$

$$= 8.14 \times 10^{-6} \text{ moles}$$

hence, $x_{p2} = 1.81 \times 10^{-5} / (1.81 \times 10^{-5} + 8.14 \times 10^{-6})$

$$= 0.690$$

and $x_{p3} = 1 - x_{p2} = 0.310$

In the ternary system, the mass of the solvent is given by the extension of the spring converted to mass via the calibration function, the details are given below.

6.6.2 Microbalance calibration

A series of 5 weights, made from aluminium foil, was used to calibrate the quartz spring; aluminium was chosen because it is inert with respect to hexane.
Table 6.3
Quartz spring calibration

<table>
<thead>
<tr>
<th>Reference No</th>
<th>mass / mg</th>
<th>Extension</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mean/cm</td>
</tr>
<tr>
<td>1</td>
<td>143.8</td>
<td>3.948</td>
</tr>
<tr>
<td>2</td>
<td>150.5</td>
<td>4.081</td>
</tr>
<tr>
<td>3</td>
<td>157.9</td>
<td>4.209</td>
</tr>
<tr>
<td>4</td>
<td>169.8</td>
<td>4.465</td>
</tr>
<tr>
<td>5</td>
<td>183.5</td>
<td>4.691</td>
</tr>
</tbody>
</table>

Least-squares techniques were used to obtain the following values for the intercept (a) and slope (b) where,

\[ \text{Extension} = a + b \text{(Mass)} \]

\[ a = 1.2326 \quad b = 0.0189 \quad r = 0.9990 \]

These results are shown graphically in Figure 6.2

unexposed initial mass equivalent = 3.985 cm = 145.63 mg

final position mass equivalent = 4.030 cm = 148.01 mg

hence, increase in mass = 148.01 - 145.63 = 2.38 mg

number of moles of hexane = \( \frac{2.38}{86.17 \times 10^3} \)
\[ = 2.76 \times 10^{-5} \text{ moles} \]

hence, the ternary mole fractions are,

\[ x_1 = \frac{2.76}{(2.76 + 1.81 + 0.81)} = 0.513 \]
\[ x_2 = \frac{1.81}{(2.76 + 1.81 + 0.81)} = 0.336 \]
\[ x_3 = 1 - (x_2 + x_1) = 0.151 \]
Linear Calibration of Quartz Spring

Extension vs. Mass

Figure 6.2

Mass/mg

Extension/cm
and the volume fractions are,

\[
\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2 + x_3 r_3} \\
= \frac{0.513 \times 1}{0.513 + 12.9 \times 0.336 + 17.5 \times 0.151} \\
= 0.068
\]

\[
\phi_2 = \frac{3.8304}{7.5001} = 0.511
\]

\[
\phi_3 = 1 - (0.068 + 0.511) = 0.421
\]

and thus, \(\phi_{23} = 0.511 + 0.421 = 0.932\)

substitution of these values into (6.10) yields,

\[
x_{1,23} = \frac{1}{(0.932)^2} \left\{ (-0.391) - (-2.617) \\
+ \frac{1}{(7.866 + 5.425) - 1}(0.932) \right\} = 1.646
\]
6.6.3 The 313K Experiments

6.6.3.1 \text{C}_{14} \text{FVA}

Table 6.4

Initial Mass = 147.04 mg : \( P^\circ = 276.8 \) mmHg

<table>
<thead>
<tr>
<th>Ref. No</th>
<th>( M_{\text{solv}} / M_{\text{polymer}} )</th>
<th>( P / P^\circ )</th>
<th>( \phi_{23} )</th>
<th>( \chi_{1(23)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0294</td>
<td>0.240</td>
<td>0.832</td>
<td>-0.6193</td>
</tr>
<tr>
<td>2</td>
<td>0.0302</td>
<td>0.240</td>
<td>0.828</td>
<td>-0.6510</td>
</tr>
<tr>
<td>3</td>
<td>0.0550</td>
<td>0.355</td>
<td>0.726</td>
<td>-0.7832</td>
</tr>
<tr>
<td>4</td>
<td>0.0536</td>
<td>0.355</td>
<td>0.731</td>
<td>-0.7452</td>
</tr>
<tr>
<td>5</td>
<td>0.0834</td>
<td>0.471</td>
<td>0.636</td>
<td>-0.8710</td>
</tr>
<tr>
<td>6</td>
<td>0.0860</td>
<td>0.471</td>
<td>0.629</td>
<td>-0.8661</td>
</tr>
<tr>
<td>7</td>
<td>0.1122</td>
<td>0.541</td>
<td>0.565</td>
<td>-0.9522</td>
</tr>
<tr>
<td>8</td>
<td>0.1111</td>
<td>0.541</td>
<td>0.567</td>
<td>-0.9336</td>
</tr>
<tr>
<td>9</td>
<td>0.1460</td>
<td>0.625</td>
<td>0.499</td>
<td>-0.9656</td>
</tr>
<tr>
<td>10</td>
<td>0.1457</td>
<td>0.625</td>
<td>0.500</td>
<td>-0.9593</td>
</tr>
</tbody>
</table>

A least-squares on all points gives

\[ \chi_{13}^\circ = -0.4162 \]
Table 6.4: Interaction Parameter vs Volume Fraction

FVA at 313K

Polymer-Solvent Interaction Parameter vs Polymer Volume Fraction

Figure 6.3
Table 6.5

Initial Mass = 146.30 mg : $P^o = 276.8$ mmHg, [$\phi_{23} = \phi_2$]

<table>
<thead>
<tr>
<th>Ref. No</th>
<th>$M_{solv}/M_{polymer}$</th>
<th>$P/P^o$</th>
<th>$\phi_{23}$</th>
<th>$\chi_{1(23)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.012</td>
<td>0.017</td>
<td>0.966</td>
<td>+ 0.117</td>
</tr>
<tr>
<td>2</td>
<td>0.010</td>
<td>0.017</td>
<td>0.971</td>
<td>+ 0.283</td>
</tr>
<tr>
<td>3</td>
<td>0.030</td>
<td>0.202</td>
<td>0.726</td>
<td>+ 1.728</td>
</tr>
<tr>
<td>4</td>
<td>0.033</td>
<td>0.202</td>
<td>0.911</td>
<td>+ 1.655</td>
</tr>
<tr>
<td>5</td>
<td>0.114</td>
<td>0.514</td>
<td>0.748</td>
<td>- 0.018</td>
</tr>
<tr>
<td>6</td>
<td>0.064</td>
<td>0.415</td>
<td>0.841</td>
<td>+ 0.222*</td>
</tr>
<tr>
<td>7</td>
<td>0.065</td>
<td>0.415</td>
<td>0.838</td>
<td>+ 0.201*</td>
</tr>
<tr>
<td>8</td>
<td>0.144</td>
<td>0.618</td>
<td>0.702</td>
<td>+ 0.088</td>
</tr>
<tr>
<td>9</td>
<td>0.140</td>
<td>0.618</td>
<td>0.707</td>
<td>+ 0.111</td>
</tr>
<tr>
<td>10</td>
<td>0.067</td>
<td>0.232</td>
<td>0.834</td>
<td>- 0.649*</td>
</tr>
<tr>
<td>11</td>
<td>0.065</td>
<td>0.232</td>
<td>0.839</td>
<td>- 0.599*</td>
</tr>
</tbody>
</table>

A least-squares on all the absorption points gives

$$\chi^o_{1,23} = +0.186$$

(desorption points are marked with an asterisk)
Table 6.5: Interaction Parameter vs Volume Fraction
EVA at 313K

![Graph showing the interaction parameter vs volume fraction for EVA at 313K. The graph includes data points for adsorption and desorption.](Image)
Table 6.6

Blend 1: (20% EVA, at 313 K)

Initial Mass = 140.0 mg : P° = 276.8 mmHg

<table>
<thead>
<tr>
<th>Ref. No</th>
<th>( \text{M}<em>{\text{solv}} / \text{M}</em>{\text{polymer}} )</th>
<th>( \text{P} / \text{P}^0 )</th>
<th>( \phi_{23} )</th>
<th>( \phi_2 )</th>
<th>( \chi_{123} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.040</td>
<td>0.213</td>
<td>0.837</td>
<td>0.279</td>
<td>+ 1.225</td>
</tr>
<tr>
<td>3</td>
<td>0.042</td>
<td>0.213</td>
<td>0.828</td>
<td>0.278</td>
<td>+ 1.187</td>
</tr>
<tr>
<td>4</td>
<td>0.079</td>
<td>0.398</td>
<td>0.721</td>
<td>0.235</td>
<td>+ 1.407</td>
</tr>
<tr>
<td>5</td>
<td>0.083</td>
<td>0.398</td>
<td>0.713</td>
<td>0.236</td>
<td>+ 1.398</td>
</tr>
<tr>
<td>6</td>
<td>0.122</td>
<td>0.517</td>
<td>0.627</td>
<td>0.208</td>
<td>+ 1.284</td>
</tr>
<tr>
<td>7</td>
<td>0.121</td>
<td>0.517</td>
<td>0.629</td>
<td>0.212</td>
<td>+ 1.483</td>
</tr>
<tr>
<td>8</td>
<td>0.145</td>
<td>0.585</td>
<td>0.586</td>
<td>0.198</td>
<td>+ 1.518</td>
</tr>
<tr>
<td>9</td>
<td>0.147</td>
<td>0.585</td>
<td>0.583</td>
<td>0.193</td>
<td>+ 1.521</td>
</tr>
<tr>
<td>10</td>
<td>0.047</td>
<td>0.213</td>
<td>0.812</td>
<td>0.273</td>
<td>+ 1.120*</td>
</tr>
<tr>
<td>11</td>
<td>0.050</td>
<td>0.213</td>
<td>0.803</td>
<td>0.269</td>
<td>+ 1.085*</td>
</tr>
</tbody>
</table>

A least-squares on all the absorption points gives

\[ \chi_{123}^{\infty} = +1.014 \]

(desorption points are marked with an asterisk)
Table 6.6: Interaction Parameter vs Volume Fraction

BLEND 1: 20% EVA (w/w), 313K

[Graph showing data points and a line]
Table 6.7:
Blend 2: (40%EVA) - 313K

Initial Mass = 145.6 mg : \( P^o = 276.8 \text{ mmHg} \)

<table>
<thead>
<tr>
<th>Ref. No</th>
<th>( M_{\text{solv}}/M_{\text{polymer}} )</th>
<th>( P/P^o )</th>
<th>( \phi_{23} )</th>
<th>( \phi_2 )</th>
<th>( \chi_{1(23)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.016</td>
<td>0.155</td>
<td>0.932</td>
<td>0.511</td>
<td>+ 1.647</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>0.154</td>
<td>0.919</td>
<td>0.572</td>
<td>+ 1.420</td>
</tr>
<tr>
<td>3</td>
<td>1.498</td>
<td>0.317</td>
<td>0.591</td>
<td>0.373</td>
<td>+ 1.109</td>
</tr>
<tr>
<td>4</td>
<td>1.494</td>
<td>0.317</td>
<td>0.591</td>
<td>0.373</td>
<td>+ 1.122</td>
</tr>
</tbody>
</table>

A least-squares calculation on all points gave \( \chi_{1,23}^\phi = +1.631 \)

6.6.4 The 353K Experiments

6.6.4.1 \( C_{14} \) FVA

Table 6.8

Initial Mass = 146.68 mg : \( P^o = 1081.7 \text{ mmHg} \) : [\( \phi_{23} = \phi_3 \)]

<table>
<thead>
<tr>
<th>Ref. No</th>
<th>( M_{\text{solv}}/M_{\text{polymer}} )</th>
<th>( P/P^o )</th>
<th>( \phi_{23} )</th>
<th>( \chi_{1(23)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.006</td>
<td>0.427</td>
<td>0.962</td>
<td>-0.4687</td>
</tr>
<tr>
<td>2</td>
<td>0.006</td>
<td>0.739</td>
<td>0.962</td>
<td>+0.1224</td>
</tr>
<tr>
<td>3</td>
<td>0.016</td>
<td>0.932</td>
<td>0.901</td>
<td>-0.6817</td>
</tr>
<tr>
<td>4</td>
<td>0.014</td>
<td>0.930</td>
<td>0.910</td>
<td>-0.1987</td>
</tr>
</tbody>
</table>

A least-squares calculation on all points gives \( \chi_{12}^\phi = +0.563 \)
Table 6.8: Interaction Parameter vs Volume Fraction

FVA at 353K

Figure 6.7
6.6.4.2 EVA

Table 6.9

Initial Mass = 134.31 mg : $P^o = 1081.7$ mmHg

<table>
<thead>
<tr>
<th>Ref. No</th>
<th>$M_{solv}/M_{polymer}$</th>
<th>$P/P^o$</th>
<th>$\phi_{23}$</th>
<th>$\chi_{1(23)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.024</td>
<td>0.066</td>
<td>0.925</td>
<td>-1.0676</td>
</tr>
<tr>
<td>2</td>
<td>0.041</td>
<td>0.130</td>
<td>0.880</td>
<td>-0.8727</td>
</tr>
<tr>
<td>3</td>
<td>0.028</td>
<td>0.083</td>
<td>0.915</td>
<td>-0.9615</td>
</tr>
</tbody>
</table>

A least-squares calculation on all points gave $\chi^{\alpha}_{13} = -1.328$

6.7 Discussion

The design and construction of this apparatus required substantial effort and the limited number of experimental results reflects the prolonged commissioning period and the equilibrium time required per measurement. One major disadvantage of the original design was that the glass suspension hook and the sample chamber were connected by a greased ground-glass joint. After a new sample was inserted and the system evacuated, this joint leaked causing pressure surge into the RHS of the glassware with mercury being sprayed from the manometer into the LHS glassware. It is believed that often this seal failed because of a redistribution of the vacuum grease as the apparatus was heated to the operational temperature. This problem was eventually solved by replacing the grease with a neoprene 'O' ring. To ensure that mercury spillage could be removed readily, the glassware was modified to retain the spillage within an external purge line. This was the reason that a low temperature of 313K was chosen for the first experiments since it was initially unclear whether the mercury spillage was occurring as a result of a pressure leak or by condensation of the mercury vapour outside the thermal envelope of the rig. In view of the high density of the mercury, which prevented a large bore manometer being used owing to fear of fracture with its associated toxicological hazards, it might have been more prudent to have used an alternative medium, for example a high boiling silicone oil. The original
design was also found to have a significant temperature gradient between the top and bottom of the box which was overcome by remounting the infrared lamps on the roof and re-positioning the circulation fan.

Another factor which reduced the number of successful experiments was the time required to achieve equilibrium. This period was found to vary between 8 and 36 hours for absorption but the experimental results suggested that desorption equilibrium was not achieved even after as long as 100 hours.

Although the primary measurements were found to be reproducible, the linear extrapolation of the interaction parameters to the condition of infinite dilution of the solvent introduced significant errors for a number of reasons. Firstly, generally there were insufficient data at low solvent concentrations to apply statistical techniques to obtain a fit for the function, and secondly, there is no reason to assume, that even at low solvent concentrations, the interaction parameter is a linear function of $\phi_{23}$. For example, if all the absorption data for EVA-Hexane at 313K are fitted as a series of polynomials of increasing order, the intercept value changes significantly as shown in Table 6.10, (it should also be noted that the assignment of data to any potential fit is arbitrary).

### Table 6.10

Coefficients for polynomial fits of EVA-Hexane data at 313K

<table>
<thead>
<tr>
<th>Order</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>Intercept at $\phi_{23} = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.0305</td>
<td>0.2162</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.186</td>
</tr>
<tr>
<td>2</td>
<td>-0.0015</td>
<td>-0.1769</td>
<td>0.4211</td>
<td>-</td>
<td>-</td>
<td>0.242</td>
</tr>
<tr>
<td>3</td>
<td>0.0002</td>
<td>-2.5202</td>
<td>6.0515</td>
<td>-3.3324</td>
<td>-</td>
<td>0.199</td>
</tr>
<tr>
<td>4</td>
<td>0.0000</td>
<td>105.7400</td>
<td>-388.3998</td>
<td>471.9492</td>
<td>-189.3873</td>
<td>-0.098</td>
</tr>
</tbody>
</table>

These data show a significant variation in their extrapolated $\chi^\infty_{13}$ values.

Values of the EVA-hexane interaction parameter change from small and positive to significantly negative over the temperature range 313 to 353K, Table 6.11, suggesting that hexane becomes a more effective solvent for EVA
which change from small and negative to small and positive.

<table>
<thead>
<tr>
<th>Method</th>
<th>Temp/K</th>
<th>$\chi_{12}^\infty$</th>
<th>$\chi_{13}^\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVS</td>
<td>313</td>
<td>0.1855</td>
<td>-0.4162</td>
</tr>
<tr>
<td>SVS</td>
<td>353</td>
<td>-1.3278</td>
<td>0.5625</td>
</tr>
<tr>
<td>IGC</td>
<td>353</td>
<td>1.7963</td>
<td>1.5361</td>
</tr>
<tr>
<td>IGC</td>
<td>373</td>
<td>2.0567</td>
<td>1.6421</td>
</tr>
<tr>
<td>IGC</td>
<td>393</td>
<td>2.2782</td>
<td>1.8190</td>
</tr>
</tbody>
</table>

The agreement between the SVS and IGC results at 353K for both systems is very poor with no obvious explanation for this difference. The variations in both the calculated values of the SVS homopolymer-hexane interaction parameters between 313 and 353K are an order of magnitude greater than those seen in the IGC results between 353 and 393K. The accuracy and reliability of the SVS results should be better than those derived from the IGC experiments since there are no unpredictable dynamic effects involved and there is no other material present which could affect the measurements, e.g. the PTFE support, but this reproducibility could not be verified owing to the limited data from the SVS experiments. Several workers have reported good agreement between IGC and SVS experiments\(^{(1,3,9)}\) and concluded that both techniques were equally valid. However, there have also been reports of noticeable discrepancies being observed between results obtained from IGC and those from SVS\(^{(4)}\) and even an inter-laboratory collaboration\(^{(10)}\) failed to resolve these differences. These discrepancies are more fully discussed in Chapter 9.

The polymer-polymer interaction parameters which were calculated at 313K for mixtures of 20 and 40\% (wt/wt) EVA and C\(_{14}\) FVA are both very large and negative, Table 6.12.
Table 6.12:

Polymer-Polymer Interaction Parameters for EVA/C_{14} FVA from Hexane Probes

<table>
<thead>
<tr>
<th>% EVA (wt/wt)</th>
<th>T / K</th>
<th>$\chi_{12}^\infty$</th>
<th>$\phi_2$</th>
<th>$\chi_{13}^\infty$</th>
<th>$\phi_3$</th>
<th>$\chi_{1.23}^\infty$</th>
<th>$\phi_3^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 SVS</td>
<td>313</td>
<td>+0.1857</td>
<td>0.355</td>
<td>-0.4162</td>
<td>0.665</td>
<td>+1.014</td>
<td>-5.515</td>
</tr>
<tr>
<td>40 SVS</td>
<td>313</td>
<td>+0.1857</td>
<td>0.621</td>
<td>-0.4162</td>
<td>0.379</td>
<td>+1.014</td>
<td>-7.110</td>
</tr>
<tr>
<td>25 IGC</td>
<td>353</td>
<td>+1.7963</td>
<td></td>
<td>+1.5361</td>
<td></td>
<td></td>
<td>-2.105</td>
</tr>
<tr>
<td>36 SVS</td>
<td>353</td>
<td>+1.7963</td>
<td></td>
<td>+1.5361</td>
<td></td>
<td></td>
<td>+0.743</td>
</tr>
</tbody>
</table>

These values predict that any mixture of less than 40% EVA (wt/wt) and C_{14} FVA would be highly miscible at this temperature. The normal range of $\chi$ values is ± 1, and thus these figures display major differences from those expected. Some doubt was felt as to the magnitude of these values and as a consequence it was decided to examine the sensitivity of the calculation.

If the 20% EVA data are taken, for example, from equation 6.11

$$\chi_{23}^\infty = (\chi_{12}^\infty \phi_2^\infty + \chi_{13}^\infty \phi_3^\infty - \chi_{1.23}^\infty) / (\phi_2^\infty \phi_3^\infty) \tag{6.11}$$

$$\chi_{12}^\infty \phi_2^\infty = 0.062$$  
$$\chi_{13}^\infty \phi_3^\infty = -0.277$$  
$$\chi_{1.23}^\infty = 1.014$$  
$$\phi_2^\infty \phi_3^\infty = 0.223$$

From these values it is apparent that $\chi_{1.23}^\infty$ dominates the calculation, and the net effect is multiplied by a factor of (1.0/0.223), or approximately 5, from the product of the polymer mixture volume fractions. Since the value of $\chi_{1.23}^\infty$ is obtained by fitting a straight line to eight data points and extrapolating this function to $\phi_{23} = 1$, the potential error is significant, i.e. if a polynomial fit is used the extrapolated intercept varies considerably, Table 6.13,
Table 6.13

Coefficients for polynomial fits of Hexane-EVA data at 353K

<table>
<thead>
<tr>
<th>Order</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>Intercept at $\phi_{23} = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.2700</td>
<td>-1.2557</td>
<td></td>
<td></td>
<td>1.014</td>
</tr>
<tr>
<td>2</td>
<td>0.8076</td>
<td>2.9379</td>
<td>-2.9504</td>
<td>0.795</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.9813</td>
<td>-2.1328</td>
<td>4.2839</td>
<td>-3.4080</td>
<td>0.724</td>
</tr>
</tbody>
</table>

(The quadratic and cubic functions are shown in Figures 6.9 and 6.10)

If the quadratic fit intercept value is now inserted into the calculation of $\chi'_{23}$,

$$\chi'_{23} = \frac{(0.062 - 0.277 - 0.795)/(0.228)}{\phi_{23} = -4.430}$$

This represents a 20% difference in the estimated polymer-polymer interaction parameter. This difference could be greatly increased if the same procedure was applied to the extrapolated values of the homopolymer-solvent interaction parameters. The significance of this effect is not unique to the SVS data presented here: a similar analysis was performed on the data reported by Panayiotou and Vera\(^{(7)}\) for the system benzene-polystyrene-poly(vinyl methyl ether) with the following results.

Table 6.14

Coefficients for polynomial fits of Benzene-PS-PVME data at 298K

(PS Wt.Fr. = 0.3337)

<table>
<thead>
<tr>
<th>Order</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>Intercept at $\phi_{23} = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2529</td>
<td>-0.0002</td>
<td></td>
<td></td>
<td>0.252</td>
</tr>
<tr>
<td>2</td>
<td>0.2628</td>
<td>-0.0316</td>
<td>0.0238</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-0.4536</td>
<td>4.5564</td>
<td>-10.7404</td>
<td>10.9795</td>
<td>0.262</td>
</tr>
</tbody>
</table>
Table 6.6: Interaction Parameter vs Volume Fraction

BLEND 1: 20% EVA (w/w), 313K

Polymer Blend Volume Fraction

Figure 6.9
Table 6.6: Interaction Parameter vs Volume Fraction

BLEND 1: 20% EVA (w/w), 313K

![Graph showing the relationship between Polymer Blend Volume Fraction and Polymer-Polymer Interaction Parameter. The graph includes data points for Adsorption and Desorption.](image-url)
Reference (7) quotes $\chi_{1,23}^p = 0.252$ at $\phi_{23} = 1$, from a linear extrapolation, but fails to record that a correlation coefficient, $r_{cc}$, of 0.007 is obtained with this fit. This situation can be improved if the order of the polynomial is increased, i.e. $r_{cc} = 0.130$ for the quadratic and $r_{cc} = 0.210$ for the cubic. If some of the carbon tetrachloride-poly(vinyl chloride)-poly($\varepsilon$-caprolactone) data at 338K from the same paper are considered,

Table 6.15
Polynomial fits of carbon tetrachloride-poly(vinyl chloride)-poly($\varepsilon$-caprolactone) data at 338K (PVC Wt.Fr. = 0.7653)

<table>
<thead>
<tr>
<th>Order</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Intercept at $\phi_{23} = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5451</td>
<td>0.5197</td>
<td>-</td>
<td>-</td>
<td>1.065</td>
</tr>
<tr>
<td>2</td>
<td>2.4150</td>
<td>-3.9755</td>
<td>2.6724</td>
<td>-</td>
<td>1.112</td>
</tr>
<tr>
<td>3</td>
<td>-13.4083</td>
<td>53.0946</td>
<td>-65.5265</td>
<td>27.0049</td>
<td>1.160</td>
</tr>
</tbody>
</table>

The correlation coefficients for the fits above are 0.8977, 0.9544 and 0.9830 respectively. These data, shown graphically in figure 6.11, demonstrate a major problem with the linear extrapolation technique. Essentially all of the points, except the last, lie on a straight line which if extrapolated to $\phi_{23} = 1$ would give $\chi_{1,23}^p = 1.029$, an 11% difference from the cubic fit. Panayiotou and Vera quote $\chi_{1,23}^p = 1.025$ which suggests that they have not included the last point in the fit, although this is not discussed in the text. These data clearly demonstrate the dilemma which arises when non-linear results are obtained, i.e. to decide whether this is truly a non-linear relationship or if the last point is erroneous, and without more information this cannot be resolved. The cubic fit gives the best correlation coefficient but the point of inflection at approximately $\phi_{23} = 0.76$ cannot be readily justified. This entire fitting procedure is without doubt a major source of error which will greatly affect the accuracy of any SVS data which are non-linear.

The only reliable conclusion that can be reached from the $\chi_{23}$ values obtained in this work is that for mixture compositions of up to 40% EVA, the polymer-polymer interaction parameters of the EVA/C$_{14}$ FVA system are likely to be significantly negative and thus favourable. This conclusion is in broad agreement with the IGC results for 353K.
Reference (7) quotes $\chi_{123}^2 = 0.252$ at $\phi_{23} = 1$, from a linear extrapolation, but fails to record that a correlation coefficient, $r_{cc}$, of 0.007 is obtained with this fit. This situation can be improved if the order of the polynomial is increased, i.e. $r_{cc} = 0.130$ for the quadratic and $r_{cc} = 0.210$ for the cubic. If some of the carbon tetrachloride-poly(vinyl chloride)-poly($\epsilon$-caprolactone) data at 338K from the same paper are considered, the results are as in Table 6.15

Table 6.15
Polynomial fits of carbon tetrachloride-poly(vinyl chloride)-poly($\epsilon$-caprolactone) data at 338K (PVC Wt.Fr. = 0.7653)

<table>
<thead>
<tr>
<th>Order</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>Intercept at $\phi_{23} = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5451</td>
<td>0.5197</td>
<td>-</td>
<td>-</td>
<td>1.065</td>
</tr>
<tr>
<td>2</td>
<td>2.4150</td>
<td>-3.9755</td>
<td>2.6724</td>
<td>-</td>
<td>1.112</td>
</tr>
<tr>
<td>3</td>
<td>-13.4083</td>
<td>53.0946</td>
<td>-65.5265</td>
<td>27.0049</td>
<td>1.160</td>
</tr>
</tbody>
</table>

The correlation coefficients for the fits above are 0.8977, 0.9544 and 0.9830 respectively. These data, shown graphically in figure 6.11, demonstrate a major problem with the linear extrapolation technique. Essentially all of the points, except the last, lie on a straight line which if extrapolated to $\phi_{23} = 1$ would give $\chi_{123}^2 = 1.029$, an 11% difference from the cubic fit. Panayiotou and Vera(7) quote $\chi_{1,23}^2 = 1.025$ which suggests that they have not included the last point in the fit, although this is not discussed in the text. These data clearly demonstrate the dilemma which arises when non-linear results are obtained, i.e. to decide whether this is truly a non-linear relationship or if the last point is erroneous, and without more information this cannot be resolved. The cubic fit gives the best correlation coefficient but the point of inflection at approximately $\phi_{23} = 0.76$ cannot be readily justified. This entire fitting procedure is without doubt a major source of error which will greatly affect the accuracy of any SVS data which are non-linear.

The only reliable conclusion that can be reached from the $\chi_{23}^2$ values obtained in this work is that for mixture compositions of up to 40% EVA, the polymer-polymer interaction parameters of the EVA/C$_{14}$ FVA system are likely to be significantly negative and thus favourable. This conclusion is in broad agreement with the IGC results for 353K.
6.8 REFERENCES

(1) P.J.T.Tait and M.A.Abushihada, Polymer, 18, 810, (1977).


Chapter 7  Optical Microscopy

7.1 Introduction

The main attraction of optical microscopy as a characterisation technique is that a direct image of the sample is obtained without a demanding sample preparation. When this instrument is coupled to a hot stage, it is possible to observe many of the thermally induced transitions that macromolecules undergo and obtain an accurate estimation of the temperatures at which they occur. The main disadvantage of the technique is poor resolution, typically 200-600 nm, which is determined by the wavelength of light being used. For many applications in polymer science this is inadequate as the effects being studied are not physically large enough.

Optical microscopy is particularly useful in the study of polymer blends since optical clarity is usually the first indication of the conditions under which two polymers are miscible. However its application is restricted because of poor resolution in systems which have similar refractive indices; this resolution can be improved by a phase contrast facility which utilises a prism to split the transmitted beam. After passing through the sample both beams are recombined in an interferometer which shears the beams vertically against each other. The presence of a phase difference is shown by interference. Caution should be used when interpreting microphotographs as deceptive results can be obtained if the blend either separates into two distinct layers, or forms a two-phase structure which has domains that are smaller than the wavelength of the incident beam.

7.2 Apparatus and Materials

This study was carried out using an Olympus BH2 microscope fitted with a phase contrast condenser and a CK20 objective. The temperature of the sample was varied by a Linkam THM 600 hot stage. The image from the microscope was monitored by a JVC KYF-30 video camera and relayed as a SVHS signal, via a Linkam VTO 232 text overlayer, to a Sony UP-5000P mavigraph printer. The polymers were annealed at 373K under vacuum for 12 hours and then left in a desiccator containing silica for another 12 hours before being analysed. The samples were prepared by depositing a small amount of bulk polymer (typically 2mg), at ambient temperature, on a glass cover slip and compressing the polymer with another slip.
7.3 Refractive Index Calculations

As a preliminary to the phase contrast experiments, the refractive indices of the copolymers were calculated using the expression proposed by Gladstone and Dale,

\[ R_{GD} = (n-1)M/\rho = (n-1)V \]  \hspace{1cm} (7.1a)

or,

\[ n = 1 + \frac{R_{GD}}{V} \]  \hspace{1cm} (7.1b)

where,

\[ R_{GD} \quad \text{Gladstone-Dale Molar Refraction index} \]

\[ n \quad \text{refractive index} \]

\[ M \quad \text{molecular weight of monomer unit} \]

\[ V \quad \text{molar volume, cm}^3\text{mol}^{-1} \]

Using Goedhart's data \(^{(1)}\), the following refractive indices were calculated,

**Table 7.1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_{GD} )</th>
<th>Mol Wt</th>
<th>( n_p ) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA</td>
<td>128.29</td>
<td>254.4</td>
<td>1.482</td>
</tr>
<tr>
<td>( C_{14} )FVA</td>
<td>290.11</td>
<td>594.8</td>
<td>1.461</td>
</tr>
</tbody>
</table>

The similarity in the refractive indices calculated above suggested that there was very little contrast between these two materials and consequently it might be difficult to resolve any morphological changes that occurred. This view was supported by some unsuccessful experiments using a polarising microscope. However, a phase contrast microscope was found to have adequate resolution.
7.4 Results

These experiments were undertaken in an attempt to resolve some of the discrepancies between the results of the other techniques. The first interest was the EVA sample itself which was already known to show some type of morphological change when heated. This material was heated at 2K min\(^{-1}\) from 313.2 to 343.2 K and the results are shown in Figure 7.1. This clearly shows crystalline structure at 313.2 K which accounts for the turbidity seen in the bulk. As the sample is heated this structure starts to disappear until 343.2 K when it either melts completely or is no longer large enough to be resolved. The turbidimetry work, chapter 3.5, showed that EVA became significantly clearer at approximately 326.2 K, yet this micrograph shows that some structure is still present at 333.2 K. \(C_{14}\) FVA was found to be optically transparent between 303.2 and 373.2 K. Two blends of differing composition were prepared by mixing the two copolymers from the bulk at room temperature and the results are described below.

Figures 7.2 a & b: Blend 1 - \{49.4% EVA (w/w)\}

These two figures show the behaviour of the blend as it was heated from 313.2 to 373.2 K at 5 K min\(^{-1}\). The mottled structure of EVA is easily seen against the formless FVA. As the temperature is increased both materials begin to expand although they remain discrete and the structure of EVA is still apparent up to 353.9 K. If the two final frames, at 363.2 and 373.3 K respectively, are studied carefully it can be seen that the phase boundary is still present. These micrographs show that at this composition of blend these materials are not miscible at temperatures between 313.2 and 373.2 K.

Figure 7.2 c: Blend 1 - Annealed at 373.2 K.

These micrographs feature Blend 1 after being annealed at 373.2 K for 10 minutes. It was thought that this apparent immiscibility may not have been a thermodynamic effect but may have arisen from poor dispersion of the polymers during the mixing process and the low mobility of these materials in the melt. To investigate this possibility another sample of Blend 1 was pretreated thermally and then heated at 5K min\(^{-1}\) from 303.2 to 373.3 K. The first image shows that after being annealed the polymers are considerably more disperse and that the EVA existed both as large mottled aggregates and small, dark circular areas. When this sample was heated it retained this general structure to 373.2 K, suggesting that these polymers are immiscible.
Figure 7.3 : Blend 2 - {16.7% EVA (w/w)}

The IGC results at 353.2 K produced negative polymer-polymer interaction parameters for both blend compositions below 44% EVA thus suggesting that the polymers were miscible under these conditions. Consequently a FVA rich blend was prepared to investigate this predicted miscibility. This blend was prepared directly from the bulk with neither polymer having any thermal history. The EVA is the dark crystalline material. As the sample was heated the EVA began to melt forming discrete circular structures. These micrographs clearly show again that these materials are immiscible under these conditions, contrary to the IGC findings.

Figure 7.4 : Blend 2 - Solution cast from chloroform

This experiment was the final attempt to observe the miscibility predicted by the IGC data. As the polymers were dissolved in chloroform before being used in the IGC experiments it was thought that this may have influenced the blend morphology. Another sample of Blend 2 was dissolved in the minimum volume of CHCl₃ and cast onto a glass cover slip. The solvent was left to evaporate naturally. From examination of the first image it is apparent that the polymers exist as a highly disperse two-phase structure after being cast from solution. The remaining micrographs show that these materials are still immiscible after being heated to 364.3 K.
7.5 Discussion

From the micrographs on the previous pages it is apparent that these material were immiscible under the conditions pertaining to this work. These results are considered reliable because the polymers neither formed two discrete layers on the microscope slide, (since both could be seen simultaneously), nor did there appear to be any change in the macroscopic surface area of each component which would have occurred had a small two-phase structure been formed. The significance of these experiments is discussed in Chapter 9.

7.6 REFERENCE

Chapter 8  Simulation of the Phase Boundary

8.1  Introduction

Many authors have tried to simulate theoretically the experimentally observed miscibility limits of various polymer mixtures using either a modified lattice model\(^{(6-8)}\) or Prigogine-Flory's equation of state\(^{(5-8)}\). The latter approach obtains a polymer-polymer interaction parameter, \(X_{23}\), by fitting to heat of mixing data. The equation of state for the spinodal condition also contains a corresponding entropic interaction parameter, defined as \(Q_{23}\). These enthalpic and entropic interaction parameters can be related via a free energy parameter, \(\bar{X}_{23}\), in an expression which is analogous to the classical expansion for the Gibbs free energy,

\[
\bar{X}_{23} = X_{23} - T \bar{V} Q_{23}
\]  \hspace{1cm} (8.1)

and,

\[
\Delta G = \Delta H - T \Delta S
\]  \hspace{1cm} (8.2)

In the majority of references cited above the spinodal boundary has been simulated by evaluating \(X_{23}\) from heat of mixing measurements and then fitting the experimentally determined spinodal to the theoretical spinodal by adjusting the value of \(Q_{23}\). Since \(Q_{23}\) has no defined physical significance, i.e. it was not part of the original equation of state concept but was introduced subsequently to allow for excess entropic effects which had been observed experimentally, and through its continued use as a fitting parameter, it is now generally considered as nothing more than a 'fudge factor'. However, it is also generally accepted that spinodal boundaries which are obtained from the original equation of state, i.e. with \(Q_{23} = 0\), commonly show very poor agreement with experimental cloud point curves, from which it can be concluded that the original model of the entropic contribution to the partition function is inadequate. Since any experiment, with the exception of calorimetry, which can be used to calculate a polymer-polymer interaction parameter, is following a free energy change the resulting interaction parameter is \(\bar{X}_{23}\). Thus by using calorimetry in conjunction with another technique, for example IGC or vapour sorption, both \(X_{23}\) and \(\bar{X}_{23}\) can be evaluated, and, from equation 8.1, \(Q_{23}\) can be calculated directly.

8.2  Procedure

The best results are obtained from Prigogine-Flory's equation of state when PVT data for pure components are available. However, an analysis is still
possible if other physical information is known about both the pure components and the binary mixture. These parameters are outlined below.

Pure Component Parameters

1. Specific volume, $v$

2. Surface area to unit core volume ratio, $s_1/s_2$

3. Thermal expansion coefficient, $\alpha$

4. Thermal pressure coefficient, $\gamma$

Mixture Parameters

5. Reduced volume, $\tilde{v}$

6. Enthalpic interaction term, $X_{23}$

7. Free energy interaction parameter, $\tilde{X}_{23}$

There are a variety of routes available to obtain these parameters, e.g.,

1. Specific volume, $v$

Specific volumes are usually obtained from reciprocal density values, $v = 1/\rho$, measured either by equal density titration or pycnometry, and some values are available in the literature\textsuperscript{3,10}. In this work, a digital densitometer, (described in section 3.3), was used to determine the density of both pure components and seven mixtures of varying composition for temperatures in the range 303 to 333K.

2. Surface area to unit core volume ratio, $s_1/s_2$

This ratio has a significant effect only when $X_{23}$ or $Q_{23}$ are also large, in which cases it acts to skew the spinodal boundary, and it is generally accepted that a rough approximation of its value is adequate under most circumstances\textsuperscript{21}. There are a selection of methods available to estimate this ratio, e.g.

2.1. The tabulated results of Bondi\textsuperscript{11}.

Reference (11) defines the van der Waals volume of a molecule as that which is impenetrable to other species with normal thermal energies, and quotes the corresponding surface area.
These data are tabulated as group contributions and by dissecting the defined segment of the polymer of interest into its constituent parts, a total value of the surface area to volume ratio can be obtained. It should be noted that these values were originally intended to enable the van der Waals volumes and radii of small molecules to be estimated and were not intended for application to polymeric structures. It should also be noted that it is the $s_3/s_2$ ratio of the segment which is calculated and not that of an entire chain, thus no chain or steric effects are considered in the estimation.

(2.2) Casting shadows$^{(12-17,19)}$.

This technique involves postulating a geometrical model of the molecule of interest, e.g. right cylinders for n-alkanes and a right cylinder with hemispherical caps for diphenyl$^{(19)}$, and casting the shadow of this model, in a variety of orientations, and determining an average projected area. By assuming that small molecules are essentially spherical and polymer molecules are cylindrical the ratio $s_3/s_2$ can be determined.

(2.3) The equation of Abe and Flory$^{(18,19)}$

$$s_3/s_4 = (r_3/r_2)^{-1/3} = (v_3^*/v_2^*)^{-1/3}$$

(8.3)

This relation is based on the assumption that the number of contact sites per molecule is proportional to the surface area of a sphere of the same hard core volume. Although this equation was originally intended to describe small, non-polar molecules, it does serve as an approximate basis for macromolecular analyses.

Results from these traditional methods, 2.1, 2.2 and 2.3 usually show poor agreement and the majority of previous workers have used some type of mean value. This work used the commercially available molecular modelling software COSMIC to estimate the value of $s_3/s_2$. This involved entering the structure of each polymeric segment into the program and obtaining the most favourable conformation of this unit by minimising the energetic effects. The software then calculated the surface area and volume of this optimal conformation. The results obtained from this approach are compared with those from the more traditional routes overleaf,
Comparable estimations of ratio of surface area to volume for the EVA/FVA mixture

<table>
<thead>
<tr>
<th>Method</th>
<th>s_3/s_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bondi</td>
<td>0.997</td>
</tr>
<tr>
<td>Abe-Flory</td>
<td>1.473</td>
</tr>
<tr>
<td>Cosmic</td>
<td>1.105</td>
</tr>
</tbody>
</table>

Since the value of s_3/s_2 determined by COSMIC lies in between the other estimations it was assumed to be at least as reliable. The value of this ratio is significant in both the determination of mixture miscibility and the shape of the resulting phase boundary.

(3) Thermal Expansion Coefficient, $\alpha$

The thermal expansion coefficient is defined as,

$$\alpha \equiv \frac{1}{v} \left[ \frac{\partial v}{\partial T} \right]_p$$

and thus differentiation of the specific volume as a function of temperature data will yield $\alpha$. Specific volume was found to be substantially linear with respect to both composition and temperature for both the pure components and the EVA/FVA mixtures and the following expression was developed in section 3.3, to characterise these functions,

$$v = (b_0 + b_1T) + (c_0 + c_1T + c_2T^2)w$$

(3.3)

where the numerical values of the coefficients and the units are as given on page 51.
By differentiating equation 3.3 with respect to temperature,

\[ \alpha = \left( b_1 + (c_1 + 2c_2T)w \right)/\nu \]  

(8.4)

Using this relationship the thermal expansion coefficient was calculated for each composition, at each temperature, as required.

(4) Thermal Pressure Coefficient, \( \gamma \)

The thermal pressure coefficient is defined as,

\[ \gamma = \left( \frac{\partial P}{\partial T} \right)_\nu \]  

(2.39)

Although direct measurements of \( \gamma \) have been carried out on polymeric materials\(^{20,21}\) the experiments are difficult and generally avoided since the term is only weakly influential in the equation of state\(^{30}\).

The most common route used to evaluate \( \gamma \) is via the Hildebrand solubility parameter, \( \delta \). The cohesive energy density, (CED), of a material is a measure of its molecular cohesion and this is related algebraically to the solubility parameter and thermal pressure coefficient as follows,

\[ P_i = T(\alpha/\beta_T) = T\gamma \]  

(8.5)

and \( P_i = m(\text{CED}) \) \hspace{1cm} (8.6)

but \( \delta^2 = (\text{CED}) \) \hspace{1cm} (8.7)

hence

\[ m\delta^2 = T\gamma \]  

(8.8)

i.e.,

\[ \gamma = \alpha/\beta_T \]  

(8.9)

where,

\[ \alpha = \text{thermal expansion coefficient, K}^{-1} \]

\[ \beta_T = \text{isothermal compressibility, atm}^{-1} \]
T = temperature, K
m = proportionality coefficient which is unity for polymers
Pi = pressure, atm

The solubility parameter of a polymer can be calculated from the sum of its group contributions in accordance with the theory of Small\(^{(22)}\). This theory assumes that the solubility parameter is a linear function of an additive structural constant, \(f_i\), defined as the 'molar attraction constant',

\[
\delta = \rho \sum f_i / M \tag{8.10}
\]

where,

\[
M = \text{molecular weight of a repeat unit, g}
\]

\[
\rho = \text{density, g cm}^{-3}
\]

Small evaluated the molar attraction constants for a selection of common functional groups and chemical sequences from vapour pressure and heat of vaporisation data. These original data have subsequently been improved by Hoy\(^{(23)}\) and Van Krevelen\(^{(24)}\).

The solubility parameters and thermal pressure coefficients of EVA and FVA were evaluated at 353K as,

Table 8.1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(\delta / (\text{cal cm}^{-3})^{0.5})</th>
<th>(\gamma / \text{atm K}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA</td>
<td>8.05</td>
<td>0.1835</td>
</tr>
<tr>
<td>FVA</td>
<td>8.07</td>
<td>0.1844</td>
</tr>
</tbody>
</table>

The temperature dependence of \(\gamma\) is given by,

\[
\gamma = \gamma_o - \gamma_o(1+2\alpha_oT)\Delta T/T \tag{8.11}
\]

or it can be calculated directly from density data if they are available.
Mixture Parameters

(5) Reduced volume, $\tilde{\nu}$

The reduced volume is a measure of the volume change that occurs on mixing two materials and is related to the hard core volume by,

$$\tilde{\nu} = \nu/\nu^*$$  (2.33)

It is commonly obtained by measuring the density of a number of blends of differing compositions and fitting these data to provide a continuous function with respect to composition. The density data obtained in this work were substantially linear with respect to composition, (Table 3.3 and Figure 3.3)

(6) Enthalpic Interaction Parameter, $X_{23}$

This parameter represents the difference in energies between homogeneous and heterogeneous contacts in the mixture and thus should be independent of both temperature and composition. It is evaluated by fitting equation 2.52c to experimental heat of mixing data using a non-linear least squares procedure,

$$\Delta H_{\text{mix}} = n_2 V_1^* \left( \phi_3 X_{23} / \tilde{\nu}_2 + P_1^* (1/\tilde{\nu} - 1/\tilde{\nu}_2) - (\phi_2^* / \phi_1^*) P_2^* (1/\tilde{\nu} - 1/\tilde{\nu}_3) \right)$$  (2.52c)

where $X_{23}$ is the adjustable parameter. This has been carried out on the heat of mixing data obtained at 348.7K, described in chapter 5, and the results are quoted in Table 8.2. The recalculated values of $\Delta H_{\text{mix}}$ were obtained by re-inserting the value of $X_{23}$, obtained from the fit, into equation 2.52c and solving for $\Delta H_{\text{mix}}$. 
Table 8.2

Measured and recalculated heat of mixing values at 348.7K

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt.Fr.EVA</th>
<th>Measured $\Delta H_{mix}/10^{-2}$Jg$^{-1}$</th>
<th>Recalculated $\Delta H_{mix}/10^{-2}$Jg$^{-1}$</th>
<th>Difference $10^{-2}$Jg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.119</td>
<td>3.804</td>
<td>4.468</td>
<td>0.664</td>
</tr>
<tr>
<td>2</td>
<td>0.243</td>
<td>7.162</td>
<td>7.647</td>
<td>0.512</td>
</tr>
<tr>
<td>3</td>
<td>0.299</td>
<td>9.005</td>
<td>8.657</td>
<td>0.348</td>
</tr>
<tr>
<td>4</td>
<td>0.361</td>
<td>10.596</td>
<td>9.440</td>
<td>-1.156</td>
</tr>
<tr>
<td>5</td>
<td>0.475</td>
<td>10.077</td>
<td>10.025</td>
<td>0.052</td>
</tr>
<tr>
<td>6</td>
<td>0.479</td>
<td>10.047</td>
<td>10.026</td>
<td>0.021</td>
</tr>
<tr>
<td>7</td>
<td>0.635</td>
<td>9.496</td>
<td>9.068</td>
<td>-0.410</td>
</tr>
<tr>
<td>8</td>
<td>0.833</td>
<td>3.257</td>
<td>5.286</td>
<td>2.029</td>
</tr>
</tbody>
</table>

Fitted value of $X_{23} = 5.667$ bar

These data are displayed in Figure 8.1. Although heat of mixing measurements were also performed at 359.3K these data have not been used in the simulation of the phase boundary for two reasons. Firstly, by definition, $X_{23}$ should be independent of temperature and consequently the two sets of data should yield the same value of $X_{23}$, and secondly, owing to time constraints, only three experimental points were recorded at 359.3K and this was felt to be insufficient to justify the fitting procedure. The $X_{23}$ value obtained at 348.7K, converted to Jcm$^{-3}$, is compared to some literature values in Table 8.3.
Heat of Mixing for EVA/FVA Mixture at 348.7K

Measured and Recalculated Values

Figure 8.1
Table 8.3
Comparison of interaction parameter values obtained from heat of mixing measurements

<table>
<thead>
<tr>
<th>Polymer Mixture</th>
<th>$\Delta X_{23}$ /J cm$^{-3}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA/FVA (tetraglyme)</td>
<td>0.567 (348.7 K)</td>
<td>this work</td>
</tr>
<tr>
<td>(4-phenoxy phenyl phenyl sulphone)</td>
<td>-40.00 (363.2 K)</td>
<td>25</td>
</tr>
<tr>
<td>(Cereclor 52) (2-ethylhexyl acetate)</td>
<td>-2.63 (363.2 K)</td>
<td>7</td>
</tr>
</tbody>
</table>

where,
tetraglyme - model compound for poly(ethylene oxide), PEO: 4-phenoxy phenyl phenylsulphone - model compound for poly(ether sulphone), PES: Cereclor 52 - model compound for chlorinated poly(ethylene), CPE: 2-ethylhexyl acetate - model compound for poly(ethylene - vinyl acetate) copolymer, EVA.

It should be noted that both PEO/PES and CPE/EVA mixtures are known to be miscible, and undergo lower critical solution type phase separation, and that the heats of mixing values quoted above are those of low molecular weight analogues, and not the polymers themselves. When allowances for these differences are made, the $X_{23}$ value obtained for this immiscible, polymeric system appears to have the correct sign and order of magnitude.

(6) Free Energy Interaction Parameter, $\bar{X}_{23}$
The free energy interaction parameter can be obtained from a variety of experiments, e.g. melting point depression (25), solvent vapour sorption (26) or
inverse phase gas chromatography\(^{(1,27)}\). This work has used the data from the IGC experiments detailed in chapter 4 because of the volume of this information.

The Flory-Huggins-Chang-Miller theory polymer-polymer interaction parameter, \( \tilde{x}_{23} \), is given by equation 4.7,

\[
\tilde{x}_{23} = \frac{V_2}{V_1} \left\{ \frac{1}{\phi_2 \phi_3} \ln \left( \frac{V_{gc,23}}{w_2 V_2 + w_3 V_3} \right) - \phi_2 \ln \left( \frac{V_{gc,22}}{V_2} \right) - \phi_2 \ln \left( \frac{V_{gc,23}}{V_2} \right) \right\}
\]

where,

\( \tilde{x}_{23} \) = true polymer-polymer interaction parameter.

\( V_1 \) = molar volume of solvent, cm\(^3\)mol\(^{-1}\)

\( V_2 \) = molar volume of polymer, cm\(^3\)mol\(^{-1}\)

\( \phi_i \) = volume fraction of component \('i'\)

\( v_i \) = specific volume of component \('i'\), cm\(^3\)g\(^{-1}\)

\( w_i \) = weight fraction of component \('i'\) in blend

To convert equation 4.7 into the corresponding equation of state expression it is necessary to firstly replace the lattice theory volume fraction with the EOS hard core volume fractions, \( \phi_i^* \),

\[
\phi_i^* \equiv 1 - \phi_2^* \equiv N_i r_i / (N_i r_i + N_2 r_2)
\]

or,

\[
\phi_i^* = w_i V_i^* / (w_1 V_1^* + w_2 V_2^*)
\]

where,

\( w_i \) = weight fraction of component \('i'\)

\( V_i^* \) = molar hard core volume of component \('i'\)

\( r_i \) = number of segments per molecule

\( N_i \) = number of molecules
As mentioned in chapter 2, the hard core volume fraction is defined as the volume which a segment of polymer would occupy at 0 K, and is more useful than a normal volume fraction because it is independent of temperature and pressure.

Since the characteristic dimension in EOS theory is an arbitrary segment of a polymer chain and the enthalpic contribution is based on the relative surface areas, it is convenient to introduce the surface fraction, \( \theta_2 \),

\[
\theta_2 \equiv 1 - \theta_3 \equiv \frac{N_2 r_2 s_2}{(N_2 r_2 s_2 + N_3 r_3 s_3)} \tag{2.46a}
\]

or,

\[
\theta_2 \equiv \frac{(s_2/s_2) \phi^*_2}{(s_3/s_2) \phi^*_2 + \phi^*_3} \tag{2.46b}
\]

where, \( s_2/s_2 = \) surface area per unit volume ratio

The non-combinatorial contribution to mixing is described by the parameter \( \chi^* \) and this can be easily calculated by reformulating equations 4.5a, 4.5b and 4.5c in terms of the hard core parameters, i.e.,

\[
\tilde{\chi}_{12} = \ln \left( \frac{RTv_2^*}{V_{gc} V_1 P_1^o} \right) - \left[ 1 - \frac{V_1}{(Mn)_2 v_2^*} \right] - \frac{P_1^o}{RT} \left( B_{11} - V_1 \right) \tag{8.11}
\]

\[
\tilde{\chi}_{13} = \ln \left( \frac{RTv_3^*}{V_{gc} V_1 P_1^o} \right) - \left[ 1 - \frac{V_1}{(Mn)_3 v_3^*} \right] - \frac{P_1^o}{RT} \left( B_{11} - V_1 \right) \tag{8.12}
\]

\[
\tilde{\chi}_{123} = \ln \left( \frac{RT(w_2v_2^* + w_3v_3^*)}{V_{gc23} V_1 P_1^o} \right) - \left[ 1 - \frac{V_1}{(Mn)_2 v_2^*} \right] \theta_2 - \left[ 1 - \frac{V_1}{(Mn)_3 v_3^*} \right] \theta_3 - \frac{P_1^o}{RT} \left( B_{11} - V_1 \right) \tag{8.13}
\]

\( \tilde{X}_{23} \) and the free volume on mixing contribution can be related explicitly to \( \chi^* \) by the corresponding states\(^{28,29}\) form of the the EOS theory,
\[ RT \chi_{(12)}^{*} = \frac{v_{1}^{*} \bar{X}_{12}}{\bar{v}_{2}} + P_{1}^{*} v_{1}^{*} \left[ \frac{1}{\bar{v}_{1}} - \frac{1}{\bar{v}_{2}} + 3 T_{1} \ln \frac{\bar{v}_{1}^{1/3} - 1}{\bar{v}_{2}^{1/3} - 1} \right] \]

(8.14)

Similarly, for a ternary system with a mixed stationary phase, equation 8.14 becomes,

\[ RT \chi_{(123)}^{*} = \frac{s_{1} v_{1}^{*}}{\bar{v}} \left( \frac{\bar{X}_{12}}{s_{1}} \theta_{2} + \frac{\bar{X}_{13}}{s_{1}} \theta_{3} - \frac{\bar{X}_{123}}{s_{2}} \theta_{2} \theta_{3} \right) \]

\[ + P_{1}^{*} v_{1}^{*} \left[ \frac{1}{\bar{v}_{1}} - \frac{1}{\bar{v}} + 3 T_{1} \ln \frac{\bar{v}_{1}^{1/3} - 1}{\bar{v}^{1/3} - 1} \right] \]

(8.15)

where,

subscript 1 refers to the IGC probe species, with 2 and 3 referring to EVA and FVA respectively in the polymer mixture.

\[ R = \text{Universal gas constant, (82.057 cm}^{-3} \text{ atm K}^{-1} \text{ mol}^{-1}) \]

\[ T = \text{absolute temperature, K} \]

\[ s_{i} = \text{surface area to volume ratio of component } i', \text{ m}^{-1} \]

\[ \theta_{i} = \text{surface fraction of component } i' \text{ in the stationary phase} \]

The polymer solvent interaction parameters, \( \bar{X}_{12} \) and \( \bar{X}_{13} \), are evaluated from the appropriate versions of equation 8.14. The value of \( s_{i} \), i.e. the surface to volume ratio for each solvent probe was also obtained from the COSMIC molecular modelling package described above and the results are quoted in Table 8.4.
Table 8.4

Values of the surface area to volume ratio for the solvents used in the IGC experiments

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$s_r / \text{Å} $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>2.294</td>
</tr>
<tr>
<td>Hexane</td>
<td>2.233</td>
</tr>
<tr>
<td>Heptane</td>
<td>2.057</td>
</tr>
<tr>
<td>Octane</td>
<td>2.200</td>
</tr>
<tr>
<td>Methanol</td>
<td>2.391</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>2.447</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.295</td>
</tr>
<tr>
<td>Methylethylketone</td>
<td>2.324</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>2.346</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>2.406</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>1.986</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.878</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>1.829</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.398</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.589</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.451</td>
</tr>
</tbody>
</table>

Once all of this information has been obtained, equation 8.15 can be solved for $\bar{x}_{23}$.

8.2 Evaluation of equation of state parameters

The EOS parameters of both the pure components and the mixture can now be derived from the physical information detailed above. The following is a brief outline of these calculations and the interdependence of these parameters.
8.2.1 The reduced volume, $\tilde{v}$, and hard core volume, $v^*$

The reduced volumes of the pure components and the mixture were calculated from equation 2.38, via the thermal expansion coefficients,

$$
\tilde{v} = \left( 1 + \frac{\alpha T}{3 (1 + \alpha_T)} \right)
$$

(2.38)

thus, $\tilde{v}_2$, $\tilde{v}_3$ and $\tilde{v}_{23}$ were obtained. Equation 2.33 relates the hard core volume of the pure components and the mixture to the reduced parameters.

$$
\tilde{v} = v/v^*
$$

(2.33)

or $$
v^* = v/\tilde{v}
$$

8.2.2 Hard core pressure, $P^*$

Equation 2.40 was used to calculate the hard core pressures of the pure components from thermal pressure coefficients and the reduced volumes.

$$
P^* = \gamma T\tilde{v}^2
$$

(2.40)

The hard core pressure of the mixture is related to the pure component values by equation 2.47,

$$
P^* = \phi_2 P_{2}^* + \phi_3 P_{3}^* - \phi_2 \phi_3 X_{23}
$$

(2.47)

8.2.3 Hard core temperature, $T^*$

The hard core temperature was obtained by solving the equation of state, equation 2.36, assuming the pressure to be substantially zero for the reduced temperatures,

$$
\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}
$$

(2.36)

and substituting these values into equation 2.34,

$$
\tilde{T} = T/T^*
$$

(2.34)

The hard core temperature of the mixture is related to the pure component values by equation 2.48,
\[
T^* = \frac{\phi_2 P_1^* + \phi_3 P_2^* - \phi_3 \theta_3 X_{23}}{\phi_2 P_1^*/T_1^* + \phi_3 P_2^*/T_2^*}
\] (2.48)

Once all of these parameters were evaluated the equation of state was used to predict the mixtures thermodynamic properties and behaviour.

8.3 Results

Tables 8.5 and 8.6 list the characteristic parameters of EVA and FVA respectively which have been calculated using the information and procedures outlined above.

**Table 8.5: EOS parameters for EVA - \( s_2 = 2.3251 \text{ Å} \)**

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>( v / \text{cm}^3 \text{ g}^{-1} )</th>
<th>( v^* / \text{cm}^3 \text{ g}^{-1} )</th>
<th>( T^* / \text{K} )</th>
<th>( P^* / \text{bar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>1.10456</td>
<td>0.88932</td>
<td>6293.3</td>
<td>4106.5</td>
</tr>
<tr>
<td>373</td>
<td>1.12269</td>
<td>0.89820</td>
<td>6508.4</td>
<td>3927.7</td>
</tr>
<tr>
<td>393</td>
<td>1.14083</td>
<td>0.90722</td>
<td>6723.8</td>
<td>3719.4</td>
</tr>
</tbody>
</table>

**Table 8.6: EOS parameters for FVA - \( s_3 = 2.0633 \text{ Å} \)**

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>( v / \text{cm}^3 \text{ g}^{-1} )</th>
<th>( v^* / \text{cm}^3 \text{ g}^{-1} )</th>
<th>( T^* / \text{K} )</th>
<th>( P^* / \text{bar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>1.09042</td>
<td>0.90087</td>
<td>6031.6</td>
<td>3909.5</td>
</tr>
<tr>
<td>373</td>
<td>1.10559</td>
<td>0.90775</td>
<td>7145.3</td>
<td>3776.8</td>
</tr>
<tr>
<td>393</td>
<td>1.12075</td>
<td>0.91477</td>
<td>7359.2</td>
<td>3621.0</td>
</tr>
</tbody>
</table>

To judge the reliability of these values the EVA results were compared with those in the literature for an EVA copolymer (EVA 45) and an EVA model compound OC-AC(7). However, the materials used in reference (7) had the following physical characteristics,

EVA copolymer: \( \tilde{M}_n = 37,700 \quad \tilde{M}_w = 256,000 \quad \tilde{M}_w/\tilde{M}_n = 6.79 \)

Model Compound: 1-methyl heptyl acetate, molecular weight = 172.3 g mol\(^{-1}\)
Since the EVA sample used in this work had a number average molecular weight one order of magnitude lower than that for the EVA sample described above, it was expected that its EOS properties would lie somewhere between those of the copolymer and the model compound. The comparison is shown in Table 8.7.

### Table 8.7

Comparison of EOS parameters for EVA45, OC-AC and EVA

<table>
<thead>
<tr>
<th>Material</th>
<th>T / K</th>
<th>( v / \text{cm}^3\text{g}^{-1} )</th>
<th>( v^* / \text{cm}^3\text{g}^{-1} )</th>
<th>T* / K</th>
<th>P* / bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA45</td>
<td>356.7</td>
<td>1.0636</td>
<td>0.9288</td>
<td>9250.3</td>
<td>3761.8</td>
</tr>
<tr>
<td>OC-AC</td>
<td>356.7</td>
<td>1.2442</td>
<td>0.9877</td>
<td>6067.2</td>
<td>2769.3</td>
</tr>
<tr>
<td>EVA</td>
<td>353</td>
<td>1.1046</td>
<td>0.8893</td>
<td>6293.3</td>
<td>4106.5</td>
</tr>
</tbody>
</table>

As anticipated, the specific volume and hard core characteristic temperature of the EVA fall between those of the EVA45 and the OC-AC. However the hard core characteristic volume and pressure do not. This discrepancy arises from the dependence of these terms on the reduced volume, \( \bar{v} \), and hence on the thermal expansion coefficient. The thermal expansion coefficient of the EVA was estimated, from the density-temperature measurements, to be an order of magnitude greater than that for either EVA45 or OC-AC,

\[
i.e. \quad \alpha_{(\text{EVA, } 353K)} = 7.52 \times 10^{-3} \text{ K}^{-1}
\]

\[
\alpha_{(\text{EVA45, } 367.7K)} = 4.51 \times 10^{-4} \text{ K}^{-1}
\]

\[
\alpha_{(\text{OC--AC, } 367.7K)} = 8.85 \times 10^{-4} \text{ K}^{-1}
\]

The \( \alpha \) values of EVA45 and OC-AC were determined by dilatometry at a single temperature. It was concluded that this discrepancy in magnitude must have arisen from the method of estimation although this could not be verified as no reference experiments were employed.

Equation of state theory gives the chemical potential of component 2 as,

\[
\frac{\partial}{\partial \phi_2} \left( \frac{\Delta \mu_1}{RT} \right)_{T,P} = 0
\]  

(8.16)
This equation is then used to derive the phase boundary from the spinodal condition defined as,

\[
\frac{1}{\phi_1} + 1 - \frac{r_1}{r_2} - \frac{P_1 V'_1}{RT'_1} \frac{\partial \bar{V}}{\partial \phi_2} \frac{1}{\bar{V}^{2/3}(\bar{V}^{1/3} - 1)} + \frac{P_1 V'_1}{RT'_{sp}} \frac{\partial \bar{V}}{\partial \phi_2} \left( \frac{1}{\bar{V}^2} - \bar{P}_1 \right)
\]

\[
+ \frac{V'_1 X_{12}}{RT'_{sp}} \left( \frac{2 \theta_2 \phi_2^2}{\bar{V}^2 \phi_2} - \frac{\phi_2^2}{\bar{V}^2} \right) - \frac{V'_1 Q_{12}}{RT'_{sp}} \frac{2 \theta_1 \phi_2^2}{\bar{V}^2 \phi_2} = 0
\]

(8.17)

where the partial derivatives are given in the equations below

\[
\frac{\partial \bar{V}}{\partial \phi_2} = \left( \frac{\partial \bar{P}}{\partial \phi_2} - \frac{1}{T} \left( \bar{P} + \frac{1}{\bar{V}^3} \right) \frac{\partial \bar{T}}{\partial \phi_2} \right)
\]

\[
= \left( \frac{2}{\bar{V}^3} - \frac{T}{\bar{V}^{2/3}} \frac{2}{3} \frac{1}{\bar{V}^{5/3}(\bar{V}^{1/3} - 1)} \right)
\]

\[
\frac{\partial \bar{P}}{\partial \phi_2} = \frac{P}{P^2} \left( P'_1 - P'_2 + X_{12} \theta_2 (\phi_1 / \phi_2 - 1) \right)
\]

\[
\frac{\partial \bar{T}}{\partial \phi_2} = \frac{T}{P} \left( \frac{P'_2}{T'_2} - \frac{P'_1}{T'_1} \right) + \frac{T}{P^*} \left( P'_1 - P'_2 + X_{12} \theta_2 (\phi_1 / \phi_2 - 1) \right)
\]

This equation was solved iteratively using the technique known as inverse parabolic interpolation in which a root of an equation is first bracketed and thereafter a parabola is fitted to successive error terms for the three 'best' trial values until the absolute value of the error is either minimised or becomes less than some preset value. The routine used was a Modula 2 version of the Pascal procedure known as Brent's method and which is fully described in Chapter 10, pp 318-322 of 'Numerical Recipes in Pascal' (31). In this particular
case a mixture composition was chosen, for which \( X_{23} \) and \( Q_{23} \) were known and the reduced parameters and composition variables at successive trial temperatures were evaluated; when the error term had been reduced to a suitable value the corresponding trial temperature was taken as \( T_{sp'} \). This process was repeated for the mixture compositions for which data were available. Collectively these solutions represent the spinodal boundary.

The results are listed in Tables 8.8, 8.9 and 8.10. In the interests of brevity and clarity the \( X_{23}, Q_{23} \) and spinodal temperatures calculated for each solvent have been combined as arithmetic means for each composition at each temperature: a full listing of the individual results is given in Appendix 1.

The standard deviation in interaction parameter values from different solvents has been calculated, and is displayed in figures 8.2, 8.3 and 8.4 as an error bar. It should be noted that a spinodal temperature is not quoted for the mixture of weight fraction 0.2515 EVA at 353K, because equation 8.18 would not converge between limits of 0 and 5000K for the \( X_{23} \) and \( Q_{23} \) values obtained.

### Table 8.8

Mean values of \( \bar{X}_{23}, Q_{23} \) and Spinodal temperature for mixtures at 353K

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>( \bar{X}_{23} )/bar</th>
<th>( Q_{23} )/bar K(^{-1} )</th>
<th>( T_{spin} )/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>-8.25</td>
<td>-0.1292</td>
<td>6.32</td>
</tr>
<tr>
<td>0.2515</td>
<td>-500.13</td>
<td>1.1750</td>
<td>-</td>
</tr>
<tr>
<td>0.2905</td>
<td>324.56</td>
<td>-0.7404</td>
<td>7.33</td>
</tr>
<tr>
<td>0.3588</td>
<td>446.40</td>
<td>-1.0214</td>
<td>5.88</td>
</tr>
<tr>
<td>0.5000</td>
<td>306.49</td>
<td>-0.6947</td>
<td>8.79</td>
</tr>
<tr>
<td>0.7496</td>
<td>212.31</td>
<td>-0.4742</td>
<td>11.52</td>
</tr>
<tr>
<td>0.8033</td>
<td>-299.59</td>
<td>0.6991</td>
<td>51.37</td>
</tr>
</tbody>
</table>
Table 8.9

Mean $\bar{X}_{23}$, $Q_{23}$ and Spinodal temperatures for the EVA/FVA mixture at 373K

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>35.07</td>
<td>0.0892</td>
<td>15.20</td>
</tr>
<tr>
<td>0.2515</td>
<td>300.10</td>
<td>-0.6436</td>
<td>9.62</td>
</tr>
<tr>
<td>0.2905</td>
<td>235.68</td>
<td>-0.5023</td>
<td>11.40</td>
</tr>
<tr>
<td>0.3588</td>
<td>183.84</td>
<td>-0.3884</td>
<td>16.24</td>
</tr>
<tr>
<td>0.5000</td>
<td>448.80</td>
<td>-0.9622</td>
<td>6.81</td>
</tr>
<tr>
<td>0.7496</td>
<td>606.83</td>
<td>-1.2971</td>
<td>4.87</td>
</tr>
</tbody>
</table>

Table 8.10

Mean values of $\bar{X}_{23}$, $Q_{23}$ and Spinodal temperature for mixture at 393K

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>164.56</td>
<td>-0.3292</td>
<td>11.45</td>
</tr>
<tr>
<td>0.2515</td>
<td>186.54</td>
<td>-0.3731</td>
<td>18.12</td>
</tr>
<tr>
<td>0.2905</td>
<td>338.31</td>
<td>-0.6853</td>
<td>8.35</td>
</tr>
<tr>
<td>0.3588</td>
<td>417.18</td>
<td>-1.1233</td>
<td>7.21</td>
</tr>
<tr>
<td>0.5000</td>
<td>574.88</td>
<td>-1.1661</td>
<td>6.81</td>
</tr>
<tr>
<td>0.7496</td>
<td>691.91</td>
<td>-1.3969</td>
<td>4.25</td>
</tr>
</tbody>
</table>

The $\bar{X}_{23}$ data at 353, 373 and 393K are displayed as functions of EVA weight fraction in Figures 8.2, 8.3 and 8.4 respectively, and the simulated spinodals are shown in Figures 8.5, 8.6 and 8.7.
Mean values of $X_{23}$ for EVA/FVA mixture at 353K

Equation of state analysis of IGC results

Figure 8.2
Mean values of X23 for EVA/FVA mixture at 373K

Equation of state analysis of IGC results

Figure 8.3
Mean values of X23 for EVA/FVA mixture at 393K

Equation of state analysis of IGC results

Figure 8.4
Simulated Spinodal from 353K Data
(Quadratic Fit)

Temperature/K

Mass Fraction EVA

Figure 8.5
Simulated Spinodal from 373K Data

(Quadratic Fit)

Temperature/K

Mass Fraction EVA

Figure 8.6
Simulated Spinodal from 393K Data

(Quadratic Fit)

Figure 8.7
8.4 Discussion

The previous results have shown that the EOS can be used to predict the thermodynamics and miscibility limits of a polymer mixture and this discussion has been subdivided into an analysis of the dominant parameters in this mathematical model, the context and validity of the predictions that have been made and the reliability of the data upon which these predictions were based.

McMaster\(^{(30)}\) demonstrated that a general form of Flory's EOS was capable of predicting both LCST and UCST behaviour, either independently or simultaneously, in theoretical polymer blends and that the simulated phase boundary could be radically altered by varying some state parameters. Olabisi\(^{(1)}\) verified some of McMaster's conclusions from studies of a blend of poly(\(\epsilon\)-caprolactone) and poly(vinyl chloride) and thus some alterations to the state parameter values were performed in this work to find out whether this model responded in a similar manner. It should be stressed that the envelope of the model was not fully characterised owing to its inherent limitations and the unlikely predictions which were obtained from the experimental data.

8.4.1 The Sensitivity of the Model

In order to understand the relative influence of some of the physical terms in this model, a series of variations was performed and the net effect on the predicted spinodal temperature recorded.

8.4.1.1 Number average molecular weight, \(M_n\)

The number average molecular weights of the components do not feature directly in the spinodal equation. Instead their influence is exerted via the interaction parameters. Three scenarios were considered,

(a) \(M_{EVA} = 10400\) \hspace{1cm} \(M_{FVA} = 10400\)

(b) \(M_{EVA} = 10000\) \hspace{1cm} \(M_{FVA} = 20000\)

(c) \(M_{EVA} = 20000\) \hspace{1cm} \(M_{FVA} = 10000\)
The recalculated data are listed in Tables 8.11, 8.12 and 8.13 respectively and are shown graphically in Figure 8.8.

Table 8.11: Scenario (a)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2390</td>
<td>202.9</td>
<td>-0.4314</td>
<td>14.43</td>
</tr>
<tr>
<td>0.5151</td>
<td>303.3</td>
<td>-0.6461</td>
<td>9.41</td>
</tr>
<tr>
<td>0.5642</td>
<td>302.6</td>
<td>-0.6438</td>
<td>9.42</td>
</tr>
<tr>
<td>0.6389</td>
<td>310.1</td>
<td>-0.6588</td>
<td>9.13</td>
</tr>
<tr>
<td>0.7597</td>
<td>622.4</td>
<td>-1.3304</td>
<td>4.34</td>
</tr>
<tr>
<td>0.9044</td>
<td>1401.8</td>
<td>-3.095</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Table 8.12: Scenario (b)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1357</td>
<td>231.25</td>
<td>-0.4947</td>
<td>12.02</td>
</tr>
<tr>
<td>0.3469</td>
<td>261.4</td>
<td>-0.5577</td>
<td>11.01</td>
</tr>
<tr>
<td>0.3930</td>
<td>242.4</td>
<td>-0.5156</td>
<td>11.99</td>
</tr>
<tr>
<td>0.4694</td>
<td>288.9</td>
<td>-0.4724</td>
<td>13.17</td>
</tr>
<tr>
<td>0.6125</td>
<td>415.8</td>
<td>-0.8881</td>
<td>6.67</td>
</tr>
<tr>
<td>0.8236</td>
<td>786.8</td>
<td>-1.6821</td>
<td>3.38</td>
</tr>
</tbody>
</table>
Effect of Varying the Molecular Weight
Cyclohexane data at 373K

Figure 8.8
<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3558</td>
<td>214.7</td>
<td>-0.4553</td>
<td>14.23</td>
</tr>
<tr>
<td>0.6800</td>
<td>422.6</td>
<td>-0.9013</td>
<td>6.69</td>
</tr>
<tr>
<td>0.7216</td>
<td>445.9</td>
<td>-0.9505</td>
<td>6.31</td>
</tr>
<tr>
<td>0.7786</td>
<td>493.7</td>
<td>-1.0522</td>
<td>5.64</td>
</tr>
<tr>
<td>0.8634</td>
<td>1052.8</td>
<td>-2.2527</td>
<td>2.55</td>
</tr>
<tr>
<td>0.9498</td>
<td>2636.6</td>
<td>-5.6478</td>
<td>0.99</td>
</tr>
</tbody>
</table>

McMaster's\textsuperscript{(30)} EOS model predicted that increasing the molecular weight of one component of the blend would reduce the mutual solubility, manifested in the corresponding spinodal temperature, and skew the phase boundary to the side of increased mass. The results obtained here also exhibit this skewing effect as the molecular weight of each component was increased but very little change was observed in the overall temperature of phase separation.

### 8.4.1.2 The Surface Area to Volume ratio ($s_2/s_3$) of the blend components.

Three scenarios were considered,

(a) $s_2 = 2.0 \times 10^{-10}$; \hspace{1cm} $s_3 = 2.0 \times 10^{-10}$; \hspace{1cm} $s_2/s_3 = 1$

(b) $s_2 = 1.0 \times 10^{-10}$; \hspace{1cm} $s_3 = 2.0 \times 10^{-10}$; \hspace{1cm} $s_2/s_3 = 0.5$

(c) $s_2 = 2.0 \times 10^{-10}$; \hspace{1cm} $s_3 = 1.0 \times 10^{-10}$; \hspace{1cm} $s_2/s_3 = 2$
The recalculated data are listed in Tables 8.14, 8.15 and 8.16 respectively and are shown graphically in Figure 8.9.

### Table 8.14: Scenario (a)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>115.0</td>
<td>-0.2402</td>
<td>11.83</td>
</tr>
<tr>
<td>0.2515</td>
<td>72.3</td>
<td>-0.1457</td>
<td>29.42</td>
</tr>
<tr>
<td>0.2905</td>
<td>44.1</td>
<td>-0.0840</td>
<td>44.62</td>
</tr>
<tr>
<td>0.3588</td>
<td>13.2</td>
<td>-0.0165</td>
<td>89.85</td>
</tr>
<tr>
<td>0.5000</td>
<td>75.2</td>
<td>-0.1512</td>
<td>32.17</td>
</tr>
<tr>
<td>0.7496</td>
<td>102.8</td>
<td>-0.2096</td>
<td>22.67</td>
</tr>
</tbody>
</table>

### Table 8.15: Scenario (b)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>236.8</td>
<td>-0.5075</td>
<td>8.78</td>
</tr>
<tr>
<td>0.2515</td>
<td>215.2</td>
<td>-0.4582</td>
<td>11.61</td>
</tr>
<tr>
<td>0.2905</td>
<td>183.8</td>
<td>-0.3891</td>
<td>13.69</td>
</tr>
<tr>
<td>0.3588</td>
<td>148.2</td>
<td>-0.3108</td>
<td>17.09</td>
</tr>
<tr>
<td>0.5000</td>
<td>274.1</td>
<td>-1.5830</td>
<td>9.39</td>
</tr>
<tr>
<td>0.7496</td>
<td>431.0</td>
<td>-0.9178</td>
<td>5.74</td>
</tr>
</tbody>
</table>
Effect of Varying the Surface Area to Volume Ratio

Cyclohexane data at 373K

Figure 8.9

Weight Fraction EVA

Zeta potential K

100.00
80.00
60.00
40.00
20.00
0.00

0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00

0 = \alpha = 1.0
0 = \beta = 0.5
0 = \gamma = 2.0
Table 8.16: Scenario (c)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>255.8</td>
<td>-0.5492</td>
<td>8.86</td>
</tr>
<tr>
<td>0.2515</td>
<td>300.2</td>
<td>-0.6439</td>
<td>8.43</td>
</tr>
<tr>
<td>0.2905</td>
<td>288.9</td>
<td>-0.6184</td>
<td>8.82</td>
</tr>
<tr>
<td>0.3588</td>
<td>279.8</td>
<td>-0.5977</td>
<td>9.16</td>
</tr>
<tr>
<td>0.5000</td>
<td>465.7</td>
<td>-1.0000</td>
<td>5.51</td>
</tr>
<tr>
<td>0.7496</td>
<td>843.2</td>
<td>-1.8070</td>
<td>2.86</td>
</tr>
</tbody>
</table>

Reference (30) reported that the relative magnitude of the surface area to volume ratio affects the symmetry of the phase boundary but only affects the spinodal temperature when the system also possesses a large enthalpic interaction parameter and Rostami$^{(8)}$ stated that an increasing $s_2/s_3$ ratio in conjunction with a constant negative value of $X_{23}$ introduced bimodality in the phase boundary. Increasing the surface area to volume ratio in this work caused suppression of the UCST behaviour in the phase boundary. These changes did not cause the position of the maximum to move.

8.4.1.3 The Thermal Expansion Coefficient

The spinodal condition is known to be extremely sensitive to the numerical value of the thermal expansion coefficient and this is confirmed by the results given by the current model. A slight variation of the thermal expansion coefficient can be seen to have a massive effect on the predicted spinodal temperature. This is most apparent in the majority of cases where convergence to a spinodal condition is not reached throughout the range of blend compositions.
To enlarge the model envelope, five scenarios, using a range of values for the thermal expansion coefficients, were examined:

(a) \( a_2 = 1.0 \times 10^{-3} \); \( a_3 = 1.0 \times 10^{-3} \); \( a_{23} = 1.0 \times 10^{-3} \);
(b) \( a_2 = 0.5 \times 10^{-4} \); \( a_3 = 0.5 \times 10^{-4} \); \( a_{23} = 0.5 \times 10^{-4} \);
(c) \( a_2 = 1.0 \times 10^{-3} \); \( a_3 = 1.0 \times 10^{-3} \); \( a_{23} = 0.75 \times 10^{-3} \);
(d) \( a_2 = 7.272 \times 10^{-4} \); \( a_3 = 8.080 \times 10^{-4} \); \( a_{23} = 7.676 \times 10^{-4} \);
(e) \( a_2 = 5.656 \times 10^{-4} \); \( a_3 = 8.080 \times 10^{-4} \); \( a_{23} = 6.868 \times 10^{-4} \);

The recalculated data are listed in Tables 8.17 to 8.22 respectively and are shown graphically in Figure 8.10.

Table 8.17: Scenario (a)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>( \bar{X}_{23}/\text{bar} )</th>
<th>( Q_{23}/\text{bar K}^{-1} )</th>
<th>( T_{\text{spin}}/\text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>943.7</td>
<td>-2.0591</td>
<td>2.57</td>
</tr>
<tr>
<td>0.2515</td>
<td>656.8</td>
<td>-1.4231</td>
<td>3.70</td>
</tr>
<tr>
<td>0.2905</td>
<td>627.8</td>
<td>-1.3577</td>
<td>3.86</td>
</tr>
<tr>
<td>0.3588</td>
<td>603.6</td>
<td>-1.3055</td>
<td>3.98</td>
</tr>
<tr>
<td>0.5000</td>
<td>804.7</td>
<td>-1.7349</td>
<td>2.99</td>
</tr>
<tr>
<td>0.7496</td>
<td>1394.1</td>
<td>-2.9955</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Table 8.18: Scenario (b)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>( \bar{X}_{23}/\text{bar} )</th>
<th>( Q_{23}/\text{bar K}^{-1} )</th>
<th>( T_{\text{spin}}/\text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>-745.0</td>
<td>1.6474</td>
<td>-</td>
</tr>
<tr>
<td>0.2515</td>
<td>-340.8</td>
<td>9.7569</td>
<td>-</td>
</tr>
<tr>
<td>0.2905</td>
<td>-346.3</td>
<td>0.7681</td>
<td>-</td>
</tr>
<tr>
<td>0.3588</td>
<td>-371.2</td>
<td>0.8211</td>
<td>-</td>
</tr>
<tr>
<td>0.5000</td>
<td>-303.5</td>
<td>0.6710</td>
<td>-</td>
</tr>
<tr>
<td>0.7496</td>
<td>-647.0</td>
<td>1.4077</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table 8.19: Scenario (c)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/ bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>579.3</td>
<td>-1.2592</td>
<td>4.85</td>
</tr>
<tr>
<td>0.2515</td>
<td>208.2</td>
<td>-0.4428</td>
<td>61.8</td>
</tr>
<tr>
<td>0.2905</td>
<td>143.8</td>
<td>-0.3018</td>
<td>$1.6 \times 10^4$</td>
</tr>
<tr>
<td>0.3588</td>
<td>44.5</td>
<td>-0.0849</td>
<td>-</td>
</tr>
<tr>
<td>0.5000</td>
<td>20.8</td>
<td>-0.0330</td>
<td>-</td>
</tr>
<tr>
<td>0.7496</td>
<td>-435.9</td>
<td>0.9523</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 8.20: Scenario (d)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>$\bar{X}_{23}$/bar</th>
<th>$Q_{23}$/ bar K$^{-1}$</th>
<th>$T_{spin}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>516.6</td>
<td>-1.1203</td>
<td>4.57</td>
</tr>
<tr>
<td>0.2515</td>
<td>369.4</td>
<td>-0.7950</td>
<td>6.72</td>
</tr>
<tr>
<td>0.2905</td>
<td>340.3</td>
<td>-0.7308</td>
<td>7.37</td>
</tr>
<tr>
<td>0.3588</td>
<td>305.6</td>
<td>-0.6538</td>
<td>8.43</td>
</tr>
<tr>
<td>0.5000</td>
<td>445.3</td>
<td>-0.9546</td>
<td>6.26</td>
</tr>
<tr>
<td>0.7496</td>
<td>680.8</td>
<td>-1.4566</td>
<td>5.89</td>
</tr>
</tbody>
</table>
Table 8.21: Scenario (e)

<table>
<thead>
<tr>
<th>Wt Fraction</th>
<th>( \bar{X}_{23} )/bar</th>
<th>( Q_{23} )/bar K(^{-1} )</th>
<th>( T_{\text{spin}} )/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>383.1</td>
<td>-0.8287</td>
<td>624.3</td>
</tr>
<tr>
<td>0.2515</td>
<td>195.0</td>
<td>-0.4140</td>
<td>25.9</td>
</tr>
<tr>
<td>0.2905</td>
<td>151.6</td>
<td>-0.3187</td>
<td>55.4</td>
</tr>
<tr>
<td>0.3588</td>
<td>86.2</td>
<td>-0.1755</td>
<td>-</td>
</tr>
<tr>
<td>0.5000</td>
<td>136.1</td>
<td>-0.2835</td>
<td>-</td>
</tr>
<tr>
<td>0.7496</td>
<td>-41.9</td>
<td>0.1025</td>
<td>-</td>
</tr>
</tbody>
</table>

Of the five thermal expansion coefficient scenarios examined only two produced interaction parameters permitting the spinodal equation to converge. This statistic alone demonstrates the influence of this variable in the EOS. McMaster\(^{(30)}\) reported that a 6% increase in an \( \alpha \) value of a model blend caused a 4.6% decrease in \( T^* \), 2.0% increase in \( P^* \) and a 1.0% decrease in \( v^* \) at 300K. Scenarios (a) and (d) produce the most consistent results and are plotted in figure 8.10. However, it should be noted that both of these scenarios produced an UCST type phase boundary, whereas the experimental phase boundaries were all LCST. Scenario (b) represents the situation when the \( \alpha \) values were an order of magnitude smaller than those measured, which produced a significantly negative \( \bar{X}_{23} \), correspondingly positive \( Q_{23} \) values and the combination of these data produced exponentially large spinodal solutions which have not been recorded. Both (c) and (e) produced spinodal temperatures at low EVA concentrations although these functions became exponential as the FVA concentration was increased. A clearer representation of the influence of \( \alpha \) was not obtained because by fixing the values of \( \alpha \), \( X_{23} \) and \( \bar{X}_{23} \), the only remaining variable was \( Q \) whose value became unrealistic and prevented the spinodal equation from converging.
Effect of varying the Thermal Expansion

Cyclohexane data at 3734K

Figure 8.10
8.4.1.4 The Q parameter

Various values of Q were used to predict the spinodal temperature while keeping the other parameters at their original values.

(a) For a temperature of 373K

<table>
<thead>
<tr>
<th>Wt. Fr</th>
<th>$T_{spin}/K$ (Q = 0.0)</th>
<th>$T_{spin}/K$ (Q = 0.005)</th>
<th>$T_{spin}/K$ (Q = -0.005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>61.7</td>
<td>64.8</td>
<td>58.8</td>
</tr>
<tr>
<td>0.2</td>
<td>96.2</td>
<td>102.8</td>
<td>90.3</td>
</tr>
<tr>
<td>0.3</td>
<td>105.7</td>
<td>112.4</td>
<td>99.3</td>
</tr>
<tr>
<td>0.4</td>
<td>99.6</td>
<td>105.7</td>
<td>94.1</td>
</tr>
<tr>
<td>0.5</td>
<td>83.9</td>
<td>88.3</td>
<td>79.9</td>
</tr>
<tr>
<td>0.6</td>
<td>62.5</td>
<td>65.2</td>
<td>60.1</td>
</tr>
<tr>
<td>0.7</td>
<td>39.6</td>
<td>40.8</td>
<td>38.5</td>
</tr>
<tr>
<td>0.8</td>
<td>20.1</td>
<td>20.4</td>
<td>19.8</td>
</tr>
<tr>
<td>0.9</td>
<td>7.2</td>
<td>7.2</td>
<td>7.1</td>
</tr>
</tbody>
</table>

These results are shown in figure 8.11. As $Q_{23}$ is increased the spinodal temperature also increases, the effect being most dramatic at the larger values of $T_{spin}$. However it was found that $T_{spin}$ increased exponentially as $Q_{23}$ approached a specific value and this was studied by increasing its value gradually. These results are given in Table 8.23 and shown in figure 8.12.
Effect of Varying the $Q$ Parameter
Cyclohexane data at 373K

Figure 8.11
Table 8.23

<table>
<thead>
<tr>
<th>$Q$</th>
<th>$T_{\text{spin}}$/K</th>
<th>$Q$</th>
<th>$T_{\text{spin}}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>5.5</td>
<td>0.015</td>
<td>-</td>
</tr>
<tr>
<td>-2.0</td>
<td>2.8</td>
<td>0.011</td>
<td>93.9</td>
</tr>
<tr>
<td>-3.0</td>
<td>1.9</td>
<td>0.012</td>
<td>94.9</td>
</tr>
<tr>
<td>-4.0</td>
<td>1.4</td>
<td>0.013</td>
<td>95.9</td>
</tr>
<tr>
<td>-5.0</td>
<td>1.1</td>
<td>0.014</td>
<td>-</td>
</tr>
<tr>
<td>-6.0</td>
<td>0.9</td>
<td>0.0135</td>
<td>96.46</td>
</tr>
<tr>
<td>-0.5</td>
<td>10.7</td>
<td>0.0138</td>
<td>96.77</td>
</tr>
<tr>
<td>-0.25</td>
<td>19.8</td>
<td>0.0139</td>
<td>96.87</td>
</tr>
<tr>
<td>-0.10</td>
<td>38.6</td>
<td>0.01391</td>
<td>96.85</td>
</tr>
<tr>
<td>-0.05</td>
<td>54.1</td>
<td>0.013915</td>
<td>96.88</td>
</tr>
<tr>
<td>0.10</td>
<td>92.9</td>
<td>0.139152</td>
<td>96.88</td>
</tr>
</tbody>
</table>

8.5 General discussion

The temperatures which satisfy the spinodal equation for the EVA/FVA mixtures quoted in Tables 8.8 - 8.10 are all below 52 K and of little practical use, because although they may reflect the physics of the system, under these conditions both polymers are significantly below their glass transition temperatures and miscibility would be prohibited by their physical state. This prediction partially supports the results of the phase contrast microscopy experiments which showed no evidence of miscibility between 303 and 523 K. It can thus be concluded, both on experimental and theoretical grounds, that these two polymers are never miscible in the bulk state. However, several features of this calculation should be noted and the results considered in context. Firstly, since the reduced parameters of the pure components and the mixture require to be evaluated at each spinodal temperature during the iterative calculation, in this case they have been linearly extrapolated over approximately 250 K. This is without doubt invalid. It was also felt that it was worth reconsidering the sources of these data, and the fundamental assumptions of the calculation.
Relationship between the Spinodal Temperature and the $Q$ Parameter

Figure 8.12
Possibly the greatest flaw in the basis of this estimation was that \( X_{23} \) is defined as being constant, and independent of temperature. This definition assumes that any density, steric or end group effects which contribute to the heat of mixing will either be incorporated in the other parameters in equation 2.52c,

\[
\Delta H_{\text{mix}} = n_2 V_1^{*} \left( \phi_2 \frac{X_{23}}{\widetilde{\nu}_2} + P_1^{*} \left( \frac{1}{\widetilde{\nu}_1} - \frac{1}{\widetilde{\nu}_2} \right) - \left( \phi_2^{*} / \phi_1^{*} \right) P_2^{*} \left( \frac{1}{\widetilde{\nu}_1} - \frac{1}{\widetilde{\nu}_2} \right) \right)
\]

(2.52c)

which they are not, or they are insignificant in relation to the contributions from the respective exchange enthalpies. Since other experiments in this current work have shown that there is very little energetic difference in the homopolymers intermolecular contacts, and no strong specific interaction between heterogeneous contacts, the enthalpy of mixing in this system may be dominated by the unaccounted physical effects. This scenario would not affect the reproducibility of the measurements since they could be precise but inaccurate. However, these alternative effects are more likely to be temperature dependent and in view of this possibility, some additional heats of mixing experiments were carried out at 359.3K and the results are given in Table 8.24.

**Table 8.24**

<table>
<thead>
<tr>
<th>Run</th>
<th>Measured ( \Delta H_{\text{mix}} / 10^{-2} \text{J g}^{-1} )</th>
<th>Recalculated ( \Delta H_{\text{mix}} / 10^{-2} \text{J g}^{-1} )</th>
<th>Difference ( 10^{-2} \text{J g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.390</td>
<td>5.957</td>
<td>0.567</td>
</tr>
<tr>
<td>2</td>
<td>7.162</td>
<td>6.497</td>
<td>-1.206</td>
</tr>
<tr>
<td>3</td>
<td>6.259</td>
<td>6.905</td>
<td>0.646</td>
</tr>
</tbody>
</table>

By fitting the data in Table 8.24 with a non-linear least squares function \( X_{23} \), at 359.3K, was estimated as 3.315bar. The recalculated values given above represent the corresponding data values from the fitted function. The difference between the \( X_{23} \) values at 348.7 and 359.3K represents a
change of about 40% over a 10.6 K range. Owing to insufficient experimental time and calorimetry data, this effect could not be studied fully and thus the influence of a heavily temperature dependent enthalpic contribution on the phase boundary was not quantitatively examined. If it is assumed that the value of $X_{23}$ would continue to decrease with increasing temperature, i.e. that heterogeneous contacts would begin to become more favourable than the homogeneous, the critical point of the predicted phase boundary would be elevated\(^{(30)}\). However, this should also be considered in context. The moduli of the mean values of $\bar{X}_{23}$ at 353K, quoted in Table 8.8, are \textit{circa} two orders of magnitude greater than those of $X_{23}$ and thus although the enthalpic value used in this simulation may be a crude approximation, it is insignificant in relation to the entropic contribution. This contribution is manifested in the value of $Q_{23}$ which itself is insignificant for the majority of values but entirely dominant over a very short range, i.e. Table 8.24 and Figure 8.12. In view of this dominance, it was apparent that a reliable estimation of $Q_{23}$ was imperative to produce a realistic simulation of the phase boundary. It is unsurprising that this term has generally been used as the fitting parameter for experimental and theoretical phase boundaries since it has the potential to alter the predicted spinodal temperature by orders of magnitude. However, the entire EOS approach to predicting the thermodynamics of mixtures will be fundamentally weakened unless a more representative partition function is adopted which accounts for the influence of physical effects on the heat of mixing and a clear model of the effects which contribute to excess entropy.
8.6 REFERENCES


(25) D. J. Walsh, S. Rostami and V. B. Singh,


(27) B. M. Mandal, C. Bhattacharya and S. N. Bhattacharya,


(31) W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vettering,
Chapter 9  Final Conclusions

The objectives of this work were to examine experimentally and characterise the thermodynamics and miscibility limits of a mixture of two copolymers, EVA and $C_{14}$ FVA, and to review the applicability of the experimental techniques which were employed to obtain the thermodynamic data.

The density measurements, (Chapter 3), showed that mixtures of all compositions were volume additive between 303 and 333K, and the thermal expansion coefficients of both the homopolymers and of each blend, which were required for an equation of state analysis, were calculated from these data. By definition, materials which are volume additive when mixed do not strongly or specifically interact and in these systems the intermolecular forces between homo-contacts must be approximately equal to those between hetero-contacts. Alternatively, volume additivity can arise in cases where the component materials do not mix on a truly molecular level and consequently the system is effectively a micro-dispersion rather than a mixture. The EVA and $C_{14}$ FVA copolymers are chemically very similar and it is likely therefore that the intermolecular forces between the homo-species would be very similar to those in the blend. On this basis, and in the absence of contrary information and for the application of an equation of state analysis, it was assumed that molecular mixing did occur. However, the ultimate conclusion from both the majority of the experimental results and the theoretical predictions is that the copolymers are immiscible in all proportions between 303 and 393K. This suggests that the density measurements, together with the thermal expansivities and reduced mixture volumes calculated from them, actually refer to dispersions of EVA and $C_{14}$ FVA rather than to mixtures. Similarly, the heats of mixing calculated in Chapter 5 would then refer to the enthalpic changes which occur when the surfaces of these materials are contacted. However the magnitude of such an enthalpic effect would be highly dependent on the interfacial area of the hetero-contact which can be assumed to be variable. The consistency of the heats of mixing data in Chapter 5 show that this is not the case. These factors all cast doubt on the validity of the unusual phase boundaries predicted in Chapter 8. In view of the importance of accurate determinations of the specific volumes and thermal expansion coefficients of component materials to an EOS treatment, it is suggested that future workers should obtain as much information as possible about the density-temperature-composition relationships of these species, preferably using more than one technique.
Differential scanning calorimetry, (Chapter 3), was used to characterise the temperature-heat capacity responses of the polymers and consequently identify any thermal transitions which they had undergone. EVA was found to have $T_g \approx 140K$ and no identifiable melt: $C_{14}$ FVA $T_g \approx 160K$ and $T_m = 300K$. A polymer-polymer interaction parameter can be obtained from DSC if one of the components of a binary mixture is crystalline and the other amorphous. For this purpose the $C_{14}$ FVA was defined as being crystalline and the depression in its melting point was measured as a function of EVA concentration. This experimental programme was abandoned because the observed depression of the $C_{14}$ FVA melting point was insignificant from which it was concluded that the copolymers did not co-crystallise and thus the presence of the EVA had no effect on the chemical potential of the $C_{14}$ FVA. DSC can also be used to examine the phase boundary of a mixture as the $T_g$ value of each component is replaced by a single transition in a miscible blend. The movements of the $T_g$ values of EVA and $C_{14}$ FVA were followed after the samples had been annealed at a range of temperatures and the predicted phase boundary was of the LCST type, occurring at between 340 and 315K across the composition range. However, some doubt arose over the validity of this prediction owing to the weak and non-reproducible nature of the salient features of the thermograms of both materials, and it was concluded that DSC was inappropriate for exploring the thermodynamics of this particular mixture. A complicating factor was the observation that EVA went from opaque to translucent when heated to about 325K and this effect was quantitatively characterised using laser turbidimetry, (Chapter 3). No reflection of this change was observed in either the density or the DSC experiments, i.e. it did not cause a change in either unit volume or heat capacity. This was most probably caused by the solubilisation of the extreme elements of either the molecular weight or the compositional distributions. As a consequence, it was decided that subsequent experiments should be performed above 325K to ensure that any manifestations of this effect were not included unwittingly in the results.

Inverse phase gas chromatography, (Chapter 4), was used to evaluate polymer-solvent and polymer-polymer interaction parameters at 353, 373 and 393K and from these data it was observed that the polymer-polymer interaction varied significantly with both composition and temperature. In general, the interaction parameters were found to be small and positive with values from EVA rich mixtures being more favourable to miscibility. The probability of mutual solubility decreased as the FVA concentration and the temperature increased. The experimental data were highly consistent and
reproducible although the polymer-polymer interaction parameters did exhibit a significant solvent dependence. Several attempts were made to correlate this dependence with either a physical characteristic of the solvent, or with the empirical functions which have been quoted in the literature, but without success. It is apparent that IGC as a technique would benefit enormously from a greater theoretical analysis, preferably from a chromatographic viewpoint, which had the object of understanding and quantifying the various processes which can occur on the column, as the elution peak appeared to contain considerably more information than that utilised by the current method of analysis. It was intended that the accuracy of the dynamic IGC results would be verified by a series of static solvent vapour sorption, SVS, experiments but owing to technical and time constraints this was not achieved. However, the normal SVS procedure of linearly extrapolating the interaction parameter vs. mixture mass fraction relationship to zero solvent concentration was found to introduce significant uncertainty in both the interaction parameters obtained in this work and those obtained by others, (Chapter 6). It was concluded that since this linear fitting procedure had no theoretical or practical basis it should be replaced by fitting the highest justifiable polynomial. It is also suggested that previously published SVS data be re-analysed using more appropriate extrapolation procedures which may affect the magnitude of the reported discrepancies between equivalent SVS and IGC data.

Heat of mixing experiments were carried out to separate the free energy of mixing into its enthalpic and entropic components (Chapter 5). The enthalpy of mixing was found to be small and positive, i.e. unfavourable to mixing, but a Flory-Huggins-Chang-Miller analysis estimated the Gibbs free energy of mixing to be negative and favourable. This suggested that the free energy change on mixing was dominated by the entropic contribution. Since gel permeation chromatography had shown that both EVA and C\textsubscript{14}FVA were low molecular weight materials, this entropic dominance was quite possible and thus a more advanced theoretical analysis should be used to predict the thermodynamics of the mixture since the simple FHCM model only considers configurational contributions whereas the equation of state theories also take account of contributions from the external degrees of freedom of the polymer chains. The equation of state approach of Flory and Prigogine was adopted on the basis that it provided a general partition function and because it was the most studied of all the EOS theories. The theoretical LCST spinodal boundaries, which predicted that these copolymers would always be miscible above about 50K, are of little practical value (Chapter 8). It is believed that
this is the first work to calculate directly the entropic correction factor, Q, and thus produce spinodal functions which do not contain a 'fudge factor'. However, in the absence of an experimental phase boundary, it is impossible to conclude whether these calculations, and thus the theory, produce realistic solutions for this mixture. It was clear from altering some of the state parameters, for both homopolymer and mixtures, that the solution of the spinodal condition was dominated by the magnitude of the Q parameter, which in turn arose from the two orders of magnitude difference between the enthalpic and free energy interaction parameters, calculated from heats of mixing and IGC respectively. It was concluded, from the two sets of heats of mixing data obtained at different temperatures, that the EOS assumption of a constant enthalpic interaction parameter for any polymer pair is dubious. However the greatest cause for doubt lay in the incompatibility of the heats of mixing results with those obtained for IGC. It should be noted that the six parameter copolymer theory of Cowie et al (1) was not employed in this work because it requires investigation of the homopolymers of each monomer unit in each copolymer, *i.e.* in this case polyethylene, polyvinylacetate and a polymer of the di-substituted C₁₄ fumaric ester.

Finally, optical microscopy, (Chapter 7), was employed to observe the behaviour of a selection of mixtures as they were heated from 313 to 373K, and the resulting micrographs demonstrated that EVA and C₁₄ FVA were not miscible in this temperature range, which supported the results from IGC, heats of mixing and the EOS predictions.

It is concluded that the *ad hoc* addition of the Q parameter will always reduce the potency of the EOS, particularly when the mixing is dominated by the entropic contribution. It is suggested that a new partition function, which directly incorporates an entropic contribution with a clear physical significance, should be considered.

The true value of this work can only be estimated if it is repeated with a low viscosity blend for which an experimental phase boundary can be determined.

**REFERENCE**

### Values of the Chi functions for Benzene at 80°C

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### Values of the Chi functions for Dichloromethane at 80°C

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### Values of the Chi functions for Methanol at 80°C

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### Appendix 1.11

#### Values of the Chi functions for 2-Propanone at 100°C

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### Appendix 2.1

#### Probe - Benzene at 80°C

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**Appendix 2.3**

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**Probe - Chloroform at 80°C**

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**Probe - Methyl Acetate at 80°C**

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### Appendix 2.4

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### Appendix 2.5

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#### Probe - Carbon tetrachloride at 100°C

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## Appendix 2.6

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### Probe - Chloroform at 100°C

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### Appendix 2.8

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### Appendix 2.9

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<td>232.8</td>
<td>-0.4685</td>
<td>11.38</td>
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<td>0.2905</td>
<td>282.2</td>
<td>-0.5696</td>
<td>9.56</td>
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<tr>
<td>0.3588</td>
<td>271.2</td>
<td>-0.5461</td>
<td>10.04</td>
</tr>
<tr>
<td>0.5000</td>
<td>217.4</td>
<td>-0.4339</td>
<td>12.41</td>
</tr>
<tr>
<td>0.7496</td>
<td>484.8</td>
<td>-0.9754</td>
<td>5.37</td>
</tr>
<tr>
<td>1.0000</td>
<td>783.4</td>
<td>0.0000</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Probe - Chloroform at 120°C

<table>
<thead>
<tr>
<th>Wt Fr</th>
<th>$X_{23}$</th>
<th>$Q_{23}$</th>
<th>$T_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>627.8</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>0.0904</td>
<td>619.1</td>
<td>-1.2705</td>
<td>4.06</td>
</tr>
<tr>
<td>0.2515</td>
<td>565.8</td>
<td>-1.1551</td>
<td>4.79</td>
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<tr>
<td>0.2905</td>
<td>503.6</td>
<td>-1.0258</td>
<td>5.41</td>
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<tr>
<td>0.3588</td>
<td>501.6</td>
<td>-1.0197</td>
<td>5.46</td>
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<tr>
<td>0.5000</td>
<td>543.2</td>
<td>-1.1013</td>
<td>5.05</td>
</tr>
<tr>
<td>0.7496</td>
<td>918.4</td>
<td>-1.8579</td>
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<tr>
<td>1.0000</td>
<td>818.7</td>
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</table>

#### Probe - Methyl Acetate at 120°C

<table>
<thead>
<tr>
<th>Wt Fr</th>
<th>$X_{23}$</th>
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<th>$T_{sp}$</th>
</tr>
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<tbody>
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<tr>
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<td>210.0</td>
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<td>10.29</td>
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<td>0.2515</td>
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<td>547.7</td>
<td>-1.1033</td>
<td>4.79</td>
</tr>
<tr>
<td>1.0000</td>
<td>1839.7</td>
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<td>-</td>
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</table>
### Probe - 2-Propanone at 120°C

<table>
<thead>
<tr>
<th>Wt Fr</th>
<th>X&lt;sub&gt;23&lt;/sub&gt;</th>
<th>Q&lt;sub&gt;23&lt;/sub&gt;</th>
<th>T&lt;sub&gt;sp&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>1721.2</td>
<td>0.0000</td>
<td>–</td>
</tr>
<tr>
<td>0.0904</td>
<td>124.3</td>
<td>-0.2458</td>
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<td>628.1</td>
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<td>1.0000</td>
<td>2011.5</td>
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<td>–</td>
</tr>
</tbody>
</table>

### Probe - Isopropanol at 120°C

<table>
<thead>
<tr>
<th>Wt Fr</th>
<th>X&lt;sub&gt;23&lt;/sub&gt;</th>
<th>Q&lt;sub&gt;23&lt;/sub&gt;</th>
<th>T&lt;sub&gt;sp&lt;/sub&gt;</th>
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</thead>
<tbody>
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<td>54.5</td>
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### Probe - Ethyl Acetate at 120°C

<table>
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<tr>
<th>Wt Fr</th>
<th>X&lt;sub&gt;23&lt;/sub&gt;</th>
<th>Q&lt;sub&gt;23&lt;/sub&gt;</th>
<th>T&lt;sub&gt;sp&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td>0.2905</td>
<td>366.9</td>
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<td>4.18</td>
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<tr>
<td>1.0000</td>
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</table>
University of Durham

Board of Studies in Chemistry

Colloquia, lectures and Seminars given by Invited Speakers

1st August 1989 to 31st July 1990

ASHMAN  Mr A (Durham Chemistry Teacher's Centre)
         The National Curriculum - An Update              11th Oct 1989

BADYAL  Dr J P S (Durham University)
         Breakthroughs on Heterogeneous Catalysis         1st Nov 1989

BECHEr  Dr J (Odense University)
         Synthesis of New Macrocyclic Systems using      13th Nov 1989
         Heterocyclic Building Blocks

BERCAW  Prof J E (California Institute of Technology)
         Synthetic and Mechanistic Approaches to          10th Nov 1989
         Ziegler-natta Polymerization of Olefins

BLESDALE Dr C (Newcastle University)
         The Mode of Action of some Anti-tumour Agents    21st Feb 1990

BOLLEN  Mr F (formerly Science Advisor, Newcastle LEA)
         What's new in Satis, 16-19                      27th Mar 1990

BOWMAN  Prof J M (Emory University)
         Fitting Experiment with Theory in Ar-OH          23rd Mar 1990

BUTLER  Dr A (St Andrews University)
         The Discovery of Penecillin: Facts and Fancies   7th Dec 1989

CAMPBELL Mr W A (Durham Chemistry Teachers Centre)
         Industrial Catalysis - Some Ideas for            12th Sep 1989
         the National Curriculum

CHADWICK Dr P (Dept of Physics, Durham University)
         Recent Theories of the Universe (with respect     24th Jan 1990
         to National Curriculum Attainment Target 16)

CHEETHAM Dr A K (Oxford University)
         Chemistry of Zeolite Cages                       8th Mar 1990
Appendix 3.2

CLARK Prof D T (ICI Wilton)
Spatially resolved Chemistry (using Nature’s Paradigm in the Advanced Materials Arena) 22nd Feb 1990

COLE-HAMILTON Prof D J (St Andrews University)
New Polymers from Homogeneous Catalysis 29th Nov 1989

CROMBIE Prof L (Nottingham University)
The Chemistry of Cannabis and Khat 15th Feb 1990

DYER Dr U (Glaxo)
Synthesis and Conformation of C-Glycosides 31st Jan 1990

FLORIANI Prof C (University of Lausanne, Switzerland)
Molecular Aggregates - A Bridge between Homogeneous and Heterogeneous Systems 25th Oct 1989

GERMAN Prof L S (USSR Academy of Sciences, Moscow)
New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes 9th Jul 1990

GRAHAM Dr D (BP Research Centre)
How Proteins Absorb to Interfaces 4th Dec 1989

GREENWOOD Prof J H (University of Leeds)
Novel Cluster Geometries in Metallaborane Chemistry 9th Nov 1989

HOLLOWAY Prof J H (University of Leicester)
Noble Gas Chemistry 1st Feb 1990

HUGHES Dr M N (King’s College, London)
A Bug’s Eye View of the Periodic Table 30th Nov 1989

HUISGEN Prof R (Universitat Munchen)

IDDON Dr B (University of Salford)
Schools’ Christmas Lecture - The Magic of Chemistry 15th Dec 1989

JONES Dr M E (Durham Chemistry Teachers’ Centre)
The Chemistry A Level 1990 3rd Jul 1989
IONES Dr M E (Durham Chemistry Teachers' Centre)
GCSE and Dual Award Science as a starting point for A level Chemistry - how suitable are they?

JOHNSON Dr G A L (Durham Teachers' Training Centre)
Some aspects of local Geology in the National Science Curriculum (attainment target 9)

KLIINOWSKI Dr J (Cambridge University)
Solid State NMR Studies of Zeolite Catalysts

LANCASTER Rev R (Kimbolten Fireworks)
Fireworks - Principles and Practice

LUNAZZI Prof L (University of Bologna)
Application of Dynamic NMR to the Study of Conformational Enantiomerism

PALMER Dr F (Nottingham University)
Thunder and Lightening

PARKER Dr D (Durham University)
Macrocycles, Drugs and Rock 'n' Roll

PERUTZ Dr R N (York University)
Plotting the Course of C-H Activations with Organometallics

PLARINOY Prof V E (USSR Academy of Sciences, Novosibirsk)
Polyfluorooindanes: Synthesis and Transformation

POWELL Dr R L (ICI)
The Development of CFC Replacements

POWIS Dr I (Nottingham University)
Spinning off in a huff: Photodissociation of Methyl Iodide

RICHARDS Mr C (Health and Safety Executive, Newcastle)
Safety in School Science Laboratories and COSHH

Appendix 3.3

21st Nov 1989

8th Feb 1990

13th Dec 1989

8th Feb 1990

12th Feb 1990

17th Oct 1989

16th Nov 1989

24th Jan 1990

9th Jul 1990

6th Dec 1989

21st Mar 1990

28th Feb 1990
ROZHKO\textsc{v}  Prof I N (USSR Academy of Sciences, Moscow) Nurshey of Perfluoroalkyl Bromides  9th Jul 1990

STODDART  Dr J F (Sheffield University)  Molecular Lego  1st Mar 1990

SUTTON  Prof D (Simon Fraser University, Vancouver BC)  Synthesis and Applications of Dinitrogen and Diazocompounds of Rhenium and Iridium  14th Feb 1990

THOMAS  Dr R K (Oxford University)  Neutron Reflectometry from Surfaces  28th Feb 1990

THOMPSON  Dr D P (Newcastle University)  The role of Nitrogen in Extending Silicate Crystal Chemistry  7th Feb 1990
This is the final version of the GFA Basic program used for data collection

! 4 byte signed integers, i.e. up to 2147483648
! strings
! 1 byte Boolean variables

exptl_pt(10000)
c(8),st_w(10),st_q(10),st_f(10),ok_q(10)
max_trys = 15000

PROCEDURE findadc

a procedure supplied with the ADC for channel allocation

rom = &HFB0000
rom+1
rom+3
rom+5
rom+7
rom+9
rom+11
rom+13
rom+15

channel = c(1)

RETURN

PROCEDURE getadc

the procedure which obtains a reading from the ADC

rd% = PEEK(channel)
rd% = PEEK(channel)

RETURN

PROCEDURE dummy

does nothing - used with a loop which monitors the keyboard

PROCEDURE co_or(ds(ncols,nlines,VAR nxpixels,nypixels)

ncx = MUL(8,SUB(nx,1))
ncy = MUL(16,SUB(ny,1))

RETURN

PROCEDURE off_set(st,VAR n_off,n_chars)

returns the offset, n_off, to centre a string and the number
of characters, n_chars, in the string st

LOCAL n0,n1,n2
n_chars = LEN(st)
n1 = 80
n_off = ADD(DIV(SUB(n1,n_chars),2),1)

RETURN
PROCEDURE clr_line(nx1,nx2,ny)
    PRINT AT(nx1,ny1);SPACE$(ADD(1,SUB(nx2,nx1)))
RETURN

PROCEDURE screen_box(nx1,ny1,nx2,ny2,n0)
    LOCAL mx1,mx2,my1,my2
    co_ords(nx1,ny1,mx1,my1)
    co_ords(nx2,ny2,mx2,my2)
    IF n0=0
        CLS
    ELSE
        DEFFILL,0
        BOUNDARY 0
        IF n0=1
            PBOX 0,my1,640,my2
        ELSE PBOX mx1,my1,mx2,my2
        ENDIF
        BOUNDARY 1
    ENDIF
    BOX ADD(mx1,4),ADD(my1,8),ADD(mx2,4),ADD(my2,8)
RETURN

PROCEDURE message(st,nx1,ny1,nx2,ny2,nb,nc)
    LOCAL jx,jy
    jx = ADD(nbx1,1)
    jy = ADD(nby1,1)
    IF nb > 0
        clr_line(jx,jy,ny1)
    ENDIF
    PRINT AT(nx1,ny1); st
    IF nc = 0
        jx = ADD(ADD(LEN(st),5), nx1)
        jy = ny1
    ELSE
        jx = nx2
        jy = ny2
    ENDIF
    LOCATE jx,jy
RETURN
PROCEDURE paws(st,ny,n0)
REM
REM     suspends program operation until next key press

LOCAL  j0,j1,k1,k2,key1
off_set(st,j0,j1)
k1 = SUB(j0,2)
k2 = ADD(j0,ADD(j1,2))
screen_box(k1,SUB(1,1),k2,ADD(ny,1),n0)
PRINT AT(j0,ny); st
key1 = INP(2)
k1 = SUB(ny,1)
FOR k2=k1 TO k1+2
   clr_line(1,80,k2)
NEXT k2

RETURN

PROCEDURE yes_or_no(n)
LOCAL  st1,st2
st1 = "YN"
REPEAT
   st2 = UPPER$(INKEY$)
   UNTIL INSTR(st1,st2)
ok_q(n) = st2 = "Y"

RETURN

PROCEDURE enter_data
REM
REM     Requests the necessary initial data for the experiment and tests dt_set
to ensure that it is >= 0.01; values of dt_set are also rounded up to the
REM     nearest 1/100 of a second. Also determines whether the run is
REM     a software test (ok_test) or the real thing (ok_real).

LOCAL  jx1,jx2,jy1,jy2,nx1,nx2,ny1
st_w(1) = "Enter the following information"
st_w(2) = "The time delay in seconds (to nearest 1/100)"
st_w(3) = "The total number of experimental points"
st_w(4) = "The percentage difference to be used in START_UP"
st_w(5) = "The number of successively increasing points"
st_w(6) = "A zero for test data consisting of random numbers"
st_w(4) = "The time interval must be at least 0.01 seconds - try again"

REM
REM     Determine coordinates of box

jx1 = 5
jx2 = 75
jy1 = 1
jy2 = ADD(jy1,MUL(7,2))

REM
nx1 = 10
nx2 = ADD(LEN(st_w(6)),nx1+5)
REPEAT
    screen_box(jx1, jy1, jx2, jy2, 1)
    ny1 = ADD(jy1, 2)
    message(st_w(1), nx1, ny1, nx2, ny2, 1)
    ADD ny1, 2
    message(st_w(2), nx1, ny1, nx2, ny2, 1)
    INPUT "", dt_set
    IF dt_set < 0.01 THEN
        ADD ny1, 6
        message(st_w(7), nx1, ny1, nx2, ny2, 1)
        DELAY 2
    ENDIF
UNTIL dt_set >= 0.01
    dt_set = 0.01*CINT(100*dt_set)
    ADD ny1, 2
    message(st_w(3), nx1, ny1, nx2, ny2, 1)
    INPUT "", n_max
    ADD ny1, 2
    message(st_w(4), nx1, ny1, nx2, ny2, 1)
    INPUT "", pct
    ADD ny1, 2
    message(st_w(5), nx1, ny1, nx2, ny2, 1)
    INPUT "", n_spec
    ADD ny1, 2
    message(st_w(6), nx1, ny1, nx2, ny2, 1)
    INPUT "", n_test
    ok_test = n_test = 0
    ok_run = NOT ok_test

REM
    IF ok_run THEN
        st_w(1) = "Enter the following additional information"
        st_w(2) = "Carrier gas flow rate (cm^3 s^{-1})"
        st_w(3) = "Column inlet pressure (mmHg)"
        st_w(4) = "Column outlet pressure (mmHg)"
        st_w(5) = "Mass of polymer on the column (g)"
    ENDIF
REM
    jy2 = ADD(jy1, MUL(6, 2))
    screen_box(jx1, jy1, jx2, jy2, 0)
    ny1 = ADD(jy1, 2)
    message(st_w(1), nx1, ny1, nx2, ny2, 1)
    ADD ny1, 2
    age(st_w(2), nx1, ny1, nx2, ny2, 1)
    INPUT "", gas_flow_rate
    ADD ny1, 2
    age(st_w(3), nx1, ny1, nx2, ny2, 1)
    INPUT "", inlet_pressure
    ADD ny1, 2
    message(st_w(4), nx1, ny1, nx2, ny2, 1)
    INPUT "", outlet_pressure
    ADD ny1, 2
    age(st_w(5), nx1, ny1, nx2, ny2, 1)
    INPUT "", wt_of_polymer
ELSE
    ENDIF
REM
RETURN
PROCEDURE time_check(dt_set)

This procedure determines when the next sample is to be taken.

LOCAL n_set,n0,n1

n_set = CINT(200*dt_set) ! expresses sample interval in 200ths of a second
n0 = TIMER ! obtains starting time

REPEAT
    n1 = TIMER
    SUB n1,n0 ! calculates time interval in 200ths
    UNTIL n1 >= n_set ! compares the current interval with that desired

RETURN

PROCEDURE exptl_pt(n)

Obtains either a random number or a measurement as appropriate

LOCAL j

time_check(dt_set)

IF ok_test
    j = RANDOM(255) ! a random number between 0 and 255
    INC j ! eliminates chance of zero, i.e. 1 to 256
ELSE
    GOSUB getadc
    j = rd%
ENDIF

RETURN

exptl_pt(n) = j

PROCEDURE compare(n,VAR ok_greater)

Tests whether the current result exceeds the previous value by
the percentage specified in the data input procedure.

LOCAL fx,x_old,x_new,ok

x_new = exptl_pt(n)

ok_greater = x_new > 0 ! avoids chance of division by zero

IF ok_greater
    x_old = exptl_pt(n-1) ! previous reading
    fx = 100*(1 - x_old/x_new)
    ok_greater = fx > pct ! compare with specified %age
ELSE
ENDIF

RETURN
PROCEDURE start_up

Monitors the specified number of successively increasing values which defines
the beginning of the experiment

LOCAL
  j, n_ok, ok, nx1, ny1
  j = 1
  n_ok = 0
  expt_tot = 0
  ADD n_trys, 1
  exptl_pt(n_ok)
  WHILE (n_ok < n_ints) AND (max_trys >= n_trys)
    INC j
    INC n_trys
    exptl_pt(j)
    compare(j, ok)
    PRINT AT (nx, ny); n_trys
    IF ok
      INC n_ok
    ELSE
      exptl_pt(1) = exptl_pt(j)
      j = 1
      n_ok = 0
    ENDIF

IF max_trys = n_trys
  st_w(1) = "The maximum permitted attempts has been reached"
  st_w(2) = "To continue enter Y else N which terminates program"
  nx1 = 10
  ny1 = 5
  message(st_w(1), nx1, ny1, nx1, ny1, 0)
  ADD ny1, 2
  message(st_w(2), nx1, ny1, nx1, ny1, 1)
  REPEAT
    st_w(3) = INKEY$
    IF LEN(st_w(3)) = 1
      st_w(3) = UPPER$(st_w(3))
    ENDIF
    UNTIL (st_w(3) = "Y") OR (st_w(3) = "N")
    IF st_w(3) = "N"
      END
    ELSE
      n_trys = 0
      expt_total = 0
      clr_line(6, 74, 5)
      clr_line(6, 74, 7)
      clr_line(nx - 5, 74, ny)
    ENDIF
  ENDIF
WEND
n_base = CINT(DIV(expt_total, n_trys))

RETURN
PROCEDURE capture

This procedure obtains the specified number of experimental values; locates the peak value together with the corresponding time and displays this information on the screen.

LOCAL jx1,jy1,jx2,jy2,nx1,nx2,ny1,nx,ny
enter_data
findadc

The first step is to halt the program just prior to introducing the sample - do this by calling for the dummy procedure

$st_w(1) = \text{"Introduce the sample, then press any key"} $
$paws(st_w(1),23,1)$

The next section compares successive readings until the specified number of points which have increased by at least the specified percentage difference have been detected.

$jx1 = 5$
$jx2 = 75$
$jy1 = 2$
$jy2 = 10$

screen_box(jx1,jy1,jx2,jy2,0)

n_ints = n_spec - 1 ! no. intervals one less than no. points
n_trys = 0

$st_w(2) = \text{"Current number of trys"}$

nx1 = 10 ! x coordinate for writing to screen
ny1 = ADD(jy1,1) ! y coordinate for writing to screen

message(st_w(2),nx1,ny1,nx1,ny1,0)

n_start= TIMER

nx = ADD(nx1,ADD(LEN(st_w(2)),5)
ny = ny1

start_up(nx,ny)

n_end = TIMER

dead_time = 0.005*(n_end - n_start)
dt_start = dead_time/n_trys

$st_w(1) = \text{"The following successive increasing values have been detected"}$

ADD ny1,2

ny = ny1

message(st_w(1),nx1,ny,65,ny,0)

ADD ny1,2

ny = ny1

nx = 25

FOR j=1 TO n_spec
    PRINT AT(nx,ny); expl_p(j)
    ADD nx,8

Next j

$st_w(1) = \text{"The time interval between the initial points = "}$

ADD ny1,2

ny = ny1

message(st_w(1),10,ny,10,ny,0)

nx = ADD(nx1,LEN(st_w(1)))

PRINT AT(nx,ny); USING "####.####", dt_start

nx = ADD(nx,8)

PRINT AT(nx,ny); "seconds"
Now collect either experimental data of random numbers in the range 0 to 255 as a simulation of experimental data

```plaintext
jx1 = 5
jx2 = 75
jy1 = 12
jy2 = 20
screen_box(jx1,jy1,jx2,jy2)
ny1 = ADD(jy1,1)
st_w(1) = "Now beginning the storage of "
st_w(2) = "experimental values"
x = ADD(LEN(st_w(1)),ADD(5,LEN(st_w(2))))
x = SUB(jx2,jx1,ADD(nx,1))
PRINT AT(nx,ny); st_w(1); n_max; st_w(2)
n_data = n_spec
n_start = TIMER
REPEAT
   INC n_data
   exp_tr_pt(n_data)
   UNTIL n_data = n_max
n_end = TIMER
di_main = 0.005*(n_end-n_start)/(n_max-n_spec-1)
```

Now find the peak value and calculate the corresponding time

```plaintext
n_data = 1;
max_val = exp_tr_pt(1)
REPEAT
   INC n_data
   m = exp_tr_pt(n_data)
   IF m > max_val
      max_value = m
      inc_val% = n_data
   ELSE
   ENDIF
   UNTIL n_data = n_max
```

peak_time = dt_start*(n_spec-1) + dt_main*(inc_val% - n_spec)
total_time = peak_time + dead_time

```plaintext
ADD ny1,2
st1 = "Time from injection to peak = ",
st0 = st1 + "####.####" + "seconds"
off_set(st0,nx1,j0)
PRINT AT(nx1,ny1); st1
nx = ADD(nx1,LEN(st1))
PRINT AT(nx,ny1); USING "####.####", total_time
PRINT AT(nx+8,ny1); "seconds"
```

```plaintext
ADD ny1,2
st1 = "Time from detection to peak = ",
PRINT AT(nx1,ny1); st1
nx = ADD(nx1,LEN(st1));
PRINT AT(nx,ny1); USING "####.####", peak_time
PRINT AT(nx+8,ny1); "seconds"
```
\[ j_0 = \text{INSTR(st1, "}") \]  ! Find position of equals sign 
\[ nx1 = nx1 + j_0 - \text{LEN("Peak Value ")}-1 \]  ! Align = sign with others 
\[ \text{ADD ny1,2} \]
\[ \text{st1 = "Peak Value = "} \]
\[ \text{PRINT AT(nx1,ny1);st1} \]
\[ \text{PRINT AT(nx1+\text{LEN(st1)},ny1); max_value;} \]
\[ \text{st1 = "To continue, press any key"} \]
\[ \text{Paws(st1,23,1)} \]

\text{RETURN}

\text{PROCEDURE} \ 	ext{filename(VAR file_title$)}

\text{REM}
\text{REM}
\text{Obtains appropriate drive (A: or B:) together with the name of the}
\text{file in which the data are to be stored. Determines the type of}
\text{experiment being carried out,i.e.(0, 1, 10, 11)}

\text{REM}
\text{REM}
\text{st_w(1) = "The method used to store data presupposes the existence"}
\text{st_w(2) = "of at least four 'folders' to store data files; these are"}
\text{st_w(3) = "CH4 UC, CH4 C, SOLVT UC and SOLVT C respectively."}
\text{st_w(1) = "Data can be stored only on drives A: and B:"}
\text{st_w(1) = "Please supply the following data:"
\text{screen_box(5,1,75,21,0)}
\text{st_q(1) = "Are the data to be stored on drive A: (y/n) ?"}
\text{st_q(2) = "Is the solvent methane (y/n)?"}
\text{st_q(3) = "Is the column coated (y/n)?"}
\text{st_q(4) = "Supply the name of the data file."}
\text{st_q(5) = "Are the CH4 UC data stored on drive A: (y/n) ?"}
\text{st_q(6) = "Supply the file name for the CH4 UC data."}
\text{st_q(7) = "Are the CH4 C data stored on drive A: (y/n) ?"}
\text{st_q(8) = "Supply the file name for the CH4 C data."
\text{REM}
\text{n = 3}
\text{k = ADD(LEN(st_w(5)),5)
\text{FOR j = 1 TO 4
\text{\quad PRINT AT(10,n); st_w(j)
\text{\quad ADD n,2
\text{NEXT j
\text{INC n
\text{PRINT AT(10,n); st_w(5)
\text{FOR j = 1 TO 3
\text{\quad ADD n,2
\text{\quad message(st_q(j),10,n,k,n,1)
\text{\quad yes_or_no(j)
\text{NEXT j
\text{ADD n,2
\text{message(st_q(4),10,n,k,n,1)
\text{INPUT st_f(4)
\text{REM
\text{IF ok_q(1)
\text{\quad st_f(1) = "a:
\text{ELSE
\text{\quad st_f(1) = "b:
\text{ENDIF
\text{IF ok_q(2)
\text{\quad st_f(2) = "\CH4_"
\text{ELSE
\text{\quad st_f(2) = "SOLVT_"
\text{ENDIF
IF ok_q(3)
    st_f(3) = "C"
ELSE
    st_f(3) = "UC"
ENDIF
file_title$ = st_f(1)+st_f(2)+st_f(3)+st_f(4)+".LST"

IF ok_q(2)
    n2 = 0
ELSE
    n2 = 1
ENDIF
IF NOT ok_q(3)
    n3 = 0
ELSE
    n3 = 1
ENDIF

expt_type = n2 + 10*n3
OPEN "O",#1,file_title$

RETURN

REM
PROCEDURE store_data

REM
Arrange for the storage of the data; experimental results
REM
from the ADC are arranged in rows of 15
REM
OPEN "O",#1,file_title$  ! opens file for writing
PRINT #1 USING "#.#,#####",total_time
PRINT #1 USING "#.#,#####",peak_time
PRINT #1 USING "#.#",n_base
PRINT #1, dt_set,""n_spec""""n_max""""pct
PRINT #1,gas_flow_rate,""inlet_pressure""""outlet_pressure""""wt_of_polymer

REM
DIV n_max,15  ! divides by 15 and truncates
MUL n_max,15  ! ensures that final value is a multiple of 15
n_data = 0
REPEAT
    j = 0
    REPEAT
        INC j
        PRINT #1, USING "#.#", exptl_pt(n_data+j);
    UNTIL j = 15
    ADD n_data,15
UNTIL n_data = n_max
CLOSE #1

RETURN

REM
PROCEDURE lose_arrow(VAR s)
LOCAL s0,n
n = LEN(s)
s0 = LEFT$(s,3)
IF s0 = "->-
    s = RIGHT$(s,SUB(n,3))
ENDIF

RETURN

REM
REM
PROCEDURE get_number(s0, VAR s1, real)
LOCAL j,k,s2
s1 = TRIM$(s1)
j = LEN(s1)
k = INSTR(s1,s0)
s2 = LEFTS(s1,k-1)
s1 = RIGHTS(s1,j-k)
real = VAL(s2)
s1 = TRIM$(s1)
RETURN
REM
REM
PROCEDURE get_data(VAR n_pts, n_peak)
LOCAL j,k,s1,file_title$
file_name(file_title$)$
OPEN "I",#1,file_title$
INPUT #1,total_time
INPUT #1,pk_time
INPUT #1,n_base
INPUT #1,s1
lose_arrow(s1)
get_number(" ",s1,dt_set)
n_peak = ROUND(pk_time/dt_set)
get_number(" ",s1,pts_spec)
n_spec = ROUND(pts_spec)
get_number(" ",s1,pts_max)
n_spec = ROUND(pts_max)
pct = VAL(s1)
REM
INPUT #1,s1
lose_arrow(s1)
get_number(" ",s1,gas_flow)
get_number(" ",s1,p_inlet)
get_number(" ",s1,p_outlet)
polymer_wt = VAL(s1)
REM
n_pts = 0
CLS
PRINT AT(20,8); "Current number of point being processed" DO UNTIL EOF(#1)
LINE INPUT #1,s1
lose_arrow(s1)
DO WHILE LEN(s1) > 4
n_pts = npts + 1
PRINT AT(38,10); n_pts
get_number(" ",s1,z)
exptl_pt(n_pts) = ROUND(z)
! proc. returns a real value ! round to integer
LOOP
n_pts = npts+1
exptl_pt(n_n_pts) = ROUND(VAL(s1))
LOOP
CLOSE #1
CLS
PRINT AT(20,10); USING "Number of experimental points \\

****",n_pts
PRINT AT(20,12); USING "Approximate point of maximum \\

****",n_peak
st0 = "To show the experimental data, press any key"
paws(st0,23,1)
RETURN
PROCEDURE exptl
PROCEDURE pplot
CLS
IF (n_pts > 640) AND (n_peak > 320)
   n_finish = n_peak + 320
   IF n_finish > n_pts
      n_finish = n_pts
   ENDIF
   n_start = n_finish - 640
ELSE
   n_start = 1
   IF n_pts > 640
      n_finish = 640
   ELSE IF (n_pts < 640)
      n_finish = n_pts
   ENDIF
ENDIF
FOR n = n_start TO n_finish
   PLOT n - n_start, 300 - exptl_pt(n)
NEXT n
st0 = "To continue, press any key"
paws(st0,23,1)
PROCEDURE partial_plot
REM Where the number of points is in excess of that which can be shown on
REM the screen, it is convenient to be able to show the general shape of the
REM curve by plotting only every nth point where n depends upon the total
REM number of experimental points.
LOCAL n,n_th,n_count,ok,j,k
CLS
n_th = n_max DIV 640 ! to determine plotting interval
INC n_th
SELECT n_th
   CASE 1
      s = ""
   CASE 2
      s = STR$(n_th) + "nd"
   CASE 3
      s = STR$(n_th) + "rd"
   CASE 4,5,6,7,8,9
      s = STR$(n_th) + "th"
ENDSELECT
REM
s = "Plotting every \( n \) point"
off_set(s,j,k)
PRINT AT(j,1);s
n_count = 0
FOR n = 1 TO n_max
   ok = (n MOD n_th) = 0
   IF ok
      INC n_count ! determine value for x-axis
      PLOT n_count, SUB(300, exptl_pt(n))
   ENDIF
NEXT n
st0 = "To continue, press any key"
paws(st0, 23, 1)
RETURN
REM
PROCEDURE plot_area
LOCAL delta_a, j, n, n_rem, n_sections, f0, f1
CLS
IF n_pts > 640
   n_rem = 640
ELSE
   n_rem = n_pts
ENDIF
n_begin = n_start
n_sections = 0
area = 0
f1 = 6/140
WHILE n_rem > 6
   delta_a = 0
   FOR j = 0 TO 6
      n = n_begin + j
      SELECT j ! Newton-Cotes weight factors for 6 strip
      CASE 0, 6
         f0 = 41
      CASE 1, 5
         f0 = 216
      CASE 2, 4
         f0 = 27
      CASE 3
         f0 = 272
      ENDSELECT
      delta_a = delta_a + f0 * SUB(exptl_pt(n), n_base)
   NEXT j
   delta_a = f1 * delta_a
ENDIF
ADD n_begin,6
SUB n_rem,6
INC n_sections
PRINT AT(10,5);
USING "Number of Integration Sections ###", n_sections
PRINT AT(10,7);
USING "Current value part area under curve #######", delta_a
PRINT AT(10,9);
USING "Cumulative value of area under curve ######.##", delta_a
PAUSE 2
WEND
RETURN
REM
REM
PROCEDURE menu
LOCAL n_type,nx,my,n,j
menustart:
  nbx1 = 5
  nby1 = 2
  nbx2 = 75
  nby2 = ADD(4,MUL(6,2))
screen_box(nbx1,nby1,nbx2,nby2,0)
st_w(1) = "There are five operations possible:"
st_w(2) = "(1) To obtain and store experimental results."
st_w(3) = "(2) To plot data which includes the peak height."
st_w(4) = "(3) To plot selected data to show the entire curve."
st_w(5) = "(4) Numerical integration to get the area under the curve."
st_w(6) = "(5) To exit from the program."
st_w(7) = "Make your selection - (1 to 5)."
off_set(st_w(5),nx,j)
y = ADD(nby1,1)
REM
FOR n = 1 TO 6 DO
  message(st_w(n),nx,ny,nx+j,ny,2,0)
  ADD ny,2
NEXT n
j = LEN(st_w(7))
REPEAT
  PRINT AT(nx,ny): st_w(7)
  LOCAT nx+j,ny
  s = INKEY$
  k = ASC(s)
UNTIL (48 < k) AND (k < 54)
n_type = k - 48
REM
SELECT n_type
CASE 1
  exptl
  GOTO menu_start
CASE 2, 3, 4
  screen_box(5,21,75,23,1)
  st = "Is it necessary to read the data from a file (y/n) ?"
  off_set(st,n,j)
  message(st,n,22,n+j,22,2,0)
  REPEAT
    s = INKEY$
    s = UPPER$(s)
    k = ASC(s)
UNTIL (k = 78) OR (k = 89)
IF s = "Y"
    get_data(n_pts,n_peak)
ENDIF
IF n_type = 2
    partial_plot
    GOTO menu_start
ENDIF
IF n_type = 3
    partial_plot
    GOTO menu_start
ENDIF
IF n_type = 4
    plot_area
    GOTO menu_start
ENDIF
CASE 5
END
ENDSELECT
paws("To continue, press any key",22,0)
RETURN
REM
DEFINITION MODULE bbmutils; (* 14th August 1990 *)

IMPORT Str,Window,IO;

TYPE
  String = ARRAY[1..80] OF CHAR;
  Words = ARRAY[0..21] OF String;
  Data = ARRAY[1..20] OF LONGREAL;
  SigFigs = ARRAY[1..20] OF CARDINAL;

VAR
  spaces : ARRAY[1..80] OF String;

PROCEDURE SpaceFill;

PROCEDURE SizeArray(w: Words; n1,n2: CARDINAL; VAR jchars,jrow:CARDINAL);

PROCEDURE NewWindow(w: Words; n1,n2: CARDINAL; m: Window.WinType;
  VAR xc1,yc1,xc2,yc2: Window.AbsCoord);

PROCEDURE OffSet(s: ARRAY OF CHAR; VAR nchars,nspaces:CARDINAL;
  xmin,xmax:CARDINAL);

PROCEDURE LocateStr(s: ARRAY OF CHAR; nxmin,nxmax,nLine:CARDINAL);

PROCEDURE WrArray(Ar: Words; ns,nf,xmin,xmax:CARDINAL; LastLine: BOOLEAN);

PROCEDURE Pause(VAR w: Words; nLines,nMessage:CARDINAL);

PROCEDURE Round(VAR n: CARDINAL; x: LONGREAL);

PROCEDURE CharDisplay;

PROCEDURE ShowData(VAR wh,wd: Words; d: Data; np: SigFigs; nh,nd: CARDINAL);

PROCEDURE bbmConcat(VAR s: String; w: Words; n1,n2: CARDINAL);

PROCEDURE AddSpaces(VAR wd: Words; nvalues:CARDINAL);

END bbmutils.

IMPLEMENTATION MODULE bbmutils;

(*# optimize( i386 => on ) *)
(*# optimize( i387 => on ) *)
(*# debug( vid => full ) *)
(*# check( index => on ) *)
(*# check( stack => on ) *)

PROCEDURE SpaceFill;
  VAR n :CARDINAL;
  BEGIN
    n := 1; spaces[1] := ' ';
    FOR n := 2 TO 80 DO Str.Concat(spaces[n],spaces[n-1],')'); END;
  END SpaceFill;
PROCEDURE SizeArray(w:Words; n1,n2:CARDINAL; VAR jchars,jrow:CARDINAL);

(* This procedure determines the largest string in an array of String; beginning at n1 and ending at n2; jchars is the length and jrow is the index of the largest string *)

VAR j,k :CARDINAL;
BEGIN
  jchars := 0;
  FOR k := n1 TO n2 DO
    j := Str.Length(w[k]);
    IF j > jchars THEN jchars := j; jrow := k END;
  END
END SizeArray;

PROCEDURE NewWindow(w:Words; n1,n2:CARDINAL; m:Window.WinType;
VAR xc1,yc1,xc2,yc2:Window.AbsCoord);

(* This procedure re-sizes the current window to accommodate an array w of String 6 spaces are added to each side of the largest string and 3 lines to each half of the window *)

VAR jmax,jrow,k,n :CARDINAL;
BEGIN
  SizeArray(w,n1,n2,jmax,jrow);
  (* determine width in terms of spaces *)
  jmax := jmax DIV 2; INC(jmax,6);
  IF jmax > 40 THEN jmax := 40 END;
  xc1 := 40 - jmax; xc2 := 40 + jmax;
  (* determine length in terms of lines *)
  k := n2 - n1 + 1;
  IF ODD(k) THEN INC(k,1) END;
  k := k DIV 2; INC(k,3);
  IF k > 11 THEN k := 11 END;
  yc1 := 12 - k; yc2 := 12 + k;
  Window.Change(m,xc1,yc1,xc2,yc2);
  Window.PutOnTop(m);
END NewWindow;

PROCEDURE OffSet(s:ARRAY OF CHAR; VAR nchars,nspaces:CARDINAL;
xc1,xc2:CARDINAL);
BEGIN
  nchars := Str.Length(s);
  nsaces := xc2 - xc1;
  DEC(nspaces,nchars);
  nsaces := nsaces DIV 2;
  INC(nspaces);
END OffSet;
PROCEDURE LocateStr(s:ARRAY OF CHAR; xc1,xc2,nLine:CARDINAL);

VAR  j,k :CARDINAL;
BEGIN
  OffSet(s,j,k,xc1,xc2);
  Window.DirectWrite(k,nLine,ADR(s),Str.Length(s));
END LocateStr;

PROCEDURE WrArray(Ar:Words; ns,nf,xc1,xc2:CARDINAL; LastLine:BOOLEAN);

(* This procedure writes the contents of an array to the current
   window which must be large enough to accommodate the text. *)

VAR  i,j,k,nmax,klast,n,nrows :CARDINAL;
BEGIN
  SizeArray(Ar,ns,nf,j,nmax);
  OffSet(Ar[nmax],j,k,xc1,xc2);
  IF LastLine THEN OffSet(Ar[nf],j,klast,xc1,xc2) END;
  i := 2;
  FOR j := ns TO nf DO
    IF (j = nf) AND LastLine THEN n := klast ELSE n := k END;
    Window.DirectWrite(n+j,ADR(Ar[j]),Str.Length(Ar[j]))
  END;
  Window.GotoXY(n+Str.Length(Ar[nf])+1,nf-ns+i);
END WrArray;

PROCEDURE Pause(VAR w:Words; nrows,nMessage:CARDINAL);

VAR  j,k,i,n,ni,nmax
    xc1,yc1,xc2,yc2
    ch
    s
    wd1,wd2
    w1,w2
    :CARDINAL;
BEGIN
  :Window.AbsCoord;
  :CHAR;
  :Words;
  :Window.WinDef;
  :Window.WinType;

(* The array containing the information to be displayed should not exceed
   5 lines of text - i.e. nrows = 4 the third line will consist of a message
   determined by the third parameter *)

  wd2 := Window.WinDef(0,0,79,24,Window.Red,Window.Black,
      TRUE,FALSE,TRUE,TRUE,Window.SingleFrame,
      Window.Yellow,Window.Black);
  w2 := Window.Open(wd2);
  IF nrows > 4 THEN
    s[0] := 'Pause has been called with too many lines of text';
    NewWindow(w,0,0,w2,xc1,yc1,xc2,yc2);
    LocateStr(s[0],xc1,xc2,3);
    HALT;
END;
nl := nrow; INC(nl);
IF nMessage = 0 THEN w[nl] := 'press the space bar to continue.';
ELSIF nMessage = 1 THEN w[nl] := 'Do you wish to continue (y/n) ?';
ELSE
END;
SizeArray(w,0,nl,j,nmax);
NewWindow(w,0,nl,w2,xc1,yc1,xc2,yc2);
WrArray(w,0,nl,xc1,xc2,TRUE);
REPEAT
  ch := CAP(IO.RdKey());
  IF ch = 'N' THEN HALT END;
UNTIL (ch = ' ') OR (ch = 'Y');
Window.Close(w2);
Window.CursorOn;
END Pause;

PROCEDURE Round(VAR n:CARDINAL; x:LONGREAL);
VAR dx :LONGLREAL;
s :String;
BEGIN
  IF x > 65535.0 THEN
    s := 'Round called with a LongReal > Maximum permitted Cardinal';
    LocateStr(s,0,79,24);
    HALT;
  END;
  n := TRUNC(x);
  dx := x - VAL(LONGREAL,n);
  IF dx >= 0.5 THEN INC(n) END;
END Round;

PROCEDURE CharDisplay;
VAR j,k,n,r,c,nchar,nrow,ncol :CARDINAL;
m1 :Window.WinType;
d1 :Window.WinDef;
BEGIN
d1 := Window.WinDef(0,0,79,25,Window.LightBlue,Window.Black,
FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
Window.Yellow,Window.Black);
m1 := Window.Open(d1);
ncol := 1; nrow := 1;
FOR nchar := 128 TO 255 DO;
  Window.GotoXY(ncol,nrow); IO.WrCard(nchar,3);
  Window.GotoXY(ncol+1,nrow+1); IO.WrChar(CHR(nchar));
  INC(ncol,5);
  IF ncol > 77 THEN INC(nrow,3); ncol := 1; END;
END CharDisplay;
PROCEDURE ShowData(VAR wh, wd: Words; d: Data; np: SigFigs; nh, nd: CARDINAL);
VAR
  j, k, n, nx, ny, xc1, xc2, yc1, yc2, nmin, k0,
  maxlines, maxchars
    : CARDINAL;
  m0, d0, ok, ch
    : Window.WinDef;
  s
    : String;
BEGIN
  (* This procedure is intended to display numerical data for debugging purposes;*
  the arrays should contain the following information:
    wh - nh lines of text for a heading;
    wd - identifiers for the numerical data;
    d - nd items of numerical data;
    np - the number of figures after the point.
    nmin should not exceed 20 though no protection is provided. *)
  nmin := 8;
  FOR n := 1 TO nd DO
    wtemp[n] := wd[n];
    (* determine number of places before decimal point *)
    k := TRUNC(ABS(d[n]));
    Str.CardToStr(VAL(LONGCARD, k), s, 10, ok);
    k := nmin - Str.Length(s);
    IF d[n] < 0.0 THEN DEC(k) END;
    Str.Append(wtemp[n], spaces[k]);
    (* obtain a string representation of the LONGREALs in
     array d to the number of places stored in np *)
    Str.FixRealToStr(d[n], np[n], s, ok);
    Str.Append(wtemp[n], s);
  END;
  wtemp[nd+1] := 'Press any Key';
  (* Find the longest string *)
  maxchars := 0;
  FOR n := 0 TO nh-1 DO
    k := Str.Length(wh[n]);
    IF k > maxchars THEN maxchars := k END;
  END;
  FOR n := 1 TO nd DO
    k := Str.Length(wtemp[n]);
    IF k > maxchars THEN maxchars := k END;
  END;
  maxlines := nh + (nd+3) + 2;
  maxchars := maxchars DIV 2; INC(maxchars, 6);
  IF maxchars > 39 THEN xc1 := 1; xc2 := 80
    ELSE xc1 := 40 - maxchars; xc2 := 40 + maxchars; END;
  maxlines := maxlines DIV 2; INC(k, 3);
IF maxlines > 12 THEN yc1 := 1; yc2 := 24
ELSE yc1 := 12 - maxlines; yc2 := 12 + maxlines; END;

d0 := Window.WinDef(0,0,79,24,Window.LightBlue,Window.Black,
FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
Window.Yellow,Window.Black);

m0 := Window.Open(d0);
Window.CursorOn;
Window.Change(m0,xc1,yc1,xc2,yc2);
Window.PutOnTop(m0);

(* Write heading *)
ny := 0;
FOR n := 0 TO nh-1 DO
  Offset(wh[n],j,k,xc1,xc2);
  INC(ny);
  Window.DirectWrite(k,ny,ADR(wh[n]),j);
END;

(* Underline last line of input *)
k0 := Str.Length(wh[nh-1]);
s := wh[nh-1];
FOR n := 1 TO k0 DO s[n] := CHR(196) END;
INC(ny);
Window.DirectWrite(k,ny,ADR(s),k0);

(* Write numerical values to window *)
Offset(wtemp[1],j,k,xc1,xc2);
FOR n := 1 TO nd DO
  INC(ny);
  Window.DirectWrite(k,ny,ADR(wtemp[n]),Str.Length(wtemp[n]));
END;

(* Pause to examine data *)
INC(ny,2);
s := wtemp[nd+1];
Offset(s,j,k,xc1,xc2);
Window.DirectWrite(k,ny,ADR(s),j);
Window.GotoXY(j+k+2,ny);
ch := IO.RdKey();
Window.Close(m0);
END ShowData;

PROCEDURE bmmConcat(VAR s:String; w:Words; n1,n2:CARDINAL);
VAR k :CARDINAL;
BEGIN
  s := "";
  FOR k := n1 TO n2 DO Str.Append(s,w[k]) END;
END bmmConcat;
PROCEDURE AddSpaces(VAR wd:Words; nvalues:CARDINAL);

(* This procedure will add spaces to the beginning of the string representation of LONGREALs when used as identifiers in ShowData. *)

VAR  n,nmax,j :CARDINAL;
BEGIN
  (* Find longest string *)
  nmax := 0;
  FOR n := 1 TO nvalues DO
    j := Str.Length(wd[n]);
    IF j > nmax THEN nmax := j END;
  END;

  (* Add extra spaces at the beginning of the string *)
  FOR n := 1 TO nvalues DO
    j := nmax - Str.Length(wd[n]);
    IF j > 0 THEN Str.Concat(wd[n],spaces[j],wd[n]) END;
  END;
BEGIN
  SpaceFill;
END  bbmutils.
DEFINITION MODULE retvols;

    TYPE
        VrtData = ARRAY[1..2] OF ARRAY[1..9] OF LONGREAL;
    VAR
        SolventRefNo : CARDINAL;
        Vret : VrtData;

PROCEDURE RetentVols80(SolventRefNo: CARDINAL);

PROCEDURE RetentVols100(SolventRefNo: CARDINAL);

PROCEDURE RetentVols120(SolventRefNo: CARDINAL);

END retvols.

IMPLEMENTATION MODULE retvols;

(*# optimize i386 => on *)
(*# optimize i387 => on *)
(*# debug vid => full *)
(*# check index => on *)
(*# check stack => on *)

(* Vret[i, n] represent mol fractions as recalculated from original wt fractions *)

PROCEDURE RetentVols80(SolventRefNo: CARDINAL);
BEGIN

    Vret[1,1] := 0.00000;  Vret[1,2] := 0.23906;
    Vret[1,3] := 0.51520;  Vret[1,4] := 0.56425;
    Vret[1,5] := 0.63894;  Vret[1,6] := 0.75975;
    Vret[1,7] := 0.90447;  Vret[1,8] := 0.92811;
    Vret[1,9] := 1.00000;

    CASE SolventRefNo OF
    | 1: (* Methanol, RPS 62, RPP 117 *)
        Vret[2,9] := 3.683;
    | 2: (* Ethanol, RPS 102, RPP 170 *)
    | 3: (* Benzene, RPS 242, RPP 343 *)
        Vret[2,9] := 27.739;

END.

<table>
<thead>
<tr>
<th>4: (* Dichloromethane, RPS 53, RPP 107 *)</th>
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</table>

<table>
<thead>
<tr>
<th>5: (* Carbon Tetrachloride, RPS 42, RPP 94 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vret[2,9] := 22.998;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6: (* Cyclohexane, RPS 249, RPP 353 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vret[2,9] := 17.859;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>7: (* Pentane, RPS 223, RPP 311 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vret[2,9] := 3.481;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8: (* Hexane, RPS 271, RPP 379 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vret[2,9] := 8.312;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>9: (* Heptane, RPS 308, RPP 429 *)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>10: (* Octane, RPS 354, RPP 483 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vret[2,9] := 47.207;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>11: (* Toluene, RPS 286, RPP 400 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vret[2,9] := 64.722;</td>
</tr>
</tbody>
</table>
12: (* 2-Butanone, RPS 167, RPP 243 *)
Vret[2,1] := 15.240;
Vret[2,3] := 12.891;
Vret[2,4] := 17.139;
Vret[2,5] := 18.185;
Vret[2,7] := 15.335;
Vret[2,8] := 13.870;

13: (* Trichloromethane, RPS 50, RPP 103 *)
Vret[2,1] := 27.734;
Vret[2,2] := 26.400;
Vret[2,3] := 22.715;
Vret[2,4] := 31.103;
Vret[2,8] := 27.166;
Vret[2,9] := 27.166;

14: (* Tetrahydrofuran, RPS 168, RPP 244 *)
Vret[2,1] := 18.115;
Vret[2,2] := 19.510;
Vret[2,3] := 15.992;
Vret[2,8] := 16.554;

15: (* Methyl Acetate, RPS 129, RPP 203 *)
Vret[2,1] := 7.435;
Vret[2,2] := 5.878;
Vret[2,4] := 8.308;
Vret[2,5] := 8.878;
Vret[2,6] := 8.159;
Vret[2,8] := 5.247;

16: (* Acetone, RPS 122, RPP 196 *)
Vret[2,1] := 6.270;
Vret[2,3] := 5.124;
Vret[2,4] := 7.008;
Vret[2,8] := 4.289;
Vret[2,9] := 5.832;

17: (* Isopropanol, RPS 134, RPP 208 *)
Vret[2,1] := 9.668;
Vret[2,2] := 17.382;
Vret[2,3] := 8.832;
Vret[2,4] := 11.462;
Vret[2,5] := 12.085;

18: (* Ethyl Acetate, RPS 172, RPP 249 *)
Vret[2,1] := 13.524;
Vret[2,2] := 13.885;
Vret[2,3] := 12.079;
Vret[2,6] := 15.958;
Vret[2,8] := 10.772;

ELSE
END;
END RetenVols80;
PROCEDURE Retent Vols100(SolVentRefNo: CARDINAL);
BEGIN
Vret[1,1] := 0.00000; Vret[1,2] := 0.23906;
Vret[1,3] := 0.51520; Vret[1,4] := 0.56425;
Vret[1,5] := 0.63894; Vret[1,6] := 0.75975;
Vret[1,7] := 0.90447; Vret[1,8] := 1.00000;
CASE SolVentRefNo OF
  | 1: (* Methanol, RPS 62, RPP 117 *)
  |     Vret[2,1] := 0.951; Vret[2,2] := 0.912;
  | 2: (* Ethanol, RPS 102, RPP 170 *)
  | 3: (* Benzene, RPS 242, RPP 343 *)
  | 4: (* Dichloromethane, RPS 53, RPP 107 *)
  | 5: (* Carbon Tetrachloride, RPS 42, RPP 94 *)
  | 6: (* Cyclohexane, RPS 249, RPP 353 *)
  | 7: (* Pentane, RPS 223, RPP 311 *)
  | 8: (* Hexane, RPS 271, RPP 379 *)
  | 9: (* Heptane, RPS 308, RPP 429 *)
END;
10: (* Octane, RPS 354, RPP 483 *)

11: (* Toluene, RPS 286, RPP 400 *)
   Vret[2,1] := 33.112;  Vret[2,2] := 34.667;

12: (* 2-Butanone, RPS 167, RPP 243 *)

13: (* Trichloromethane, RPS 50, RPP 103 *)

14: (* Tetrahydrofuran, RPS 168, RPP 244 *)

15: (* Methyl Acetate, RPS 129, RPP 203 *)

16: (* Acetone, RPS 122, RPP 196 *)

17: (* Isopropanol, RPS 134, RPP 208 *)

18: (* Ethyl Acetate, RPS 172, RPP 249 *)

ELSE
END;

END RetentVols100;
PROCEDURE RetentVols120(SolVentRefNo: CARDINAL);
BEGIN

Vret[1,1] := 0.00000;  Vret[1,2] := 0.23906;
Vret[1,3] := 0.51520;  Vret[1,4] := 0.56425;
Vret[1,5] := 0.63894;  Vret[1,6] := 0.75975;
Vret[1,7] := 0.90447;  Vret[1,8] := 1.00000;

CASE SolVentRefNo OF
| 1: (* Methanol, RPS 62, RPP 117 *)
  | Vret[2,1] := 0.021;  Vret[2,2] := -0.1030;
  | Vret[2,3] := -0.1115;  Vret[2,4] := -0.0393;
  | Vret[2,7] := 0.035;  Vret[2,8] := 0.035;
| 2: (* Ethanol, RPS 102, RPP 170 *)
| 3: (* Benzene, RPS 242, RPP 343 *)
| 4: (* Dichloromethane, RPS 53, RPP 107 *)
| 5: (* Carbon Tetrachloride, RPS 42, RPP 94 *)
| 6: (* Cyclohexane, RPS 249, RPP 353 *)
| 7: (* Pentane, RPS 223, RPP 311 *)
  | Vret[2,1] := 0.845;  Vret[2,2] := 0.624;
  | Vret[2,3] := 0.691;  Vret[2,4] := 0.744;
  | Vret[2,5] := 0.794;  Vret[2,6] := 0.901;
  | Vret[2,7] := 0.694;  Vret[2,8] := 0.301;
| 8: (* Hexane, RPS 271, RPP 379 *)
| 9: (* Heptane, RPS 308, RPP 429 *)
<table>
<thead>
<tr>
<th>10: (* Octane, RPS 354, RPP 483 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 14.077;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 14.105;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 14.159;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 15.289;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 15.091;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 14.185;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 14.209;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 11.177;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>11: (* Toluene, RPS 286, RPP 400 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 18.108;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 19.208;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 19.494;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 20.072;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 20.056;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 19.253;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 20.181;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 16.155;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>12: (* 2-Butanone, RPS 167, RPP 243 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 3.638;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 3.865;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 3.809;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 4.065;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 4.154;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 4.559;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 4.249;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 3.575;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>13: (* Trichloromethane, RPS 50, RPP 103 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 6.636;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 7.135;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 7.688;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 7.656;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 7.766;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 7.954;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 8.281;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 6.813;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>14: (* Tetrahydrofuran, RPS 168, RPP 244 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 7.265;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 7.673;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 7.702;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 8.029;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 8.137;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 7.718;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 8.122;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 6.350;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>15: (* Methyl Acetate, RPS 129, RPP 203 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 1.395;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 1.426;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 1.372;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 1.533;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 1.659;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 1.882;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 1.559;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 1.362;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>16: (* Acetone, RPS 122, RPP 196 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 1.104;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 1.117;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 1.076;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 1.185;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 1.313;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 1.621;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 1.267;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 1.096;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>17: (* Isopropanol, RPS 134, RPP 208 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 1.757;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 1.786;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 1.815;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 1.939;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 2.079;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 2.561;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 2.202;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 1.944;$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>18: (* Ethyl Acetate, RPS 172, RPP 249 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{ret}[2,1] := 3.271;$</td>
</tr>
<tr>
<td>$V_{ret}[2,2] := 3.427;$</td>
</tr>
<tr>
<td>$V_{ret}[2,3] := 3.386;$</td>
</tr>
<tr>
<td>$V_{ret}[2,4] := 3.659;$</td>
</tr>
<tr>
<td>$V_{ret}[2,5] := 3.772;$</td>
</tr>
<tr>
<td>$V_{ret}[2,6] := 4.036;$</td>
</tr>
<tr>
<td>$V_{ret}[2,7] := 3.787;$</td>
</tr>
<tr>
<td>$V_{ret}[2,8] := 3.148;$</td>
</tr>
</tbody>
</table>

ELSE
END;
BEGIN
  RetentVols120;
END retvol.
DEFINITION MODULE rjmutils;

IMPORT Window,Str,bbmutils,IO,FIO,Graph;
FROM bbmutils IMPORT Words,String,spaces,Data,SigFigs;
FROM MATHLIB IMPORT Exp,Log,Sqrt;

TYPE  CharSet = SET OF CHAR;
CardSet = SET OF CARDINAL;
VrtData = ARRAY[1..2] OF ARRAY[1..9] OF LONGREAL;

CONST  
CtoK = 273.16; GasConst = 8.3144; (* J/(mol K) *)

(* Constants for the effect of temperature on the calculation of the specific volume of polymer blends. *)
a0b0 = 1.02976406; a0b1 = 7.58275052E-4;
a1b0 = 2.25513866E-3; a1b1 = 1.48485124E-4; a1b2 = 3.29117195E-11;

(* Constants for the physical properties of the polymers *)
SegMolWt2 = 254.4; sigmaG2 = 3147.3; NoAvMolWt2 = 3290.0;
SegMolWt3 = 594.89; sigmaG3 = 4982.4; NoAvMolWt3 = 10400.0;

VAR  
(* Global *)
MolWt,Tcrt,Pcrt,ZRa,Omegan,Rho20,OmeganSRK,
VpA,VpB,VpC,VpD,b0,b1,b2,VP,TdegC,Vast,
SolubilityParameter,
v1,vred1,vstar1,Pstar1,Pred1,Tred1,Tstar1,
v2,vred2,vstar2,v3,vred3,vstar3,Pstar2,Pstar3,
Pred2,Pred3,Tred2,Tred3,Tstar2,Tstar3,
v3,vred23,vstar23,vbarN,
P,Pstar23,Pred23,TdegK,Tstar23,Tred23,phi2,phi3,
phistar2,phistar3,theta2,theta3,
StoVRatio1,StoVRatio2,StoVRatio3,
WtFr,dPred,dTred,dvred
LOAD:
SolventRefNo : LONGREAL;
SolventName : CARDINAL;
Vret : String;
VrtData : VrtData;
Debug : ARRAY[1..20] OF BOOLEAN;

PROCEDURE CubeRoot(x:LONGREAL):LONGREAL;

PROCEDURE SetDebugParams(nLines: CARDINAL);

PROCEDURE CancelDebug;

PROCEDURE SolventChoice(VAR SolventRefNo: CARDINAL;
DISPLAYMenu: BOOLEAN; VAR SolventName: String);

PROCEDURE ProbePhysProps(SolventRefNo: CARDINAL);

PROCEDURE VPmmHg(VAR VP: LONGREAL; TdegC: LONGREAL;
SolventRefNo: CARDINAL);

PROCEDURE HBT(VAR Vsat,Kval: LONGREAL; TdegC,Psystem: LONGREAL);

PROCEDURE RackettSD(VAR Vsat: LONGREAL; TdegC: LONGREAL);
PROCEDURE AlphaCalc(VAR alpha: LONGREAL; TdegC: LONGREAL);

PROCEDURE RSD(VAR vt,alpha,kval: LONGREAL; TdegC,Psys: LONGREAL);

PROCEDURE ProbeCharProps(TdegC:LONGREAL);

PROCEDURE PolymerSpecVol(VAR SpVol,Alpha: LONGREAL;
TdegC,WtFrEVA: LONGREAL);

PROCEDURE MassFromMol(VAR wm2,wm3: LONGREAL; MolFr2: LONGREAL);

PROCEDURE SegmtFromMol(VAR ws2,ws3: LONGREAL; MolFr2: LONGREAL);

PROCEDURE MolFromMass(VAR mf2,mf3: LONGREAL; WtFr2: LONGREAL);

PROCEDURE PolymerProps(TdegC,WtFrEVA:LONGREAL);

END rjmutils.

IMPLEMENTATION MODULE rjmutils;

(* amended 14th October to avoid the need for displaying the probe menu *)

(* amended 15th August to include Debug parameters 12,13 for RosWalsh *)

(* amended 13th August to include procedures for obtaining mass fractions from mol fractions;
segment fractions from mole fractions and mol fractions from mass fractions *)

(*# optimize( i386 => on ) *)
(*# optimize( i387 => on ) *)
(*# debug( vid => full ) *)
(*# check( index => on ) *)
(*# check( stack => on ) *)

PROCEDURE CubeRoot(x:LONGREAL): LONGREAL;

VAR
  xroot :LONGREAL;
  w :Words;

BEGIN
  IF x <= 0.0 THEN
    w[0] := 'CubeRoot called with argument <= zero';
    bbmutils.Pause(w,0,1);
  ELSE
    xroot := Exp(Log(x)/3.0);
    RETURN xroot;
  END;
END CubeRoot;
PROCEDURE SetDebugParams(nLines:CARDINAL);

VAR
    nx,nx,nx1,yc1,xc2,xc2,j,k,LastLine,
    j0,k0,m :CARDINAL;
    ok :BOOLEAN;
    ch2 :CHAR;
    w :Words;
    m0 :Window.WinType;
    d0 :Window.WinDef;

BEGIN

    w[0] := 'Display of Numerical Data';
    w[1] := 'Do you wish values from ProbePhysProps (y/n) ?';
    w[2] := 'Do you wish values from VPmmHg (y/n) ?';
    w[3] := 'Do you wish values from HBT (y/n) ?';
    w[4] := 'Do you wish values from RackettSD (y/n) ?';
    w[5] := 'Do you wish values from AlphaCalc (y/n) ?';
    w[6] := 'Do you wish values from RSD (y/n) ?';
    w[7] := 'Do you wish values from ProbeCharProps (y/n) ?';
    w[8] := 'Do you wish values from PolymerProps (y/n) ?';
    w[9] := 'Do you wish values from Bviral (y/n) ?';
    w[10] := 'Do you wish values from ChiCalc (y/n) ?';
    w[11] := 'Do you wish values from XijBar (y/n) ?';
    w[12] := 'Do you wish values from PartDerivs (y/n) ?';
    w[13] := 'Do you wish values from Spinodal (y/n) ?';

    d0 := Window.WinDef(0, 0, 79, 24, Window.LightBlue, Window.Black,
                        FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
                        Window.Yellow,Window.Black);

    m0 := Window.Open(d0);
    Window.CursorOn;
    bmbutils.NewWindow(w[0],nLines,m0,xc1,yc1,xc2,yc2);
    ny := 1; LastLine := yc2 - yc1 - 2;
    bmbutils.LocateStr(w[0],0,xc2-xc1,ny);
    INC(ny);
    bmbutils.OffSet(w[1],j,k,0,xc2-xc1);
    n := 0;
    w[21] := 'To change other debug commands enter y else n';
    bmbutils.OffSet(w[21],j,k,0,xc2-xc2);

    REPEAT
        INC(n); INC(ny); m := nLines-n+1;
        j := Str.Length(w[m]);
        Window.WriteByte(k,ny,ADR(w[m]),j);
        Window.GotoXY(j+k-1,ny);
        REPEAT
            ch1 := CAP(IO.RdKey());
            UNTIL (ch1 = 'Y') OR (ch1 = 'N');
            Debug[m] := ch1 = 'Y';
            Window.WriteByte(k0,LastLine,ADR(w[21]),j0);
            Window.GotoXY(j0+k0+2,LastLine);
        REPEAT
            ch2 := CAP(IO.RdKey());
            UNTIL (ch2 = 'Y') OR (ch2 = 'N');
            Window.GotoXY(1,LastLine);
            Window.CtrEot;
        UNTIL (n = nLines) OR (ch2 = 'N');
    Window.Close(m0);
END SetDebugParams;
PROCEDURE CancelDebug;
    VAR n:
BEGIN
    FOR n := 1 TO 20 DO Debug[n] := FALSE END;
END CancelDebug;

PROCEDURE SolventChoice(VAR SolventRefNo: CARDINAL;
                        DisplayMenu: BOOLEAN; VAR SolventName: String);

LABEL skip;
VAR
    nx1,nx2,nx3,nnline,n1,n2,n3,j,k:
    ch:
    s,t,w:
    range:
    m0:
    d0:
BEGIN
    s[1] := 'Methanol';
    s[2] := 'Ethanol';
    s[3] := 'Benzene';
    s[4] := 'Dichloromethane';
    s[7] := 'Pentane';
    s[8] := 'Hexane';
    s[9] := 'Heptane';
    s[10] := 'Octane';
    s[12] := '2-Butanone';
    s[14] := 'Tetrahydrofuran';
    s[15] := 'Methyl Acetate';
    s[16] := '2-Propanone';
    s[17] := 'Isopropanol';
    s[18] := 'Ethyl Acetate';
    t[1] := 'Methyl Alcohol';
    t[2] := 'Ethyl Alcohol';
    t[3] := 'Benzol';
    t[4] := 'Methylene Chloride';
    t[7] := 'Amyl Hydride';
    t[8] := 'Caproyl Hydride';
    t[9] := 'Heptyl Hydride';
    t[10] := 'Octyl Hydride';
    t[11] := 'Methyl Benzene';
    t[12] := 'Methyl Ethyl Ketone';
    t[13] := 'Chloroform';
    t[14] := 'Tetramethylene Oxide';
    t[15] := '';
    t[16] := 'Acetone';
    t[17] := 'Isopropyl Alcohol';
    t[18] := '';

    w[1] := 'Systematic Name';
    w[2] := 'Trivial Name';
    w[3] := 'Reference No.';
    w[4] := 'Enter the reference number for the solvent ';
    w[5] := 'Your choice was outside the permitted range - try again !';

    (* Note if the menu is not displayed then the user program must ensure the value of SolventRefNo is within {1..18} while excluding 3 and 14 *)

    IF NOT DisplayMenu THEN GOTO skip END;

    n1 := 5;  w[6] := spaces[n1];
    n2 := 14;  w[7] := spaces[n2];
    n3 := 15;  w[8] := spaces[n3];
    Str.Concat(w[9],w[6],w[1]);
    Str.Append(w[9],w[7]);
    Str.Append(w[9],w[2]);
    Str.Append(w[9],w[8]);
    Str.Append(w[9],w[3]);
d0 := Window.WinDef(0,0,79,24,Window.LightBlue,Window.Black,
FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
Window.Yellow,Window.Black);

m0 := Window.Open(d0);
Window.CursorOn;
nline := 1;
Window.DirectWrite(1,nline,ADR(w[9]),Str.Length(w[9]));
ch := CHR(196);
w[10] := spaces[78];
FOR j := 1 TO 78 DO w[10,j] := ch END;
INC(nline);
Window.DirectWrite(1,nline,ADR(w[10]),Str.Length(w[10]));
nx1 := 6; nx2 := 35; nx3 := 67;

FOR j := 1 TO 18 DO
  INC(nline);
  Window.DirectWrite(nx1,nline,ADR(s[j]),Str.Length(s[j]));
  Window.DirectWrite(nx2,nline,ADR(t[j]),Str.Length(t[j]));
  Window.GotoXY(nx3,nline);
  IO.WrCard(j,2);
END;

range := CardSet(1,3..18);
INC(nline,2);
bbmutils.Offset(w[4],j,k,0,79);
REPEAT
  Window.TextColor(Window.LightBlue);
  Window.GotoXY(1,nline);
  Window.ChrEol;
  bbmutils.LocateStr(w[4],0,79,nline);
  Window.GotoXY(j+k,nline);
  SolventRefNo := IO.RdCard();
  IF NOT (SolventRefNo IN range) THEN
    Window.TextColor(Window.Yellow);
    bbmutils.LocateStr(w[5],0,79,nline+1)
END;
UNTIL SolventRefNo IN range;
Window.Close(m0);

.skip: SolventName := s[SolventRefNo];
END SolventChoice;

PROCEDURE ProbePhysProps(SolventRefNo:CARDINAL);
VAR
  nx,ny,j,k,xc1,yc1,xc2,yc2 :CARDINAL;
  s :String;
  wh,wd :Words;
  d :Data;
  np :SigFigs;
  ...
Appendix 5.20

BEGIN

CASE SolventRefNo OF

1: (* Methanol, RPS 62, RPP 117 *)
MolWt : 32.042;
 Omega : 0.556;
 Rho20 : 0.7914;
 VpA : -8.54796;
 b0 : -0.1750799;
 SolubilityParameter : 0.000;
 StoVRatio1 : 2.3909E-10;

2: (* Ethanol, RPS 102, RPP 170 *)
MolWt : 46.069;
 Omega : 0.644;
 Rho20 : 0.7893;
 VpA : -8.51838;
 b0 : -0.7548748;
 SolubilityParameter : 0.000;
 StoVRatio1 : 2.3909E-10;

3: (* Benzene, RPS 242, RPP 343 *)
MolWt : 78.011;
 Omega : 0.212;
 Rho20 : 0.8765;
 VpA : -6.98273;
 b0 : -0.37822731;
 SolubilityParameter : 9.147;
 StoVRatio1 : 2.3980E-10;

4: (* Dichloromethane, RPS 53, RPP 107 *)
MolWt : 84.933;
 Omega : 0.199;
 Rho20 : 1.3266;
 VpA : -7.35739;
 b0 : -0.40527635;
 SolubilityParameter : 9.879;
 StoVRatio1 : 2.9857E-10;

5: (* Carbon Tetrachloride, RPS 42, RPP 94 *)
MolWt : 153.823;
 Omega : 0.193;
 Rho20 : 1.594;
 VpA : -7.07139;
 b0 : -0.94192552;
 SolubilityParameter : 8.582;
 StoVRatio1 : 1.8290E-10;

6: (* Cyclohexane, RPS 249, RPP 353 *)
MolWt : 84.162;
 Omega : 0.212;
 Rho20 : 0.7785;
 VpA : -6.96009;
 b0 : -0.32696438;
 SolubilityParameter : 8.182;
 StoVRatio1 : 2.3354E-10;

END
Appendix 5.21

<table>
<thead>
<tr>
<th>7: (* Pentane, RPS 223, RPP 311 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MolWt := 72.151; Tcrit := 469.65; Pcrit := 33.7;</td>
</tr>
<tr>
<td>Omega := 0.251; OmegaSRK := 0.2522;</td>
</tr>
<tr>
<td>Rho20 := 0.6262; ZRa := 0.26853; Vast := 0.3113;</td>
</tr>
<tr>
<td>VpA := -7.28936; VpB := +1.53679;</td>
</tr>
<tr>
<td>VpC := -3.08367; VpD := -1.02456;</td>
</tr>
<tr>
<td>b0 := -0.34472727; b1 := +0.75926287; b2 := -0.26023873;</td>
</tr>
<tr>
<td>SolubilityParameter := 7.012;</td>
</tr>
<tr>
<td>StoVRatio1 := 2.2937E-10;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8: (* Hexane, RPS 271, RPP 379 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MolWt := 86.178; Tcrit := 507.43; Pcrit := 30.1;</td>
</tr>
<tr>
<td>Omega := 0.299; OmegaSRK := 0.3007;</td>
</tr>
<tr>
<td>Rho20 := 0.6603; ZRa := 0.26355; Vast := 0.3682;</td>
</tr>
<tr>
<td>VpA := -7.46765; VpB := +1.44211;</td>
</tr>
<tr>
<td>VpC := -3.28222; VpD := -2.50941;</td>
</tr>
<tr>
<td>b0 := -0.34109856; b1 := +0.76502185; b2 := -0.35116533;</td>
</tr>
<tr>
<td>SolubilityParameter := 7.242;</td>
</tr>
<tr>
<td>StoVRatio1 := 2.2328E-10;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>9: (* Heptane, RPS 308, RPP 429 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MolWt := 100.205; Tcrit := 540.26; Pcrit := 27.4;</td>
</tr>
<tr>
<td>Omega := 0.349; OmegaSRK := 0.3507;</td>
</tr>
<tr>
<td>Rho20 := 0.6837; ZRa := 0.26074; Vast := 0.4304;</td>
</tr>
<tr>
<td>VpA := -7.46768; VpB := +1.37068;</td>
</tr>
<tr>
<td>VpC := -3.53620; VpD := -3.20243;</td>
</tr>
<tr>
<td>b0 := -0.33914149; b1 := +0.66524786; b2 := -0.84928651;</td>
</tr>
<tr>
<td>SolubilityParameter := 7.423;</td>
</tr>
<tr>
<td>StoVRatio1 := 2.0565E-10;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10: (* Octane, RPS 354, RPP 483 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MolWt := 114.232; Tcrit := 568.83; Pcrit := 24.9;</td>
</tr>
<tr>
<td>Omega := 0.398; OmegaSRK := 0.3998;</td>
</tr>
<tr>
<td>Rho20 := 0.7025; ZRa := 0.25678; Vast := 0.4904;</td>
</tr>
<tr>
<td>VpA := -7.91211; VpB := +1.38007;</td>
</tr>
<tr>
<td>VpC := -3.80435; VpD := -4.50132;</td>
</tr>
<tr>
<td>b0 := -0.34577078; b1 := +0.84347227; b2 := -0.50695659;</td>
</tr>
<tr>
<td>SolubilityParameter := 7.554;</td>
</tr>
<tr>
<td>StoVRatio1 := 2.1990E-10;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>11: (* Toluene, RPS 286, RPP 400 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MolWt := 92.141; Tcrit := 591.79; Pcrit := 41.0;</td>
</tr>
<tr>
<td>Omega := 0.263; OmegaSRK := 0.2651;</td>
</tr>
<tr>
<td>Rho20 := 0.8669; ZRa := 0.26455; Vast := 0.3137;</td>
</tr>
<tr>
<td>VpA := -7.28607; VpB := +1.38091;</td>
</tr>
<tr>
<td>VpC := -2.83433; VpD := -2.79186;</td>
</tr>
<tr>
<td>b0 := -0.35415461; b1 := +0.87470561; b2 := -0.28391941;</td>
</tr>
<tr>
<td>SolubilityParameter := 8.907;</td>
</tr>
<tr>
<td>StoVRatio1 := 2.5886E-10;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>12: (* 2-Butanone, RPS 167, RPP 243 *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MolWt := 72.107; Tcrit := 536.78; Pcrit := 42.1;</td>
</tr>
<tr>
<td>Omega := 0.320; OmegaSRK := 0.3188;</td>
</tr>
<tr>
<td>Rho20 := 0.8054; ZRa := 0.26248; Vast := 0.2523;</td>
</tr>
<tr>
<td>VpA := -7.71476; VpB := +1.71061; (* ZRa calculated *)</td>
</tr>
<tr>
<td>VpC := -3.68770; VpD := -0.75169;</td>
</tr>
<tr>
<td>b0 := +0.21880959; b1 := +2.64087032; b2 := +0.41155558;</td>
</tr>
<tr>
<td>SolubilityParameter := 9.038;</td>
</tr>
<tr>
<td>StoVRatio1 := 2.3244E-10;</td>
</tr>
</tbody>
</table>
Appendix 5.22

| 13: (* Trichloromethane, RPS 50, RPP 103 *)
| MolWt = 119.378;  Tcrt = 536.40;  Prct = 53.7;
| Omega = 0.218;  OmegaSRK = 0.2181;
| Rho02 = 1.4832;  ZRa = 0.27498;  Vast = 0.2245;
| VpA = -6.95546;  VpB = +1.16625;
| VpC = -2.13970;  VpD = -3.44421;
| b0 = -0.2165469;  b1 = +1.28817983;  b2 = +0.27776848;
| SolubilityParameter = 9.240;
| StoVRatio1 = 1.8777E-10;

| 14: (* Tetrahydrofuran, RPS 168, RPP 244 *)
| MolWt = 72.107;  Tcrt = 540.15;  Prct = 51.9;
| Omega = 0.217;  OmegaSRK = 0.2227;
| Rho02 = 0.8892;  ZRa = 0.25523;  Vast = 0.2308;
| VpA = +9.1069;  VpB = +2768.38;  VpC = -46.9;
| (* Uses RPP equation 3 *)  
| b0 = +0.0000000;  b1 = +0.0000000;  b2 = +0.0000000;
| SolubilityParameter = 9.317;
| StoVRatio1 = 2.0000E-10;

| 15: (* Methyl Acetate, RPS 129, RPP 203 *)
| MolWt = 74.080;  Tcrt = 506.80;  Prct = 46.9;
| Omega = 0.326;  OmegaSRK = 0.3205;
| Rho02 = 0.933;  ZRa = 0.55238;  Vast = 0.2262;
| VpA = -8.05406;  VpB = +2.56375;
| VpC = -5.12994;  VpD = +0.16125;
| b0 = -0.73216340;  b1 = -0.36768303;  b2 = -1.92009995;
| SolubilityParameter = 0.000;
| StoVRatio1 = 2.0000E-10;

| 16: (* Acetone, RPS 122, RPP 196 *)
| MolWt = 58.080;  Tcrt = 508.15;  Prct = 47.0;
| Omega = 0.304;  OmegaSRK = 0.3149;
| Rho02 = 0.790;  ZRa = 0.24494;  Vast = 0.2080;
| VpA = -7.45514;  VpB = +1.20200;
| VpC = -2.43926;  VpD = -3.35590;
| b0 = -0.34055397;  b1 = +0.82971338;  b2 = -1.49459151;
| SolubilityParameter = 9.712;
| StoVRatio1 = 2.0000E-10;

| 17: (* Isopropanol, RPS 134, RPP 208 *)
| MolWt = 60.096;  Tcrt = 508.76;  Prct = 47.6;
| Omega = 0.665;  OmegaSRK = 0.6637;
| Rho02 = 0.786;  ZRa = 0.24962;  Vast = 0.2313;
| VpA = -8.16927;  VpB = -9.43213E-2;
| VpC = -8.10040;  VpD = -7.85;
| b0 = -0.44005976;  b1 = -0.01017017;  b2 = -3.30505211;
| SolubilityParameter = 0.000;
| StoVRatio1 = 2.0000E-10;

| 18: (* Ethyl Acetate, RPS 172, RPP 249 *)
| MolWt = 88.107;  Tcrt = 523.20;  Prct = 38.3;
| Omega = 0.362;  OmegaSRK = 0.3595;
| Rho02 = 0.901;  ZRa = 0.25389;  Vast = 0.2853;
| VpA = -7.68521;  VpB = -1.36511;
| VpC = -4.08980;  VpD = -1.75342;
| b0 = -0.66912027;  b1 = -0.31486861;  b2 = -1.72062881;
| SolubilityParameter = 9.044;
| StoVRatio1 = 2.0000E-10;
ELSE
END;

IF Debug[1] THEN
    wh[0] := 'Physical Properties of '; 
    Str.Append(wh[0],SolventName);
    wd[1] := 'Molecular Weight '; 
    wd[8] := 'VpA '; 
    wd[10] := 'VpC '; 
    wd[12] := 'b0 '; 
    wd[13] := 'b1 '; 
    wd[14] := 'b2 '; 
    wd[16] := '1.0E10 * StoVRatio1 '; 
    d[16] := StoVRatio1*1.0E10; np[16] := 4;
    bbnutils.ShowData(wh,wd,d,np,1,16);
END;

END ProbePhysProps;

PROCEDURE VPmmHg(VAR VP:LONGREAL; TdegC:LONGREAL;
    SolventRefNo:CARDINAL);

VAR
    x,x15,x3,x6,f1,f2,t : LONGLREAL;
    r : CardSet;
    wh,wd : Words;
    d : Data;
    np : SigFigs;

BEGIN
    t := TdegC + CtoK;
    r := CardSet{1..13,15..18};
    IF SolventRefNo IN r THEN
        x := 1.0 - t/Tcrlit; x15 := x*Sqrt(x);
        x3 := x15*x15; x6 := x3*x3;
        f1 := (VpA*x + VpB*x15 + VpC*x3 + VpD*x6)/(1.0 - x);
        f2 := Pcrit*Exp(t1);
    ELSE
        f1 := VpA - VpB/(t + VpC);
        f2 := Exp(f1);
    END;
    VP := 750.0*t2;
    IF Debug[2] THEN
        wh[0] := 'Test Output from Procedure VPmmHg';
        wd[1] := 'Temperature (degC) '; 
        wd[2] := 'Vapour Pressure (mmHg)'; 
        bbnutils.ShowData(wh,wd,d,np,1,2);
    END;
END VPmmHg;
PROCEDURE HBT(VAR Vsat,Kval:LONGREAL; TdegC,Psyst:P:LONGREAL);

(* The calculation of liquid saturated molar volumes using the Hankinson-Brobst-Thomson technique as detailed in Reid, Prausnitz and Polling, pp 55 et seq. *)
(* Extended in an attempt to calculate the isothermal compressibility K *)

CONST
  a = -1.52816;
  b = +1.43907;
  c = -0.81446;
  d = +0.190454;
  aa = -9.070217;
  bb = +62.45326;
  dd = -135.1102;
  ff = +4.79594;
  gg = +0.250047;
  hh = +1.14188;
  jj = +0.0861488;
  kk = +0.0344483;

VAR
  VrZero,Vrdelta,Tr,x1,x2,x3,x4,Vstar,
  cc,ee,beta,V1,V2,V3,dP,Pbar :LONGREAL;
  wh,wd :Words;
  v :Data;
  np :SigFigs;

BEGIN
(* The value of the Debug Parameter is 3 *)
(* This procedure cannot be used without re-introducing OmegaSRK into the Physical Constants Procedure *)

VPmnmHg(VP,TdegC,SolventRefNo);
VP := VP/750.0;

(* Use Rho20 to calculate Vstar *)
Tr := (20.0 + CtoK)/Tcrit;
x3 := 1.0 - Tr; x1 := CubeRoot(x3); x2 := x1*x1; x4 := x3*x1;
VrZero := 1.0 + a*x1 + b*x2 + c*x3 + d*x4;
Vrdelta := (e + Tr*(f + Tr*(g + Tr*h)))/(Tr - 1.00001);
Vstar := MolWt/(Rho20*VrZero*(1.0 - OmegaSRK*Vrdelta));

(* Next evaluate the terms that are independent of Pressure *)
cc := jj + kk*OmegaSRK;
cc := Exp(ff + OmegaSRK*(gg + OmegaSRK*hh));
beta := Pcrit*(-1.0 + aa*x1 + bb*x2 + dd*x3 + ee*x4);
Pbar := 1.01325*Psyst; dP := 0.05*Pbar;
IF dP < 0.5 THEN dP := 0.5 END;

V1 := Vsat*(1.0 - cc*Log((beta + Pbar - dP)/(beta + VP)));
V2 := Vsat*(1.0 - cc*Log((beta + Pbar)/(beta + VP)));
V3 := Vsat*(1.0 - cc*Log((beta + Pbar + dP)/(beta + VP)));

(* K is defined as -(1/V)(dV/dP) *)
Kval := -0.5*(V3 - V1)/V2/dP;
IF Debug[3] THEN
wh[0] := 'Test Output from Procedure HBT';
wd[1] := 'Temperature (degC)';
wd[3] := 'Vsat (cm3/mol)';
wd[4] := 'Volume at 0.5 bar';
wd[5] := 'Volume at 1.0 bar';
wd[6] := 'Volume at 1.5 bar';
wd[7] := 'Estimate of 1.0E6*K';

bbmutils.ShowData(wh,wd,v,np,1,7);

END;

END HBT;

PROCEDURE RackettSD(VAR Vsat:LONGREAL; TdegC:LONGREAL);
CONST r = 0.285714285;
VAR phi,Tr,TrRef,f1,f2 :LONGREAL;
wh,wd :Words;
v :Data;
np :SigFigs;

BEGIN
Tr := (TdegC + CtoK)/Tcrit; TrRef := (20.0 + CtoK)/Tcrit;
phi := Exp(r*log(1.0-Tr)) - Exp(r*log(1.0-TrRef));
Vsat := (MolWt/Rho20)*Exp(phi*log(ZRa));

IF Debug[4] THEN
wh[0] := 'Test Output from Procedure RackettSD';
wd[1] := 'Temperature (degC)';

bbmutils.ShowData(wh,wd,v,np,1,2);

END;

END RackettSD;

PROCEDURE AlphaCalc(VAR alpha:LONGREAL; TdegC:LONGREAL);
VAR v0,v1,v2,t1,t2 :LONGREAL;
wh,wd :Words;
d :Data;
np :SigFigs;

BEGIN
(* Debug parameter is 5 *)

(* The liquid phase volumes have been calculated from the RackettSD equation in preference to the Hankinson-Brobst-Thomson technique because the former gave results which were in better agreement with the only available test data: *)
alpha = 0.001487 for acetone at 20 degC
RSD gave 0.001462 while HBT gave 0.001516

RackettSD(v0,TdegC);  t1 := TdegC-0.5;
RackettSD(v1,t1);  t2 := TdegC+0.5;
RackettSD(v2,t2);
alpha := (v2-v1)/v0;

IF Debug[5] THEN
  wh[0] := 'Output from Procedure AlphaCalc';
  wd[1] := 'Temperature (degC)';
  wd[2] := 'Calculated Alpha (/deg)';
  bbmutilis.ShowData(wh,wd,d,np,1,2);
END;
END AlphaCalc;

PROCEDURE RSD(VAR vt,alpha,kval:LONGREAL; TdegC,Psystem:LONGREAL);
VAR
  Tr,Pr,Kt,Kr,Tref,Pbar,dP,
  Rhotandp,Rhotm,Rhotp,Rhopp,Rhopp
  Bi :LONGREAL;
  wh,wd :ARRAY [0..4],[0..3] OF LONGREAL;
  d :Data;
  np :SigFigs;
BEGIN
  sum := 0.0;
  FOR n := 0 TO 4 DO
    IF n = 0 THEN x := 1.0 ELSE x := Pr*x END;
    sum := sum + Bi[n,i]*x;
  END;
  RETURN sum;
END FuncAi;

PROCEDURE FuncK(Tr,Pr:LONGREAL):LONGREAL;
VAR
  n :CARDINAL;
  sum,x,Ai
BEGIN
  sum := 0.0;
  FOR n := 0 TO 3 DO
    Ai := FuncAi(Pr,n);
    IF n = 0 THEN x := 1.0 ELSE x := Tr*x END;
    sum := sum + Ai*x;
  END;
  RETURN sum;
END FuncK;
BEGIN

Bi[0,0] := +1.6368;
Bi[1,0] := -0.04615;
Bi[2,0] := +2.1138*1.0E-3;
Bi[3,0] := -0.7845*1.0E-5;
Bi[4,0] := -0.6923*1.0E-6;

Bi[0,1] := -1.9693;
Bi[1,1] := +0.21847;
Bi[2,1] := -8.0028*1.0E-3;
Bi[3,1] := -8.2823*1.0E-5;
Bi[4,1] := +5.2604*1.0E-6;

Bi[0,2] := +2.4638;
Bi[1,2] := -0.36461;
Bi[2,2] := +12.8763*1.0E-3;
Bi[3,2] := +14.8059*1.0E-5;
Bi[4,2] := -8.6895*1.0E-6;

Bi[0,3] := -1.5841;
Bi[1,3] := +0.25136;
Bi[2,3] := -11.3805*1.0E-3;
Bi[3,3] := -9.5672*1.0E-5;
Bi[4,3] := +2.1812*1.0E-6;

(* This procedure for the adjustment of known liquid density for temperature and pressure is by Rea, Spencer and Danner (1973) and is quoted by Walas in Phase Equilibria in Chemical Engineering, Butterworth. It can be made to yield values of both isobaric thermal expansion and isothermal compressibility; the system pressure is assumed to be in atmospheres but note that Pc is in bar hence Pressystem is multiplied by 1.01325 *)

(* Calculate alpha *)
Tref := 20.0 + CtoK; Pbar := 1.01325*Pressystem;
Tr := Tref/Tcrt; Pr := Pbar/Pcrt;
Kr := FuncK(Tr,Pr);

Tr := (TdegC + CtoK)/Tcrt;
Kt := FuncK(Tr,Pr);
Rhotandp := Rho20*Kt/Kr;
Tr := (TdegC + 0.5 + CtoK)/Tcrt;
Kt := FuncK(Tr,Pr);
Rhotp := Rho20*Kt/Kr;
Tr := (TdegC + 0.5 + CtoK)/Tcrt;
Kt := FuncK(Tr,Pr);
Rhotm := Rho20*Kt/Kr;

alpha := (1.0/Rhotp - 1.0/Rhotm)/(1.0/Rhotandp);

(* Calculate isothermal compressibility; determine a value for dP (say) 5% of Pressystem but never less than 0.5 bar *)

dP := 0.05*Pbar;
IF dP < 0.5 THEN dP := 0.5 END;
Tr := (TdegC + CtoK)/Tcrt;
Pr := (Pbar + dP)/Pcrt;
Kt := FuncK(Tr,Pr);
Rhopp := Rho20*Kt/Kr;
Pr := (Pbar - dP)/Pcrt;
Kt := FuncK(Tr,Pr);
Rhopm := Rho20*Kt/Kr;

kval := -0.5*(1.0/Rhopp - 1.0/Rhopm)/(1.0/Rhotandp)/dP;
IF Debug[6] THEN
wh[0] := 'Output from Procedure RSD';
wd[1] := 'Density at 20C and Psystem';
wd[2] := 'Density at T and Psystem';
wd[3] := 'Density at T+0.5 and Psystem';
wd[4] := 'Density at T-0.5 and Psystem';
wd[5] := 'Density at T and Psystem+dp';
wd[7] := 'Calculated Alpha*1.0E3 (/deg)';
wd[8] := 'Calculated Kval*1.0E6 (/bar)';
d[1] := Rho20;
d[2] := Rhotandp;
d[3] := Rhotp;
d[4] := Rhotm;
d[5] := Rhopp;
d[7] := alpha*1.0E3;
d[8] := kval*1.0E6;
bbmutils.ShowData(wh, wd, d, np, 1, 8);
END;
END RSD;

PROCEDURE ProbeCharProps(TdegC;LONGBREAL);
VAR
  x, alpha, f, TdegK, Pval, Psat, DeltaSq, Kval : LONGBREAL;
  wh, wd : Words;
  d, np : Data;
  SigmaFigs : SigFigs;
BEGIN
  (* Debug parameter is 7 *)
  TdegK := TdegC + CtoK;
  AlphaCalc(alpha, TdegC);
  f := alpha*TdegK;
  x := (3.0 + 4.0*f)/(3.0 + 3.0*f);
  vred1 := x*x*x;
  RackettRD(v1, TdegC);
  v1 := v1/MolWt;
  vstar1 := v1/vred1;
  Tred1 := (x - 1.0)/x/vred1;
  Tstar1 := TdegK/Tred1;

  IF SolubilityParameter > 0.0 THEN
    DeltaSq := SolubilityParameter*SolubilityParameter;
    Pstar1 := 10.0*DeltaSq*vred1*vred1*4.1868;
    (* bar *)
  ELSE
    HBT(Psat, Kval, TdegC, 1.0);
    Pstar1 := alpha*vred1*vred1*TdegK/Kval;
  END;
IF Debug[7] THEN
  wh[0] := 'Procedure ProbeCharProps - Data for ';  
  Str.Append(wh[0],SolventName);
  wd[1] := 'Temperature (degC)
  wd[2] := 'Calculated vred1
  wd[3] := 'Calculated v1 (cm3/g)
  wd[4] := 'Calculated vstar1 (cm3/g)
  wd[6] := 'Calculated Tred1
  wd[7] := 'Calculated Tstar1 (K)
  wd[8] := 'Calculated Pstar1 (Bar)
  wd[9] := 'Calculated Pstar1 (J/cm3)
  d[9] := 0.1*Pstar1; np[9] := 1;
  bbmunits.ShowData(wh,wd,d,np,1,9);
END;
END ProbeCharProps;

PROCEDURE PolymerSpecVol(VAR SpVol,Alpha: LONGREAL;
                           TdegC,WtFrEVA: LONGREAL);

(* The specific volume is a function of composition and temperature; the data were first correlated in terms of mass fraction EVA and the relationship was found to be linear. The resulting coefficients were then plotted against temperature and it was decided to use a linear function for a0 and a quadratic for a1. *)

VAR
  a0,a1,deriv : LONGREAL;
  debug        : BOOLEAN;
  wh,wd        : Words;
  d             : Data;
  np            : SigFigs;
BEGIN
  a0 := a0b0 + a0b1*TdegC;
  a1 := a1b0 + TdegC*(a1b1 + a1b2*TdegC);
  SpVol := a0 + a1*WtFrEVA;
  deriv := a0b1 + WtFrEVA*(a1b1 + 2.0*a1b2*TdegC);
  Alpha := deriv/SpVol;
  debug := FALSE;
  IF debug THEN
    wh[0] := 'Debug Results for PolymerSpecVol';
    bbmunits.ShowData(wh,wd,d,np,1,4);
  END;
END PolymerSpecVol;
PROCEDURE MassFromMol(VAR wm2,wm3:LONGREAL; MolFr2:LONGREAL);
VAR numerator,denominator :LONGREAL;
BEGIN
  numerator := MolFr2*NoAvMolWt2;
  denominator := numerator + (1.0 - MolFr2)*NoAvMolWt3;
  wm2 := numerator/denominator; wm3 := 1.0 - wm2;
END MassFromMol;

PROCEDURE SegmtFromMol(VAR ws2,ws3:LONGREAL; MolFr2:LONGREAL);
VAR numerator,denominator :LONGREAL;
BEGIN
  numerator := MolFr2*SegMolWt2;
  denominator := numerator + (1.0 - MolFr2)*SegMolWt3;
  ws2 := numerator/denominator; ws3 := 1.0 - ws2;
END SegmtFromMol;

PROCEDURE MolFromMass(VAR mf2,mf3:LONGREAL; WtFr2:LONGREAL);
VAR numerator,denominator :LONGREAL;
BEGIN
  numerator := WtFr2/NoAvMolWt2;
  denominator := numerator + (1.0 - WtFr2)/NoAvMolWt3;
  mf2 := numerator/denominator; mf3 := 1.0 - mf2;
END MolFromMass;

PROCEDURE PolymerProps(TdegC,WtFrEVA:LONGREAL);
VAR TdegK, alpha, alpha2, alpha3, p, xw2, xw3,
delta2, delta3, g2at25c, g3at25c, g2, g3, S2toS3,
v2at25c, v3at25c, dToverT, a2at25c, a3at25c :LONGREAL;
nx, ny, n, xc1, yc1, xc2, yc2, j, k :CARDINAL;
ok :BOOLEAN;
s0, s1, s2 :String;
PP, Ph :Words;
PPvals :Data;
np :SigFigs;
BEGIN
  (* The Debug parameter is 8 *)
  (* Step 1 - calculate volume functions *)
  TdegK := TdegC + CtoK;
  PolymerSpecVol(v2,alpha2,TdegC,1.0);
  PolymerSpecVol(v3,alpha3,TdegC,0.0);
  p := alpha2*TdegK;
  xw2 := (3.0+4.0*p)/(3.0+3.0*p);
  vred2 := xw2*xw2*xw2;
  p := alpha3*TdegK;
  xw3 := (3.0+4.0*p)/(3.0+3.0*p);
  vred3 := xw3*xw3*xw3;
  vstar2 := v2/vred2; vstar3 := v3/vred3;

  (* According to paper by Rostami and Walsh, p319, the product rbar*N*vstar is calculated as vbarN *)

xw2 := WtFrEVA; xw3 := 1.0 - xw2;
vrbarN := xw2*vstar2 + xw3*vstar3;
PPvals[10] := vrbarN;
PolymerSpecVol(v23, alpha, TdegC, WtFrEVA);
p := alpha*TdegK;
p := (3.0+4.0*p)/(3.0+3.0*p);
vred23 := p*p*p; vstar23 := v23/vred23;

IF Debug[8] THEN
    Ph[0] := 'Volume Functions';
    Ph[1] := ' at ';
    Str_FixRealToStr(TdegC,0,Ph[2],ok);
    Ph[3] := ' degC';
    bbmutlks,bbmConcat(Ph[5],Ph,1,3);
    Str_Append(Ph[0],Ph[5]);
    Ph[1] := ' For EVA, FVA and Blends';
    FOR n := 1 TO 10 DO np[n] := 5 END;
    bbmutlks.ShowData(Ph,PP,PPvals,np,2,10);
END;

(* Step 2 - calculate the characteristic pressures. *)
(* The first step is to calculate the gamma values at 250C *)

PolymerSpecVol(v2at25c,a2at25c,25.0,1.0);
PolymerSpecVol(v3at25c,a3at25c,25.0,0.0);
delta2 := sigmaG2/SegMolWt2/v2at25c;
delta3 := sigmaG3/SegMolWt3/v3at25c;
g2at25c := delta2*delta2/298.15;
g3at25c := delta3*delta3/298.15;

(* The next step is to calculate the temperature correction for gamma in accordance with the method given by Rostami *)

dToverT := (TdegK - 298.16)/TdegK;
g2 := g2at25c*(1.0 - (1.0 + 2.0*a2at25c*TdegK)*dToverT);
g3 := g3at25c*(1.0 - (1.0 + 2.0*a3at25c*TdegK)*dToverT);

(* Pressures obtained from the relationship Pstar = gamma * vred * vred * TdegK are in units of cal/cm3; to convert to bar multiply by 10.0 * 4.1868 *)
Pstar2 := 41.868*2*TdegK*vred2*vred2;
Pstar3 := 41.868*3*TdegK*vred3*vred3;

(* Step 3 - calculate the temperature functions. *)
p := CubeRoot(vred2);
Tred2 := (p - 1.0)/(vred2*p); Tstar2 := TdegK/Tred2;
p := CubeRoot(vred3);
Tred3 := (p - 1.0)/(vred3*p); Tstar3 := TdegK/Tred3;
IF Debug[8] THEN
    Ph[0] := 'Temperature and Pressure Functions';
    Ph[1] := 'for EVA, FVA and Blends';
    Str.Append(Ph[1],Ph[5]);
    bbumutils.ShowData(Ph,PP,PPvals,np,2,6);
END;

(* Step 4 - Calculate the volume/segment fractions together with the
surface fractions. Note the phi values are based on number
average molecular weights. *)

StoVRatio2 := 2.0000E-10; StoVRatio3 := 1.0000E-10;
S2toS3 := 2.0000;
xw2 := WtFrEVA; xw3 := 1.0 - xw2;
phi3 := xw3*v3/v23;
phi2 := xw2*v2/v23;

phistar3 := xw3*vstar3/(xw2*vstar2 + xw3*vstar3);
phistar2 := 1.0 - phistar3;
g2 := 1.0/S2toS3;
theta3 := g2*phistar3/(g2*phistar3 + phistar2);
theta2 := 1.0 - theta3;

IF Debug[8] THEN
    FOR n := 1 TO 6 DO np[n] := 6 END;
    PPvals[7] := 1.0E10*StoVRatio2;
    PPvals[8] := 1.0E10*StoVRatio3;
    Ph[0] := 'Segment and Surface Area Functions';
    bbumutils.ShowData(Ph,PP,PPvals,np,2,8);
END;

END PolymerProps;

BEGIN
    CancelDebug;
END rbumutils.
MODULE X23Optim;

(*# optimize (i386 -> on ) *)
(*# optimize (i387 -> on ) *)
(*# debug ( vid -> full ) *)
(*# check ( index -> on ) *)
(*# check ( stack -> on ) *)

(* An optimization program for X23 - 24th May 1990 *)
(* sum of squares of the error term using Brent method *)

IMPORT Window,Str,bbutils,rjutils,IO,Graph;
FROM bbutils IMPORT ShowData,Words,String,spaces,Data,SigFigs;
FROM MATHLIB IMPORT Exp,Log,Sqrt;
FROM rjutils IMPORT CubeRoot,SetDebugParams,SolventChoice,
ProbePhysProps,VPmmHg,HBT,RackettSD,
AlphaCalc,RSD,ProbeCharProps,PolymerProps;

FROM rjutils IMPORT
CtoK, GasConst, (* J/(mol K) *)
MolWt,Tcrit,Pcrit,ZRa,Omega,Rho20,OmegaSRK,
VpA,VpB,VpC,VpD,b0,b1,b2,VP,TdegC,Vast,
SolubilityParameter,
v1,vred1,vstar1,Pstar1,Pred1,Tred1,Tstar1,
v2,vred2,vstar2,v3,vred3,vstar3,Pstar2,Pred3,
Pred2,Pred3,Tred2,Tred3,Tstar2,Tstar3,
v23,vred23,vstar23,vbarN,
P,Pstarb,Predb,TdegK,Tstarb,Tredb,
phi2,phi3,phistar2,phistar3,
theta2,theta3,dPred,dTred,dvred,
SolventRefNo,SolventName,Vref,Debug;

TYPE CharSet = SET OF CHAR;
CardSet = SET OF CARDINAL;

VAR
Error,X23,t1,t2,t3 :LONGREAL;
ch :CHAR;
wh,wd :Words;
s :String;
j,k,n,px,ny,xc1,xc2,yc1,yc2,nData1,nData2 :CARDINAL;
m0,m1 :Window.WinType;
d0,d1 :Window.WinDef;
ok,db :BOOLEAN;
dHData,WtFr,X23vals,dHCalc,d :Data;
np :SigFigs;

PROCEDURE Func(X23:LONGREAL; n1,n2:CARDINAL):LONGREAL;

VAR
t0,t1,t2,t3,t4,Error :LONGREAL;
j,k :CARDINAL;
BEGIN
  Error := 0.0;
  FOR n := n1 TO n2 DO
    IF n <= 8 THEN TdegC := 75.5 ELSE TdegC := 86.1 END;
    PolymerProps(TdegC,WtFr[n]);
(* Pstar is in bar thus each term in the RHS will have units of cm^3 bar/g hence the dHData must be multiplied by 10 to convert J/g to cm^3.bar/g *)

t0 := 10.0*dHData[n]/vbarN;
t1 := phi2*Pstar2*(1.0/vred2 - 1.0/vred23);
t2 := phi3*Pstar3*(1.0/vred3 - 1.0/vred23);
t3 := phi2*theta3*X23/vred23;
t4 := t0 - t1 - t2 - t3;
Error := Error + t4*14;
END;
RETURN Error;
END Func;

PROCEDURE Brent(VAR Answer,Error:LONGREAL;
ax,bx,cm,tol:LONGREAL; Display:BOOLEAN);

LABEL Finish;
CONST
itmax = 100; zeps = 1.0E-8; cgold = 0.3819660;
VAR
a,b,d,e,etemp,fx,fw,fv,
p,q,r,tol1,tol2,u,v,w,x,xm
iter
:LONGREAL;
CARDINAL;

xc1,xc2,yc1,yc2,j,k,nx,ny,ni
sw
s1,s2,s3
ch
m0
:d:WINDOW;WinType;
:d:Window.WinDef;
:BOOLEAN;

PROCEDURE Sign(a,b:LONGREAL):LONGREAL;
BEGIN
IF b >= 0.0 THEN RETURN ABS(a)
ELSE RETURN ABS(b)
END;
END Sign;

BEGIN
IF Display THEN
    d0 := Window.WinDef(0,0,79,24,Window.LightBlue,Window.Black,
FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
    Window.Yellow,Window.Black);
    m0 := Window.Open(d0);
    Window.CursorOn;
    xc1 := 15; xc2 := 65; yc1 := 1; yc2 := 23;
    Window.Change(m0,xc1,yc1,xc2,yc2);
    ni := 2;
    s2 := 'Press any key to continue';
    s3 := 'N ' x F(x)';
    Window.DirectWrite(5,1,ADR(s3),Str.Length(s3));
END;
(* a and b must be in ascending order *)
IF ax < cx THEN a := ax ELSE a := cx END;
IF ax > cx THEN b := ax ELSE b := cx END;

(* initialization *)
v := bx; w := v; x := v; e := 0.0;
f := Func(x,nData1,nData2);
f := fx; f := fx;

(* Main Program Loop *)
FOR iter := 1 TO itmax DO
    x := 0.5*(a+b); tol1 := tol*ABS(x) + zeps; tol2 := tol1 + tol1;

    IF ABS(x - xm) <= tol2 - 0.5*(b-a) THEN
        Answer := x; Error := fx;
        IF Display THEN
            bbsutils.Offset(s2,j,k,xc1,xc2);
            Window.DirectWrite(k,yc2-2,ADR(s2),j);
            Window.GotoXY(k+j+1,yc2-2);
            ch := IO.RdKey();
        END;
        GOTO Finish;
    ELSE
        IF Display THEN
            INC(ni);
            nx := 4;
            Window.GotoXY(nx,ni); IO.WrCard(iter,3);
            INC(nx,10);
            Str.FixRealToStr(x,10,s1,ok);
            Window.DirectWrite(nx,ni,ADR(s1),Str.Length(s1));
            IF fx < 0.0 THEN INC(nx,19) ELSE INC(nx,20) END;
            Str.FixRealToStr(fx,10,s1,ok);
            Window.DirectWrite(nx,ni,ADR(s1),Str.Length(s1));
            IF ni > 19 THEN
                ni := 2;
                bbsutils.Offset(s2,j,k,0,50);
                Window.DirectWrite(k,yc2-2,ADR(s2),j);
                Window.GotoXY(k+j+1,yc2-2);
                ch := IO.RdKey();
                Window.Clear;
                Window.DirectWrite(5,1,ADR(s3),Str.Length(s3));
            END;
        END;
    END;
END;

IF ABS(e) > tol1 THEN (* Construct trial parabolic fit *)
r := (x-w)*(fx-fv);
q := (x-v)*(fx-fw);
p := (x-v)*q - (x-w)*r;
q := 2.0*(q-r);
IF q > 0.0 THEN p := -p END;
q := ABS(q); etemp := e; e := d;
IF (ABS(p) >= ABS(0.5*q*ctemp)) OR (p <= q*(a-x)) OR (p >= q*(b-x))
THEN IF x >= xm THEN e := a-x ELSE e := b-x END;
d := cgold*e;
ELSE
d := p/q; u := x+d;
IF (u-a < tol2) OR (b-u < tol2) THEN d := Sign(tol1,xm-x) END;
(* of IF ABS(p) > .loop*)
ELSE
IF x >= xm THEN e := a-x ELSE e := b-x END;
d := cgold*e;
END; (* of IF ABS(e) > tol12 ...loop *)

IF ABS(d) >= tol1 THEN u := x + d ELSE u := x + Sign(tol1,d) END;
fu := Func(u,nData1,nData2);

IF fu <= fx THEN
IF u >= x THEN a := x ELSE b := x END;
v := w; fv := fw; w := x; fw := fx;
x := u; fx := fu;
ELSE
IF u < x THEN a := u ELSE b := u END;
IF (fu <= fw) OR (w = x) THEN v := w; fv := fw; w := u; fw := fu;
ELSE
IF (fu <= fv) OR (v = x) OR (v = w)
THEN v := u; fv := fu END;
END;
(* of IF (fu <= fx) condition. *)
(* of FOR loop. *)

sw[0] := 'Permitted number of iterations exceeded';
sw[1] := 1;
sw[2] := 'Current best answer is ';
sw[3] := 1;
Str.FixRealToStr(b,10,sw[4],ok);
Str.Append(sw[2],sw[4]);
bmutils.Pause(sw,3,0);
Answer := x; Error := fx;

Finish:
IF Display THEN Window.Close(m0) END;
END Brent;

BEGIN
(* Data at 75.5 degC - all data in Joules/gram *)
WtFr[1] := 0.1193; dHDdata[1] := 3.804E-2; 
WtFr[8] := 0.8333; dHDdata[8] := 3.257E-2; 

(* Data at 86.1 degC *)
WtFr[9] := 0.2991; dHDdata[9] := 5.390E-2; 
WtFr[10] := 0.3613; dHDdata[10] := 7.703E-2; 
wh[0] := 'Estimation of X23 by Minimisation of Error';
wd[1] := 'The value of X23 for data at 75.5°C is';
wd[2] := 'The value of X23 for data at 86.1°C is';
wd[3] := 'The value of X23 for combined data is';
wd[4] := 'To continue, press any key';

SetDebugParams(8);
db := TRUE;
nData1 := 1; nData2 := 8;
Brent(X23,Error,0,0,5,0,10,0,1.0E-6,db);
X23vals[1] := X23;

nData1 := 9; nData2 := 11;
Brent(X23,Error,0,0,5,0,10,0,1.0E-6,db);

nData1 := 1; nData2 := 11;
Brent(X23,Error,0,0,5,0,10,0,1.0E-6,db);

FOR n := 1 TO 3 DO np[n] := 8 END;
ShowData(wh,wd,X23vals,np,1,3);

(* The recalculation of the dHData values using the optimised values of X23 *)

FOR n := 1 TO 11 DO
    IF n <= 8 THEN TdegC := 75.5 ELSE TdegC := 86.1 END;
    PolymerProps(TdegC,WtFr[n]);
    t1 := phi2*Pstar2*(1.0/vred2 - 1.0/vred23);
    t2 := phi3*Pstar3*(1.0/vred3 - 1.0/vred23);
    t3 := phi2*theta3*X23/vred23;

    (* As calculated, the energy term will have units of cm3 bar / g 
       thus to convert J/g it is necessary to multiply by 0.1 *)
    dHCalc[n] := 0.1*vrbarN*(t1 + t2 + t3);
END;

wh[0] := 'A comparison of the experimental heat of mixing';
wh[1] := ' data with the values recalculated using the ';
wh[2] := ' optimised X23 values at 75.5 and 86.1 degC. ';
FOR n := 1 TO 11 DO
    StrFixRealToStr(100.0*dHData[n],4,wd[n],ok);
    d[n] := 100.0*dHCalc[n]; np[n] := 4;
END;
bbmutils.AddSpaces(wd,11);
ShowData(wh,wd,d,np,4,11);
END X23Optim.
(* data(stack_size=>9000H) *)
MODULE XbarAll;

(* Last edited Tuesday 14th August 1990 *)

(*# optimize (i386 => on ) *)
(*# optimize (i387 => on ) *)
(*# debug (vid => full ) *)
(*# check (index => on ) *)
(*# check (stack => on ) *)

IMPORT bbumutils, rjmutils, retvols, I0, FIO, MATHLIB, Window, Str;
FROM FIO IMPORT File;
FROM MATHLIB IMPORT CubeRoot, SetDebugParams, SolventChoice,
                 ProbePhysProps, VPmmHg, HBT, RackettSD,
                 AlphaCalc, RSD, ProbeCharProps,
                 PolymerSpecVol, MassFromMol, SegmFromMol,
                 MolFromMass, PolymerProps;
FROM retvols IMPORT RetentVol80, RetentVol100, RetentVol120;
FROM bbumutils IMPORT Words, String, spaces, Data, SigFigs;
FROM rjmutils IMPORT CtoK, GasConst,
                   (* J/(mol K) *)
                   SegMolWt2, sigmaG2, SegMolWt3,
                   sigmaG3, NoAvMolWt2, NoAvMolWt3,
                   MolWt, Tcrt, Prct, ZRa, Omega, Rho20, OmegaSRK,
                   VpA, VpB, VpC, VpD, b0, b1, b2, VP, TdegC, Vast,
                   SolubilityParameter,
                   v1, vred1, vstar1, Pstar1, Pred1, Tred1, Tstar1,
                   v2, vred2, vstar2, v3, vred3, vstar3, Pstar2, Pstar3,
                   Pred2, Pred3, Tred2, Tred3, Tstar2, Tstar3,
                   v23, vred23, vstar23, vbarRN,
                   P, Pstar23, Pred23, TdegK, Tstar23, Tred23, phi2, phi3,
                   phistar2, phistar3, theta2, theta3,
                   StoVRatio1, StoVRatio2, StoVRatio3,
                   WfFr, dPred, dTred, dvred,
                   SolventRefNo, SolventName,
                   Debug;
FROM retvols IMPORT Vret;

TYPE
  CharSet = SET OF CHAR;
  CardSet = SET OF CARDINAL;

LABEL Omit;

VAR
  B11, Vret2, Vret3, Chi12, Chi13, Chi12star, 
  Chi13star, X12bar, X13bar, error                     : LONGREAL;
  nSet;                                                  : CardSet;
  w, PP, wtfrr                                        : Words;
  s, ResFile                                          : String;
  Chi23, Chi23prime, Chi23star, Chi23sandp,            : Data;
  Chi123, Chi123star, X23bar, Q23                     : BOOLEAN;
  FileOutput                                          : File;
  FileHandle                                         : File;
PROCEDURE FileData(VAR wh,w: Words; d: Data; np: SigFigs;
   nh,nd: CARDINAL; FileHandle: File);

VAR
   n : CARDINAL;
   ok : BOOLEAN;
   ch : CHAR;
   s  : String;

BEGIN

   (* This procedure is intended to write numerical data to a file identified by
      FileHandle; the array w should contain identifiers for the numerical data
      held in array d. nd should not exceed 20 though no protection is provided. *)

   FOR n := 1 TO nh-1 DO
      FIO.WrStr(FileHandle,wh[n-1]);
      FIO.WrLn(FileHandle);
   END;

   FIO.WrCard(FileHandle,nd,2);
   FIO.WrLn(FileHandle);

   s := wh[nh-1];
   FOR n := 1 TO Str.Length(wh[nh-1]) DO s[n] := CHR(196) END;
   FIO.WrStr(FileHandle,wh[nh-1]);
   FIO.WrLn(FileHandle);
   FIO.WrStr(FileHandle,s);
   FIO.WrLn(FileHandle);

   FOR n := 1 TO nd DO
      FIO.WrStr(FileHandle,w[n]);
      FIO.WrStr(FileHandle,s);
      Str.FixRealToStr(d[n],np[n],s,ok);
      FIO.WrStr(FileHandle,s);
      FIO.WrLn(FileHandle);
   END;
   FIO.WrLn(FileHandle);
END FileData;

PROCEDURE Bviral(VAR B11: LONGREAL; TdegC: LONGREAL);

VAR
   f0,f1,tr1,tr2,tr3,tr8,br1,br2,
   Bb,bbm,Btsonop : LONGREAL;
   ok : BOOLEAN;
   Bw,Bh : Words;
   Bv : Data;
   np : SigFigs;
BEGIN
(*the Debug Parameter is 9 *)

tr1 := (TdegC + CtoK)/Tcrit;
tr2 := tr1*tr1; tr3 := tr2*tr2; tr8 := tr3*tr3*tr2;
f0 := 0.1445 - 0.330/tr1 - 0.1385/tr2 - 0.0121/tr3 - 0.000607/tr8;
f1 := 0.0637 + 0.331/tr2 - 0.423/tr3 - 0.008/tr8;
br1 := f0 + Omega*f1;

f0 := Log(tr1)/tr1;
br2 := b0 + f0*(b1 + f0*b2);

f1 := Pcrit/GasConst/Tcrit;
Bbmm := br2/f1; Bsonop := br1/f1;
IF (SolventRefNo = 14) OR (SolventRefNo = 15)
    THEN B11 := Bsonop
    ELSE B11 := Bbmm
END;

IF Debug[9] THEN
    Bh[0] := 'Estimated values of 2nd Virial Coefficients';
    Bh[2] := 'at a temperature of ';
    Str_FixRealToStr(TdegC,0,Bh[3],ok);
    Bh[4] := 'degC';
    bbumils.bbmConcat(Bh[1],Bh,2,4);
    bbumils.ShowData(Bh,Bw,Bv,np,2,2);
END;
END Bvirial;

PROCEDURE ChooseTdegC(nDegC: CARDINAL): LONGREAL;
VAR
    tdegc : LONGREAL;
BEGIN
    IF nDegC = 1 THEN tdegc := 80.0
    ELSEIF nDegC = 2 THEN tdegc := 100.0
    ELSE tdegc := 120.0
    END;
    RETURN tdegc;
END ChooseTdegC;

PROCEDURE ChiValues(VAR Npts: CARDINAL;nDegC,SolventRefNo: CARDINAL;
                      FileOutput: BOOLEAN; FileHandle: File);

CONST
    GasConst = 83.144; (* Bar cm3 / (Mol K) *)

(* as vapour pressure data have been amended to bar it
is convenient to redefine R in appropriate units. *)
VAR
  f0,f1,V1,V2,V3,Vstar1,Vstar2,Vstar3,w2,
  Veva,VFva,w3,TdegC,TdegK,
  term1,term2,term3,term4,r,rstar   :LONGREAL;
  n,m                                 :CARDINAL;
  ok,debug                             :BOOLEAN;
  Cw,Ch                                :Words;
  Cv,WF                                :Data;
  np                                   :SigFigs;

PROCEDURE F1(a,b,c:LONGREAL):LONGREAL;
BEGIN
  RETURN Log(a*b/c);
END  F1;

PROCEDURE S1(a,b,c:LONGREAL):LONGREAL;
BEGIN
  RETURN a-b-c;
END  S1;

BEGIN
  (* Debug parameter is 10 *)
  debug := FALSE;
  TdegC := ChooseTdegC(nDegC);
  TdegK := TdegC+CtoK;
  ProbePhysProps(SolventRefNo);
  ProbeCharProps(TdegC);
  VPmmHg(VP,TdegC,SolventRefNo); VP := VP/750.061; (* to bar *)
  Bvrials(B11,TdegC);

  (* Load the values of the retention volumes. *)

  IF  nDegC = 1 THEN Npts := 9; RetentVols80(SolventRefNo);
  ELSIF nDegC = 2 THEN Npts := 8; RetentVols100(SolventRefNo);
  ELSE  Npts := 8; RetentVols120(SolventRefNo);
  END;

  (* Chi12 and Chi13 values from Eqn 2 of Bhatt.. et al
    after obtaining v2 and v3 for pure polymers *)

  f0 := VP/GasConst;
  V1 := v1*MolWt;
  f1 := CtoK/V1/f0;
  term2 := f0*(B11 - V1)/TdegK;

  (* For 100% EVA the weight fraction is always 1.0 and
  the retention volume is always Vret[2,Npts] *)

  WF[Npts] :=1.0000;  Veva :=Vret[2,Npts];
  PolymerProps(TdegC,1.0);
  V2 :=v2*NoAvMolWt2;  (* only evaluated once *)
  term3 :=1.0 - V1/V2;
  term1 :=F1(f1,v2,Veva);
  Chi12 :=S1(term1,term2,term3);
(* For 100% FVA the weight fraction is always 0.0 and 
the retention volume is always Vret[2,1]*)

\[WF[1] := 0.0000; Vfva := Vret[2,1];\]
\[V3 := v3 * NoAvMol/W13;\] (* only evaluated once *)
\[term3 := 1.0 - V1/V3;\]
\[term1 := V1f1/v3, Vfva;\]
\[Chi13 := S1(term1, term2, term3);\] (* only evaluated once *)
\[r := V2/V1;\]

(* Chi23prime values from Eqn 3 *)
FOR n := 2 TO Npts-1 DO

(* Convert the mol fraction Vret[1,n] to mass 
fractions prior to the call to PolymerProps *)
MassFromMol(w2, w3, Vret[1,n]);
WF[n] := w2;
PolymerProps(TdegC, w2);
term1 := Exp(phi2 * Log(v2)) * Exp(phi3 * Log(v3));
term2 := Exp(phi2 * Log(Veva)) * Exp(phi3 * Log(Vfva));
term3 := w2 * v2 + w3 * v3;
Chi23prime[n] := Log((term1 * Vret[2,n]) / (term2 * term3)) / (phi2 * phi3);

(* Chi23 values now obtained by multiplying prime 
values by the ratio V2/V1 *)
Chi23[n] := r * Chi23prime[n];
END;

IF Debug[10] OR FileOutput THEN

(* The first 3 sections need only be done once for all the output sections *)
Str.FixRealToStr(TdegC, 0, Ch[7], ok); Ch[8] := ' degC';
bbmutil.bbmConcat(Ch[1], Ch, 4, 8);

bbmutil.bbmConcat(Ch[2], Ch, 4, 6);
FOR n := 1 TO Npts DO Str.FixRealToStr(WF[n], 4, Cw[n], ok) END;
FOR n := 1 TO Npts DO np[n] := 4 END;

Ch[0] := 'Values of Chi12, Chi13 and Chi23prime';
Cv[Npts] := Chi12; Cv[1] := Chi13;
FOR n := 2 TO Npts-1 DO Cv[n] := Chi23prime[n] END;
IF Debug[10] THEN bbmutil.ShowData(Ch, Cw, Cv, np, 3, Npts) END;
IF FileOutput THEN FileData(Ch, Cw, Cv, np, 3, Npts, FileHandle) END;

Ch[0] := 'Values of Chi12, Chi13 and Chi23';
FOR n := 2 TO Npts-1 DO Cv[n] := Chi23[n] END;
IF Debug[10] THEN bbmutil.ShowData(Ch, Cw, Cv, np, 3, Npts) END;
IF FileOutput THEN FileData(Ch, Cw, Cv, np, 3, Npts, FileHandle) END;
END;
Appendix 5.43

(* Chi12star and Chi13star values from Eqn 2 of Bhatt.. et al *)

Vstar1 := vstar1*MolWt;  (* only evaluated once *)
F1 := CtoK/Vstar1/f0;
term2 := f0*(B11 - Vstar1)/TdegK;
Vstar2 := vstar2*SegMolWt2;
term3 := 1.0 - Vstar1/Vstar2;
term1 := F1(f1,vstar2,Veva);
Chi12star := S1(term1,term2,term3);
Vstar3 := vstar3*SegMolWt3;
term3 := 1.0 - Vstar1/Vstar3;
term1 := F1(f1,vstar3,Vfva);
Chi13star := S1(term1,term2,term3);
rstar := Vstar2/Vstar1;

(* Chi23sandp values from Eqn 3 *)

FOR n := 2 TO Npts-1 DO
  (* convert mol fractions to mass fractions *)
  MassFromMol(w2,w3,Vrel[1,n]);
  (* call procedure to get phisstar2,phisstar3 *)
  PolymerProps(TdegC,w2);
  term1 := Exp(phisstar2*Log(vstar2))*Exp(phisstar3*Log(vstar3));
  term2 := Exp(phisstar2*Log(Veva))*Exp(phisstar3*Log(Vfva));
  term3 := w2*v2 + w3*v3;
  Chi23sandp[n] := -Log((term1*Vrel[2,n])/(term2*term3))/(phi2*phi3);

(* Chi23star values now obtained by multiplying prime values by the ratio Vstar2/Vstar1 *)

Chi23star[n] := rstar*Chi23sandp[n];
END;

IF Debug[10] OR FileOutput THEN
  Ch[0] := 'Values of Chi12star, Chi13star and Chi23sandp';
  Cv[Npts] := Chi12star; Cv[1] := Chi13star;
  FOR n := 2 TO Npts-1 DO Cv[n] := Chi23sandp[n] END;
  IF Debug[10] THEN bmbutils.ShowData(Ch,Cw,Cv,ap,3,Npts) END;
  IF FileOutput THEN FileData(Ch,Cw,Cv,ap,3,Npts,FileHandle) END;
END;

(* Calculation of Chi123 *)

F1 := CtoK/f0/V1;
term2 := f0*(B11 - V1)/TdegK;
FOR n := 2 TO Npts-1 DO
  (* calculate wt.frs. from mol frs. *)
  MassFromMol(w2,w3,Vrel[1,n]);
  PolymerProps(TdegC,w2);
  term3 := (1.0 - V1/V2)*phi2;
  term4 := (1.0 - V1/V3)*phi3;
  term3 := term2 + term3 + term4;
  Chi123[n] := Log(f1*v23/Vrel[2,n]) - term3;
END;
(* Calculation of Chi23star *)

f1 := CtoK/T0/Vstar1;
term2 := f0*(B11*Vstar1/TdegK);
FOR n := 2 TO Npts-1 DO
  (* calculate wt.frs. from mol frs. *)
  MassFromMol(w2,w3,Vret[1,n]);
  PolymerProps(TdegC,w2);
  term3 := (1.0 - Vstar1/Vstar2)*phistar2;
  term4 := (1.0 - Vstar1/Vstar3)*phistar3;
  term3 := term2 + term3 + term4;
  Chi123star[n] := Log(f1*Vstar23/Vret[2,n]) - term3;
END;

IF Debug[10] OR FileOutput THEN
  Ch[0] := 'Values of Chi12, Chi13 and Chi123';
  Cv[Npts] := Chi12; Cv[1] := Chi13;
  FOR n := 2 TO Npts-1 DO Cv[n] := Chi123[n] END;
  IF Debug[10] THEN bmutils.ShowData(Ch,Cw,Cv,np,3,Npts) END;
  IF FileOutput THEN FileData(Ch,Cw,Cv,np,3,Npts,FileHandle) END;
  Ch[0] := 'Values of Chi12star, Chi13star and Chi123star';
  Cv[Npts] := Chi12star; Cv[1] := Chi13star;
  FOR n := 2 TO Npts-1 DO Cv[n] := Chi123star[n] END;
  IF Debug[10] THEN bmutils.ShowData(Ch,Cw,Cv,np,3,Npts) END;
  IF FileOutput THEN FileData(Ch,Cw,Cv,np,3,Npts,FileHandle) END;
END;
END ChiValues;

PROCEDURE Xijbar(nDegC,SolventRefNo:CARDINAL;
                   FileOutput:BOOLEAN; FileHandle:File);

CONST
  GasConst = 83.144;
  (* Bar cm3 / (Mol K) *)

VAR
  t0,t1,t2,t3,t4,Vstar1,TdegK,w2,w3,r,
  OptimValue,f0,p0,q0,p1,q1,p2,q2 :LONGREAL;
  n,Npts :CARDINAL;
  ok :BOOLEAN;
  s :String;
  Cw,Ch,Ctemp :Words;
  Cv,Cwf :Data;
  np :SigFigs;

BEGIN
  OptimValue := 5.566;
  (* units bar using only data at 75.5 degC *)
  ChiValues(Npts,nDegC,SolventRefNo,FALSE,FileHandle);

  TdegC := ChooseTdegC(nDegC);
  TdegK := TdegC + CtoK;
  f0 := GasConst*TdegK;

  (* X12bar and X13bar are calculated from Eq 5 *)

(* X12bar *)
Vstar1 := vstar1*MolW;
p0 := (CubeRoot(vred1) - 1.0);
t0 := p0/(CubeRoot(vred2) - 1.0);
q0 := Fstar1*Vstar1;
p1 := 1.0/vred1 + 3.0*Tred1*Log(t0);
t1 := q0*(p1 - 1.0/vred2);
t2 := f0*Chi12star;
X12bar := (vred2/Vstar1)*(t2 - t1); Cwf[Npts] := 1.000;

(* X13bar *)
t0 := p0/(CubeRoot(vred3) - 1.0);
t1 := q0*(p1 - 1.0/vred3);
t2 := f0*Chi13star;
X13bar := (vred3/Vstar1)*(t2 - t1); Cwf[1] := 0.000;

(* X23bar is calculated from Eq 9 *)
p2 := X12bar*theta2 + X13bar*theta3;
q2 := theta2*theta3;

FOR n := 2 TO Npts-1 DO
  MassFromMol(w2,w3,Vret[1,n]); Cwf[n] := w2;
  PolymerProps(TdegC,w2);
  t0 := p0/(CubeRoot(vred23) - 1.0);
  t1 := q0*(p1 - 1.0/vred23);
  t2 := f0*Chi122star[n];
  t3 := (vred23/Vstar1)*(t2-t1) - p2;
  X23bar[n] := -(t3*StoVRatio2/StoVRatio1)/q2;
  Q23[n] := (OptimValue - X23bar[n])/(TdegK*vred23);
END;

  (* Develop Heading *)
  Ch[0] := 'Calculated values for X23bar and Q23';
  Ch[3] := ' at ';
  Str.FixRealToStr(TdegC,0,Ch[4],ok);
  Ch[5] := ' degC';
  bbumutils.bbmConcat(s,Ch,1,5);
  Ch[1] := s;
  Ch[2] := 'X23bar is in bar and Q23 in bar/K';
  bbumutils.bbmConcat(s,Ch,3,9);
  Ch[3] := s;
  FOR n := 1 TO Npts DO Str.FixRealToStr(Cwf[n],4,Cwf[n],ok)END;
  bbumutils.AddSpaces(Cw,Npts);
  FOR n := 1 TO Npts DO Str.Append(Cwf[n],spaces[5]) END;
  Str.FixRealToStr(X12bar,4,Ctemp[1],ok);
  Str.FixRealToStr(X12bar,4,Ctemp[Npts],ok);
  FOR n := 2 TO Npts-1 DO
    Str.FixRealToStr(X23bar[n],4,Ctemp[n],ok)
  END;
  bbumutils.AddSpaces(Ctemp,Npts);
  FOR n := 1 TO Npts DO Str.Append(Cw[n],Ctemp[n])END;
Cv[1] := 0.0; Cv[Npts] := 0.0;
FOR n := 2 TO Npts-1 DO Cv[n] := Q23[n] END;
FOR n := 1 TO Npts DO np[n] := 4 END;
IF Debug[11] THEN bmbutils.ShowData(Ch,Cw,Cv,np,3,Npts)END;
IF FileOutput THEN FileData(Ch,Cw,Cv,np,4,Npts,FileHandle) END;
END;
END Xijbar;

BEGIN
SetDebugParams(11);
nSet := CardSet(1,2,3);

w[0] := 'Do you wish to write the results to a file (y/n)? ';
w[2] := 'Enter the file name (up to 8 chars )';
w[4] := 'Enter an integer {1,2 or 3} to select a';
w[6] := 'temperature of 80, 100 or 120 degC';
w[8] := 'Do you wish to repeat with another probe (y/n)?';
FOR n := 1 TO 7 BY 2 DO w[n] := '' END;

d0 := Window.WinDef(0,0,79,24,Window.LightBlue,Window.Black,
FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
Window.Yellow,Window.Black);
m0 := Window.Open(d0);
Window.CursorOn;
bmbutils.NewWindow(w,0,6,m0,xc1,yc1,xc2,yc2);
Window.Clear;
ny := 2;
bmbutils.OffSet(w[0],j,ny,xc1,xc2);
Window.DirectWrite(nx,ny,ADR(w[0]),j);
Window.GotoXY(nx+j+1,ny);
REPEAT
  ch := CAP(IO.RdKey());
  FileOutput := ch = 'Y';
UNTIL FileOutput OR (ch = 'N');
Window.GotoXY(1,ny);
Window.ClrEol;

IF FileOutput THEN
  INC(ny,2);
  j := Str.Length(w[2]);
  Window.DirectWrite(nx,ny,ADR(w[2]),j);
  Window.GotoXY(nx+j+1,ny);
  IO.RdStr(ResFile);
  Str.Append(ResFile,'Res');
  FileHandle := FIO.Create(ResFile);
END;

INC(ny,2);
Window.DirectWrite(nx,ny,ADR(w[4]),Str.Length(w[4]));
INC(ny,2);
j := Str.Length(w[6]);
REPEAT
  Window.DirectWrite(nx,ny,ADR(w[6]),j);
  Window.GotoXY(j+nx+1,ny);
  Window.ClrEol;
  Window.GotoXY(j+nx+1,ny);
  nDegC := IO.RdCard();
UNTIL nDegC IN nSet;
Window.Clear;
Window.Hide(m0);

TdegC := ChooseTdegC(nDegC);

FOR nprobe := 3 TO 18 DO
   IF nprobe = 14 THEN GOTO Omit END;
   SolventRefNo := nprobe;
   SolventChoice(SolventRefNo,FALSE,SolventName);
   Xijbar(nDegC,SolventRefNo,FileOutput,FileHandle);

Omit:
   END;

IF FileOutput THEN FIO.Close(FileHandle) END;

END XbarAll.
MODULE Spinodal;
(* Re-edited Wednesday 15th August 1990 *)

(*# optimize( i386 => on ) *)
(*# optimize( i387 => on ) *)
(*# debug( vid => full ) *)
(*# check( index => on ) *)
(*# check( stack => on ) *)

IMPORT bbuatl, rjmutils, retvols, FO, FIO, MATHLIB, Window, Str;

FROM FIO IMPORT File;
FROM MATHLIB IMPORT Exp, Log, Sqrt;
FROM rjmutils IMPORT CubeRoot, SetDebugParams, SolventChoice,
  ProbePhysProps, VPmmHg, HBT, RackettSD,
  AlphaCalc, RSD, ProbeCharProps,
  PolymerSpecVol, MassFromMol, SegmtFromMol,
  MolFromMass, PolymerProps;

FROM retvols IMPORT RetentVols80, RetentVols100, RetentVols120;

FROM bbuatl IMPORT Words, String, spaces, Data, SigFigs;

FROM rjmutils IMPORT CtoK, SegMolWt2, sigmaG2, SegMolWt3, sigmaG3,
  NoAvMolWt2, NoAvMolWt3,
  MolWt, Tcrit, Pcrit, Zeta, Omega, Rho20, OmegaSRK,
  VPa, VPb, VPc, VpD, b0, b1, b2, VP, TdegC, Vast,
  SolubilityParameter,
  v1, vred1, vstar1, Pstar1, Pred1, Tred1, Tstar1,
  v2, vred2, vstar2, v3, vred3, vstar3, Pstar2, Pstar3,
  Pred2, Pred3, Tred2, Tred3, Tstar2, Tstar3,
  v23, vred23, vstar23, vbarN,
  P, Pstarb, Predb, TdegK, Tstarb, Tredb,
  phi2, phi3, phistar2, phistar3, theta2, theta3,
  WtFr, dPred, dTred, dvred,
  StoVRatio1, StoVRatio2, StoVRatio3,
  SolventRefNo,
  SolventName,
  Debug;

FROM retvols IMPORT Vret;

TYPE CharSet = SET OF CHAR;
CardSet = SET OF CARDINAL;

CONST GasConst = 83.144;
(* redefined as bar cm3 / (mol K) *)

VAR
X23, Q23, wfr
j, k, n, a, x, c1, c2, y, y, c2
m0, m1
d0, d1
ok
ch
s
w
d
np

:LONGREAL;
:CARDINAL;
:Window.WinType;
:Window.WinDef;
:BOOLEAN;
:CHAR;
:String;
:Words;
:Data;
:SigFigs;
PROCEDURE ShowReal(Var s: String; r: LONGREAL; nplaces, nx, ny: CARDINAL);
VAR ok : BOOLEAN;
BEGIN
Str.FixRealToStr(r, nplaces, s, ok);
Window.DirectWrite(nx, ny, ADR(s), Str.Length(s));
END ShowReal;

PROCEDURE PartDerivs(Trial: LONGREAL);
VAR
v3red23, factor, B, C, D, x, y, z, p, q, vroot : LONGREAL;
j, k, n : CARDINAL;
PDvals : Data;
s, s1 : String;
w, PD, Ph : Words;
np : SigFigs;
BEGIN
(* Using the nomenclature derived by Zhikuan et al, Polymer, 1983, Vol 24, 263 *)

Pstarb := Pstar2*phistar2 + Pstar3*phistar3
- phistar2*theta3*X23; (* R&W Eqn 5 *)
p := phistar2*Pstar2/Tstar2;
q := phistar3*Pstar3/Tstar3;
Tstarb := Pstarb/(p + q); (* R&W Eqn 6 *)
Predb := P/Pstarb; Tredb := Trial/Tstarb;
B := P/(Pstarb*Pstarb)*
(Pstar2 - Pstar3 - X23*theta3*(1.0 - theta2/phistar3));
dPred := B; (* R&W Eqn 27 *)

C := Tredb*B/Predb + (Pstar3*Tred3 - Pstar2*Tred2)/Pstarb;
dTred := C; (* R&W Eqn 28 *)
v3red23 := vred23*vred23*vred23; vroot := CubeRoot(vred23);
x := B - C*(Predb/Tredb + 1.0/(Tredb*vred23*vred23));
y := Tredb*(3.0*vroot - 2.0);
z := 3.0*vred23*vroot*vroot*(vroot - 1.0)*(vroot - 1.0);
D := x/(2.0/v3red23 - y/z);
dvred := D;

IF Debug[12] THEN
Ph[0] := 'Values of Blend Parameters';
FOR n := 1 TO 2 DO np[n] := 2 END;
FOR n := 3 TO 4 DO np[n] := 6 END;
bbmutils.ShowData(Ph, PD, PDvals, np, 1, 4);

Ph[0] := 'Values of Partial Derivatives';
FOR n := 1 TO 3 DO np[n] := 8 END;
bbmutils.ShowData(Ph, PD, PDvals, np, 1, 3);
END PartDerivs;
PROCEDURE ErrorTerm(TrialK:LONGREAL; db:BOOLEAN):LONGREAL;
VAR
Vstar2,vroot,TrialC :LONGREAL;
j,k,n,xc1,xc2,yc1,yc2 :CARDINAL;
lc :LONGCARD;
ok :BOOLEAN;
s0,s1 :String;
t :Data;
wh,wd :Words;
np :SigFigs;
BEGIN
(* NOTE Vstar2 is defined as the molar hard core volume of component 2
   - suggest we try NoAvMolWt2*vstar2 *)

TrialK := TrialK - CtoK;
PolymerProps(TrialC,WtFr);
PartDerivs(TrialK);
Vstar2 := NoAvMolWt2*vstar2;

t[1] := 2.0*theta3*theta3*theta2/(phistar2*phistar3);

(* the ratio of r2/r3 has been fixed as 0.73972 *)

IF db THEN

wh[0] := 'Value of Terms in Error Function';
FOR n := 1 TO 8 DO
  Str.CardToStr(VAR(longcard,n),s0,10,ok);
  Str.Concat(wd[n],Term,s0);
  np[n] := 6;
END;
bbmutils.ShowData(wh,wd,t,np,1,8);
END;
RETURN t[8];
END

PROCEDURE zBrent(VAR answer:LONGREAL; x1,x2,tol:LONGREAL; Display:BOOLEAN);
LABEL Finish;
CONST itmax = 1000; eps = 1.0E-14;
VAR
a,b,c,d,e,min1,min2,min,fa,fb,fc,
p,q,r,s,tol1,xm :
iter
xc1,xc2,yc1,yc2,j,k,ni,ni,w :

s1,s2,s3 :String;
ch :CHAR;
m3 :Window.WinType;
d3 :Window.WinDef;
ok,db :BOOLEAN;
BEGIN
  db := FALSE;
  a := x1; fa := ErrorTerm(a,db);
  b := x2; fb := ErrorTerm(b,db);
  IF fa*fb > 0.0 THEN
    w[0] := 'Root must be bracketed in search procedure'
    w[1] := ',';
    bbumits.Pause(w,1,0);
    GOTO Finish;
  END;

  IF Display THEN
    d3 := Window.WinDef(0,0,79,24,Window.LightBlue,Window.Black,
      FALSE,FALSE,FALSE,TRUE,
      Window.SingleFrame,
      Window.Yellow,Window.Black);
    m3 := Window.Open(d3);
    Window.CursorOn;
    xc1 := 15; xc2 := 65; yc1 := 1; yc2 := 24;
    Window.Change(m3,xc1,yc1,xc2,yc2);
    ni := 2;
    s2 := 'Press any key to continue'
    s3 := 'N
      x
      F(x)
      Window.DirectWrite(5,1,ADR(s3),Str.Length(s3));
  END;

  fc := fb;
  FOR iter := 1 TO itmax DO
    IF fb*fc > 0.0 THEN c := a; fc := fa; d := b-a; e := d; END;
    IF ABS(fc) < ABS(fb) THEN
      a := b; b := c; c := a;
      fa := fb; fb := fc; fc := fa;
    END;
    tol1 := 2.0*eps*ABS(b) + 0.5*tol;
    xm := 0.5*(c - b);
    IF (ABS(xm) <= tol1) OR (fb = 0.0) THEN
      answer := b;
      IF Display THEN
        bbumits.Offset(s2,j,k,xc1,xc2);
        Window.DirectWrite(k,yc2-2,ADR(s2),j);
        Window.GotoXY(k+j+1,yc2-2);
        ch := IO.RdKey();
      END;
      GOTO Finish;
    END;
  END;

  IF (ABS(c) >= tol1) AND (ABS(fa) > ABS(fb)) THEN
    s := fb/fa;
    IF a = c THEN p := 2.0*xm*s; q := 1.0 - s;
    ELSE
      q := fa/fc; r := fb/fc;
      p := s*(2.0*xm*q*(q-r) - (b-a)*(r-1.0));
      q := (q-1.0)*(r-1.0)*(s-1.0);
    END;
IF p > 0.0 THEN q := -q END;
  p := ABS(p);
  min1 := 3.0*xm*q - ABS(tol1*q);
  min2 := ABS(e*q);
  IF min1 < min2 THEN min := min1
      ELSE min := min2
  END;
  IF 2.0*p < min THEN e := d; d := p/q;
      ELSE d := xm; e := d;
  END;
ELSE
d := xm; e := d;
END;
a := b; fa := fb;
IF ABS(d) > tol1 THEN b := b+d
ELSE
  IF xm >= 0.0 THEN b := b + ABS(tol1)
      ELSE b := b - ABS(tol1)
  END;
END;
fb := ErrorTerm(b,db);
IF Display THEN
  INC(ni);
  nx := 4;
  Window.GotoXY(nx,ni); IO.WrCard(iter,3);
  INC(nx,10);
  ShowReal(s1,b,10,nx,ni);
  IF fb < 0.0 THEN INC(nx,19) ELSE INC(nx,20) END;
  ShowReal(s1,fb,10,nx,ni);
  IF ni > 20 THEN
    ni := 2;
    bbumuls.OffSet(s2,j,k,0,50);
    Window.DirectWrite(k,yc2-2,ADR(s2),j);
    Window.GotoXY(k+j+1,yc2-2);
    ch := IO.RdKey();
    Window.Clear;
    Window.DirectWrite(5,1,ADR(s3),Str.Length(s3));
  END;
END;
END;
w[0] := 'Permitted number of iterations exceeded';
w[1] := 'i';
w[2] := 'Current best answer is ';
w[3] := 'i';
Str.FixRealToStr(b,10,w[4],ok);
Str.Append(w[2],w[4]);
bbumuls.Pause(w,3,0);
answer := b;

Finish:
  IF Display THEN Window.Close(m3) END;
END zBrent;
BEGIN

SetDebugParams(13);

w[0] := 'The Calculation of the Spinodal Temperature';
w[1] := 'Enter the expl. temperature        ';
w[2] := 'Enter the wt fr EVA';
w[3] := 'Enter Q23 (bar/K)  ';
w[4] := 'Calculated Spinodal Temperature (K)';
w[5] := 'Do you wish to repeat the calculation (y/n)?'

D0 := Window.WinDef(0,0,79,24,Window.LightBlue,Window.Black,
FALSE,FALSE,FALSE,TRUE,Window.SingleFrame,
Window.Yellow,Window.Black);

m0 := Window.Open(D0);
Window.CursorOn;
bmutils.NewWindow(w,0,8,m0,xc1,yc1,xc2,yc2);

REPEAT

Window.Clear;

ny := 2;
bmutils.Offset(w[0],j,nx,xc1,xc2);
Window.DirectWrite(nx,ny,ADR(w[0]),j);

bmutils.Offset(w[1],j,nx,xc1,xc2);
INC(ny,2);

j := Str.Length(w[1]);
Window.DirectWrite(nx,ny,ADR(w[1]),j);
Window.GotoXY(nx+j+1,ny);
Texptl := IO.RdLngReal();
INC(ny,2);

j := Str.Length(w[2]);
Window.DirectWrite(nx,ny,ADR(w[2]),j);
Window.GotoXY(nx+j+1,ny);
WtFr := IO.RdLngReal();
INC(ny,2);

j := Str.Length(w[3]);
Window.DirectWrite(nx,ny,ADR(w[3]),j);
Window.GotoXY(nx+j+1,ny);
Q23 := IO.RdLngReal();
Window.Clear;

P := 1.01325; (* atmospheric pressure bar *)
X23 := 5.667; (* bar *)

SolventChoice(SolventRefNo,FALSE,SolventName);
zBrent(TdegK,5.0,1000.0,0.0001,Debug[13]);

INC(ny,2);

j := Str.Length(w[4]);
Window.DirectWrite(nx,ny,ADR(w[4]),j);
ShowReal(s,TdegK,2,nx+j+1,ny);
INC(ny,2);
bmutils.Offset(w[5],j,nx,xc1,xc2);
Window.DirectWrite(nx,ny,ADR(w[5]),j);
Window.GotoXY(nx+j+1,ny);

REPEAT

ch := CAP(IO.RdKey());
UNTIL (ch = 'Y') OR (ch = 'N');

ch = 'N';

END Spinodal.