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Vacuum microbalance studies of the thermodynamics of non-electrolyte liquid mixtures.

Price, G. J.

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Vacuum Microbalance Studies of the Thermodynamics of Non-Electrolyte Liquid Mixtures

A Thesis submitted by **G. J. Price**
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G J Price

Dedication

This Thesis is dedicated to the Memory of my Father.

Acknowledgements

My first acknowledgement must be to my Supervisor, Dr. A. J. Ashworth. I am deeply grateful for his continued help, advice, encouragement and, at times, patience. I also thank him for the use of his previously constructed apparatus and for performing the glassblowing involved in the project.

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Finally, I must thank my Mother for her continuing support and encouragement.

Contents

Memorandum

The work described in this Thesis was carried out in the Physical Chemistry Group of the School of Chemistry, University of Bath, between September 1981 and July 1984 and has not been submitted for any other degree. It is the original work of the author except where indicated otherwise by appropriate acknowledgement or reference.

Summary

The work described in this Thesis is concerned with the application of vapour sorption techniques employing vacuum microbalances to the study of liquid mixtures.

A conventional quartz beam microbalance was used to measure the absorption of a range of volatile organic solutes by poly(dimethyl siloxane), PDMS, to determine infinite dilution activity coefficients and interaction parameters which agreed well with results from a joint gas-liquid chromatographic investigation. A slight dependence of these properties on polymer molecular weight and on the polymer to solid support ratio was detected. Results from the absorption of hexane by mixtures of PDMS with squalane or DNP were used to calculate inter-solvent interaction parameters and these were shown to give reasonable predictions of the miscibility limits of the mixtures.

A recently developed magnetic suspension vacuum microbalance was shown to give accurate results for polymer solutions over a wide concentration range using PDMS as an example. Meaningful values of the partial molar enthalpy of mixing were measured for benzene and hexane with PDMS. A number of solution theories were applied to these results but they did not predict satisfactory solution properties in the high polymer concentration region.

Previous work on the retention behaviour of mixtures of squalane and DNP was extended using three polar absorbates: chloroform, dichloromethane and ethyl acetate. It was found that predictions of the partition coefficients using the Purnell-Andrade equation were in error by up to 10% while those using the Tiley-Perry relationship agreed with experiment to within, on average, 3-4%.

Variation of absorption with absorbent liquid loading in the

benzene-PDMS and ethyl acetate-squalane or DNP systems was examined and the results suggested that adsorption occurred at the gas-liquid interface as well as at the surface of the solid support.

Chapter 1

Introduction and Theoretical

At the 1978 Faraday Discussion[1] on 'Structure and Motion in Molecular Liquids', Joel Hildebrand wrote "Few topics in Physical Chemistry have evoked so many theories but so little consensus as the liquid state". The work presented in this Thesis will describe the measurement of thermodynamic properties of some types of non-electrolyte liquid mixtures using vapour sorption techniques employing vacuum microbalances.

Substances normally exist in one of three phases: solid, liquid or gas. The former is readily identifiable as having a well defined shape, while the other two are easily differentiated since a gas will completely fill a container, whereas a liquid, while taking up the shape of the container, will not necessarily fill it. The behaviour of gases is approximately described over a wide range of conditions by the 'Ideal' or 'Perfect' gas laws derived by Boyle, Charles and others[2] in the 1700's, and more recent equations such as that of Van der Waals[3] allow calculation of gaseous properties to a fair degree of accuracy. The advent of diffraction and other methods including computer simulation during this century has also allowed a reasonable description of most types of solid to be made. However, no such fortunate situation exists as far as liquids are concerned.

The calculation and prediction of the properties of liquids and particularly their mixtures is an important problem in Chemistry and is of considerable practical value as well as being of academic and theoretical interest. Most chemical reactions take place in solution and so an accurate theory of the liquid state would allow better prediction of solvent and solution properties with consequent economy of time and effort. There are, though, a considerable number of different types of liquid mixtures. The simplest are mixtures of liquefied noble gases and the range covers mixtures of simple alkanes, more complex non-electrolytes including polymers, to mixtures of liquid metals and molten salts. Another area of wide interest is that of electrolyte solutions, where electrostatic interactions have to be taken into account, this becoming increasingly important in the application to aqueous solutions in the growing area of biotechnology. It should though be realised that, for many applications, exact results are not necessary and often a readily calculable estimate of reasonable accuracy is preferable to an exact answer that is more difficult to obtain.

The work described in this Thesis is exclusively concerned with the thermodynamics of mixtures of non-electrolytes. The technique used was to measure the vapour pressure over a solution, the composition of which was determined using a vacuum microbalance. This technique requires knowledge of the vapour composition and, with the apparatus used, requires the vapour to be a single component so that only one of the compounds in solution can be appreciably volatile. In general, polymers are involatile so that their solutions are suitable for study by this method. The growth of the polymer and plastics industry over the past two decades has led to a wide interest in polymer solutions since polymer processing, e.g. casting of films or spinning of fibres, often occurs from solution. Some aspects of the application of these experimental methods to polymer solution thermodynamics including their phase equilibria are described in Chapters 5 and 6 of this Thesis and the prediction of these properties from various solution theories is described in Chapter 7.

Since the early 1960's, the technique of gas-liquid chromatography, GLC, has been used for the study of solution thermodynamics and has been shown to be a useful technique.[4] However, doubts have been expressed about its use with polymers and a comparison of GLC results with those obtained by the static vapour sorption methods is presented in Chapter 4 and these doubts discussed. The problem of competing retention mechanisms in GLC has also been investigated using static methods and the results for several systems are presented in Chapter 8. The use of solvent mixtures to obtain conditions suitable for particular analyses needs prediction of the properties of the mixture from those of the pure components. This work is discussed with the results for several systems in Chapter 9.

1.1. THEORIES OF LIQUIDS AND LIQUID MIXTURES

Two basic directions of approach have been used in attempting to derive a satisfactory theory of liquids. One approach attempts to extrapolate the properties of gases and involves the transition from interactions between pairs of gas molecules to the multiple collisions found in liquids. The other approach starts with the more or less lattice-like structure of a solid and attempts to relax the structure to simulate the properties of a liquid. Both of these have been used to contribute to solution theory but neither has proved to be totally satisfactory.

It might be felt that an accurate theory of the behaviour of pure liquids would be a prerequisite for the treatment of solutions (the terms 'solution' and 'liquid mixture' being used interchangeably). However, the prediction of solution properties from fundamental molecular parameters is not usually necessary and of much more interest is the prediction in terms of the behaviour of the pure liquids of which the solution is composed, these being taken as reference states.

1.2. IDEAL SOLUTIONS

The simplest model of a solution is that describing an 'Ideal Solution'. There are various ways of defining an ideal solution[5] but perhaps the most useful in terms of experimentally observable properties, and especially in view of the techniques used in the work described in this Thesis, is that an ideal solution obeys Raoult's Law at all temperatures. This was determined by Raoult[6] from work on the vapour pressure of ether solutions and relates the pressure of a solvent 1, p_1, to the vapour pressure of the pure solvent, p_1°, by

$$p_1 = p_1^\circ x_1 \tag{1.1}$$

where x_1 is the mole fraction of the solvent in the solution. This definition was used by Guggenheim to show that for a solution to be ideal it was necessary for the components to mix in all proportions and at all temperatures with no heat or volume change,[7] and that this implied that they should have the same size and shape and, for a binary solution,[8] intermolecular energies between components in the solution, ε_{12}, related to those between the pure components ε_{11} and ε_{22} by $\varepsilon_{12} = (\varepsilon_{11} + \varepsilon_{22})/2$.

Experimental measurements have shown that few solutions could be classed as ideal even over a narrow range of concentrations, those most closely approximating to ideal behaviour being mixtures of chemically similar compounds, e.g. hexane and heptane or benzene and toluene. The ideal model then is not very successful in describing the properties of real solutions but has been very useful in providing a reference state, deviation from which can be used to gauge these properties.

1.3. NON-IDEAL SOLUTIONS

To compare real solutions with the ideal concept, Lewis[9,10] introduced the concepts of fugacity and activity. The activity of a component, a_1, is the ratio of the fugacity of the component in solution to that of the pure component at the same temperature. The fugacity is a measure of the tendency of molecules to move from the liquid to the vapour phase and, assuming the vapour phase behaves according to the ideal gas laws, can be represented by the vapour pressure of the component. (One should be careful to differentiate between ideal gas behaviour of the vapour and ideal solution behaviour of the liquid, these being unrelated concepts.) The activity coefficient, γ, can be defined as a measure of the deviation of a solution from ideality and may be expressed as a modification to the Raoult's Law expression

$$p_1 = p_1^{\circ} x_1 \gamma_1 \tag{1.2}$$

or equivalently,

$$\gamma_1 = a_1/x_1$$

For an ideal solution, $\gamma = 1$. Hence from measurements of vapour pressure and composition, the deviation from ideality of a solution may be calculated.

1.4. THERMODYNAMICS OF SOLUTION

The molar free energy of mixing of a solution, ΔG^M is related in the usual way to the molar entropy of mixing, ΔS^M, and molar enthalpy of mixing, ΔH^M, at temperature T.

$$\Delta G^M = \Delta H^M - T\Delta S^M \tag{1.3}$$

However, for an ideal solution, by definition, $\Delta H^M = 0$ so that $\Delta G^M = -T\Delta S^M$. An expression for ΔS^M of an ideal solution is readily calculable since all molecules have the same size and shape. Thus the entropy of mixing arises merely from the greater number of ways of arranging the molecules relative to the pure components. It may be shown that[11]

$$\Delta S^{M(id)} = -R \sum_i x_i \ln x_i \tag{1.4}$$

where $\sum_i$ represents the summation over all components i, and the superscript (id) denotes an ideal value. Thus, for an ideal solution,

$$\Delta G^{M(id)} = -RT \sum_i x_i \ln x_i \qquad (1.5)$$

The partial derivative of the free energy with respect to the concentration of one component, i, is the partial molar free energy $\overline{\Delta G_i}$, termed the chemical potential, μ_i, of the component.

$$\mu_i = \partial(\Delta G_i)/\partial x_i = \overline{\Delta G_i} \qquad (1.6)$$

It can easily[11] be shown that the chemical potential of a component i in a solution is given by

$$\mu_i = \mu_i^\circ + RT \ln a_i \qquad (1.7)$$

where μ_i° is the chemical potential of a reference state, conventionally taken as that of the pure liquid. Since for ideal solutions the activity is given by the mole fraction,

$$\mu_i^{(id)} = \mu_i^\circ + RT \ln x_i \qquad (1.8)$$

or, for non-ideal solutions

$$\mu_i = \mu_i^\circ + RT \ln(x_i\gamma_i) \qquad (1.9)$$

As a further comparison with ideal solutions, a series of 'Excess' properties can be defined which represent the difference between the property of a real solution and its ideal value. For example, considering the chemical potentials,

$$\begin{aligned} \mu_i^E &= \mu_i - \mu_i^{(id)} \\ &= [\mu_i^\circ + RT \ln(\gamma_i x_i)] - [\mu_i^\circ + RT \ln x_i] \\ &= RT \ln \gamma_i \qquad (1.10) \end{aligned}$$

Equation (1.10) gives the link between the experimentally measurable activity coefficient and the thermodynamic properties under investigation. Since the chemical potential is a free energy parameter, it can be split into entropic and enthalpic contributions.

$$\mu_i^E = \overline{\Delta G_i^E} = \overline{\Delta H_i^E} - T\,\overline{\Delta S_i^E} \qquad (1.11)$$

where the superscript 'E' denotes an excess property. Combining equations (1.10) and (1.11),

$$\ln \gamma_i = \overline{\Delta H}_i^E / RT - \overline{\Delta S}_i^E / R \qquad (1.12)$$

This equation also shows that determination of activity coefficients over a range of temperatures can yield values for the excess partial molar heats and entropies of mixing since

$$\overline{\Delta H}_i^E = R(\partial \ln \gamma_i / \partial (1/T)) \qquad (1.13)$$

and

$$\overline{\Delta S}_i^E = -R(\ln \gamma_i - \overline{\Delta H}_i^E / RT) \qquad (1.14)$$

1.5. THERMODYNAMICS OF PHASE EQUILIBRIUM

Solutions that behave ideally must, by definition, be miscible in all proportions at all temperatures. However it is a common occurrence that mixtures of some liquids, e.g. water and carbon tetrachloride, do not mix. A qualitative idea of the phase behaviour of a system can be obtained from the thermodynamic condition that, for a closed system at constant temperature and pressure, the free energy will be at a minimum. Hence, for miscibility, the free energy change on mixing must be negative. Consideration of equation (1.3) shows that if ΔH^M is negative or zero and ΔS^M positive then a negative free energy of mixing results and a miscible system would be expected.

If ΔH^M and ΔS^M are both negative then miscibility might be expected at low temperatures but phase separation may occur at higher temperatures as the $-T\Delta S^M$ term becomes dominant. The highest temperature at which a single phase can exist is the 'Lower Critical Solution Temperature' - 'LCST'. Conversely if ΔH^M and ΔS^M are both positive then the opposite argument would apply, with the positive ΔH^M term being dominant at low temperatures so that phase separation might be expected. The lowest temperature at which a single phase can exist is the 'Upper Critical Solution Temperature' - 'UCST'.

Since ΔH^M and ΔS^M are themselves functions of temperature they can change sign so that both UCST and LCST behaviour can be observed in some systems.

However, the condition that the free energy of mixing is negative, while necessary, is not a sufficient one for phase separation. Consider a binary mixture having a molar free energy of mixing-composition curve of the type shown in Figure 1-1.

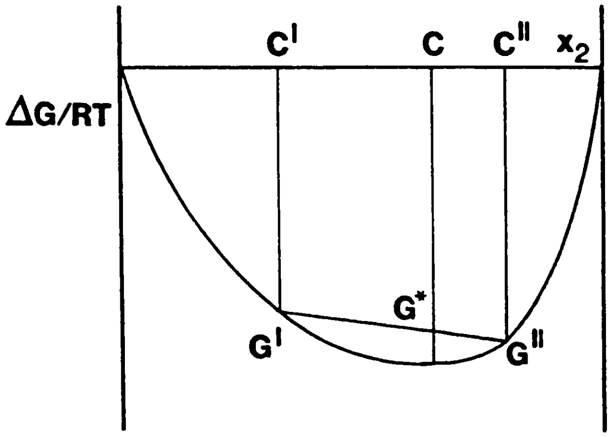


FIGURE 1-1: FREE ENERGY OF MIXING FOR A MISCIBLE SYSTEM

Note that here only the isothermal separation of a binary liquid mixture into two phases is considered. If a mixture of composition C were to separate into two phases of compositions C^I and C^{II}, then the free energies of mixing of the two phases will be G^I and G^{II} and the total free energy of mixing of the system G*. Thus, the two phase system will have a higher free energy of mixing than the single phase system so that the system will be thermodynamically stable with respect to phase separation. It is clear that this applies to any region of the curve having a positive curvature and so if the curve is concave upward throughout then the system will be completely miscible at the temperature considered.

However, if the curve is not of this form and has a region of negative curvature as in Figure 1-2 then by the same argument the free energy of mixing of the system of composition C will be lowered by splitting into two phases of compositions C^I and C^{II} so that the system is thermodynamically unstable with respect to phase separation.

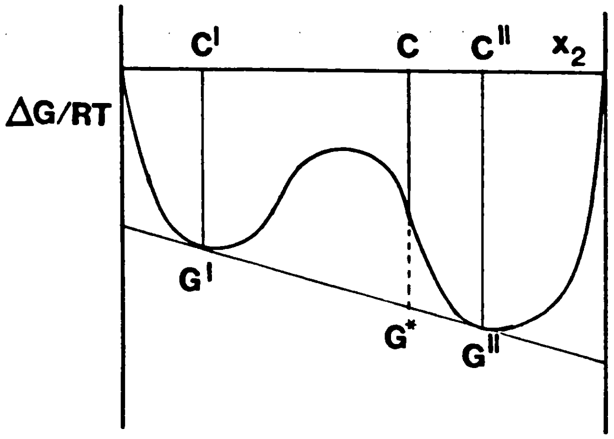


FIGURE 1-2: FREE ENERGY OF MIXING FOR A PARTIALLY MISCIBLE SYSTEM

The thermodynamic condition for equilibrium between two phases is that the chemical potentials of each component in each phase and hence change in chemical potential should be equal. Thus for a binary system of components 1 and 2 in phases I and II,

$$\Delta\mu_1^I = \Delta\mu_1^{II} \quad ; \quad \Delta\mu_2^I = \Delta\mu_2^{II} \qquad (1.15)$$

From equation (1.6), it is clear that $\Delta\mu$ at any concentration is given by the gradient of the tangent to the G(x) curve, where G(x) is the function describing the variation of free energy of mixing with mole fraction of one component. Thus equation (1.15) is satisfied when the gradients $G'(x)$ are equal and thus the compositions of the coexisting phases are given by the points of contact of a double tangent as drawn in Figure 1-2. Hence, in principle, if an expression for the free energy-concentration function is available then the compositions of the conjugate solutions can be predicted.

1.6. THEORETICAL MODELS OF SOLUTION

Equation (1.12) indicates that deviations from solution ideality and contributions to the partial molar free energy of mixing can arise from two sources; a non-ideal entropy of mixing or, since $\Delta H^{M(id)} = 0$, a non-zero enthalpy of mixing. These two contributions were first treated separately and then combined to give a theory for the description of real solutions. It has been found that all of the systems studied in the work covered in this Thesis are best treated using theories applicable to polymer solutions and so, except in as far as they have been used to contribute to polymer solution theory, accounts of low molecular weight systems will not be given and the reader is referred to specialist texts by Rowlinson and Swinton[12] and others.[13,14]

1.6.(i) Regular Solutions

The concept of regular solutions was introduced by Hildebrand[15] and assumes an ideal entropy of mixing but a non-zero heat of mixing. The original definition[16] was as a solution "involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition". The basic assumption involved in Regular Solution theory is that of completely random mixing, thermal agitation being assumed to prevent any clustering, solvation or specific interaction effects. Hildebrand and Scott conclude that this is satisfied for solutions of small, non-polar molecules except near the critical point.

The first attempts to treat enthalpy changes on mixing liquids were based on the Van der Waals equation of state applied to liquids[17] by Van Laar[18] who assumed that interactions in the solution obeyed Berthelot's 'Geometric Mean Rule'.[19] The equations he proposed found some use in correlating heat of mixing data·but were not found to be useful over wide ranges of conditions.

In 1919, Hildebrand[20] introduced the concept of a 'cohesive energy density', 'c.e.d.' as a measure of the intermolecular forces in a liquid, this being defined as the energy of vapourization per unit volume. This was developed further by Scatchard[21] who, assuming random mixing, zero volume change on mixing and that intermolecular energies depended only on distance and not on the surrounding species, proposed

$$\Delta H^M = (x_1V_1^\circ + x_2V_2^\circ)\ \phi_1\phi_2\ A_{12} \qquad (1.16)$$

where V° is the molar volume, ϕ the volume fraction and A_{12} a constant representing the differences in interactions in the mixture and in the pure components. If the c.e.d. is taken as a measure of this interaction, again assuming Berthelot's Rule,

$$A_{12} = (\delta_1 - \delta_2)^2$$

where δ is the square root of the c.e.d., termed the 'Solubility Parameter'. Thus, in Scatchard's notation,

$$\Delta H^M = (x_1V_1^\circ + x_2V_2^\circ)\ \phi_1\phi_2(\delta_1 - \delta_2)^2 \qquad (1.17)$$

An equation of the same form was derived by Hildebrand and Wood[22] using intermolecular potential energies and distribution functions, and has been shown to correlate the heats of mixing of many systems. The solubility parameter treatment is not implicit in Regular Solution Theory but is perhaps the most commonly used variant of it.

1.6.(ii) Athermal Solutions

This treatment of solutions starts from the opposite premise to that of Regular Solutions, assuming that there is zero enthalpy of mixing but a non-ideal entropy of mixing.

In early work, it had been assumed that the entropy of mixing would not depend on the size and shape of molecules and that they would obey the ideal expression (equation (1.4)). This was questioned by Fowler and Rushbrooke[23] who used a pseudo-lattice theory of liquids to show that mixtures of different sized molecules would not be ideal. Similar methods were used to show that ideal behaviour can only occur in systems where the component molecules have similar size and shape.

Using a similar lattice theory, Flory[24,25] and Huggins[26,27] independently derived expressions which lead to the following for the mixing entropy

$$\Delta S^M = -R \sum_i x_i \ln \phi_i \qquad (1.18)$$

where ϕ_i is the volume fraction defined by

$$\phi_i = x_i V_i^\circ / \sum_i x_i V_i^\circ \qquad (1.19)$$

For a binary mixture,

$$\phi_1 = x_1 / (x_1 + rx_2) \quad ; \quad \phi_2 = rx_2 / (x_1 + rx_2)$$

where r is the ratio of the molar volumes. The calculation was performed by assuming that the larger molecule can be split into a number of segments, r, each of the same size as a solvent molecule and that any site on the lattice can be occupied by any segment, subject to the restriction that adjacent segments of the larger molecule must lie on adjoining lattice sites. The entropy of mixing is then calculated by finding the number of ways of arranging n_1 smaller molecules and rn_2 polymer segments on $(n_1 + rn_2)$ lattice sites. Comparison of equations (1.4) and (1.18) show that the ideal entropy of mixing expression is merely a special case of the more general treatment since $\phi_i = x_i$ if $r = 1$ as in the ideal case.

From above,

$$\Delta S^E = \Delta S^M - \Delta S^{M(id)}$$

$$= -R \left(\sum_i x_i \ln \phi_i - \sum_i x_i \ln x_i\right)$$

Using this it can be shown[28] that the partial molar entropy of mixing can be given as

$$\overline{\Delta S}_1^M = -R\,\{\ln(1-\phi_2) - (z/2)\ln[1 - (2\phi_2/z)(1-1/r)]\} \qquad (1.20)$$

where z is the coordination number of the lattice i.e. the number of nearest neighbours of a particular segment. For large r and large z, as in the case of polymer solutions, equation (1.20) can be closely approximated by

$$\overline{\Delta S}_1^M = -R\,[\ln(1-\phi_2) + (1-1/r)\phi_2] \qquad (1.21)$$

1.7. FLORY-HUGGINS POLYMER SOLUTION THEORY

It might be thought that, since the two approaches outlined in the previous Sections start from opposite assumptions, combining them in a single theory could hardly be justified. However, it has been found[28] that approximations made to account for non-random mixing cause very small differences in the calculated values of the thermodynamic properties. Thus it is possible to retain the simplifying assumption of random mixing and combine the above treatments to derive an expression for the free energy of mixing.[29,30]

The Flory-Huggins (FH) expression for the combinatory entropy of mixing, equation (1.21), is retained, the term 'combinatory' denoting that this entropy arises only from size and shape effects and neglects any other contributions due, for example, to specific interactions in the solution. It is assumed on this simple model that these former effects are the only contributions to ΔS^M.

The enthalpic contribution to the free energy is obtained along similar lines to that in the Regular Solution treatment described earlier. If the contact interaction energy between polymer segments is w_{22}, between solvent molecules w_{11} and between polymer segment and solvent molecule w_{12} then the energy change on formation of unlike contacts, Δw, is

$$\Delta w = w_{12} - (w_{11} + w_{22})/2 \qquad (1.22)$$

By considering the numbers of contacts in a solution, a very similar expression to those of Van Laar and Scatchard (Section 1.6.(i) is obtained

$$\Delta H^{M} = (x_1 V_1^{\circ} + x_2 V_2^{\circ})\ RT\ \phi_1\ \phi_2\ \chi \qquad (1.23)$$

where χ is a dimensionless 'interaction parameter' given by

$$\chi = z\Delta w/RT.$$

Equations (1.18) and (1.23) may be combined to give an expression for the molar free energy of mixing,

$$\Delta G^{M} = RT\ [x_1 \ln \phi_1 + x_2 \ln \phi_2 + (x_1 + r x_2)\ \phi_1\ \phi_2\ \chi\ ] \qquad (1.24)$$

From this, the chemical potential of mixing for component 1 is given by

$$\Delta\mu_1 = (\mu_1 - \mu_1^{\circ}) = \overline{\Delta G}_1 = RT\ [\ln(1-\phi_1) + (1-1/r)\ \phi_2 + \chi\ V_1^{\circ}\ \phi_2^{2}] \qquad (1.25)$$

Note that in some cases the $\chi\ V_1^{\circ}\ \phi_2^{2}$ term is simply listed as $\chi\phi_2^{2}$. This involves a slight redefinition of the interaction parameter to be in terms of per unit volume of solvent and throughout the following work this definition of χ will be used unless specified otherwise. It should also be noted that the expressions contain no parameters dependent on the form of hypothetical lattice used and inclusion of such parameters, e.g. z, have not been found to significantly improve the theory but make the expressions considerably more complex.[31]

Equations (1.24) and (1.25) are generally known as the 'Flory-Huggins expressions'. The above treats the polymer as a single component whereas in reality a polymer will usually consist of a range of homologous species with a range of chain lengths. The same methods may be used to derive an equation for any number of components, i

$$\Delta G^{M}/RT = \sum_{i} x_i \ln \phi_i + \sum \chi_{ij}\ \phi_i\ \phi_j\ .\ \sum r_i\ x_i \qquad (1.26)$$

where $\sum_{i}$ denotes summation over all components i and $\sum$ summation over all pairs of components in the mixture.

1.7(i) Limitations of Flory-Huggins Theory

A major deficiency of the theory is the assumption of a lattice model to calculate the combinatorial entropy. Adoption of a lattice for the pure components is probably not too serious but the use of the same lattice for both, requiring the same size and shape of polymer segment and solvent molecule is more questionable. Many alternative expressions to equation (1.21) have been proposed but these become mathematically complex without making the fit to experimental results significantly better. Further justification for the use of equation (1.21) can be found since Hildebrand[32] and Longuet-Higgins[33] have given alternative derivations of the expression without the need to use a lattice model.

Other assumptions of the simple F-H theory are those of random mixing and zero volume change on mixing implicit in the use of the Van Laar type enthalpy term. The former is probably not too serious for solutions of non-polar compounds but any polarity or other effects that could cause specific interactions to occur would cause error. There is also ample evidence to show that appreciable volume changes can take place on mixing polymers and solvents so that neglect of these is a potentially serious defect in the theory.

The thermodynamic expressions above contain a single parameter, χ, which is easily calculable from experimental results over a range of conditions. According to the theory, χ should be independent of concentration and inversely proportional to temperature, so that the success of the theory can be judged by these criteria. Early results for rubber in benzene[34] showed good agreement with theory for a single value of χ. However, measurements at different temperatures[35] showed that the enthalpic and entropic effects differed from those predicted. Gee and Orr[35] concluded that the deficiencies in ΔH^M and ΔS^M were mutually compensating so that the expression for the free energy is a reasonable working approximation. Baughan *et al.*[36] found that solutions of nitrocellulose in some solvents gave concentration independent interaction parameters while in others χ was found to show considerable variation. Since then there has been ample evidence[37] to show that, in general, χ values are not independent of concentration and that the inverse temperature relation does not hold over large ranges.

Another deficiency of the theory was revealed in the early 1960's after it was found by Freeman and Rowlinson[38] that some polymer solutions show both Upper and Lower critical solution behaviour as this is not predictable with an expression for χ consistent with the F-H theory discussed.

Despite obvious shortcomings, F-H theory was a vast improvement over any previous description of polymer solutions and has found extensive use since its inception. However modifications have been suggested to improve the quantitative aspects of the theory.

1.8. THE COMBINATORIAL ENTROPY

A number of contributions must occur to the entropy of mixing in addition to the combinatorial or configurational effects discussed earlier. However, as will be shown in the next Section these are most easily dealt with by modifications to the interaction parameter and so only an expression for ΔS^{comb} will be considered here.

The F-H expression (equation (1.21)) can be derived in a number of ways and, in general, has been retained for the majority of work done to the present time. However r, the size ratio of the segments, should be independent of temperature and this cannot be so unless both components have the same coefficient of expansion if r is defined as above. To overcome this problem, Flory[39] retained equation (1.18) as the best estimation of ΔS^{comb} but with the redefinition of ϕ as a 'segment' or 'hard core volume' fraction using the characteristic core volume ν^* as the basis of the calculation rather than the molar volumes. The characteristic volume is calculated from the coefficient of expansion, α, and density, ρ, using

$$\nu^* = 1/\rho \{1 + [\alpha T/3(1+\alpha T)]\}^3 \qquad (1.27)$$

The segment fraction is defined by

$$\psi_1 = w_1 \nu_1^*/(w_1\nu_1^* + w_2\nu_2^*) \qquad (1.28)$$

where w_i is the weight (or weight fraction) of component. (In some cases where no differentiation between segment and volume fractions is necessary the symbol ϕ will be retained.) The size ratio, r, is then defined by

$$r = M_1 \nu_1^* / M_2 \nu_2^* \qquad (1.29)$$

where M_1 is the molecular weight of the component.

Alternative expressions for ΔS^{comb} were derived by Hildebrand[32] and Tompa[30,40] and these suggested that the ideal and F-H expressions represent limits for ΔS^{comb} and the actual value lay between these depending on the size and shapes of the molecules concerned. More recently Lichtenthaler *et al.*[41] have used similar methods and proposed an alternative expression which contains the F-H expression together with terms derived from the sizes and dimensions of the segments which effectively comprise a correction to equation (1.18) to account for the bulkiness of the components. This has been applied to solutions of poly(dimethyl siloxane) and the authors claim an improved fit to experimental data but, as yet, the expression has not gained widespread use. Prausnitz and Donnohue[42] have produced a simplified version which allows interpolation between the ideal and F-H values in terms of a parameter, p, calculable from the dimensions of the molecules concerned.

Thus far, despite attempts at improvement, equations (1.18) and (1.21) are usually retained for most polymer solution work.

1.9. THE INTERACTION PARAMETER

The expressions in the previous Section were developed only to account for configurational effects and neglect any effects due to specific interactions between neighbouring segments, which have so far been assumed to contribute only to the enthalpy of mixing.

In Section 1.4. the difference between the entropy of mixing and its ideal value was designated the 'excess' entropy. In a similar manner the difference between the entropy of mixing and that given by the F-H expression can be designated the 'Residual' entropy. Thus,

$$\begin{aligned} \Delta S^{M} &= \Delta S^{R} + \Delta S^{comb} \\ &= \Delta S^{R} + R \sum_{i} x_{i} \ln \phi_{i} \qquad (1.30) \end{aligned}$$

In a similar manner the residual free energy, ΔG^{R}, and residual chemical chemical potential, $\Delta\mu^{R}$, can be defined by

$$\Delta G^{R} = \Delta G^{M} - RT \sum_{i} x_{i} \ln \phi_{i} \qquad (1.31)$$

$$\Delta\mu_{1}^{R} = \Delta\mu_{1} - RT\,[\ln(1-\phi_{2}) + \phi_{2}(1-1/r)] \qquad (1.32)$$

If $\Delta\mu_{1}^{R}$ is represented by $RT\,\phi_{2}^{2}\,\chi$, the interaction parameter, χ, may be called the 'Reduced Residual Chemical Potential' (the reduction factor being $RT\,\phi_{2}^{2}$) and by using equation (1.21) for $\overline{\Delta S}^{comb}$ the F-H equation (1.25) may be used for the chemical potential of mixing, except that χ is redefined as outlined here and not merely a representation of the exchange enthalpy. The enthalpic and entropic contributions to χ can be separated by defining two parameters χ_{H} and χ_{S} respectively whereby

$$\chi_{H} = \overline{\Delta H}/RT\,\phi_{2}^{2} \quad ; \quad \chi_{S} = -\overline{\Delta S}^{R}/R\,\phi_{2}^{2} \qquad (1.33)$$

Clearly,

$$\chi = \chi_{H} + \chi_{S} \qquad (1.34)$$

This may also be considered by redefining Δw as a free energy parameter to include entropic effects in equation (1.22).

This treatment still assumes a single value of χ for each system and so retains the deficiencies noted earlier. However, Tompa[30] has shown that some of the problems such as the prediction of phase equiiibrium can be overcome by assuming a concentration dependence and suggested a power series of the form

$$\chi = \chi^{\circ} + \chi'\phi_2 + \chi''\phi_2^2 + \ldots.. \qquad (1.35)$$

Similarly, χ_H and χ_S can be expanded in power series of the same form.

1.10. PREDICTION OF INTERACTION PARAMETERS

The term 'interaction parameter' is perhaps somewhat of a misnomer as it suggests a parameter accounting only for interactions between the species. The definition of χ as a free energy parameter is more useful but the term 'interaction parameter' is in common usage for χ. The F-H expression for ΔS^{comb} is generally accepted so that most developments in polymer solution theory have attempted to predict and correlate values for χ.

1.10.(i) Solubility Parameter Theory

As mentioned in Section 1.6.(i) the differences in the solubility parameters of two compounds can be taken as a measure of their intermolecular energies. Adapting equation (1.17) for use here it may be shown that

$$\chi = V_1^{\circ}(\delta_1 - \delta_2)^2 / RT \qquad (1.36)$$

or, if the solubility parameters are considered to account only for enthalpic effects,

$$\chi_H = V_1^{\circ}(\delta_1 - \delta_2)^2 / RT \qquad (1.37)$$

Extensive lists of solubility parameters for solvents and polymers have been published[43] and the method has found extensive use[44] in, for example, solvent selection for particular systems. However, although it is a useful qualitative guide it does have serious drawbacks as a predictive method. Firstly there is no way of directly measuring δ_2 for a polymer and often only estimates are available. This treatment cannot give information on the concentration dependence of χ and can only predict endothermic or athermal heats of mixing whereas some systems such as poly(isobutylene) and the n-alkanes[45] show negative values.

The use of a relatively new method for determining polymer solubility parameters and their use in predicting some polymer solution properties will be discussed in Chapter 7.

1.10.(ii) Corresponding States Theory

In the 1950's, Prigogine and co-workers developed a theory based on the cell model of liquids and the corresponding states principle which was later applied to polymer solutions.[46-48] The treatment is used to express values of properties under interest in a reduced form; a form where they are divided by a known characteristic value of the property. The 'cell model' was used to derive these characteristic properties assuming a molecule or segment of the liquid is constrained to move within a 'cell' of nearest neighbours subject to a specified intermolecular potential described by a known partition function.

A reduced equation of state for the pure components was derived relating values of volume, pressure and temperature and, by plotting one set of variables against another, a series of smooth curves was found. This law of 'corresponding states' was then applied to solutions by assuming that the relations held for solutions as well as for the pure components, the solution reduction parameters being assigned as averages of their pure component values. The theory leads to elaborate expressions for the thermodynamic properties and its application to polymer solutions has been summarised and applied with some success by Patterson and co-workers.[49,50] Janini and Martire[51] applied a simplified version of the theory to mixtures of n-alkanes, also with some success.

However, this theory has not been applied to any of the results presented in this Thesis so that further details will not be given here.

1.10.(iii) Flory's Equation of State Theory

During the middle 1960's, Flory and co-workers proposed a new theory of polymer solutions. Like Prigogine he realised that a theory needed to take into account properties of the pure components as well as their mixtures and proposed a third contribution to the thermodynamic functions. As well as the combinatorial effects and exchange enthalpy considered by the older theories, there is also an 'equation of state' or 'free volume' effect arising from volume and density changes of the solution on mixing. Flory rejected the cell model of liquids as a basis for his treatment since it suggests a high degree of order in the liquid and also the graphical procedures needed to calculate the reduction parameters are subject to error in many cases.

To overcome this Flory and co-workers[39,52,53] started with a partition function similar in form to that of Prigogine but assuming hard sphere repulsion between segments and that intermolecular energies arose from contacts between segment surfaces. The work led to an equation of state which can be expressed in its reduced form

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{\frac{1}{3}}/(\tilde{v}^{\frac{1}{3}}-1) - (\tilde{v}\tilde{T})^{-1} \qquad (1.38)$$

The reduced volume $\tilde{v}$ may be calculated from the thermal expansion coefficient, α, using

$$\tilde{v} = \{1 + [\alpha T/3(1+\alpha T)]\}^{3} \qquad (1.39)$$

and the characteristic pressure p^* is calculated from the thermal pressure coefficient, τ, using

$$p^* = \tilde{v}^{2}T\tau \qquad (1.40)$$

and the reduced pressure by $\tilde{p} = p/p^*$. Substitution of $\tilde{v}$ into equation (1.38) with $\tilde{p} = 0$ allows calculation of T^*. This reduced equation of state was found[39] to predict pure component properties reasonably well with the exception of their temperature dependence.

In order to extend the treatment to mixtures, two assumptions are made. Core volumes are assumed to be additive and the intermolecular energy is assumed to depend on the surface areas of contact of the molecules or segments. Since the assignment of segments is essentially arbitary, equal size segments are chosen for convenience so that $v_1^* = v_2^* = v^*$. (The absence of a subscript for a property denotes that it refers to the mixture.) From this it follows that

$$p^* = \psi_1 p_1^* + \psi_2 p_2^* - \psi_2 \theta_1 X_{12} \tag{1.41}$$

and

$$T^* = p^*/(\psi_1 p_1^*/T_1^* + \psi_2 p_2^*/T_2^*) \tag{1.42}$$

In these equations, ψ represents the segment fraction defined by equation (1.28) and θ is the site or surface fraction, calculated using

$$\theta_1 = \psi_1/(\psi_1 + \psi_2(s_2/s_1)) \tag{1.43}$$

where s_2/s_1 is the ratio of the surface to volume ratios of the component segments. X_{12} is the energy interchange parameter which reflects the relative strengths of polymer-solvent and polymer-polymer or solvent-solvent contacts. It is formally similar to the Δw parameter of the Flory-Huggins theory. In some systems, as will be seen later, it has been found necessary to introduce another parameter, Q_{12}, to account for an entropic contribution to X_{12} such that

$$X_{12} = X_{12}' - \tilde{v}TQ_{12} \tag{1.44}$$

Using these definitions, expressions for the thermodynamic properties such as heats, residual entropies and volumes of mixing can be derived. However the work covered in this Thesis is only concerned with the chemical potentials and so they will not be reproduced here.

The residual chemical potential, χ, is given by

$$RT\,\phi_2^2\,\chi = p_1^* V_1^* [3\tilde{T}_1 \ln\{(\tilde{v}_1^{\frac{1}{3}}-1)/(\tilde{v}^{\frac{1}{3}}-1)\} + \tilde{v}_1^{-1} - \tilde{v}^{-1}] + V_1^* X_{12} \theta_2^2/\tilde{v} \tag{1.45}$$

where V_1^* is the molar characteristic volume ($V_1^* = M_1 v_1^*$). Thus, specification of p*, ν* and T* for each component allows estimation of the interaction parameter, χ, of a system subject to availability of values for X_{12} and s_2/s_1. The former is usually calculated from a single measurement of one thermodynamic quantity such as the heat of mixing to infinite dilution. The surface to volume ratio can be calculated from molecular models, bond length data or from group contribution data,[54] although in some cases s_2/s_1 has been used as a further adjustable parameter to improve the fit of the theory to experimental results.

The theory was first applied to mixtures of low molecular weight liquids[55] and was found to give reasonable prediction of properties. Application of equation (1.45) to interaction parameters for polymer-solvent systems[56,57] also gave encouraging results.

The application of this treatment to solutions of poly(dimethyl siloxane) in hexane and benzene and particularly the molecular weight dependence will be discussed in Chapter 7.

1.10.(iv) Other Polymer Solution Theories

Although the theories described in the previous two sections are probably those most often used, many others have been suggested as improvements on classical Flory-Huggins theory. Some of these are alterations of the two treatments above. For instance, Pollin and Fried,[58] use the Flory 'equation of state' theory but assume a different energy-volume relationship. This was designed for application to low molecular weight liquids as was Libermann's simplification of the same treatment[59] leading to equations for the excess properties free from empirical parameters. Flory's theory was also simplified for application to polymer solutions by Bonner and Prausnitz[60] and this was followed by Schotte[61] to give more predictive equations with a single parameter. Shiomi *et al.*[62] modified the combining rules and claim to have improved the fit of the Flory theory to PDMS solutions, but at the expense of an extra parameter and no significant improvement to the prediction of concentration dependences of χ.

Other workers have suggested alternative thermodynamic expressions based on other treatments. Heil and Prausnitz[63] used a local composition method and developed equations for the free energy of mixing and miscibility limits of polymer-solvent systems. A similar model with corrections for non-random mixing was used, along with Flory's theory, by Renuncio *et al.* and applied to PDMS solutions.[64] Dayantis used a free volume concept to derive expressions for the entropy[65] and enthalpy[66] of mixing of polymer solutions. Maron[67] has used parameters derived from the concentration and temperature dependence to describe the behaviour of solutions of rubber in benzene to a reasonable degree of accuracy. Over a number of years Huggins[68,69] has developed a theory which stresses the contact energies between polymer surfaces and assumes a pseudo-chemical equilibrium between the species. As a final example Sanchez and Lacombe have used a 'lattice fluid' model to propose a new equation of state[70] which they have applied to solutions of low molecular weight[71] compounds and polymers.[72]

This brief survey is by no means a comprehensive list of all theories of polymer solutions and their modifications but serves to illustrate some of the approaches taken. However, despite this large body of work the two treatments outlined in Sections 1.10.(ii) and 1.10.(iii) are by far the most often used, particularly that due to Flory *et al.* and none of the newer theories, as yet, has gained widespread popularity.

1.11. THE UNIFAC GROUP CONTRIBUTION METHOD

As mentioned earlier, for many applications in industrial or engineering environments a reasonable estimate of the properties of a system is sufficient. The UNIFAC (UNIfied Functional group Activity Coefficient) method is designed to give this and is particularly useful in systems where little or no experimental data is available. It is an adaptation of earlier group contribution theories whereby the components comprising a solution are split into a number of groups whose properties are assumed to be independent of the environment in which they occur and are additive. Fredenslund and co-workers developed the method[73-75] to treat the vapour-liquid equilibrium properties of normal solutions and this was adapted for use with polymer solutions by Oishi and Prausnitz.[76]

The basis of the method is that each type of molecule in the solution is split into a number of groups, these being defined as any convenient group such as methyl, methylene, carbonyl etc. This allows treatment of solutions in terms of the properties of a comparatively small number of groups rather than the enormous number of molecules that can be made using them.

Four basic parameters are needed for the application of the UNIFAC method. The first two are the group volume constant R and group surface area constant Q. These are calculated from Van der Waals volumes and areas as computed by Bondi[77] and normalised with respect to a methylene group in poly(ethylene) using parameters calculated by Abrams and Prausnitz.[78] Extensive lists of R and Q values have been published.[75] For any molecule i of molecular weight M_i and containing $n_k^{(i)}$ groups of type k the molecular volume and surface parameters r_i and q_i are given by

$$r_i = (\sum_k n_k^{(i)} R_k) / M_i \qquad (1.46)$$

$$q_i = (\sum_k n_k^{(i)} Q_k) / M_i \qquad (1.47)$$

The other two parameters needed are the group interaction parameters, w_{ij}, and are representative of energetic interactions in the solutions. Lists of w_{ij} have been published[75] and are of the form

$$\left.\begin{aligned} w_{ij} &= \exp - [(u_{ij} - u_{ii})/RT] \\ w_{ji} &= \exp - [(u_{ij} - u_{jj})/RT] \end{aligned}\right\} \quad (1.48)$$

where u_{ij} represents the potential energy of an ij pair. From equations (1.48) it is clear that $w_{ij} \neq w_{ji}$ so that two values are needed for each pair of groups. The values are calculated by minimising the deviation of the fit of the UNIFAC equations from a large range of reliable experimental data for the vapour-liquid equilibrium of binary systems. In principle any range of accurately known properties could be use, but this is the most common application of UNIFAC and so is most often used.

1.11.(i) Application of the UNIFAC Method

The original treatment calculates the activity coefficient of a solution but as this is not such a useful concept with polymer solutions, it has been adapted to give the activity of the solution. This is assumed to arise from two contributions, a 'combinatorial' effect as discussed earlier and a 'residual' effect due to energetic interactions. In their adaptation of the method Oishi and Prausnitz have added a third contribution due to free volume effects as suggested by Flory. Thus the activity of component 1 is given by

$$\ln a_1 = \ln a_1^{comb} + \ln a_1^{R} + \ln a_1^{FV} \quad (1.49)$$

The combinatorial effect is calculated using an expression derived from Staverman's statistical mechanical methods[78] and is given by

$$\ln a_1^{comb} = \ln \phi_1 + \phi_2 + (zM_i q_i/2) [\ln (\theta_1/\phi_1) - (1-\phi_1/\theta_1)] \quad (1.50)$$

In this expression, q_i is given by equation (1.47), ϕ is the UNIFAC segment fraction given by

$$\phi_1 = w_i r_i / \sum_i w_i r_i \qquad (1.51)$$

and θ the surface fraction,

$$\theta = w_i q_i / \sum_i w_i q_i \qquad (1.52)$$

where w_i is the weight or weight fraction of species i in solution.

The residual contribution is given by

$$\ln a_1^R = \sum_k n_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad (1.53)$$

Γ_k is the group residual activity of group k in the solution and $\Gamma_k^{(i)}$ that in pure liquid component i. These may be calculated by summing the interactions over all pairs of groups.

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m w_{mk}\right) - \sum_m \left(\theta_m w_{km} / \sum_n w_{nm}\right)\right] \qquad (1.54)$$

The same equation can be used for $\Gamma_k^{(i)}$ with appropriate assignment of m and n.

The residual contribution accounts for inter group interactions and so the free volume contributions are given by Flory's expression with X_{12} set to zero. Thus[76]

$$\ln a_1^{FV} = 3c_1 \ln \left[(\tilde{v}_1^{\frac{1}{3}}-1)/(\tilde{v}^{\frac{1}{3}}-1)\right] - c_1 \left[(\tilde{v}_1/\tilde{v}-1)(1-\tilde{v}_1^{\frac{1}{3}})^{-1}\right] \qquad (1.55)$$

The parameter $3c_1$ is the number of external degrees of freedom set to 1·1 by comparison with experimental results. Oishi and Prausnitz give approximate expressions for the reduced volumes.[76]

$$\tilde{v}_1 = v_i / 15{\cdot}17 \; b \; r_1 \qquad (1.56)$$

and for the mixture by

$$\tilde{v} = (w_1 v_1 + w_2 v_2)/[15{\cdot}17 \; b \; (w_1 r_1 + w_2 r_2)] \qquad (1.57)$$

where v_i is the specific volume of the component. The factor b is set to 1·28 to achieve agreement with experimental data.

The overall activity of the solvent (component 1) in a polymer solution may be estimated using equation (1.49) and an estimate of the Flory-Huggins interaction parameter may be made by using equation (1.25) adapted to represent the activity of the component.

1.11.(ii) Usefulness of the UNIFAC Method

By its nature, any group contribution method is necessarily approximate since the behaviour of a given group will be slightly different in different environments. For example the carbonyl group in, for example, acetone might be expected to behave similarly to one in another ketone such as butanone, but not to one in an aldehyde or a carboxylic acid. Obviously the accuracy of the method increases as greater distinction is made between the groups but it becomes less useful as a greater number of parameters is needed. However the method is attractive in principle since it allows estimation of the properties of a large number of liquids and solutions from knowledge of parameters for a fairly small number of functional groups. The original development of UNIFAC was to predict activity coefficients for use in phase equilibrium calculations where no experimental data was available and was shown to correlate with around seventy per cent of published data up to 1977. It is a fairly simple method to apply and with published parameters is applicable to a wide range of systems.

The UNIFAC method is applied to experimental data for PDMS in a number of solvents in Chapter 7. In particular the ability to predict the molecular weight variation is examined and a modification for use where one experimental result is available is proposed.

1.12. THE APPLICATION OF GAS-LIQUID CHROMATOGRAPHY TO SOLUTION THERMODYNAMICS

Chromatographic methods in their various forms have become extremely useful over the past two or three decades, particularly as analytical methods but also for carrying out separation and purification of compounds. Also, particularly in the case of gas-liquid chromatography, they have been used as means of obtaining physicochemical data.[4,79] The basis of chromatography is the separation of two compounds by their distribution between a mobile phase (liquid, vapour or gas) which moves over or through a stationary phase (solid or liquid). The first use of chromatography was by the Russian biochemist, Tswett, in 1906 when he used a form of liquid-solid chromatography to separate coloured plant pigments. The first quantitative use was by Martin and Synge[80] who won the 1954 Nobel Prize for their development of a liquid-liquid partition system and the 'plate' theory to describe chromatographic behaviour. Some years later Martin and James[81] used an inert solid to support a liquid over which a gaseous mobile phase was passed and so developed gas-liquid chromatography, GLC. The technique was applied to physicochemical measurements and early results included boiling points, heats of solution and partition coefficients.[82-84]

In GLC as normally used the stationary phase is an involatile liquid, usually coated onto an inert solid to give a thin film of large surface area, although in some cases the liquid is spread onto the inside of a capillary tube. The mobile phase is an inert gas, usually nitrogen or helium and it is into this stream that the sample is injected to flow over the liquid. The speed at which the sample moves through the column of stationary phase depends on its distribution between the liquid and gas phases, so that different samples, having different distributions, will move through the column at different speeds and so can be separated.

The GLC method has several advantages over traditional static techniques of measurement. When the apparatus is set up, the GLC method is much more rapid, typically taking a few minutes for each determination. Also, since a separation method is used, purity of the compounds is unimportant and several can be included in one experiment provided that they are resolvable and do not interact with each other.

The apparatus can be made very compact and to fit in an oven so that large temperature ranges can be covered. Another advantage is that very small samples are needed, the technique being suitable for sub-milligram samples provided that detectors of sufficient sensitivity are available. At these amounts the sample is effectively at infinite dilution so that a sample molecule may be considered to be surrounded only by molecules of the stationary phase and the interactions in the system are determined only by the intermolecular forces between the two species. The majority of GLC work has been done in this concentration region but some workers have extended the method for use at finite concentrations.[85,86]

A thorough discussion of the GLC method is outside the scope of this Thesis (see Reference 4) but the basic measurement made is the retention volume of a component, V_N, this being the volume of mobile phase required to elute the sample from the column. A partition coefficient, K, relating the concentrations in each phase may be defined as

$$K = \frac{\text{concentration of sample in liquid phase}}{\text{concentration of sample in mobile phase}}$$

It is clear that

$$K = V_N/v_L \tag{1.58}$$

where v_L is the volume of stationary phase liquid in the column. GLC has been widely used to measure activity coefficients and these are related to the retention volume by

$$\gamma_1 = RT\ w_L\ /\ V_N\ p_1^\circ\ M_L \tag{1.59}$$

where w_L is the weight of stationary phase used and M_L its molecular weight, though for accuracy corrections for non-ideality of the gas phase must be made. Combination of these two expressions leads to the following relation between K and γ

$$K = RT\ /\ \gamma_1\ p_1^\circ\ v_L^\circ \tag{1.60}$$

A quantity more usually quoted in chromatographic work is the specific retention volume V_g given at a column temperature T by

$$V_g = (273\ V_N) / (T\ w_L) \qquad (1.61)$$

This will be important in the discussion of polymer properties measured by static and GLC methods in Chapter 4 and is related to the activity coefficient by

$$\gamma_1 = 273\ R / V_g\ p_1^\circ\ M_L \qquad (1.62)$$

In early uses of the technique it was suggested that GLC would not measure equilibrium properties but would somehow depend on dynamic factors. There is now, though, ample evidence that, provided the measurements are made with proper attention to all experimental variables, the GLC results are valid.[4] Squalane was often used as a stationary phase and early static-GLC comparisons were performed using this compound.[87] These were complicated by inaccuracy of static techniques at low concentrations but good agreement was found with the results of Ashworth and Everett[87] and McGlashan and Williamson.[88] A more accurate apparatus was used by Ashworth[89] to show good agreement for results with hydrocarbons in squalane and dinonyl phthalate with the GLC results of Purnell and Conder.[90] Sewell and Stock[91] have shown similar agreement for chlorinated hydrocarbons in these stationary phases. However, when using polymeric stationary phases, further doubts have been expressed as to the validity of GLC results. A fuller discussion of this appears in Chapter 4 where a comparison of static and GLC results for a number of compounds in poly(dimethyl siloxane) will be presented.

1.13. COMPETING RETENTION MECHANISMS

The presence of a number of phases in a GLC system can lead to a number of concurrent adsorption and solution processes taking place which can complicate and confuse results and conclusions. As well as solution of the sample in the bulk stationary phase, other possible processes contributing to sample retention are adsorption at the gas-liquid and solid-liquid interfaces. In addition, if there is any uncovered support material present adsorption of sample onto the solid can take place.

1.13.(i) Adsorption at the Liquid Surface

Considering equation (1.58), if the retention volume is plotted against the amount of liquid phase, a straight line passing through the origin should be obtained. This has been found in general for hydrocarbon samples in non- or moderately polar stationary phases but discrepancies were sometimes noted at very low liquid loadings and these were attributed to adsorption onto the solid support. Martin,[92] however, noted that for polar samples the plots did not extrapolate to zero for zero loading and that the elution orders of some compounds could be changed with low loadings of liquid in the column. He suggested that this was due to adsorption at the gas-liquid interface so that the surface region of the liquid contained a higher concentration than the bulk liquid. Although this was doubted by other workers it was later confirmed by independent static results obtained by Martin[93] and Martire *et al.*[94,95]. Pecsok and co-workers[96] found that not only did the plot not extrapolate to zero when using β,β' thiodipropionitrile as stationary phase but that retention increased at low loadings. As a polar phase such as this should cover all the active sites on the solid, the observed results were also attributed to gas-liquid interfacial adsorption. To account for this, Martin[93] proposed a new retention equation,

$$V_N = Kv_L + K_I A_I \qquad (1.63)$$

where K again represents the bulk partition coefficient and K_I that for the liquid surface region, defined as the ratio of the excess surface concentration per unit area (i.e. the difference between the concentration in the surface region and that in the bulk liquid) to that in the mobile phase. A_I is the gas-liquid interfacial area. This equation assumes the two contributions to be independent and is only valid at infinite dilution. This is probably an oversimplification but the expression has been used to explain the results in several systems such as those referred to above.

In general, liquid surface adsorption effects were found in systems of non-polar samples in polar, but not in non-polar, stationary phases. Pecsok and Gump[97] subsequently showed, using static methods, that the effects were also noticeable with polar samples such as acetone and methanol on non-polar stationary phases such as squalane, although in these cases it was more difficult to rule out solid support effects.

In order to test the gas-liquid adsorption hypothesis Martin and Martire and Pecsok made measurements on the surface tension of systems showing these effects in GLC. By definition,

$$K_I = \Gamma_1/c \tag{1.64}$$

where Γ_1 is the surface excess concentration and c the concentration in the mobile phase. This can be related to the surface tension, σ, using the Gibbs adsorption theorem[98] which may be stated as

$$\Gamma_1 = -(1/RT)\ (d\sigma/d \ln a_1) \tag{1.65}$$

Approximating the activity of solution by the mole fraction at low concentrations, this may be transformed into

$$\Gamma_1 = -(x_1/RT)\ (d\sigma/dx_1) \tag{1.66}$$

These studies showed the two methods to give reasonable agreement, but to achieve this the comparison had to be performed in such a way as to exclude the surface areas since these values for solid supports and supported liquids are often uncertain.

1.13.(ii) Adsorption on the Solid Support

Interaction of the sample with the solid support is thought to take place in most GLC systems but to widely differing extents depending on the components involved. If only bulk solubility and adsorption on the solid support contribute to retention then a similar expression to equation (1.63) can be used.

$$V_N = K v_L + K_S A_S \qquad (1.67)$$

where A_S is the surface area of the solid support and K_S a 'solid' partition coefficient given by the ratio of the adsorbed sample per unit area to its concentration in the mobile phase.

Two forms of interaction with the solid support are possible. If the support is not completely covered then adsorption onto bare solid is possible in addition to adsorption of sample from the bulk liquid phase. These effects are often difficult to separate and so are often treated as a single phenomenon (although cases of the former effect are rarer), it normally being detected by variation of the sample size used.[4] Solid supports are often treated with 'silanizing' agents which replace active sites on the surface by inert organosilicone groups and so reduce the tendency for adsorption.

1.13.(iii) General Equation for Retention

The presence of more than one retention mechanism is probably the case for the majority of GLC systems. Bulk phase partition usually provides the greatest contribution but the other effects cannot be dismissed without careful consideration of the systems under study. While for physicochemical studies these effects are usually undesirable, they are not always unwelcome since they can, in some cases, be used to change the relative retentions of compounds and so can be useful for analytical separations.

A generalised retention equation combining those discussed earlier has been proposed

$$V_N = K\ v_L + K_I\ A_I + K_S\ A_S \qquad (1.68)$$

This equation assumes infinite dilution and independence of the retention contributions. The presence of these can be detected by varying the amount of liquid phase in the column. Equation (1.68) can be written as

$$V_N/v_L = K + K_I\ (A_I/v_L) + K_S\ (A_S/v_L) \qquad (1.69)$$

Thus, it follows that if (V_N/v_L) is independent of v_L then only bulk partitioning is present. If surface area values are available then the other contributions to the retention can be measured.[4]

1.14. MIXED STATIONARY PHASES IN GAS-LIQUID CHROMATOGRAPHY

Since samples have different retentions in different stationary phases, it should be possible to create a phase with the required properties for a particular separation by combining two (or more) liquids. This, though, requires knowledge of the behaviour of a mixed phase relative to that of the separate liquids. Two types of mixed stationary phase columns are possible. A 'Mixed-Bed' column consisting of a mechanical mixture of packings coated with the separate liquids can be made allowing no mixing of the two liquids. Alternatively the two liquids can be mixed prior to coating onto the solid to give a 'Mixed-Solvent' column. This second type allows interactions between the liquids to take place.

It has been a point of discussion for some considerable time whether these two systems would behave in the same or in a completely different manner, experimental evidence often having been conflicting.[99] Keller and Stewart[100] provided a theoretical analysis that suggested the two methods, along with two separate columns connected in sequence, should produce equivalent results and that differences would be kinetic rather than thermodynamic in origin. This conclusion was also reached by McFadden.[101] Conversely, Young[102] concluded that the two types of column should produce different results and similar suggestions were made by Waksmundzki and Suprynowicz[103] and Acree[104,105]

In an attempt to explain quantitatively the behaviour of 'mixed solvent' stationary phases, Purnell and Vargas de Andrade[106] proposed the following for a binary phase of components 1 and 2

$$K_{12} = \phi_1 K_1 + \phi_2 K_2 \qquad (1.70)$$

where K_{12} is the partition coefficient of the mixed phase, K_1 and K_2 the partition coefficients of the separate components and ϕ is the volume fraction of component in the mixture. They based this on a number of measurements in various mixtures of stationary phases together with a large number of literature results in which they found the linear dependence of retention behaviour suggested by equation (1.70). In a mixed bed column, the components would be expected to act independently so that the retentions would be additive and a linear composition dependence expected. Thus this equation implies that a 'mixed-solvent' column should have the same characteristics as a 'mixed-bed' column of the same overall composition. The relationship cannot be derived for a miscible mixture from conventional solution theory and implies that there is no interaction between the two liquids. To account for the observed behaviour, Laub and Purnell[107,108] proposed a 'micropartitioning' theory of liquids whereby the two liquids do not intimately mix but exist as small, microscopically immiscible groups of the separate components, solutions they term 'diachoric'.

As well as the works cited above, the experimental results of Littlewood and Wilmott[109] and Perry and Tiley[110] cast doubt on equation (1.70), differing from the linear relation by up to 20-30%. Also, more recently, Laub and Chien[111] have reported deviations of up to 10% for mixtures of dinonyl phthalate and squalane and this has been confirmed by Ashworth and co-workers[112-114] using static methods of measurement.

An alternative to equation (1.70) was suggested by Perry and Tiley[110] which they derived from classical Flory-Huggins solution theory.

$$\ln K_{12} = \phi_1 \ln K_1 + \phi_2 \ln K_2 + \phi_1 \phi_2 X_{12} \qquad (1.71)$$

The symbols have the same meaning as above and X_{12} is the Flory-Huggins interaction parameter between the liquids comprising the mixed phase. They successfully used this relation to explain the behaviour of dinonyl phthalate-trinitrotoluene mixtures and Ashworth and co-workers have shown the relation to predict retention behaviour to within 1% for dinonyl phthalate-squalane systems.[112-114]

Tiley[115] has pointed out that equations (1.70) and (1.71) can never have the same form except in the special case that $K_1 \approx K_2$ and $X_{12} \approx 0$ but, that on calculating the expected deviation for a number of conditions, found that equation (1.70) was often obeyed to a reasonable degree of approximation.

1.15. SYSTEMS STUDIED IN THIS THESIS

The previous work by Ashworth and co-authors cited above investigated the behaviour of dinonyl phthalate and squalane using a number of non-polar (hydrocarbons and carbon tetrachloride) and one moderately polar (diethyl ether) solutes. Extension of this study to more polar solutes was desirable but one problem that had been noticed in using the vacuum microbalance apparatus with polar absorbates was that vapour was absorbed by components of the balance such as gaskets and electrical insulation as well as by the sample under study. This made measurement of the equilibrium conditions difficult and also cast doubt on whether equilibrium was in fact established. This was not found to be a problem when using chlorinated hydrocarbons but was a serious interference when ethyl acetate was used. As will be seen in Chapter 2, the new Magnetic Suspension vacuum microbalance has no components in contact with vapour and so this apparatus was used to study the ethyl acetate-dinonyl phthalate-squalane system. The adsorption processes were studied by measuring absorption isotherms over a range of liquid loadings and the behaviour of mixed stationary phases investigated. After confirming that adsorption effects were negligible, the mixed phase behaviour was also studied using chloroform and dichloromethane to extend the previous work.

Chapter 2

Experimental

The weighing balance is probably the oldest and amongst the most often used of all apparatus in the Chemistry laboratory. Its use enabled some of the earliest and most fundamental laws of science to be discovered. In view of this the use of balances weighing in the sub-milligram range, and particularly those for use in connection with vacuum apparatus is a relatively recent development. Over the past twenty years or so several types of commercial vacuum microbalance have become available reflecting the increasingly large range of potential uses of this type of equipment.[116,117] Before discussing the application of vacuum microbalances in solution thermodynamic studies, it is pertinent to briefly outline other experimental methods that are available.

The thermodynamic property being measured is the activity of solvent in a solution and three main methods have been employed, these and other lesser used techniques to find Flory-Huggins interaction parameters having been reviewed by Orwoll.[37] GLC has mainly been used at infinite dilution though occasionally it has been applied to finite concentration studies.[85] The other methods are vapour sorption and osmotic pressure measurements. These complement each other since the former is generally carried out at high concentrations while the latter finds greatest use for dilute solutions.

Vapour sorption methods for studying polymer solutions, which include methods involving vacuum microbalances, have been reviewed by Bonner.[118] The use of equation (1.2) for the calculation of activity coefficients and other derived quantities requires the measurement of two variables, the composition of the solution and its vapour pressure. (It is assumed in these methods, as is the case in all the work described in this Thesis, that only one component is appreciably volatile and the pressure above a solution is due solely to solvent vapour.) The methods involve either preparing solutions of known composition and measuring their vapour pressures or include some means of determining the composition. This latter technique normally involves a microbalance though one notable exception is the piezoelectric absorption detector which determines the change in oscillation frequency of a quartz crystal covered in a thin film of involatile material as the weight of absorbed vapour increases.[119]

2.1. THE USE OF VACUUM MICROBALANCES FOR SOLUTION STUDIES

The earliest type of vacuum microbalance used for this work was the McBain-Bakr[120] apparatus in which the weight change was determined by the change in length of a calibrated quartz spring used to suspend the sample from a convenient reference point, while the pressure was measured with a mercury manometer. Apparatus of this type has been used for studies closely related to those involved in this Thesis[121,122] and continue in use even to the present time.[123,124] The length of the spring is usually measured to an accuracy of ±0·02 mm. As an example, the springs used by Ashworth and Hooker[122] had a sensitivity of around 1 mm mg^{-1} and had a total capacity of about 500 mg giving a 'load to precision ratio' - 'LPR' - of ~$2{\cdot}5 \times 10^4$.

The main disadvantage of this apparatus is that measurements become increasingly inaccurate at low concentrations of absorbate. For example results for the absorption of hydrocarbons into squalane or dinonyl phthalate below a mole fraction of ~0·3 were shown to be too inaccurate for reliable extrapolation to infinite dilution,[122] this being an important area of work for these techniques. To overcome these problems, more sensitive commercial balances employing a quartz beam were adapted for this type of study.[97,125] The quartz beam (QB) balance used in this study had a maximum load of 2 g and was operated on a range giving a precision of 0·01 mg giving an LPR of

2×10^5. This apparatus was shown to give precise results down to an absorbate mole fraction of ~0·05 so allowing reliable extrapolation to infinite dilution.[121] The main disadvantage of this apparatus is that, as absorbate pressures increase, components of the balance begin to absorb vapour so that large concentration ranges cannot be covered. Thus the main application of this apparatus has been in the measurement of results up to a mole fraction of ~0·04 for extrapolation to infinite dilution to compare, for example, with results obtained by GLC.

A more recent development in vacuum microbalance technology is a balance in which the sample is magnetically suspended. The balance mechanism is completely separated from the sample under study so that no interaction between balance components and absorbate vapour can take place. The magnetic suspension (MS) balance used in this work had a maximum load of 30 g and was used with a precision of 0·1 mg giving an LPR of $\sim 3 \times 10^5$. This is similar to the QB balance and so results accurate enough for reliable extrapolation were obtainable but over a much wider concentration range. Thus the MS balance combines the attributes of the other two types of balance and has been shown to give similar results for one system.[126]

It should be noted that the LPR values given above represent maximum values. In reality some of the load would be taken up with solid support and also sufficient capacity would have to be left on the balance to allow for the weight gain due to absorption so the actual LPR values applicable to the present work would be lower than those quoted here.

In the apparatuses employing commercial vacuum microbalances, electronic quartz Bourdon or capacitance gauges have been used to measure the vapour pressure giving greater accuracy than can be obtained with a mercury manometer.

2.2. THE VACUUM SYSTEM

The same basic design of Pyrex glass vacuum system was used with both the types of microbalance used. A schematic diagram is shown in Figure 2-1.

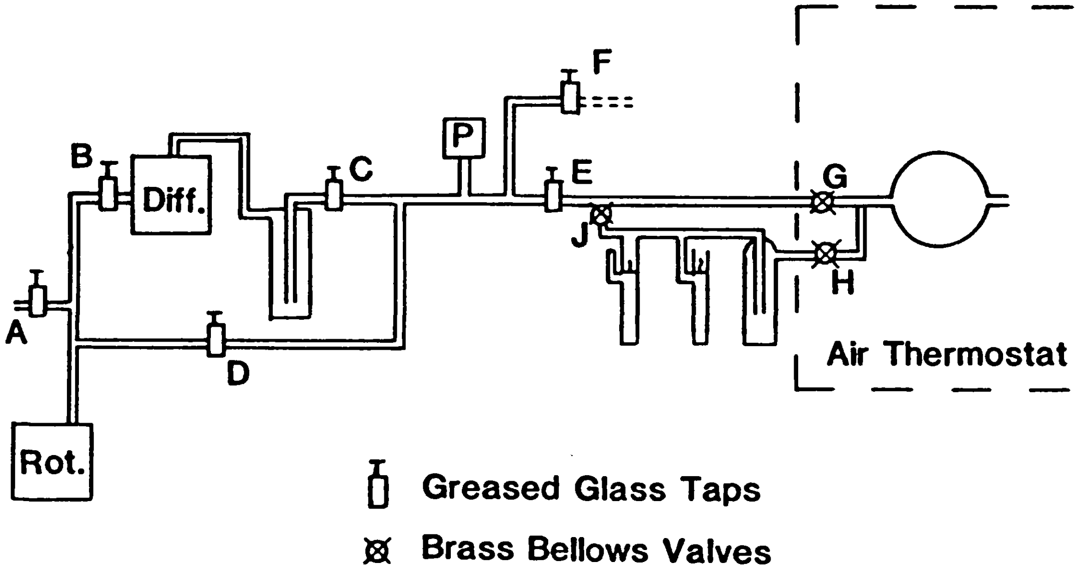


FIGURE 2-1: SCHEMATIC DIAGRAM OF THE VACUUM SYSTEM

Basic vacuum pumping was provided by means of an Edwards rotary vacuum pump in conjunction with an Edwards oil vapour diffusion pump and a liquid nitrogen cold trap giving a vacuum $\leq 10^{-4}$ torr. A by-pass line allowed the rotary pump to pump on the system or to act as backing for the diffusion pump. The pressure in the pumping line was monitored using an Edwards 'Pirani-14' vacuum gauge (P) which was periodically calibrated against a McLeod gauge on another vacuum apparatus. Taps A-F were greased, ground glass taps (except on the MS balance apparatus where A and B were 'Teflon' greaseless taps). The line containing tap F was necessary only when using a Texas Instruments Bourdon pressure gauge which required a reference vacuum line. The main pumping line led to the absorption chamber and microbalance, a subsidiary line being taken to the absorbate reservoir.

Taps G, H and J, those in contact with absorbate vapour, were 'Hoke' brass bellows valves to prevent interaction of the vapours with tap greases. The reservoir consisted of the absorbate in a break seal ampoule, a fresh ampoule into which the absorbate could be sealed after use and a small trap to prevent small pieces of glass from the broken seals reaching and scoring the bellows valves.

The absorption chamber of the apparatus consisted of the microbalance hang-down tube(s) connected to the pressure gauge via a 2 ℓ glass bulb and to the vacuum and absorbate lines. The bulb was included to minimise pressure build-up from leakage or outgassing during the recording of an isotherm and to ensure that the pressure drop due to absorption would be relatively small so that measurements could be made at essentially predetermined concentrations.

2.3. THE QUARTZ BEAM VACUUM MICROBALANCE

The quartz beam (QB) balance used was a Sartorius model 4012 balance. It was based on the traditional beam balance design where the sample and tare weights are suspended from opposite ends of a beam supported by a central horizontal torsion wire. Movement of the beam is monitored to provide information on changes of weight of the sample. A diagram of the apparatus is shown in Figure 2-2.

Prior to the recording of an absorption isotherm the balance was calibrated. This was done with the air thermostat and balance at the temperature needed for the isotherm. The method used was that provided by the manufacturers except that silver weights were added to each side of the balance so that the calibration was carried out in the load region where measurements were to be made.

The absorbent sample (see Section 2.6.) was hung from the right hand side of the balance and silica glass tare weights added to the left hand side. This material was chosen since it had a similar

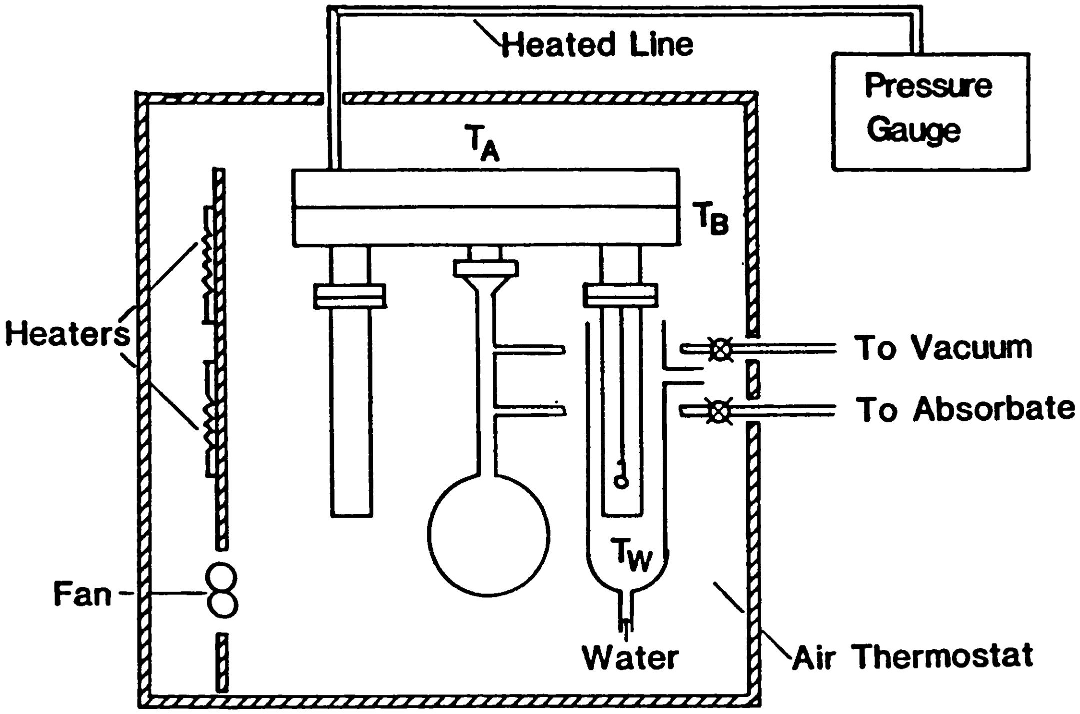


FIGURE 2-2: THE QUARTZ BEAM MICROBALANCE APPARATUS

density to the absorbent sample and thus eliminated the need for buoyancy corrections as both tare and sample were in the admitted vapour. The balance was operated on ten times the basic range allowing monitoring of a weight change of up to 200 mg to a precision of 0·01 mg. The tare weight was 1·8 g to allow the maximum load of the balance (2 g) to be used. The hang-down tubes surrounding the sample and tare weights were made of copper to ensure good heat transfer and were connected to the microbalance housing by 'Leybold' couplings employing 'Viton' rubber gaskets. Connection to the glass vacuum line was by means of another joint employing a 'Viton' gasket.

The thermal environment around the balance was controlled by enclosing the balance along with the absorption chamber of the apparatus in an air thermostat. This was heated to within a degree or so of the required temperature by a background heater, and fine control of the temperature achieved using a control heater operated by a mercury contact thermometer. A circulating fan was used to eliminate temperature gradients as far as possible. Both the air temperature, T_A, and the balance temperature, T_B, were monitored using mercury-in-glass thermometers and were controlled to ±0·1°C at a temperature just above that of the isotherm to ensure that the recorded vapour pressure was that in equilibrium with the sample. The temperature around the sample was controlled by circulating water from a thermostat around the hang-down tube and was monitored using a special thermometer calibrated as in Section 2.10 and controlled to ±0·01°C using a 40 W heater in conjunction with a mercury contact thermometer. All of the work described in this Thesis using this apparatus was carried out at a nominal temperature of 30°C, the actual temperatures are shown in Table 2-1.

TABLE 2-1: TEMPERATURES USED FOR RECORDING AN ISOTHERM AT 30°C

WATER	29·84* ± 0·01°C
AIR	30·1 ± 0·1 °C
BALANCE	30·1 ± 0·1 °C

*see Section 2.10

The pressure in the apparatus was measured with a Texas Instruments quartz Bourdon gauge operated with a 1000 torr head allowing determination of pressures up to atmospheric with a precision of ±0·01 torr. The gauge was connected to the microbalance by means of a glass line heated to well above 31°C.

2.4. THE MAGNETIC SUSPENSION VACUUM MICROBALANCE

The magnetic suspension (MS) vacuum microbalance is a relatively new type of balance, much of the development work having been carried out by Th. Gast in Berlin.[127,128] It was designed to fulfil a need for a microbalance in which the sample under analysis was in a different enclosure from the balance mechanism so that hazardous or corrosive vapours could be studied, e.g. the halogens or hydrogen halide vapours. The basis of the balance is that the absorbent sample is suspended from a magnet held by a magnetic field from another magnet attached to a beam balance. The magnetic coupling is shown schematically in Figure 2-3.

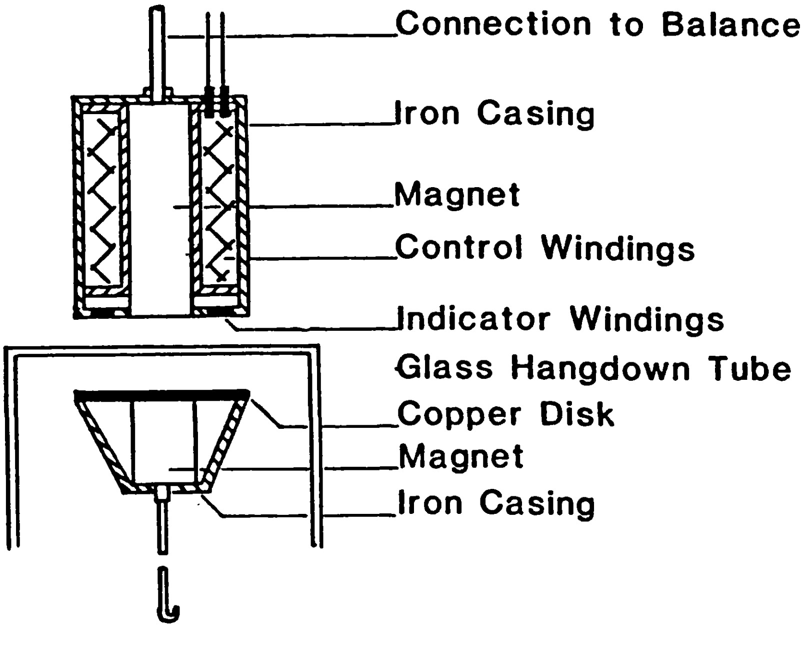


FIGURE 2-3: MAGNETIC COUPLING FOR THE MAGNETIC SUSPENSION MICROBALANCE

As may be seen, the only part of the balance in the hang-down tube and in contact with vapour is the lower magnet assembly which can be covered in protective material, e.g. glass or 'Teflon', if hazardous vapours are to be used. In the current work, the outer iron casing was found not to interact with absorbate vapour and was used as supplied although the original plastic support and stalk for the magnet had to be replaced .[126]

The sample under study is suspended from the lower magnet by means of a non-magnetic alumel wire. The upper magnet is surrounded by a control winding through which current can be passed to change the magnetic field in order to maintain a constant distance between the two magnets, this being determined by the field strength measured by an indicator winding. Movement of the upper magnet and the beam is monitored to give information on the weight changes of the sample.

The balance used was a Sartorius model 4201 commercial vacuum microbalance. It was mounted on a thick concrete plinth supported by brick columns to minimise vibrations. The experimental apparatus is shown in Figure 2-4.

The outer casing and baseplate of the balance form a thermostat through which thermostatted water was circulated. In addition the balance mechanism was surrounded by an air thermostat operated in the same way as that in the QB balance apparatus described in Section 2.3. Temperature gradients were again eliminated by the use of a circulating fan and monitoring the temperature at the top and bottom of the enclosure showed that the gradient rarely exceeded 0·1°C.

The Pyrex glass hang-down tube around the sample passed through a hole in the plinth and was attached to the upper portion of the absorption chamber surrounding the lower magnet by means of a Vacuum Generators Ltd. rotatable 'con-flat' coupling employing a copper gasket, and was connected to the vacuum and absorbate lines by a similar coupling. The lower portion of the hang-down tube which enclosed the sample was surrounded by a water jacket to control the temperature at which the isotherm was recorded and this was enclosed in a second air thermostat. The temperatures employed are shown in

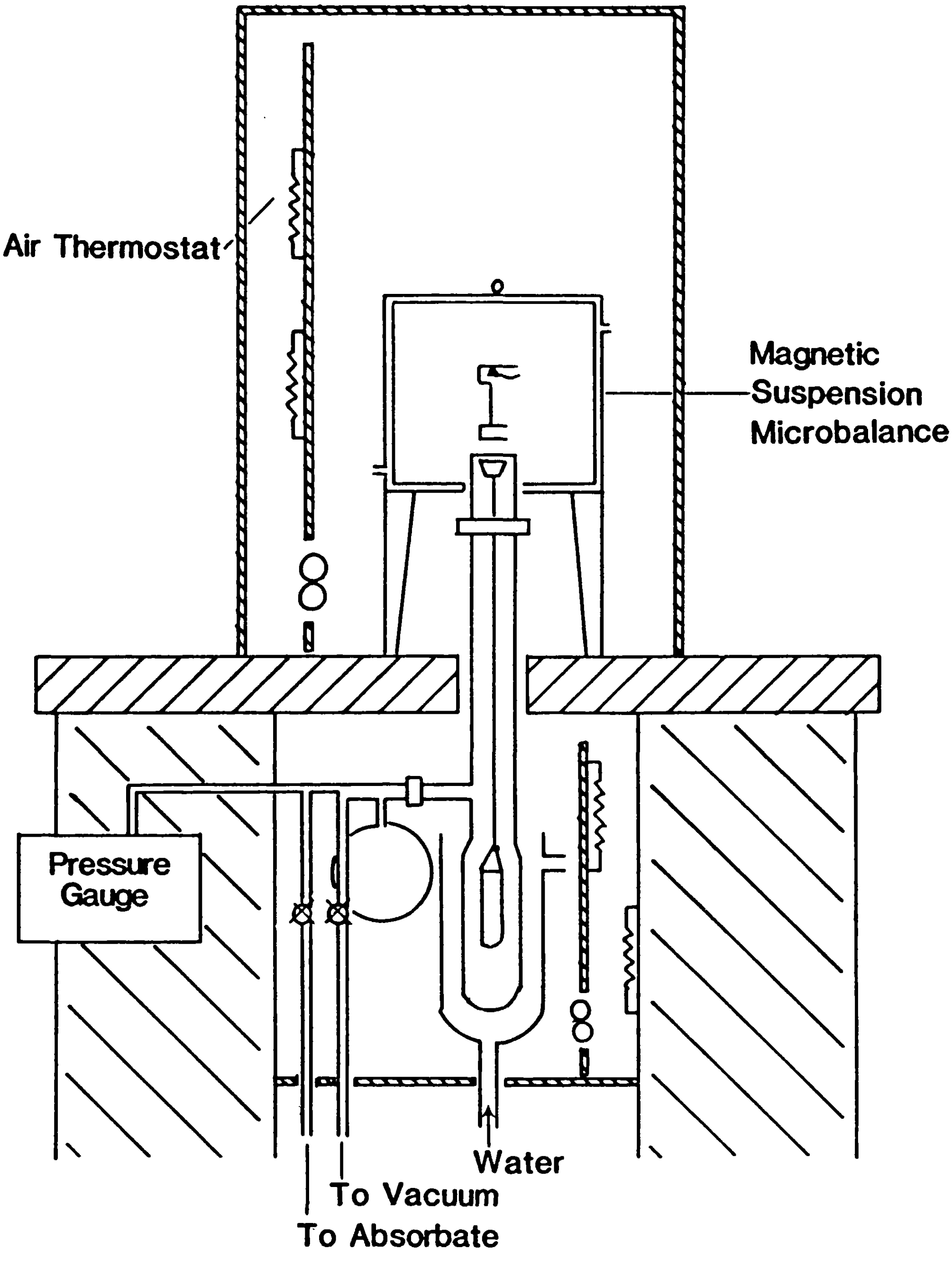


FIGURE 2-4: THE MAGNETIC SUSPENSION MICROBALANCE APPARATUS

Table 2-2 and were set so that the lower water temperature was slightly lower than the others so that the recorded pressure was the true equilibrium vapour pressure.

TABLE 2-2: TEMPERATURES (°C) USED FOR MAGNETIC SUSPENSION BALANCE

NOMINAL TEMPERATURE	WATER JACKET*	LOWER AIR THERMOSTAT	UPPER AIR THERMOSTAT	JACKET HOUSING
25	24•94	25•2	26•0	31•0
30	29•84	30•3	31•0	31•0
35	34•93	35•4	35•9	36•0

*see Section 2.10

The water circulated around the sample was controlled to ±0•01°C and the other temperatures to ±0•1°C.

The pressure gauge was connected to the absorption chamber via a glass line surrounded by heating tape. Two types of pressure gauge were used, a Texas Instruments quartz Bourdon gauge with a 1000 torr head or an M.K.S. Instruments 'Baratron' capacitance gauge with a range of 100 torr, both gauges allowing measurement with a precision of 0•01 torr.

Development of the apparatus[126,129] showed the need for the temperature and humidity of the laboratory containing the apparatus to be kept within certain limits to prevent load drift by the balance. This was achieved by controlling the room temperature using a cooling unit or an electric radiator controlled via a mercury contact thermometer. It was usually possible to control the room temperature to within ±1°C, keeping the humidity to ±6% during the course of an experiment.

The measurement of an isotherm to high pressures of absorbate, the work for which this apparatus was developed, could take a period of several days and so it was important to ensure that the balance did not show any appreciable load drift with time. Previous work at 30°C[126] had shown the drift to be of the order of ±0·1 mg day^{-1}. To check this at the other temperatures employed in this work, a 20 g brass weight was suspended from the balance and all conditions set as if an absorption isotherm was to be recorded. The system was evacuated to <10^{-4} torr and the mass of the weight recorded over a two week period. The results are shown in Figure 2-5 and lead to values of the long term drift of 0·16 mg day^{-1} at 25°C and -0·09 mg day^{-1} at 35°C, the maximum daily variation being of the order of 0·5 mg. Over the course of a day the minimum weight of vapour usually absorbed was around 500 mg so that these variations were considered to be negligible.

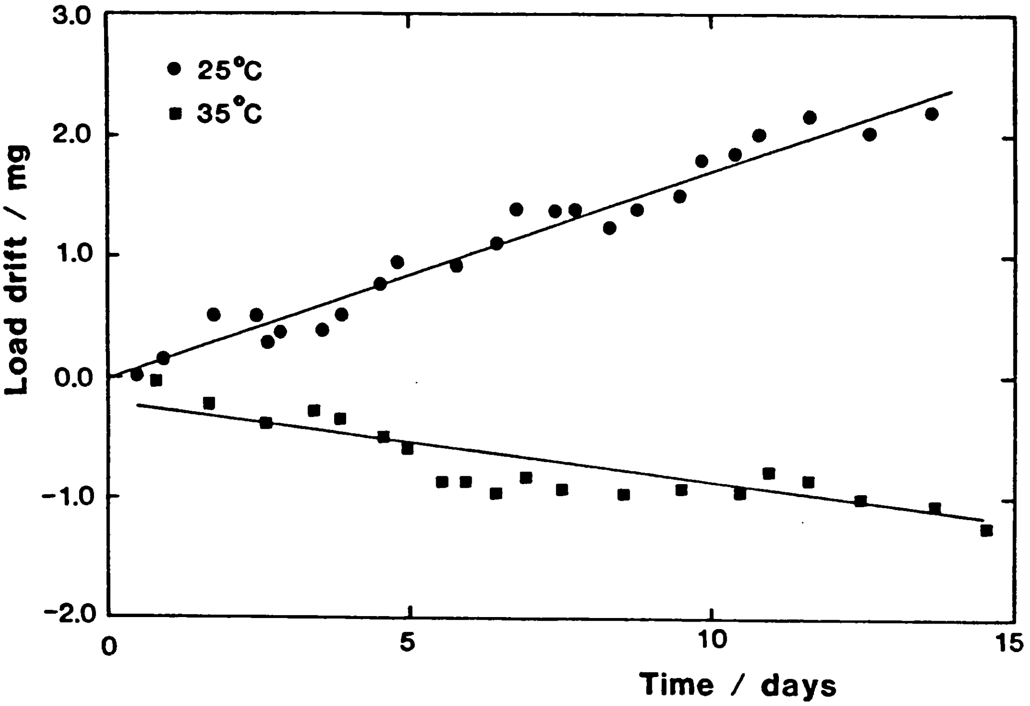


FIGURE 2-5: BALANCE STABILITY AT 25 AND 35°C

2.5. BUOYANCY CORRECTIONS

Since the MS microbalance has a single hang-down wire and sample, any recorded weight changes will be subject to buoyancy effects. These arise from apparent weight changes due to displacement of a fluid around a sample being weighed and are accounted for by the well known Principle of Archimedes which states that the apparent weight change experienced will be equivalent to the weight of the fluid displaced. In the present work there are three main effects to consider:

(i) the upthrust on the sample due to changing pressures of vapour in the absorption chamber;

(ii) the upthrust on the absorbed liquid due to the changing pressure;

(iii) the effects of counter weights in the balance mechanism being in air rather than under vacuum.

To account for these for each absorbate used, the change in weight of a 20 g brass weight with vapour pressure was determined using the same conditions as for an absorption isotherm. Also, the change of weight with changing air pressure was determined. Prior to the recording of an absorption isotherm an 'isotherm' was recorded using air rather than absorbate vapour and the change in weight with air pressure found by a linear least squares fit to account for the slight absorption of air into the absorbent liquid which occurs.

Defining the symbol $\bar{w}$ to be the rate of change of weight with pressure, i.e. $\bar{w} = dw/dp$, then if $\bar{w}_A^S$ is the value for the sample in air, $\bar{w}_A^B$ that for the brass weight in air and $\bar{w}_V^B$ that for the brass weight in vapour, the ratio of the densities, ρ, of the vapour and air is given by

$$\rho_V/\rho_A = \bar{w}_V^B / \bar{w}_A^B$$

This was used to calculate the buoyancy corrections as follows:

<u>(i)</u> Changing upthrust on sample due to pressure in system.

Upthrust = weight of vapour displaced

= (volume of sample) x (density of vapour)

$= V_S\rho_V$

$$\text{since} \qquad \bar{w}_A^S = (V_S\rho_A)/p,$$

$$\text{Upthrust} = \bar{w}_A^S\,(\rho_V/\rho_A)p$$

where p is the pressure of vapour in the system. This causes an apparent loss in weight and so must be added to the recorded weight. This correction also accounts for the upthrust on the hang down wire and lower magnet assembly since these are present in each determination of $\bar{w}$.

(ii) Changing upthrust on absorbed vapour due to pressure.

$$\begin{aligned}\text{Upthrust} &= \text{weight of vapour displaced}\\ &= (\text{volume of liquid absorbed})\ \rho_V\\ &= (W_0/\rho_L)\ \rho_V\end{aligned}$$

where W_0 is the indicated weight of absorbed vapour and ρ_L the density of liquid absorbate. Thus,

$$\text{Upthrust} = (W_0/\rho_L)(\rho_V/\rho_A)\rho_A\cdot p$$

The density of air at atmospheric pressure, ρ_A^{760} may be obtained from tables.[130] It is assumed that the density of air at pressure p(torr) is given with negligble error by

$$\rho_A = (p/760)\rho_A^{760}$$

Thus,

$$\text{apparent weight change} = (\rho_V/\rho_A)(\rho_A^{760}/760\rho_L)W_0p$$

This also causes an apparent weight loss and so must be added to W_0.

(iii) Upthrust on balance mechanism weights

The counter weights of the balance are made of nickel-chromium steel which has a density of 7·88 g cm^{-3}. Thus

$$\begin{aligned}\text{upthrust on weights} &= (\text{volume of weights})\rho_A\\ &= (W_0/7{\cdot}88)\rho_A\end{aligned}$$

Since the balance is at atmospheric pressure ρ_A may be obtained from tables at the appropriate temperature for the upper air thermostat.

This causes an apparent gain in weight and so is subtracted from W_0.

Thus, the true weight, W, at an indicated weight of W_0 and pressure p is given by the combination of these effects

$$W = W_0 + [\bar{w}_A^S + W_0(\rho_A/\rho_L)](\rho_V/\rho_A)p - (W_0\rho_A/7{\cdot}88) \qquad (2.1)$$

Of these effects, the first is by far the most important and can contribute up to 10 mg at an indicated weight of 1 g. The second effect is important only at high pressures while the third is not very significant, typically comprising a correction of 0·1 – 0·5 mg at an absorbed weight of 1 g.

2.6. PREPARATION OF ABSORBENT SAMPLES

In the majority of cases, the absorbent sample consisted of a thin liquid film spread onto an inert diatomaceous earth solid support to give a high surface area and reduce the time needed to reach equilibrium during absorption. All of the samples used on the MS apparatus were contained in buckets approximately 12 cm in length and 2·5 cm in width, made by folding aluminium foil and were suspended from the hang-down wire by a short length of fuse wire. Two types of sample container were used with the QB balance. One was similar to that described above but was approximately 3 cm long and 1 cm wide while the other was a Pyrex glass bulb of suitable dimensions. Duplicate runs on the same absorbent system showed the sample container to have no influence on the results.

The MS balance has a capacity of 30 g but in this work a sample weight around 20 g was used to allow a maximum absorption of 10 g of vapour. The samples were prepared by weighing the required amount of solid support into a dried preweighed 100 cm^3 beaker followed by addition of sufficient liquid absorbent to give the desired liquid loading. This was dispersed using a suitable solvent (60-80°C boiling range petroleum ether was used for squalane or dinonyl phthalate and ethyl acetate for poly(dimethyl siloxane)) to form a slurry and the mixture swirled to coat the solid. The solvent was allowed to evaporate while protecting the sample from the ingress of dust before final heating to constant weight in an oven at 80-90°C. The resulting sample was stirred to ensure uniformity and then weighed into the aluminium bucket. Excess sample was discarded and the beaker reweighed to account for any liquid coated onto walls of the beaker rather than the solid support.

In previous work[112-114] a similar technique was used to prepare samples for use on the QB balance but the possibility had been suggested that a considerable amount of material was not coated onto the support but adhered to the glass beaker. This possibility was eliminated by weighing the absorbent and solid support directly into the balance bucket followed by addition of the dispersing solvent. The sample weight was ~1·8 g allowing an uptake of ~200 mg to reach the 2 g capacity of the microbalance. It was found that this technique could not be used for the MS balance since the large amount of solvent needed tended to leak through the folds in the aluminium foil. As will be shown in Chapter 4, results obtained using samples prepared by these techniques were found to be in good agreement but the latter technique was always used for samples on the QB apparatus.

During the study of adsorption effects in Chapter 8 it was necessary to record isotherms on bulk liquid absorbents. To increase the area of absorption, and reduce the time taken for the experiment, the liquid was placed in three glass trays around 2·5 cm in diameter and 7 mm deep held by a frame of stiff steel wire. A depth of ~1 mm in each tray was used to give a sample weight of 2 - 2·5 g of absorbent.

2.7. RECORDING OF ISOTHERMS

The same basic method was used for work on each apparatus. The sample was loaded onto the balance and the hang-down tube(s) refitted, the gaskets being changed between each experiment on the QB balance and new copper gaskets being used after two samples had been studied on the MS balance. The apparatus was then evacuated and pumped to a pressure of $<10^{-4}$ torr, as indicated on the 'Pirani' gauge, for 48-72 hours as circumstances dictated. When a new absorbate was used, or after every two or three absorption isotherms recorded, it was outgassed by surrounding the ampoule with liquid nitrogen to freeze the absorbate and pumped on for ~5 minutes. The pumps were then isolated and the absorbate distilled into an adjacent limb of the reservoir followed by repumping. This was repeated until no pressure increase was observed on opening the frozen absorbate to the Pirani gauge.

Immediately prior to the commencement of an experiment the absorption chamber was isolated from the pumps and left for 20-30 minutes before being opened to the Pirani gauge. This allowed calculation of the rate of pressure increase due to leakage or outgassing which would cause an error in the pressure measurement during an isotherm. The upper limit of this taken as acceptable was that needed to cause a 0·1 - 0·5% error over the expected duration of an experiment. If this rate was satisfactorily low, pumping was carried out for around 15 minutes to re-establish the best vacuum during which the zero readings of weight and pressure were recorded. (The calibration of the MS microbalance was also carried out at this stage using the method recommended by the manufacturers.) The pumps were then isolated (Taps G and H closed), absorbate vapour allowed (via Tap H) to contact the sample and the weight absorbed followed on a chart recorder. When equilibrium conditions were established, taken as no weight increase over at least a ten minute period and a thirty minute period at high pressures on the MS apparatus, the weight change, vapour pressure and temperatures were recorded. A further amount of absorbate was then admitted and the procedure repeated to determine the required number of results. Usually eight points were measured at 0·05 mole fraction intervals up to 0·4 on the QB microbalance and a similar number over a wider concentration range recorded on the MS apparatus, though in some cases as many as 10-12 points were recorded. When using the QB apparatus, it was sometimes noted that the pressure and weight readings began to fall after attainment of equilibrium, presumably due to absorption by gaskets etc. When this occurred the position of equilibrium was taken at the maximum on the chart recorder trace rather than waiting a further ten minutes. This problem did not occur on the MS balance but when used at very high relative pressures (i.e. $p/p^\circ >$ 0·90) it was sometimes noted that the small temperature variations in the apparatus caused small oscillations of ~0·5 mg in weight and ~0·05 torr in pressure. These are very small compared to the indicated values and the readings were recorded in the centre of the oscillations.

When the final result had been recorded the absorbate reservoir was surrounded with liquid nitrogen and the absorbate removed from the sample by opening Tap H to condense it into the reservoir. For the MS apparatus, this was done in 5-10 torr intervals, the absorbate being allowed to desorb from the sample between each stage since it was found that the absorbent sample would 'fluff' out of the bucket if the absorbate were removed too quickly. This was not found to be a problem on the QB balance.

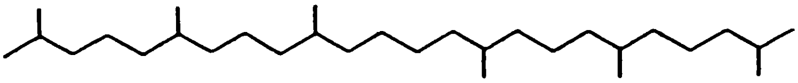
When all the vapour had been removed, the sample was opened to the pumps to remove the final traces of absorbate before being removed from the balance. It was then left for 24-48 hours to re-equilibrate with the atmosphere before being reweighed to determine whether any absorbent had been lost.

2.8. MATERIALS

The solid support used throughout was a 'Celite 545 AW' diatomaceous earth of mesh size BSS 100-120 supplied by Phase Separations Ltd. and was used as received.

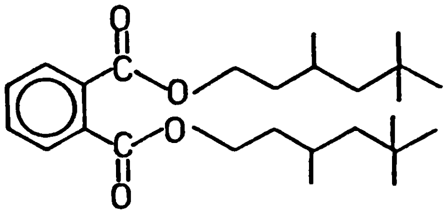
The squalane, SQ, 2,6,10,15,19,23-hexamethyl tetracosane was a Hopkin and Williams Ltd. sample supplied as a GLC reagent. It was used without further purification.

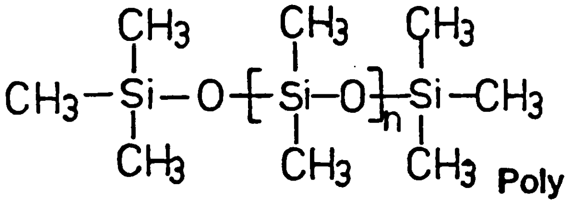
The dinonyl phthalate, DNP, nominally bis(3,5,5 trimethylhexyl)-1,2-benzene dicarboxylate was a BDH sample supplied for GLC. It was also used as received (see discussion in Chapter 9).



Squalane

Dinonyl Phthalate





$$CH_3-Si(CH_3)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-CH_3$$

Poly(dimethyl siloxane), PDMS

The poly(dimethyl siloxane) polymers, PDMS, were Dow Corning Ltd. DC 200 silicone fluids sold according to their approximate viscosities. Those used were those sold as 50, 100, 350, 1000 and 12500 cs viscosity and were used without further purification, except for the last which was treated by Hooker[131] to remove low molecular weight species using the procedure of Flory and Crescenzi.[132] As a check to confirm the absence of volatile materials in the polymer, a ~350 mg sample was suspended from a McBain-Bakr vacuum microbalance and maintained at a pressure of $<10^{-5}$ torr for seven days. No weight change was detected showing the polymers to be free of volatiles.

The hydrocarbon absorbates used on the QB balance were National Physical Laboratory high purity samples supplied in break seal ampoules and were handled under vacuum throughout. The certificated purity is shown in Table 2-3. The dichloromethane and chloroform used were BDH Ltd. 'Aristar' compounds. Both of these contain ethanol (as 0·1 and 2·0 volume per cent respectively) as a stabiliser against radical decomposition. They were purified before use by passage down a column of BDH Ltd. Brockman Grade 1 basic alumina, 25 cm long and 2 cm in diameter. The alumina was heated for 2 hours at 120°C prior to use and GLC analysis on a DNP column at 50°C was used to confirm the removal of the ethanol and showed the purity to be greater than 99·9%.

The absorbates used on the MS balance were as follows: benzene and cyclohexane were BDH Ltd. 'Research Grade' materials. The n-hexane used was a high purity sample from Fluka A.G. and the ethyl acetate a BDH Ltd 'Aristar' sample. All were used without further purification and the quoted purity is shown in Table 2-3. These absorbates were not supplied in break seal ampoules but were placed into a clean tube attached by a mercury seal to a vacuum frame. Liquid nitrogen was used to freeze the liquid and the apparatus evacuated. It was then distilled under vacuum into a break seal ampoule and outgassed by an alternate freeze-thaw procedure before being sealed under vacuum and transferred to the microbalance frame.

TABLE 2-3: QUOTED PURITY (MOLE PER CENT) OF ABSORBATES

QB BALANCE		MS BALANCE	
SAMPLE	QUOTED PURITY	SAMPLE	QUOTED PURITY
Benzene	99·99	Benzene	>99·9
Cyclohexane	99·98	Cyclohexane	>99·9
n-Pentane	99·84	n-Hexane	>99·7
n-Hexane	99·99	Ethyl Acetate	>99·5
n-Heptane	99·97		
Dichloromethane	>99·9		
Chloroform	>99·5		

2.9. MEASUREMENT OF POLYMER PROPERTIES

The five polymer samples used will be differentiated by assigning a Roman numeral from I to V with increasing molecular weight. The highest molecular weight sample (PDMS V) had been found to have a molecular weight of 89000 by measuring an intrinsic viscosity of 37·0 cm^3 g^{-1} in toluene at 25°C[131] and applying the relation of Barry.[133] The relative viscosity method was tried with the lower molecular weight polymers but these were found to give small differences in flow time between the solutions and pure solvents leading to inaccurate results. A Hewlett Packard 301A vapour pressure osmometer was tried but this was found to be difficult to calibrate and also gave inaccurate results.

As well as the intrinsic viscosity relation used by Hooker, Barry[133] also gives a relationship for the dependence of bulk liquid (or oil) viscosity on molecular weight and so this method was applied to the other polymer samples.

Two new PSL suspended level viscometers were used, one Size 5 and the other a Size 7. They were supplied with certified calibration constant, K, such that the viscosity of a liquid in centistokes is given by

$$\eta = Kt$$

where t is the flow time in seconds. The viscometers were cleaned in ethyl acetate, chromic acid, distilled water and acetone before being dried at 110°C. They were filled with the PDMS sample under study and immersed in a water bath controlled at 25·0 ± 0·1°C by a Tempunit TU14 temperature controller so that both calibration marks were beneath the surface of the water. The sample was drawn into the upper bulb and allowed to flow out under gravity, the time for flow between the two marks being noted. All times quoted are the average of at least three determinations within 0·2 s.

The molecular weights were calculated using[133]

$$\log(\eta) = 1{\cdot}00 + 0{\cdot}0123\ M_n^{\frac{1}{2}}$$

and the results are summarised in Table 2-4.

TABLE 2-4: MOLECULAR WEIGHTS OF PDMS SAMPLES

SAMPLE	VISCOMETER CONSTANT	FLOW TIME /S	VISCOSITY /CS	MOLECULAR WEIGHT	ASSUMED VALUE
PDMS I	0·1021	501·9	51·24	3329	3350
PDMS II	0·1021	970·3	99·07	6556	6550
PDMS III	1·061	326·1	345·99	15657	15650
PDMS IV	1·061	907·9	963·28	26012	26000

The density of the highest molecular weight polymer was assumed to conform to the value found by Flory and Shih[134] for a polymer of molecular weight 100000. The densities of the other samples were measured using density bottles.

Two density bottles were successively cleaned with chromic acid, distilled water and acetone before being dried and weighed. They were filled with a new sample of triply distilled mercury and immersed as far as possible in a water bath controlled at 29·85 ± 0·1°C, measured using the same thermometer as was used for determining the absorption isotherms, and left for one hour to equilibrate. The stoppers were then inserted and left for a further 15-20 minutes before being removed from the bath, dried and set aside for thirty minutes before being reweighed. The calibration was repeated with doubly distilled water. To check the density of the water, two 50 ± 0·1 cm^3 'A' grade volumetric flasks were weighed and filled with the water at 29·85 ± 0·1°C and the weight of water determined. After allowance for the expansion of the glass[130] from the calibration temperature of the flask at 20°C the density of the water was calculated and the calibration of the density bottles carried out in the same manner as with mercury. After the calibration runs, the bottles were cleaned as above and filled with a sample of polymer as appropriate and the above procedure used to determine the weight of PDMS contained in each bottle at 29·85°C. This was done for each polymer sample in turn.

All weights were recorded on a Mettler H10W four figure analytical balance and were taken as the average of at least three weighings within 0·2 mg. When calculating the densities, allowance was made for buoyancy effects during the weighings.

The results are summarised in Table 2-5.

TABLE 2-5: DENSITY/g cm^{-3} OF PDMS SAMPLES AT 30°C

DENSITY OF WATER/g cm^{-3} : A. 0·99230 B. 0·99231

AVERAGE : 0·9923 g cm^{-3}

VOLUME OF BOTTLE I /cm^3 = (H_2O) 10·907 (Hg) 10·900 (Av) 10·904

VOLUME OF BOTTLE II/cm^3 = (H_2O) 10·401 (Hg) 10·392 (Av) 10·398

SAMPLE	DENSITY/g cm^{-3}		
	BOTTLE I	BOTTLE II	AVERAGE
PDMS I	0·9523	0·9523	0·9523
PDMS II	0·9570	0·9572	0·9571
PDMS III	0·9615	0·9619	0·9617
PDMS IV	0·9644	0·9642	0·9643

2.10. CALIBRATION OF THERMOMETERS

The thermometers used to monitor the water temperature during the recording of the absorption isotherms were 10°C range Anshultz thermometers. The temperatures were read by placing them in such a position that the reflection from a graduation could be seen reflected in the mercury column. By lining up the graduation and its reflection, parallax errors were eliminated. The temperature was adjusted so that the top of the mercury thread lay on a particular mark and the same mark was used for each isotherm.

To check the actual value of the temperature the thermometer was attached to a Tinsley type 5187 SA platinum resistance thermometer (PRT). This was placed in an insulated water bath and the temperature adjusted using a Tempunit TU14 controller to give the same reading as during the recording of an isotherm. The resistance of the PRT was determined using a Tinsley 5840 resistance bridge which supplied a

1μA current to the PRT and measures the potential difference across it. The bridge gave a readout of the resistance which was related to the temperature by an NPL calibration chart supplied with the PRT. The resistance at a particular set temperature was found to vary by up to ±0·3 m Ω which corresponded to a temperature change of ±0·002°C which is undetectable on the mercury thermometers. The results are summarised in Table 2-6.

TABLE 2-6: CALIBRATION OF THERMOMETERS

NOMINAL TEMPERATURE/°C	RESISTANCE /Ω	ACTUAL TEMPERATURE/°C
25	27·06371 ± 0·00030	24·94
30	27·54134 ± 0·00021	29·84
35	28·03607 ± 0·00010	34·93

2.11. DETERMINATION OF CLOUD POINT OF PARTIALLY MISCIBLE MIXTURES

The cloud point of a partially miscible mixture is the concentration where the clear mixture just becomes turbid. In this work, measurements were required at a single temperature, 30°C, so that an oven accurately controllable at this temperature was necessary. Determination of whether a mixture was miscible was found to be quite difficult in some cases, particularly with the low molecular weight polymers where the refractive indices are quite similar, but it was found that shaking the mixture or observing it through a low power microscope considerably eased the difficulties. Thus, the ideal situation would have been a large thermostatically controlled glove box but, since this was not available, an existing thermostatted cabinet was adapted for use.

The cabinet consisted of a box constructed of asbestolite material with a removable front cover. The box was heated by means of heating mats controlled by a mercury contact thermometer and variation was reduced by enclosing the front in thick polythene sheeting which was adapted so that samples could be placed and manipulated in the box without too serious a disturbance to the temperature. Observation over a 36-hour period showed the temperature to be constant to ±0·2°C.

The cloud points were determined by weighing out sufficient of the two liquids under study into small sample tubes to give total samples of ~0·5 g covering a range of compositions. These were dissolved in ethyl acetate to give clear solutions and placed in the thermostat at 29·8 ± 0·2°C to allow the solvent to evaporate, this taking from 24-48 hours. In most cases direct visual examination was used to determine whether the mixture was clear (i.e. miscible) or cloudy or separated into two layers (i.e. immiscible). In the cases where this was uncertain, some of the liquid was drawn into a capillary tube and observed against a ruled grid with a low power (20x) binocular microscope.

When the range of miscible mixtures had been found, it was successively narrowed down by covering lesser composition ranges until the cloud point was determined to within 0·1 per cent by weight.

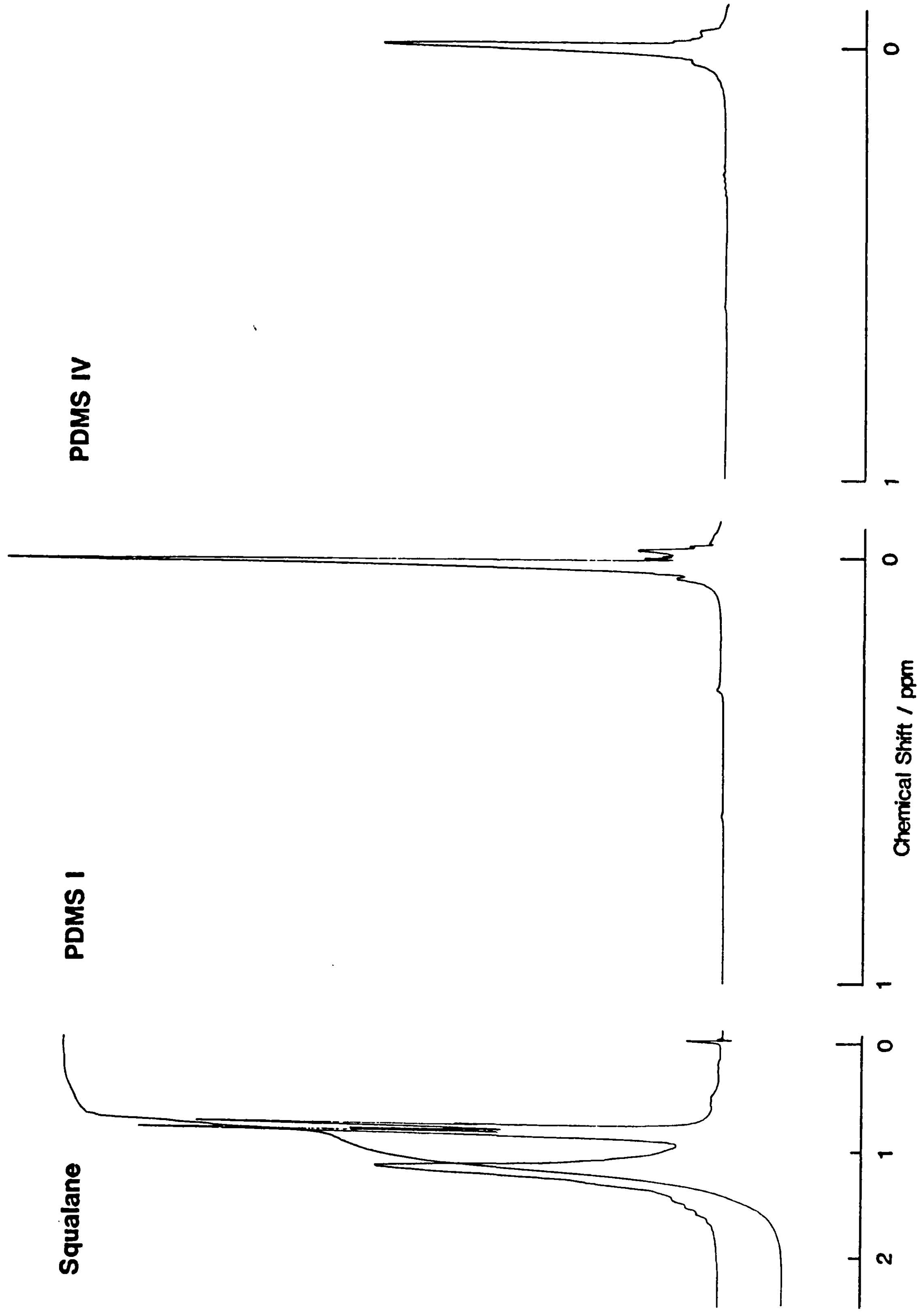
2.12. SPECTROSCOPIC MEASUREMENT OF PHASE COMPOSITIONS

As a check on the phase compositions measured by the cloud points a spectroscopic method was used to measure them. Approximately equal amounts of the two liquids under investigation were weighed into a 10 cm^3 capacity sample bottle to a total weight of ~1·5 g. The bottles were then filled with ethyl acetate and gently swirled to dissolve the liquids. This was then placed in the thermostatted cabinet described in the previous Section and the solvent was allowed to evaporate. This procedure was repeated to ensure thorough mixing of the liquid mixture and the samples left for a week for complete evaporation of solvent and separation of the mixture into two layers.

Samples of the upper layer were removed using a fine tipped glass pipette and transferred to small sample tubes taking care not to draw up any of the lower phase. Liquid from around the phase boundary was discarded and the lower layers sampled in a similar manner.

Allen and co-workers[135] used a similar method with PDMS and poly(isobutylene) employing infra-red spectroscopy for the analysis. Spectra of the compounds involved in the present work showed that this would have been suitable for PDMS/DNP mixtures but that the only suitable bands in the spectra of SQ and PDMS occurred in the same region and so interfered. DNP has a series of peaks in the ultra violet absorption spectrum but PDMS has no peak in the 190–450 nm range normally considered. However, nuclear magnetic resonance spectroscopy was found to be suitable.

The 'shift' of the absorptions in hydrogen nmr are normally measured relative to the signal of tetramethyl silane, TMS, $Si(CH_3)_4$, this being arbitrarily assigned to zero. The PDMS spectra consist of single peaks close to zero as can be seen from Figure 2-6. The spectra of DNP and SQ are also shown and can be seen to be well separated from those of the polymers and so the integrals over each peak can easily be assigned to the compounds. The samples from each mixture taken as above were dissolved in ~0·5 cm^3 *deutero*-chloroform ($CDCl_3$) and transferred to cleaned nmr tubes. Spectra were recorded on a Varian Associates EM 360 60 MHz spectrometer. The spectra in Figure 2-6 were recorded on a JEOL 100 MHz spectrometer and so might be expected to give a greater resolution between the peaks. However, the resolution of the 60 MHz spectrometer was sufficient for the present



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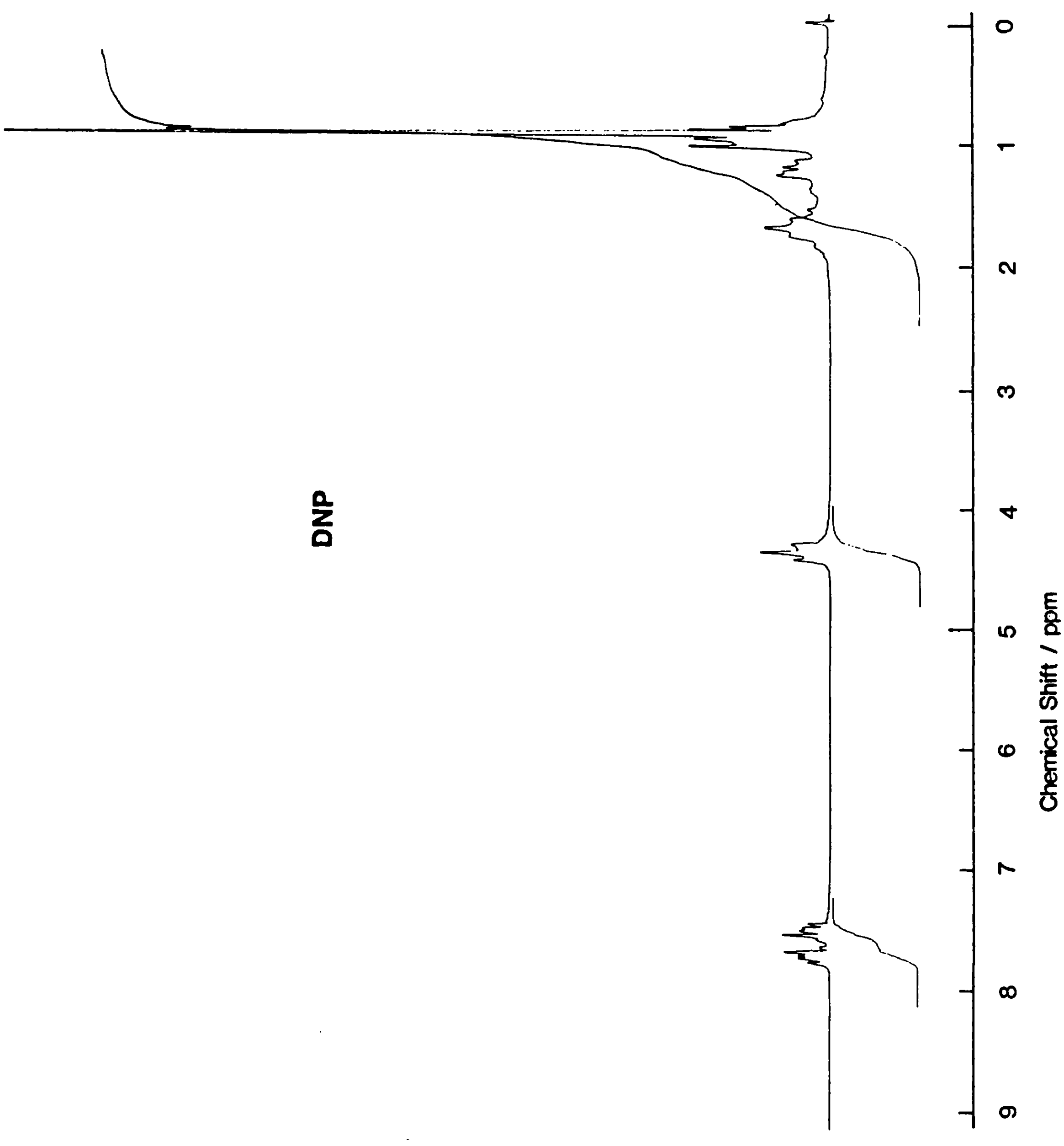

FIGURE 2-6: NMR SPECTRA OF DNP, SQUALANE AND PDMS

work as the main interest was in the integral trace.

The spectra were recorded using a 0–10 ppm sweep range on a 0·05 mG RF power and using a 5 min. sweep time. As well as the basic spectrum, the integral of the area of each peak was recorded and this was used as the basis of the calculations as outlined in Chapter 3 since the peak area is proportional to the concentration of that species in the solution.

Chapter 3

Treatment of Results

The absorption isotherms recorded during the work described in this Thesis are tabulated in Appendix I. They will not be listed here but will be considered as the results are quoted and discussed in the following Chapters. This Chapter will be used to show how the results were obtained from the experimental observations.

3.1. ACTIVITY COEFFICIENTS AND INTERACTION PARAMETERS

The activity coefficient of component 1 in a solution was calculated using equation (1.2)

$$\gamma_1 = p_1/p_1^o x_1$$

where by the nature of the work involved component 1 is the absorbate. The experimental measurements of the weight of absorbent, w_2, and the weights of absorbed vapour, w_1, were used with the molecular weights M to calculate the mole fraction, x_1, using

$$x_1 = (w_1/M_1) / (w_1/M_1 + w_2/M_2) \qquad (3.1)$$

and this combined with the measured vapour pressures p_1 and the saturated vapour pressure at the isotherm temperature p_1^o to calculate the activity coefficient. However mole fraction based activity coefficients are not very useful when dealing with polymer solutions since generally the polymer molecular weight is known only approximately and as Patterson *et al.* [136] have pointed out values based on mole fractions tend to be rather unwieldy. Therefore when PDMS was used as an absorbent, volume or segment faction based activity coefficients were employed using equation (3.2).

$$\gamma_1^V = p_1/p_1^o \phi_1 \qquad (3.2)$$

The volume fraction, ϕ_1, was calculated from the experimentally measured weights and the component densities using

$$\phi_1 = w_1/\rho_1 / (w_1/\rho_1 + w_2/\rho_2) \qquad (3.3)$$

Activity coefficients based on segment fractions, γ_1^S, were calculated by replacing ϕ_1 in equation (3.2) by Ψ_1 as defined by equation (1.28).

The calculated activity coefficients were corrected for fugacity and vapour phase non-ideality. This was done using the equation of Everett and Penny[137]

$$\ln\gamma_1 = \ln(p_1/p_1^\circ x_1) + (V_1^\circ - B)(p_1^\circ - p_1)/RT + (B/RT)^2({p_1^\circ}^2 - p_1^2)/2 \tag{3.4}$$

The inclusion of V_1°, the molar volume of the liquid absorbate, accounts for the effect of changing pressure on the activity of the solution and that of B, the absorbate second virial coefficient, accounts for vapour non-ideality. The values of the pure component data used in the calculations are given in Section 3.6.

3.2. ANALYSIS OF BINARY SYSTEMS

The results for $\ln\gamma_1$ from the preceding Section were used with the Flory-Huggins expression (equation 1.25) suitably rearranged with equation (1.10) to calculate the F-H interaction parameter χ

$$\chi = [\ln a_1 - \ln(1-\phi_2) - (1-1/r)\phi_2] / \phi_2^2 \tag{3.5}$$

where a_1 is the activity of the solutions, given by $x_1\gamma_1$, $\phi_1\gamma_1^V$ or $\psi_1\gamma_1^S$. The observed concentration dependence of χ was accounted for by the assumption of a linear dependence of the form

$$\chi = \chi^\circ + \chi' \phi_2 \tag{3.6}$$

The values of χ° and χ' that best fit the experimental results were found by performing a linear least squares fit[138] of the χ and ϕ values. The fit of the results to the relation implied by equation (3.6) was judged by calculation of a regression coefficient, the value of which approaches 1·0 for a perfect fit.

The sum of χ° and χ' is the infinite dilution interaction parameter, χ^∞ (i.e. the value at zero concentration of absorbate). Adapting equations (1.10) and (1.25) to infinite dilution, leads to

$$\ln\gamma_1^\infty = \ln(1/r) + (1-1/r) + \chi^\infty \tag{3.7}$$

so that an activity coefficient could be calculated. It was converted to the values based on the various concentration scales since they are interrelated:

$$a_1 = \gamma_1 x_1 = \overset{w}{\gamma_1} w_1 = \overset{V}{\gamma_1} \phi_1$$

where W_1 is the weight fraction, then at infinite dilution it may be shown that

$$^{\infty}\gamma_1^{w} = {}^{\infty}\gamma_1^{V} (\rho_2/\rho_1)$$

and

$$^{\infty}\gamma_1^{w} = {}^{\infty}\gamma_1 (M_2/M_1)$$

Also the infinite dilution partition coefficient between vapour and absorbent phases, K, was calculated from equation (1.60).

The values of $\chi°$ and χ' were used to calculate the best fit values of χ at each of the experimental concentrations and these fed into equation (3.5) to calculate a $\ln\gamma_{fit}$ value, the value that $\ln\gamma$ would have if the interaction parameter had its best fit value. These were compared to the experimental values and the fit of the data to the Flory-Huggins theory gauged by calculating a 'root mean square deviation', 'RMSD', for the N experimental points where,

$$\text{RMSD} = [{}^{N}\Sigma\ (\ln\gamma_{1_{fit}} - \ln\gamma_1)^2/N]^{\frac{1}{2}} \qquad (3.9)$$

In a similar manner, the best fit values of χ and $\ln\gamma_{fit}$ values were calculated at 0·1 intervals across the concentration range.

The recorded absorption isotherms are tabulated in Appendix I in the form of weight absorbed at each pressure together with appropriate derived quantities. The weights of absorbent used are also shown and the regression coefficient and RMSD values given as an indication of the fit to theory.

The computer program 'FLO-HUG' used to analyse the absorption isotherms is discussed and reproduced in Appendix II.

3.3. ANALYSIS OF TERNARY SYSTEMS

The results for the absorption of vapour into a two component stationary phase were analysed in two ways. Firstly they were treated as a pseudo-binary system, the absorbent being considered to be a single component with properties represented by the weighted average of the separate components. In this case

$$x_A = (w_A/M_A)/(w_A/M_A+w_B/M_B+w_C/M_C) \quad (3.10)$$

and similarly for the other concentration scales. In the discussion that follows it will be convenient to change the subscripts to avoid confusion. Thus for a ternary system, A refers to the absorbate while B and C refer to the involatile absorbents. The size ratio, r_{BC}, was treated as the molar average of the molar volumes,

$$r_{BC} = (x_B V_B^\circ + x_C V_C^\circ)/V_A^\circ \quad (3.11)$$

where x_B is the mole fraction of component in the absorbent phase. The pseudo-binary interaction parameter, χ, can then be calculated in the same manner as in the previous Section.

This treatment was used to calculate γ^∞ and partition coefficient values for use in the discussion on mixed stationary phase behaviour in Chapter 9.

The ternary systems were also analysed in terms of the full Flory-Huggins equation for a ternary system which is derivable from the equation (1.26) for a multicomponent system. This may be stated as

$$\ln a_A = \ln \phi_A + (1-1/r_{BC}) + (1-\phi_A)(\phi_B \chi_{AB}+\phi_C\chi_{AC}-\phi_B\phi_C\chi_{BC}) \quad (3.12)$$

Results for absorption into the two separate absorbents together with those for the mixture were used to calculate the best fit interaction parameters. The parameter between the involatile components χ_{BC} was assumed to be independent of concentration while the dependence of the interaction parameters for absorbate with absorbent was assumed to have the form

$$\chi_{AB} = \chi_{AB}^\circ + [\phi_A/(\phi_A+\phi_B)]\ \chi_{AB}' \quad (3.13)$$

and similarly for χ_{AC}. The results were analysed by a least squares fit to find the best fit values of the five interaction parameters

χ°_{AB}, χ'_{AB}, χ°_{AC}, χ'_{AC} and χ_{BC}. These were fed into equation (3.12) to find $\ln\gamma_{fit}$ values and an RMSD calculated using equation (3.9) to describe the fit of the data to the F-H theory.

3.4. CURVE FITTING BY A LEAST SQUARES PROCEDURE

Among the commonest methods of statistically analysing a set of results in terms of a known function is to perform 'Least Squares Fit'. This involves the minimization of the sum of the squares of the deviations of the experimental data from the function. Relatively simple formulae arise when only one set of observations is subject to error and a linear function is involved. However when the function is more complicated and both sets of observations subject to error the analysis is more complex. The following general account is adapted from work by Wilson[139] and Wentworth,[140] the symbols here being those commonly used and not as used elsewhere in this Thesis.

Consider a function, F, dependent on parameters p,q,... etc. and calculated from experimental observations x and y. The condition that any point, i, lies exactly on the required curve is

$$F_i = F(x_i, y_i, p, q, \ldots) = 0$$

where x_i and y_i here represent adjusted values of the experimental observations $(x_i + \Delta x_i)$ and $(y_i + \Delta y_i)$. If approximate values of the parameters $p + \Delta p$, $q + \Delta q$, etc. are available then an error term, ΔF_i, will result where

$$F_i + \Delta F_i = F(x_i+\Delta x_i,\ y_i+\Delta y_i,\ p+\Delta p,\ q+\Delta q, \ldots) = 0 \qquad (3.14)$$

Equation (3.14) may be expanded in a Taylor series about the deviations. Writing F' for a partial differential of F, e.g. $F'_x = \partial F/\partial x$ and retaining only linear terms of the series,

$$F_i + \Delta F_i = F_i + F'_{x_i}\,\Delta x_i + F'_{y_i}\,\Delta y_i + F'_p\,\Delta p + F'_q\,\Delta q \ \ldots \text{ etc.} = 0$$

The sum of the squares of the deviations of the N experimental points, S_N, is given by

$$S_N = {}^N\Sigma\ w_x\ (\Delta x_i)^2 + {}^N\Sigma\ w_y\ (\Delta y_i)^2 \tag{3.15}$$

where w_x and w_y are the statistical weights (the reciprocal of the variances) of the observations. For a least squares fit, S_N must be minimized subject to the conditions imposed by equation (3.14). This may be done by differentiating equation (3.15) and setting to zero. Hence,

$$\delta S_N = 2\{{}^N\Sigma\ w_x\ \Delta x_i\ \delta(\Delta x_i) + {}^N\Sigma\ w_y\ \Delta y_i\ \delta(\Delta y_i)\} = 0 \tag{3.16}$$

Differentiating equation (3.14) noting F_i to be zero,

$$F'x_i\ \delta(\Delta x_i) + F'y_i\ \delta(\Delta y_i) + F'p\ \delta(\Delta p) + F'q\ \delta(\Delta q) + \dots \text{etc.} = 0 \tag{3.17}$$

Multiplying each term of equation (3.17) by an arbitrary constant, λ_i, and subtracting from equation (3.16) leads to

$$\begin{aligned} {}^N\Sigma(w_x\Delta x_i - \lambda_i F'x_i)\delta(\Delta x_i) + {}^N\Sigma(w_y\Delta y_i - \lambda_i F'y_i)\delta(\Delta y_i) + {}^N\Sigma\ \lambda_i\ F'p\ \delta(\Delta p) \\ + {}^N\Sigma\ \lambda_i\ F'q\ \delta(\Delta q) + \dots \text{etc.} \end{aligned} \tag{3.18}$$

If these constants, termed 'Lagrange Multipliers' are chosen so that the coefficients of N of the variations are unity, then the remaining variations must be independent. Thus, if equation (3.18) is to hold their coefficients must also vanish. Thus

$$\begin{aligned} w_x\ \Delta x_i - \lambda_i\ F'x_i &= w_y\ \Delta y_i - \lambda_i\ F'y_i = 0 \\ {}^N\Sigma\ \lambda_i\ F'p &= {}^N\Sigma\ \lambda_i\ F'q = \dots \text{etc.} = 0 \end{aligned} \tag{3.19}$$

Defining L_i such that

$$L_i = F'x_i^2/w_x + F'y_i^2/w_y$$

then equations (3.19) may be used to eliminate Δx_i and Δy_i from (3.14) giving

$$\Delta F_i = L_i\ \lambda_i + F'p\ \Delta p + F'q\ \Delta q + \dots \text{etc.}$$

Rearranging to solve for λ_i,

$$\lambda_i = (1/L_i)(\Delta F_i - F'p\ \Delta p - F'q\ \Delta q - \dots \text{etc.}) \tag{3.20}$$

Substituting equation (3.20) in equations (3.19), and so on for all sets of parameters. By appropriate substitution and rearrangement, this can be expressed as

$$\begin{aligned} a_1 &= b_{11}\Delta p + b_{12}\Delta q + \ldots \text{ etc.} \\ a_2 &= b_{21}\Delta p + b_{22}\Delta q + \ldots \text{ etc.} \end{aligned} \qquad (3.21)$$

and so on. Equations (3.21) represent a set of simultaneous linear equations which may be solved to find Δp, Δq etc. and these may be used to adjust the original values of p, q etc. to achieve a better fit. These can then be used as the estimates and the procedure repeated until sufficient accuracy is obtained. The simultaneous equations may be solved by a number of techniques but the most straightforward for adaption to a computer method is that of 'Gaussian elimination', details of which are in most mathematical and computing texts.[141]

3.5. LEAST SQUARES FIT TO EXPERIMENTAL DATA

To apply the treatment of the previous Section to the experimental data for the ternary systems, the function F, on which the analysis is based, is obtained by subtracting the Flory-Huggins expression of $\ln\gamma_1$ from that for the experimental value. Defining the fugacity corrections by

$$c_1 = (V_A^\circ - B)\, p_A^\circ/RT \quad , \quad c_2 = (Bp_A^\circ/RT)^2/2$$

then the experimental activity coefficient is given by

$$\ln\gamma_A = \ln(a_A/x_A) + c_1(1-a_A) + c_2(1-a_A^2) \qquad (3.22)$$

where a_A ($= p_A/p_A^\circ$) is the activity of the solution.

From the Flory-Huggins theory,

$$\ln\gamma_A = \ln(\phi_A/x_A) + (1-\phi_A)(1-1/r) + (1-\phi_A)^2\chi \qquad (3.23)$$

where χ is given by

$$\chi = [\phi_B/(\phi_B+\phi_C)]\chi_{AB} + [\phi_C/(\phi_B+\phi_C)]\chi_{AC} - [\phi_B\phi_C/(\phi_B+\phi_C)^2]\chi_{BC} \tag{3.24}$$

with χ_{AB} and χ_{AC} defined by equation (3.13). Combining equations (3.22) and (3.23),

$$F = \ln(a_A/\phi_A) + (1-\phi_A)(1-1/r) + (1-\phi_A)^2\chi - c_1(1-a_A) - c_2(1-a_A^2) = 0 \tag{3.25}$$

The experimental observations for the fit (x_i and y_i) are taken as the volume fractions ϕ_A and activity a_A of absorbate. The parameters (p,q, etc.) on which F depends correspond to the five interaction parameters. The differentials required for the fit are:

$$F'x_i = (\partial F/\partial a_A) = c_1 + 2c_2a_A + (1/a_A)$$

$$F'y_i = (\partial F/\partial \phi_a) = -(1/\phi_A) - (1/x_A) + 2(\phi_A-1)\chi + (1-\phi_A)^2$$
$$\{[\phi_B/(\phi_A+\phi_B)]^2[\chi'_{AB}/(\phi_B+\phi_C)] + [\phi_C/(\phi_A+\phi_C)]^2[\chi'_{AC}/(\phi_B+\phi_C)]\}$$

F'_p, F'_q etc. are given by the partial differentials of F with respect to the interaction parameters

$$(\partial F/\partial \chi^\circ_{AB}) = (1-\phi_A)\phi_B \; ; \; (\partial F/\partial \chi'_{AB}) = [\phi_A/(\phi_A+\phi_B)][\partial F/\partial \chi^\circ_{AB}]$$

$$(\partial F/\partial \chi_{BC}) = -\phi_B\phi_C$$

$$(\partial F/\partial \chi^\circ_{AC}) = (1-\phi_A)\phi_C \; ; \; (\partial F/\partial \chi'_{AC}) = [\phi_A/(\phi_A+\phi_C)][\partial F/\partial \chi^\circ_{AC}]$$

The initial estimates of χ°_{AB}, χ°_{AC} and χ_{BC} were found from the application of equation (3.24) to the middle points of the isotherms for the separate absorbents and the mixture (or the equimolar mixture if more than one was used) and those for χ'_{AB} and χ'_{AC} were set to zero.

The analysis described in the previous Section was then applied to the data to calculate the best fit values of the interaction parameters. The equations used above describe the fit for mole fraction based activity coefficients. The same method can be applied to volume fraction based values for use with polymer absorbents with appropriate adjustment of the expressions used. The computer program 'FLO-HUG-TERNARY' used for the calculation is described and reproduced in Appendix II.

3.6. PURE COMPONENT PROPERTIES

The properties of the absorbates required for the application of the methods described in this Chapter were obtained from literature sources. The values and their sources are listed in Table 3-1.

Similarly the required properties of the absorbent samples are shown in Table 3-2.

Key to Table 3-1

a. Antoine constants from Ref. 142
b. Antoine constants from Ref. 143
c. Antoine constants from Ref. 144
d. Antoine constants from Ref. 145
e. Extrapolated from data of Ref. 146
f. Ref. 147
g. Ref. 148
h. Ref. 149
i. Ref. 150
j. Ref. 151
k. Calculated from densities and molecular weights
l. Ref. 152

TABLE 3-1: PROPERTIES OF PURE ABSORBATES

ABSORBATE	TEMPERATURE /°C	p°/torr	$-B^{e}$ /dm^3 mol^{-1}	DENSITY /g cm^{-3}	MOLAR VOLUME^{k} /cm^{3}mol^{-1}	MOLECULAR WEIGHT^{l}	ν* /cm^3 g^{-1}
n-Pentane	30	612·39^a	1·147	0·6165^f	117·03	72·149	
n-Hexane	25	150·42^a	1·935	0·6549^g	131·59	86·177	1·1544^g
n-Hexane	30	185·86^a	1·845	0·6502^g	132·54	"	1·1565^g
n-Hexane	35	228·89^a	1·758	0·6457^g	133·46	"	1·1576^g
n-Heptane	30	58·07^a	2·721	0·6753^f	148·39	100·23	
Benzene	25	94·90^a	1·478	0·8738^h	89·40	78·113	0·8860^h
Benzene	30	118·76^a	1·492	0·8684^h	89.95	"	0·8885^h
Benzene	35	147·87^a	1·357	0·8632^h	90·50	"	0·8910^h
Cyclohexane	25	97·29^a	1·717	0·7738^i	108·76	84·161	1·0012^i
Cyclohexane	30	121·15^a	1·702	0·7692^i	109·41	"	
Ethyl Acetate	30	119·17^b	2·040	0·8878^j	99·24	88·106	
Chloroform	30	240·80^c	1·160	1·4705^j	81·18	119·378	
Dichloromethane	30	519·83^d	0·810	1·3071^j	64·98	84·933	

TABLE 3-2: PROPERTIES OF PURE ABSORBENTS

ABSORBENT	TEMPERATURE /°C	MOLECULAR WEIGHT	DENSITY /g cm^{-3}	MOLAR VOLUME^{f} /ℓ mol^{-1}	CHARACTERISTIC VOLUME /cm^{3} g^{-1}
DNP	30	418·62^{a}	0·9630^{d}	0·4374	0·8705^{d}
SQ	30	422·82^{a}	0·8017^{d}	0·5274	1·0336^{d}
PDMS I	30	3350^{b}	0·9523^{b}	3·518	0·8489^{g}
PDMS II	30	6550^{b}	0·9571^{b}	6·843	0·8462^{g}
PDMS III	30	15650^{b}	0·9618^{b}	16·27	0·8432^{g}
PDMS IV	30	26000^{b}	0·9643^{b}	26·96	0·8415^{g}
PDMS V	25	89000^{c}	0·9698^{e}	92·18	0·8395^{e}
PDMS V	30	" ^{c}	0·9654^{e}	92·18	0·8410^{e}
PDMS V	35	" ^{c}	0·9610^{e}	92·18	0·8424^{e}

Key to Table 3-2

a. Ref. 152

b. Chapter 2 of this Thesis

c. Ref. 131

d. Ref. 122

e. Ref. 134

f. Calculated from molar volumes and molecular weights

g. Ref.153

3.7. EXPERIMENTAL ERRORS IN ABSORPTION ISOTHERMS

The main object in the majority of the work described in this Thesis was to use the static results obtained at finite concentrations to extrapolate properties to infinite dilution. For this, and in comparing results to those of other workers, it is important to have an estimate of the accuracy of these properties and to achieve this the effects of experimental error on the results must be considered.

As discussed in Chapter 2, pressure measurements were made to a precision of ±0·01 torr. The weight of absorbed vapour was measured to ±0·01 mg on the QB balance and to ±0·10 mg on the MS microbalance but, since the latter employed an approximately ten-fold larger sample, the relative precision was similar although this depended to a certain extent on the liquid loadings of the samples. Higher loadings led to greater absorption and therefore to a greater relative precision. The accuracy of the results changed depending on the total pressure and absorbed weight and so were not constant across the concentration range.

To estimate the experimental errors, the isotherm for n-hexane in PDMS V at 30°C on the QB microbalance was used as an example and the experimental error of the results at the lowest and highest concentrations considered. The first point was at a pressure of ~10 torr and a weight of ~3 mg while the corresponding values for the highest result were ~79 torr and ~30 mg respectively. Approximately 300 mg of polymer was used.

Assuming the densities to be exact (see later) the usual equations derived from the standard treatment of the calculus of errors[154] were applied to equation (3.3) and suggested errors in the volume fraction ϕ_1 of 0·4% and 0·05% for the two points. The value of p° calculated from Antoine constants should be accurate to ±0·1 torr and combining this with the errors in pressure and concentration leads to uncertainties of 0·55% and 0·08% in the activity coefficients γ_1^V. Errors in the fugacity corrections were found to have negligible effect. Continuing the calculations through led to the experimental errors listed in Table 3-3.

TABLE 3-3: PERCENTAGE EXPERIMENTAL ERRORS FOR PDMS V-n-HEXANE AT 30°C

	ϕ_1	γ_1^V	$\ln\gamma_1^V$	χ
LOWEST CONCENTRATION	0·46	0·55	0·40	0·94
HIGHEST CONCENTRATION	0·05	0·08	0·04	0·40

Thus, on extrapolation to infinite dilution the assumption of a 0·5% error in $\ln^{\infty}\gamma_1^V$ and 1% in χ^{∞} would appear to be reasonable. Thus, for this particular system the errors amount to ±0·005 in $\ln\gamma^{\infty}$ and ±0·004 for χ^{∞}. The same calculation applied to other PDMS-absorbate systems showed these to be typical of the expected errors so that in the discussion of results in the following Chapters an experimental error of ~1% in the infinite dilution interaction parameter will be assumed.

The use of an interactive computing system such as the micro-computer on which these results were calculated allowed ready identification of the major sources of error. It was a simple matter to run the program with each expected error included in turn to determine the effect on the calculated values of $\ln^{\infty}\gamma_1^V$ and χ^{∞}. This was done for the above system with the results shown in Table 3.4.

TABLE 3-4: SOURCES OF EXPERIMENTAL ERRORS FOR n-HEXANE-PDMS V AT 30°C

VARIABLE	ESTIMATED ERROR	PERCENTAGE ERROR $\ln^{\infty}\gamma_1^V$	PERCENTAGE ERROR χ^{∞}
p_1°	±0·1 torr	0·03	0·10
B	±0·05 $dm^3\ mol^{-1}$	0·02	0·07
ρ_1	±0·0002 $g\ cm^{-3}$	0·02	0·07
ρ_2	±0·0002 $g\ cm^{-3}$	0·01	0·05
w_2	±0·2 mg	0·05	0·19

It was found that errors of ±5000 in the polymer molecular weight, 0·1 $dm^3\ mol^{-1}$ in the polymer molar volume and 0·02°C in temperature caused no effect (the effect of temperature in p_1^o having been considered in Table 3-4).

Inspection of the table shows that the major source of error is in the measurement of the amount of polymer used, w_2, this accounting for a large part of the observed error. The error in p_1^o also causes a significant contribution but the others are fairly small in comparison to the total errors expected.

Although details will not be presented here, the same calculation was applied to the absorption results to be discussed in Chapters 8 and 9. This showed that the same level of experimental error, i.e. around 0·5%, would be applicable for the mole fraction based activity coefficients and partition coefficients that were measured.

3.8. CALCULATION OF PHASE LIMITS FROM SPECTROSCOPY

From Section 2.12. the peak area in a hydrogen nmr spectrum, measured by its integral, is proportional to the number of hydrogen atoms giving rise to the signal. This may be used to measure the concentration of a component as follows.

Consider two components; A having H_A hydrogen atoms per molecule of molecular weight M_A and giving rise to a peak integral I_A, and similarly for B. Then for a mixture of w_A of A and w_B of B (w is the weight),

$$I_A \propto (w_A/M_A)\, H_A \qquad ; \qquad I_B \propto (w_B/M_B)\, H_B$$

Inserting proportionality constants K and dividing,

$$\frac{I_A}{I_B} = \left(\frac{K_A\, H_A\, M_B}{K_B\, H_B\, M_A}\right) \frac{w_A}{w_B} = K_{AB}\ \frac{w_A}{w_B} \qquad (3.26)$$

since all terms in the bracket are constant. By measuring I_A/I_B for a mixture of known composition, the constant K_{AB} can be calculated.

To check this, three mixtures of DNP and PDMS I were made up at approximately 1:3, 1:1 and 3:1 compositions and their nmr spectra recorded. The calculated values of K_{AB} were 1·075, 1·054 and 1·062 respectively, showing that it does not depend to any great extent on composition and confirming the analysis used.

This method was applied to each of the systems studied (see Chapter 6) except for PDMS V which was not used due to shortage of material. A calibration spectrum was recorded using a mixture of known composition and the technique outlined in Chapter 2. This was used to calculate the constant K_{AB} and this value used in conjunction with the spectra of the mixtures under study to calculate the ratio of the concentrations of the two components in the phases (w_1/w_2). This was converted to a percentage by weight of polymer, W_2, using

$$\begin{aligned} W_2 &= 100\ w_2/(w_1+w_2) \\ &= 100/(1+w_1/w_2) \qquad (3.27) \end{aligned}$$

The results are shown in Table 3-5.

TABLE 3-5: PHASE LIMITS FOR DNP-PDMS AND SQ-PDMS SYSTEMS AT 30°C

SYSTEM	K_{AB}	I_1/I_2	w_1/w_2	W_2
DNP-PDMS I	2·463	0·689	0·279	78·1
DNP-PDMS II	2·035	0·509	0·250	79·9
DNP-PDMS III	2·205	0·453	0·211	82·9
DNP-PDMS IV	2·956	0·569	0·193	83·9
SQ-PDMS I	3·408	2·100	0·616	61·9
SQ-PDMS II	3·369	1·427	0·424	70·2
SQ-PDMS III	3·656	1·144	0·313	76·2
SQ-PDMS IV	4·181	0·894	0·214	82·4

Chapter 4

Determination of Interaction Parameters in PDMS Solutions for Comparison with GLC Results

As discussed in the Introduction to this Thesis, GLC has been found to be a useful technique for the study of physicochemical properties of solution. The use of GLC with polymeric stationary phases has been developed by Guillet and co-workers[155] and has been shown to be capable of providing information on a range of polymer properties. Guillet and Smidsrod[156] were the first to use GLC to measure activity coefficients and heats of solution for polymer systems. There had been doubts about the validity of the GLC technique when applied to polymers but Patterson[136] *et al.* described ways of overcoming these. Newman and Prausnitz[157] found reasonable agreement for the measured interaction parameters of polystyrene and poly(isobutylene) with those from static results, although their values were slightly lower. Summers and co-workers[158] found similar agreement of their results for PDMS with the static values of Patterson *et al.*[159] However, Lichtenthaler and co-workers[160,161] obtained GLC results for PDMS giving specific retention volumes 6-12% higher leading to χ values lower by 0·06 - 0·11 which is outside the experimental error of the technique. A combined study by these groups[162] showed notable discrepancies between static and GLC results and also between the retention volumes obtained in inter- and intra-laboratory comparisons. This involved the exchanging of PDMS samples and pre-packed columns. and showed that results obtained on a particular column agreed to within 3%, although one laboratory consistently produced results about 2% higher than the other. However, results from columns prepared in the different laboratories with the same polymer were divergent by up to 10%, suggesting the column preparation technique to be the most important of the variables investigated. The GLC values of Hammers *et al.* for PDMS are also lower than corresponding static results. Patterson *et al.*[165] also found disagreement in GLC and static results for χ in polyethylene and, with Guillet,[166] showed that potential errors in determining the amount of polymer in the column could cause large differences in results. Despite the large amount of work done using GLC with polymer systems, the reason for these discrepancies has never been fully resolved.

Thus, it was felt to be important to establish whether the GLC and static methods would give identical results or, if not, whether the previously noted differences with PDMS were peculiar to this system or a manifestation of more fundamental differences. Previous static results for PDMS had been obtained on McBain-Bakr balances and so lacked precision at low concentrations. Isotherms were therefore measured on the Quartz Beam vacuum microbalance in order to give a reliable extrapolation for comparison with GLC results at infinite dilution. A joint study was initiated to compare the results obtained with those of R.J. Laub and co-workers in the U.S.A. on a sample of polymer taken from the same batch using GLC.

Preliminary comparison of static results[131] with GLC results extrapolated from higher temperatures[167] suggested that there were significant differences but that, as previously suggested, they could be explained by difficulties in determining the amount of polymer used. This is usually measured either, as recommended by Guillet, by calcination of the sample or by solvent extraction. The former technique is inappropriate in this case due to the siloxane backbone of the polymer. Hence the GLC samples in this study were analysed by repeated solvent extraction of polymer from the solid support held in a soxhlet thimble, taking care to account for extractable materials in the thimble and support, until constant weight was achieved. The microbalance samples were ~1·8 g in weight containing ~300 mg of polymer and would have been rather small for this kind of analysis so difficulties in measuring the weight of polymer were overcome by changing the method of sample preparation as outlined in Section 2.6. to ensure that no polymer could be lost. After determination of each absorption isotherm the sample was allowed to re-equilibrate with the atmosphere and reweighed. In no case was there a change of more than 0·1 mg in the sample weight.

The isotherms for the absorption of a number of compounds into the highest molecular weight PDMS sample were measured using the techniques described in Chapter 2 and are listed in Table AI-1 in Appendix I. Infinite dilution activity coefficients and interaction parameters were calculated using the methods of Section 3.2. The results are shown in Table 4-1 together with those of Hooker[131] determined using the original method of sample preparation. Also shown are the GLC results of Laub and co-workers.

TABLE 4-1: INFINITE DILUTION INTERACTION PARAMETERS AND ACTIVITY COEFFICIENTS FOR PDMS V AT 30°C

ABSORBATE	STATIC				GLC	
	$^{\infty}\gamma_1^{V*}$	$^{\infty}\gamma_1^{V}$	$^{\infty}\gamma_1^{W}$	χ^{∞}	$^{\infty}\gamma_1^{W}$	χ^{∞}
n-Pentane	3·861	3·884	6·082	0·3580	6·092	0·360
n-Hexane	4·039	4·036	5·991	0·3965	6·023	0·402
n-Heptane	4·250	4·286	6·128	0·4569	6·135	0·458
Cyclohexane	4·246	4·291	5·386	0·4578	5·378	0·456
Benzene	5·732	5·799	6·448	0·7588	6·404	0·752
Chloroform		5·210	3·421	0·6515	3·366	0·640
Dichloromethane		6·735	4·975	0·9081	4·937	0·901

*From Reference 131.

The results for the static isotherms were calculated in terms of volume fraction for the reasons discussed in Chapter 3. These activity coefficients are compared in Table 4-1 and may be seen to agree to within an average of 0·74%, the maximum deviation being 1·15%. This is within the experimental error of the method as determined in Section 3.7. and therefore shows that the original sample preparation technique did not, in fact, cause large errors in the weight of polymer used.

Patterson *et al.*[136] have commented that the most convenient basis on which to calculate GLC results is that of weight fraction and these are shown in Table 4-1 along with those derived from the static results. The interaction parameters are also shown. Comparison of these results shows that the activity coefficients agree to an average of 0·35%, the only system showing a greater difference than 1% being chloroform. The interaction parameters agree to within an average of 0·84% with chloroform again being the most divergent but even here the difference is 1·75% which is within the combined experimental error of the techniques and shows the agreement between the two methods to be very good. It should be noted that these figures differ slightly from those in the original publication[168] since the difference between the GLC and the average of the two static results was considered there. Also the results for the two chlorinated hydrocarbons were not obtained until after the original work had been completed and so were not included in that comparison. A discussion of the agreement between the static results and those of other workers will be deferred until Chapter 5.

4.1. VARIATION OF PROPERTIES WITH POLYMER LOADING

One of the original objections to the use of GLC to study solution thermodynamics was that it was not known whether spreading the stationary phase as a thin film on the solid support would lead to differences from the properties of the bulk liquid,[4] and this was suggested as a cause of the discrepancy between static and GLC results in polymers. Prausnitz *et al.*[169] used the GLC technique employing capillary columns with the polymer coated onto the walls of a column rather than a solid support. This results in a thicker liquid film and they found significant differences between interaction parameters calculated from results on these columns and those on packed columns, though the effect was smaller with PDMS than other polymers. They concluded "polymer-solvent interactions for thin polymer films are not the same as those in bulk polymer." However, Braun and Guillet[170] doubted the values of film thicknesses quoted and ascribed the differences to non-attainment of equilibrium with the relatively high flow rates and film thicknesses used, rather than to different sorption processes being present. Lipatov and Nesterov[171] also found significant variation of properties with film thickness for a number of polymers. Commonly, when packed columns are used in GLC they contain relatively small amounts of polymer, liquid loadings (i.e. the percentage of stationary phase that is polymer) of less than 10% being usual, e.g. the 4-8% used by Laub *et al.* for the previously discussed work.[168] It is known that, particularly with more polar compounds, variation of liquid loading can result in a variation of retention properties[4] and this has also been suggested for hydrocarbon samples, although the effects should be smaller, due to the effects described in Section 1.13.

Using PDMS as the stationary phase, Summers *et al.*[158] found no change of retention for loadings greater than 7·7% but significantly lower results for a loading of 6·2% and suggested that this was due to adsorption on uncovered support, despite finding no detectable retention on a column of bare 'Chromosorb' support material. Ashworth[129] studied the adsorption of benzene on bare 'Celite', the solid support employed here, and at a relative pressure (p/p°) of 0·5 found an adsorption of 0·28 mg/g support. For the approximately 20% loaded samples employed in this work, there would be about 1·3 - 1·4 g of solid support leading to a maximum adsorption of about 0·4 mg or 1% of the total vapour absorbed by the PDMS sample at $p/p^{\circ} = 0{\cdot}49$. However, it should be stressed that this represents a maximum value and in reality many of the more active sites on the solid would be covered by the polymer and these values would be considerably reduced.

It was felt that, of the systems initially studied, benzene-PDMS would show the greatest tendency for adsorption effects. To determine the magnitude of these, absorption isotherms were recorded over a series of liquid loadings and these are listed in Table AI-2 of Appendix I. The results are shown as plots of interaction parameter versus concentration in Figure 4-1 and the infinite dilution results are summarised in Table 4-2.

As can be seen, changing from loadings of about 6% to 20-30%, as more commonly used for static measurements, can cause significant differences in the measured values. The isotherms for 20% and 30% loadings are well within experimental error suggesting that in these cases bulk solubility is the major retention process and that adsorption effects are negligible. However, the results for the 10% and 20% loaded samples are significantly different and those for the 6% sample even lower. The trend in $\ln{}^{\infty}\gamma_1^{V}$ values may be explained qualitatively since any adsorption effect would cause an apparent increase in the weight of vapour absorbed at a given pressure leading to a higher apparent concentration.

Thus $\phi^{(real)} < \phi^{(app)}$

and since $\ln\gamma_1^V = \ln(p_1/p_1^\circ\phi_1)$

it follows that $\ln\gamma_1^{V(app)} < \ln\gamma_1^{V(real)}$

TABLE 4-2: EFFECT OF LIQUID LOADING ON INFINITE DILUTION PROPERTIES OF BENZENE PDMS V AT 30°C

LIQUID LOADING/%	$\ln^\infty\gamma_1^V$	χ^∞
6·22	1·7518	0·7528
9·34	1·7543	0·7553
20·31	1·7578	0·7588
28·84	1·7581	0·7591

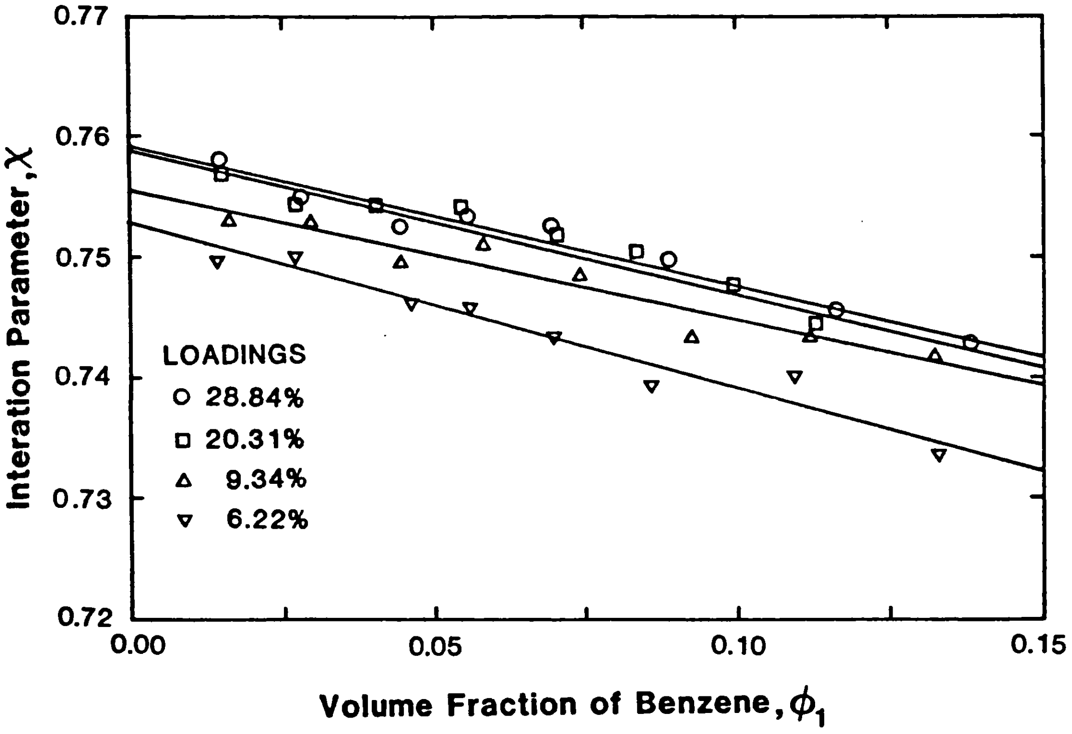

FIGURE 4-1: EFFECT OF LIQUID LOADING ON ABSORPTION OF BENZENE BY PDMS V AT 30°C

Since lower loadings will usually result in a higher surface area of liquid exposed to the vapour and thinner films, the possibility of adsorption effects would be enhanced at lower loadings, leading to a decrease in the observed activity coefficient and this is seen in the observed trend. The table shows that differences of >1% can be caused by neglect of liquid loading effects and, while small, this may partly explain the non-agreement of different sets of results. In particular it should be noted that the χ^{∞} value of 0·7528 for a 6·2% loaded sample agrees very well with that of 0·752 obtained by Laub *et al.* on a column of 4-8% loading. The measurements by Summers and co-workers[158] were the average of a number of results quoted as agreeing to within 1%. With this precision the differences between results on samples with loadings >10% would not have been detectable and so adsorption effects may occur at higher loadings than they suggested. In view of this, and their finding of negligible retention on bare support, their conclusion of adsorption onto exposed solid would appear to be in error since a loading of ~10% would cover all the available support. However, the results may be explained by the assumption of other adsorption processes and this will be returned to later in Chapter 8.

4.2. VARIATION OF PROPERTIES WITH MOLECULAR WEIGHT

The possibility that different polymer samples might have different properties is another factor which must be considered when comparing the results of various workers. The most obvious difference between samples of the same polymer is in the chain length and molecular weight. The static and GLC results described here were obtained on a polymer of molecular weight 89000; Summers *et al.* and Lichtenthaler *et al.* employed samples of ~5 x 10^5 and Hammers *et al.* ~30000. Patterson and co-workers[172] found a significant difference of χ^{∞} between two PDMS samples which they ascribed to molecular weight and Gallin[173] found variations of up to 10% in retention volumes with molecular weights of 3700–30000, both these studies being at 60°C. Conversely, Muramoto[153] found that the interaction parameter for methyl ethyl ketone in PDMS at 30°C was independent of molecular weights above ~4600. Thus it was decided to investigate the effect of polymer molecular weight on the infinite dilution properties.

However, prior to this absorption isotherms were measured for benzene in the lowest molecular weight sample used (PDMS I) to determine whether the adsorption effects noted above were enhanced at lower molecular weights. The results are tabulated in Table AI-3 of Appendix I and plotted in Figure 4-2.

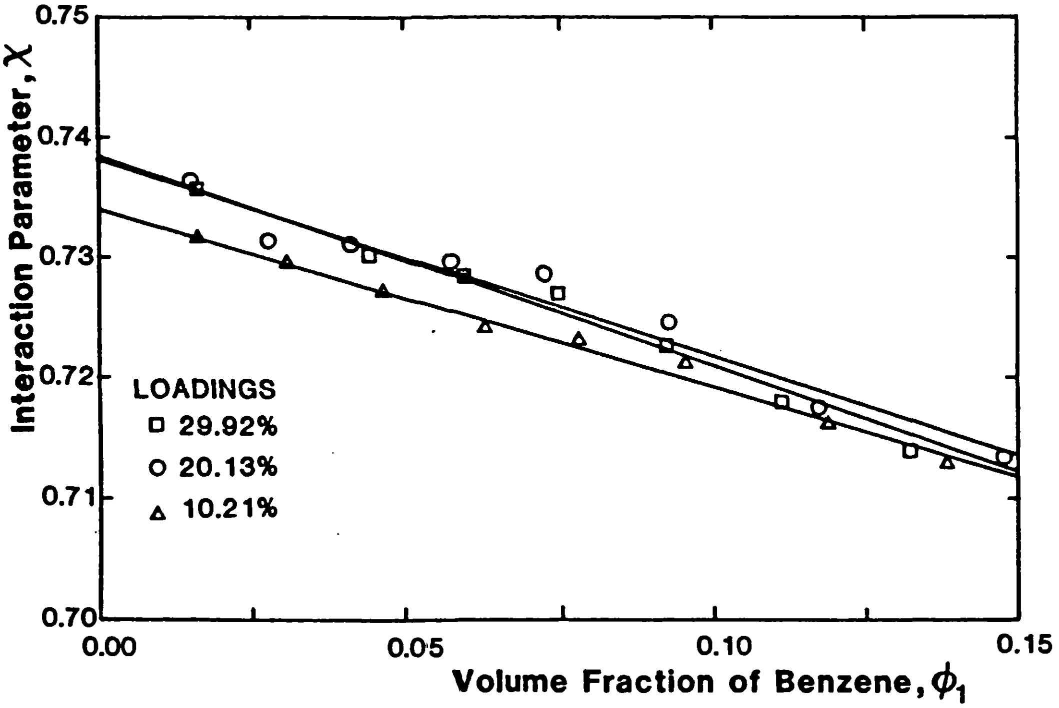

FIGURE 4-2: EFFECT OF LIQUID LOADING ON ABSORPTION OF BENZENE BY PDMS I AT 30°C

The infinite dilution values are summarised in Table 4-3.

A similar trend is found to that observed with the higher molecular weight polymer with lower values obtained at lower loadings.

Again the 20% and 30% isotherms indicate that adsorption effects are unimportant at high loadings, but the results for the 10% sample are significantly lower. The effects are of a similar magnitude for both polymer samples.

TABLE 4-3: EFFECT OF LIQUID LOADING ON INFINITE DILUTION PROPERTIES OF BENZENE-PDMS I AT 30°C

LIQUID LOADING/%	$\ln {}^{\infty}\gamma_1^V$	χ^{∞}
10·21	1·7074	0·7340
20·13	1·7119	0·7383
29·22	1·7127	0·7385

To investigate the effect of molecular weight on the systems studied absorption isotherms were measured for four other polymer samples of varying molecular weight in addition to the PDMS V used for the original study. The results are shown in Tables AI-4 and AI-5 in Appendix I and as plots of interaction parameter against concentration in Figure 4-3. Activity coefficients and interaction parameters extrapolated to infinite dilution are shown in Table 4-4. The results show that varying the molecular weight in the range 3350-89000 can cause differences in χ^{∞} of 0·026 (~7%) in hexane values and 0·02 (~3%) for benzene, which are well outside the experimental error of the method.

However, the PDMS samples in the studies detailed above which had originally shown disagreement had molecular weights in the range 30000-500000. Figure 4-4 shows the variation of χ^{∞} with logarithm of molecular weight. The logarithmic scale is not meant to imply any relationship but was used to give a more convenient scale. The figure

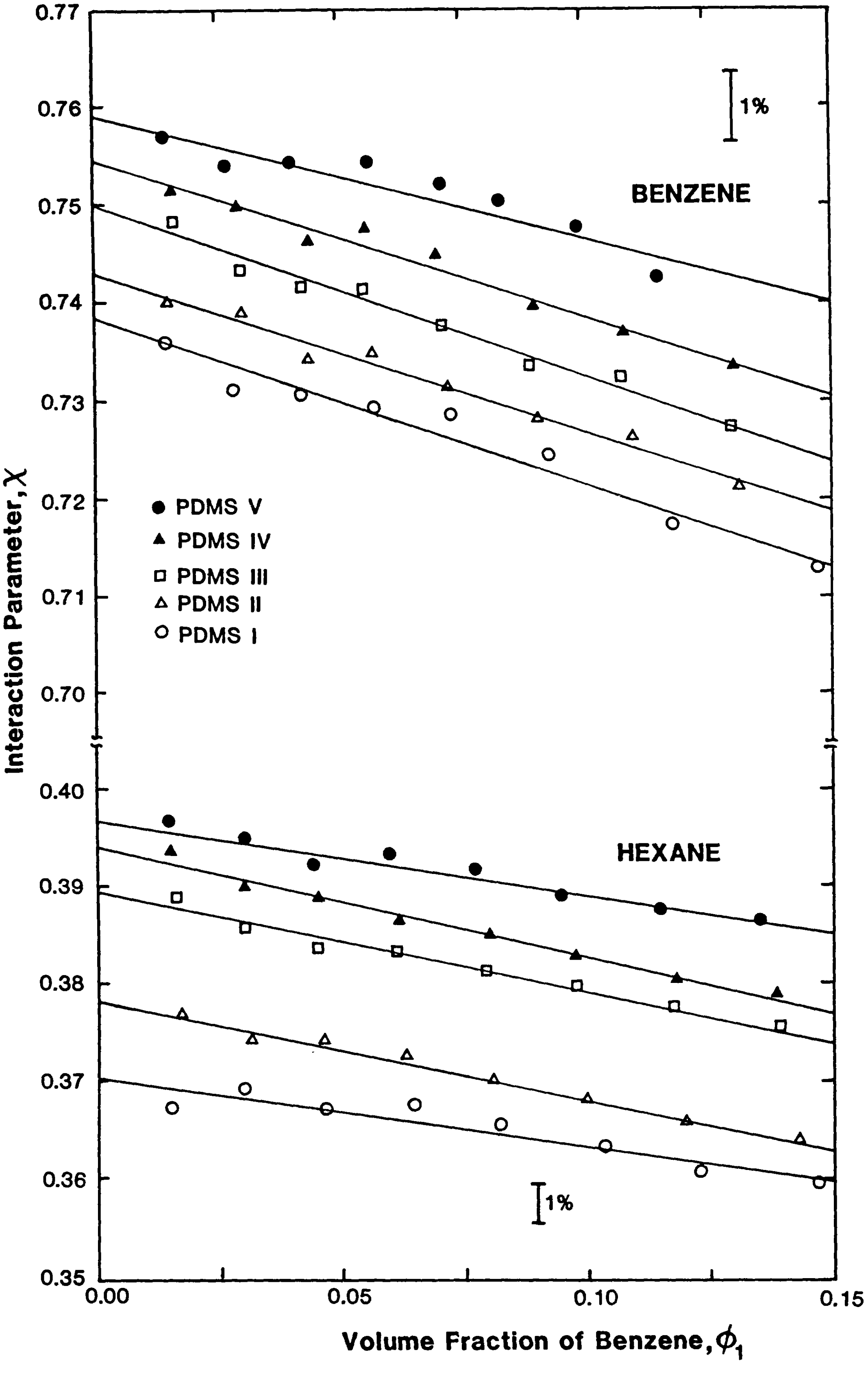

FIGURE 4-3: EFFECT OF MOLECULAR WEIGHT ON INTERACTION PARAMETERS FOR PDMS SOLUTIONS IN BENZENE AND HEXANE AT 30°C

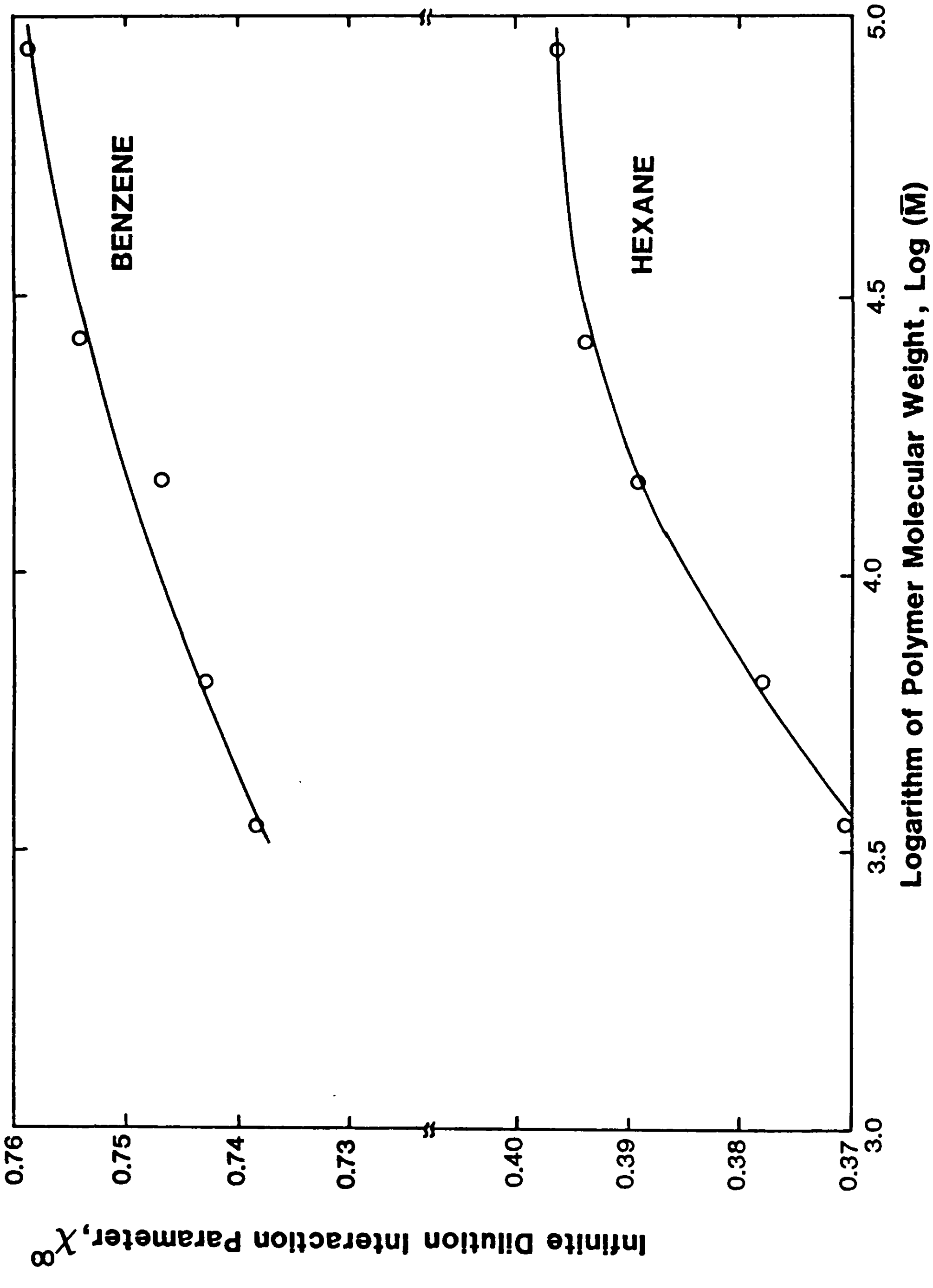

FIGURE 4-4: EFFECT OF MOLECULAR WEIGHT ON INFINITE DILUTION INTERACTION PARAMETERS FOR PDMS SOLUTIONS IN BENZENE AND HEXANE AT 30°C

TABLE 4-4: EFFECT OF POLYMER MOLECULAR WEIGHT ON INFINITE DILUTION PROPERTIES OF PDMS AT 30°C

POLYMER	HEXANE		BENZENE	
M.Wt.	${}^{\infty}\gamma_1^{V}$	χ^{∞}	${}^{\infty}\gamma_1^{V}$	χ^{∞}
3350	3·7195	0·3704	5·5439	0·7383
6550	3·8914	0·3780	5·6387	0·7428
15650	3·9797	0·3893	5·7208	0·7469
26000	4·0110	0·3939	5·7602	0·7543
89000	4·0358	0·3965	5·7990	0·7588

shows that for molecular weights above about 30000 there is a very small variation in χ^{∞} which is of the order of the experimental error expected. Thus, within the ranges generally used for this type of study, the polymer molecular weight would not be an important factor in the values of χ^{∞} obtained.

4.3. CONCLUSIONS

The results of this work and the GLC values of Laub *et al.* on an identical sample of polymer have been shown to agree within experimental error and differences noted between the two techniques appear to be due to experimental conditions rather than to any fundamental effects. The main cause of these differences may be attributed to difficulties in determining the amount of polymer used. However, perhaps it should be stressed that these conclusions should only be applied to this system and before it could be extended to general applicability a study of more systems, particularly of a more polar nature should be undertaken.

Variations in the molecular weight of the polymer samples used have been shown to cause appreciable differences in values of interaction parameters and activity coefficients at infinite dilution, but in the range used in previous studies by other workers the variation is insufficient to explain the apparent differences found. However, it would be as well to consider the possibilities of differences in results arising from this source when comparing results on different polymer samples. Also to be considered, particularly in GLC when a supported polymer is used, is the loading of polymer. Ideally loadings of around 20% should be used to ensure that bulk solubility is the only sorption process taking place but if, as is common in GLC studies, lower loadings are used, care should be taken to account for any possible errors arising from adsorption effects.

Chapter 5

The Use of the Magnetic Suspension Vacuum Microbalance for the Study of Polymer Solutions

As was mentioned in Section 2.4., the potential for the use of the Magnetic Suspension vacuum microbalance stems from the precision with which it may be used combined with the high relative solvent pressures that may be employed, allowing a wide range of concentrations to be covered. The development of the present apparatus was carried out by Ashworth[126] who showed that results very similar to those using other microbalances could be obtained for the hexane-squalane system. In order to assess the use of the MS balance for the study of polymer solutions, PDMS was chosen as a 'test' polymer. There were two main reasons for this choice. Firstly, as was discussed in Chapter 4, the thermodynamic properties of PDMS are well documented in the literature and so gave a good basis for comparing the balance with other methods. Secondly, it is one of the few high molecular weight polymers that is a liquid around room temperature to give a rapid attainment of equilibrium and ensure that the period required to record an isotherm to high pressures is not too long.

The experimental methods described in Chapter 2 were used to measure absorption isotherms for benzene, cyclohexane and hexane in PDMS V and activity coefficients and interaction parameters were calculated. Results for the first two absorbates were compared with those of other workers and, as a more stringent test of the balance, the temperature dependence of the absorption of benzene and hexane was studied and heats of mixing calculated for comparison with calorimetric studies. The results are given in Tables AI-6 to AI-8 in Appendix I.

5.1. COMPARISON OF MICROBALANCES

Previous experience had shown that the interaction parameters were more susceptible to small variations in experimental measurements than the activity coefficients, so the comparisons were based on this quantity.

The results for the variation of interaction parameter with concentration for benzene and hexane in PDMS V at 30°C on the MS and QB microbalances are shown in Figure 5-1. (Only the highest molecular weight polymer sample was employed in the work described in this Chapter so that the designation 'V' will be dropped for the discussion.)

For benzene, both the results from 10% and 20% loaded samples on the QB balance are shown. The MS balance results were obtained using samples of 10% loading. For the greater part of the concentration range studied the results agree to within 1%. The infinite dilution results for the 10% loaded samples with benzene are 1·7576 and 1·7545 for $\ln^{\infty}\gamma_1^V$ and 0·7588 and 0·7555 for χ^{∞} for the QB balance and MS balance respectively. The corresponding results for hexane are 1·3958 and 1·3950, and 0·3973 and 0·3965, again showing excellent agreement between the two sets of apparatus. In the latter case the sample loadings are different but this would not be expected to cause as large differences in this system as with benzene as the absorbate. Thus, the two microbalances give results agreeing to well within experimental error.

5.2. COMPARISON WITH OTHER WORKERS

The majority of recent polymer solution work has employed the segment fraction as the basis of calculation as outlined in Section 1.8. The absorption isotherms for cyclohexane and benzene at 25°C were analysed on this basis and are shown in Figure 5-2 as a plot of χ^* against ψ, together with the results of Patterson *et al.*[159] and Flory and Shih.[174] The former of these data sets was obtained on a polymer of molecular weight 5 x 10^5 and the latter of 1 x 10^5 and both employed McBain-Bakr quartz spring microbalances.

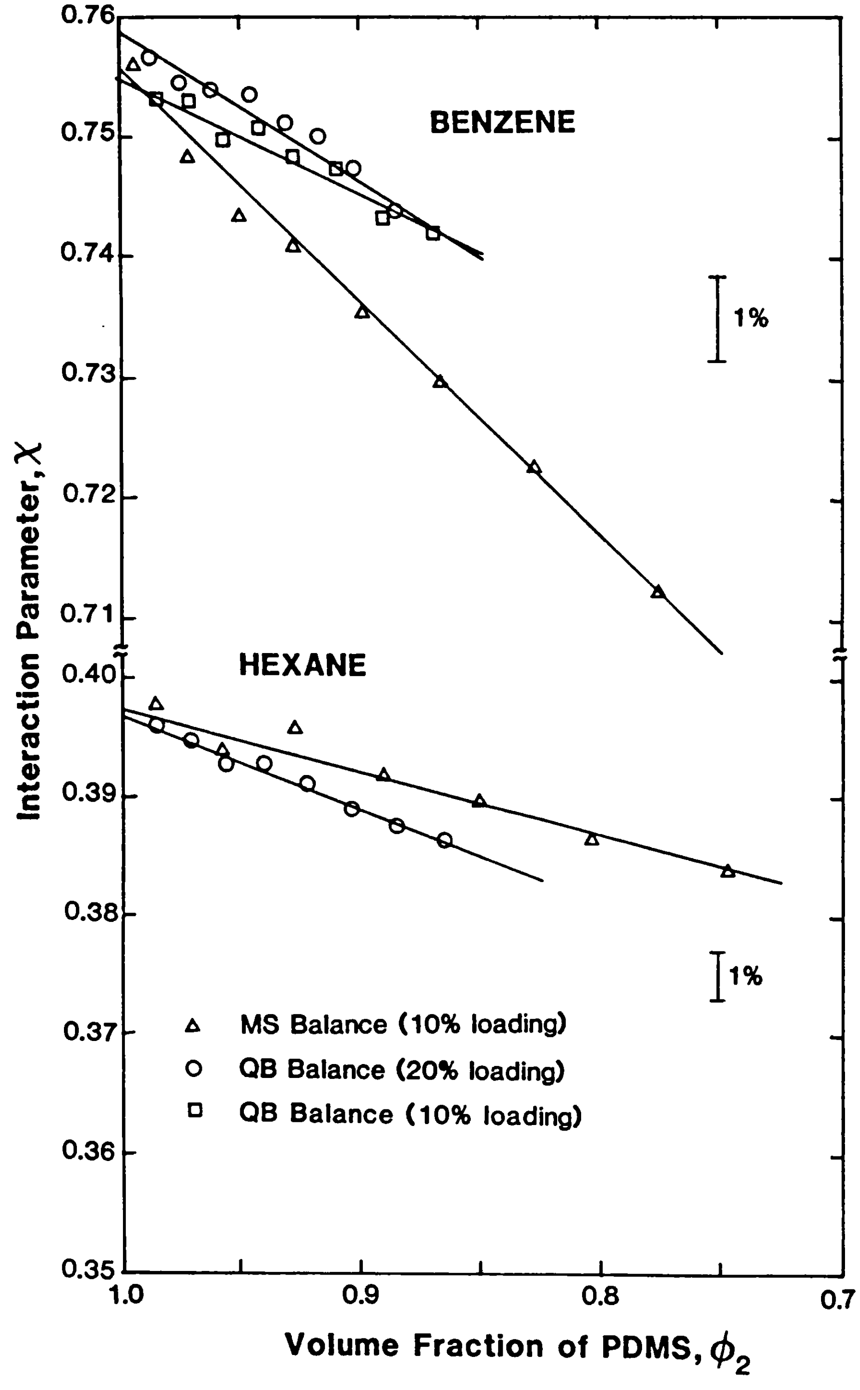

FIGURE 5-1: COMPARISON OF INTERACTION PARAMETERS OBTAINED ON THE MAGNETIC SUSPENSION AND QUARTZ BEAM MICROBALANCES AT 30°C

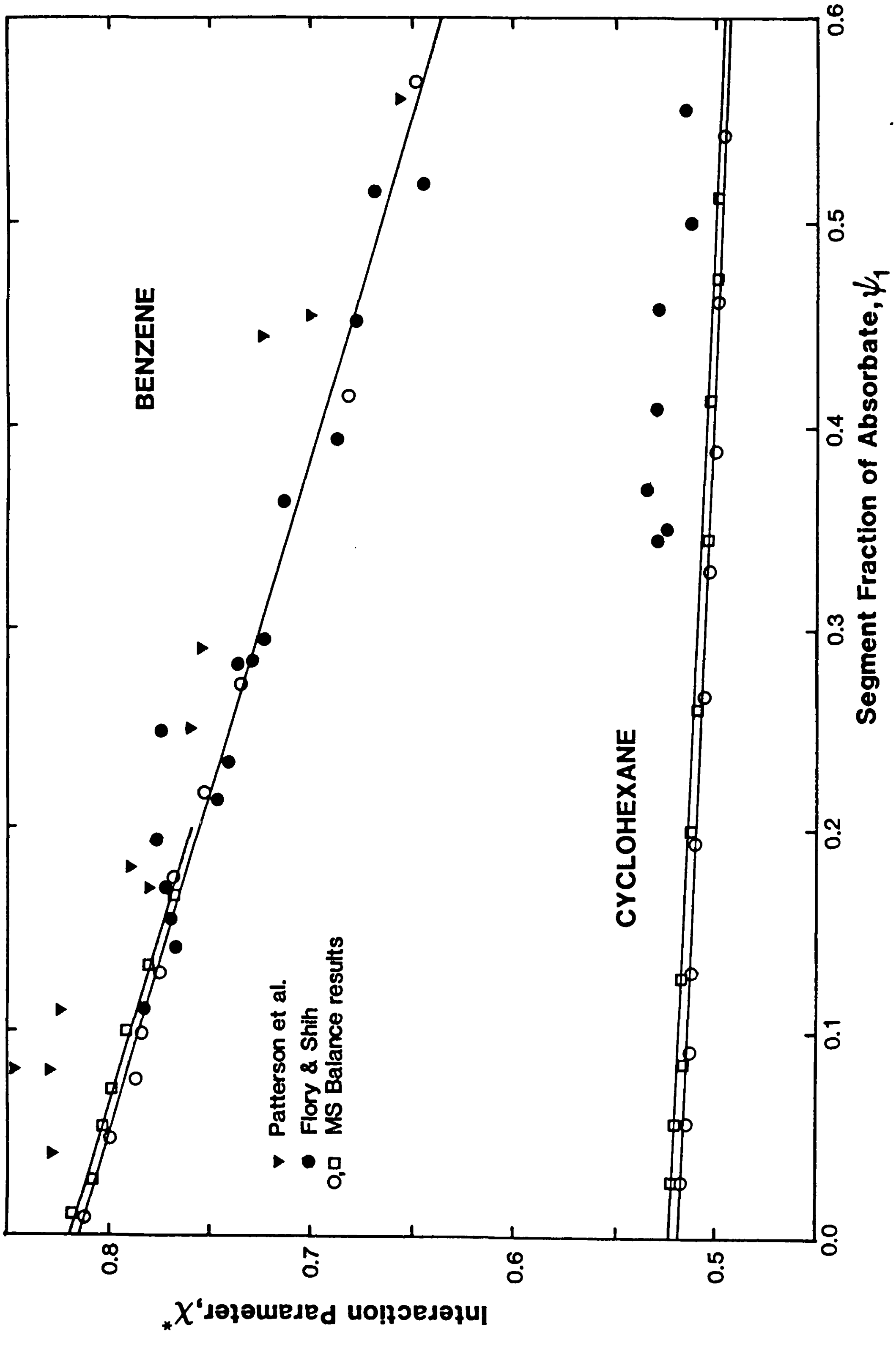

FIGURE 5-2: CONCENTRATION VARIATION OF INTERACTION PARAMETER FOR CYCLOHEXANE AND BENZENE IN PDMS AT 30°C

Two isotherms for each absorbate were determined and, as can be seen from Figure 5-2, the reproducibility of the results is within 0·004 across the concentration range which is well within the experimental error of the method. As in earlier work the relationship of χ^* with segment fraction was found to be linear with the correlation coefficients of regression as listed in Tables AI-6 and AI-7 exceeding 0·99 in each case.

The agreement between the results and those of Flory and Shih for benzene are excellent as regards both the magnitude and concentration dependence of χ^*, but those of Patterson *et al.* are slightly higher, especially at low concentrations. This may well be due to the lower precision of the McBain-Bakr balance at low absorbate pressures and weights. The MS balance results also show much less scatter due to the greater precision of this apparatus. Patterson *et al.* claim an accuracy of 0·01 to 0·05 for their interaction parameters, so that the two works do agree within experimental error, but the results from the present work are virtually an order of magnitude more precise.

For the cyclohexane isotherms the agreement with the results of Flory and Shih is not as good. There is a similar concentration dependence of χ^* but the values in the current work are 0·02 - 0·03 lower. This is outside the experimental error expected and the reason for this disagreement is not clear, especially in view of the agreement of the two sets of MS balance results. Brotzman and Eichinger[175] determined values of interaction parameters for this system at 30°C and also found their results to be lower than those of Flory and Shih. They do not show their values but give an equation for the dependence of interaction parameter on concentration calculated on a volume fraction basis which is slightly lower than the results reported here as would be expected when taking into account the temperature differences.

No vapour sorption results could be found for hexane in PDMS. (Several GLC results were discussed in Chapter 4.) Sugamiya and co-workers[176] determined χ^* at 20°C for a polymer of molecular weight 15000 in hexane using osmotic pressure measurements. This technique works at low polymer concentrations rather than the high concentrations involved in vapour sorption techniques and in the range $\psi_2 = 0{\cdot}19 - 0{\cdot}38$ they found $\chi^* = 0{\cdot}417 - 0{\cdot}420$. This can be compared to the results from the current work at a number of temperatures displayed in Figure 5-3 and, bearing in mind the differences in temperature and concentration, the results appear to be in reasonable agreement.

5.3. MEASURABLE CONCENTRATION RANGE

It had been hoped that the MS balance would allow results to be measured over the whole concentration range. However, it was found that the practical limit was around an absorbate segment fraction of 0·6. This situation is demonstrated by Figure 5-4 which is based on an absorption isotherm for cyclohexane. It can be seen that the result at $\psi_1 = 0{\cdot}54$ corresponds to a relative pressure of 0·95 and it was found that small pressure variations in this region, even those caused by small temperature fluctuations in the apparatus, can cause appreciable changes in χ^* leading to variable results. Figure 5-4 can also be used to demonstrate the very narrow range of mole fractions covered, the first result at a segment fraction of 0·026 corresponds to a mole fraction of 0·96 but a relative pressure of 0·114. Thus, a large range of relative pressures causes a reasonably large range of segment fractions but a narrow range of mole fractions, showing that the former is a better concentration scale on which to base the results.

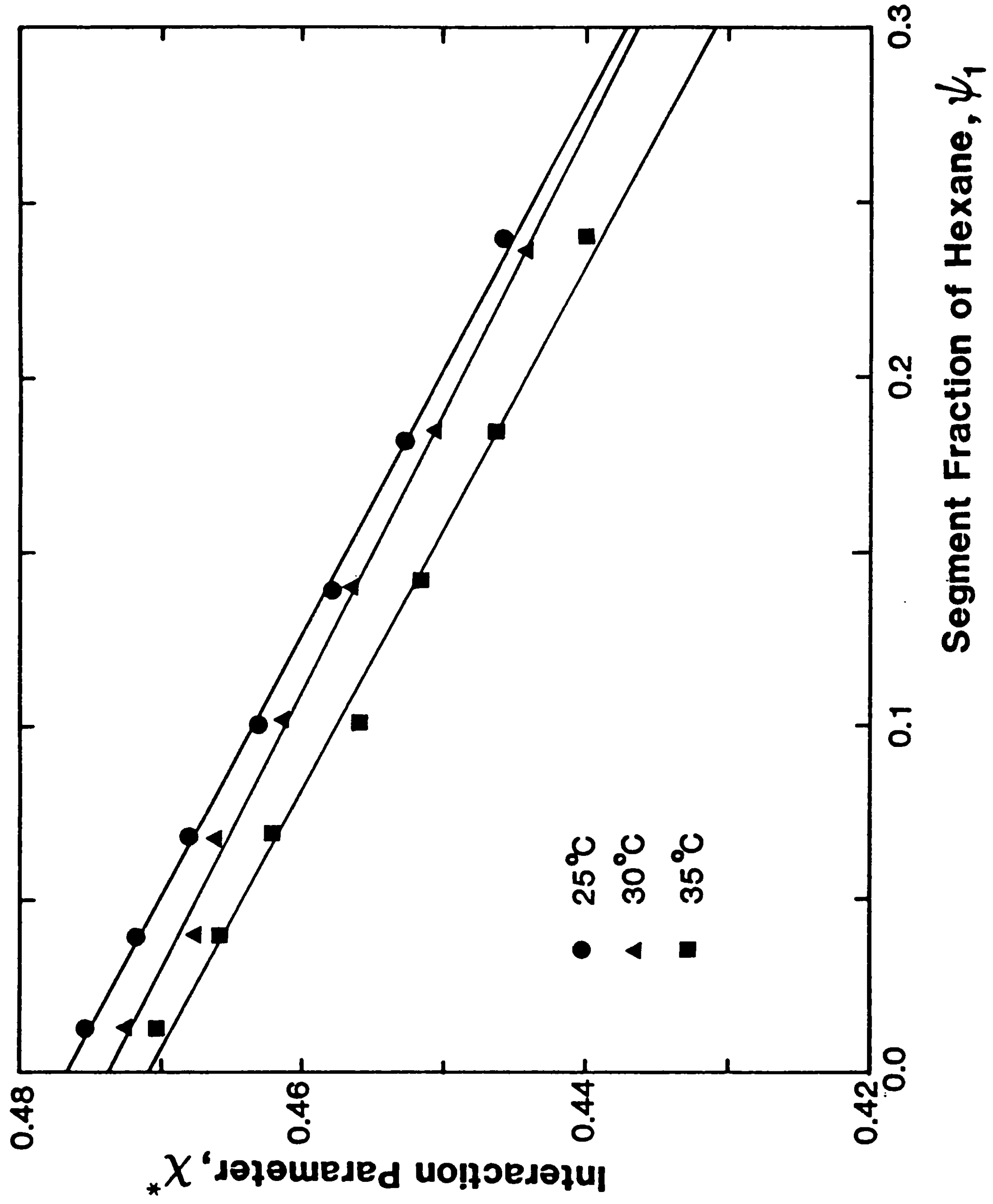

FIGURE 5-3: TEMPERATURE VARIATION OF INTERACTION PARAMETER FOR HEXANE IN PDMS

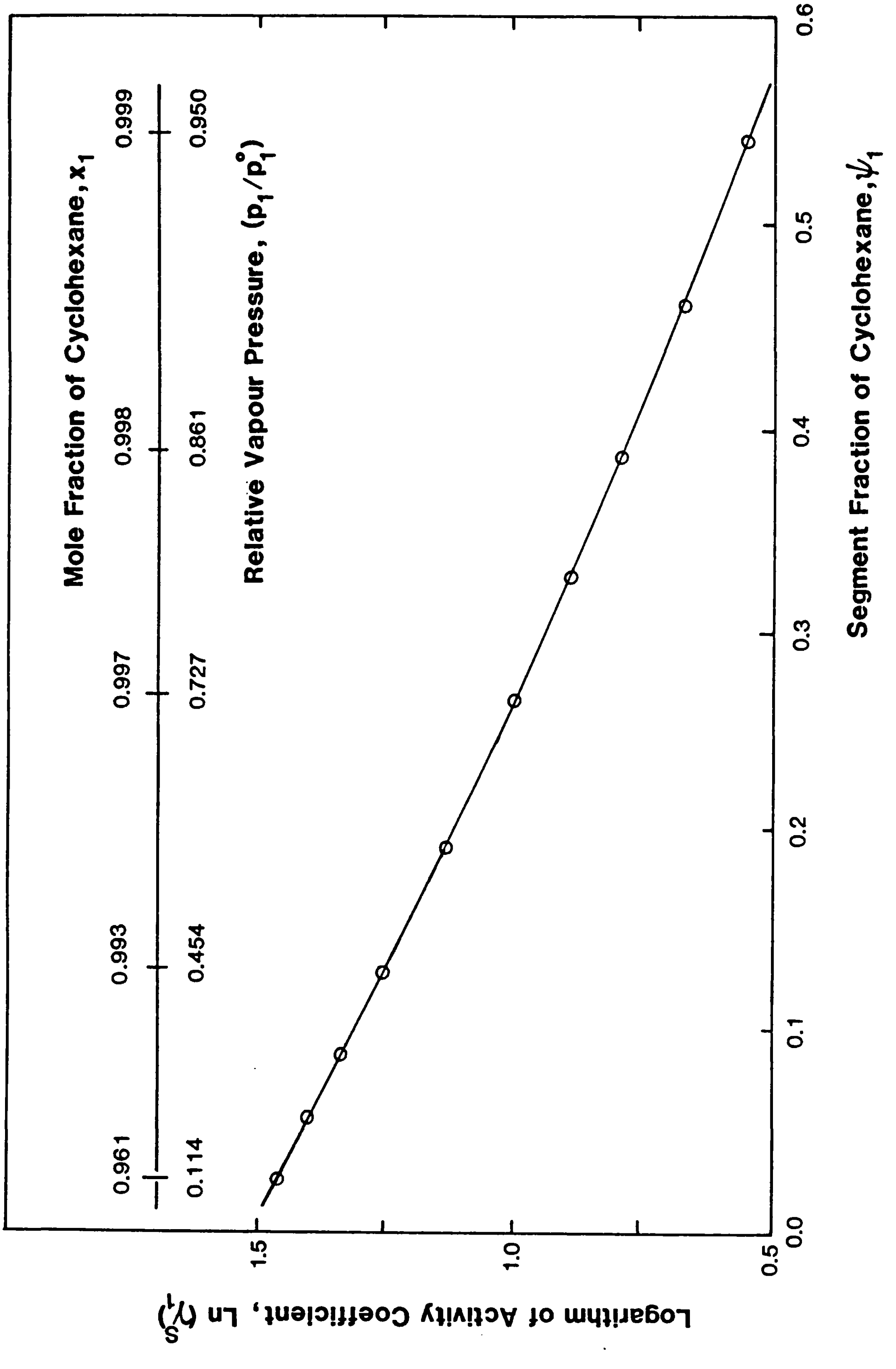

FIGURE 5-4: VARIATION OF ACTIVITY COEFFICIENT FOR CYCLOHEXANE IN PDMS AT 30°C ON VARIOUS CONCENTRATION SCALES

5.4. PARTIAL MOLAR ENTHALPIES OF MIXING

As shown in Section 1.4., the temperature variation of activity coefficients enables partial molar heats of mixing to be calculated. Thus from the activity coefficient measurements for hexane and benzene over the (nominal) temperature range of 25-35°C, the partial molar enthalpies, enthalpic and entropic contributions to the interaction parameter have been calculated at 30°C.

Patterson *et al.*[136] have shown that when using segment fractions to calculate the combinatorial contribution to the free energy that ΔS^{comb} is temperature independent so that the variation of the logarithm of activity coefficient and interaction parameter should be equivalent. Thus, the partial molar heat of mixing of the absorbate, $\overline{\Delta H}_1^M$ can be calculated from

$$\overline{\Delta H}_1^M = R\,\frac{\partial \ln \gamma_1^S}{\partial(1/T)} = R\,\frac{\partial \chi^*}{\partial(1/T)} \qquad (5.1)$$

To simplify the calculation, it was assumed that $\overline{\Delta H}_1^M$ was independent of temperature so that it could be calculated from

$$\overline{\Delta H}_1^M(30) = R\left\{\frac{\ln \gamma_1^S(35) - \ln \gamma_1^S(25)}{(1/308) \qquad (1/298)}\right\} \qquad (5.2)$$

or the corresponding expression with χ^* replacing $\ln \gamma_1^S$.

Since experimental measurements were made at different concentrations, equation (5.2) was applied to the best fit values of χ^* and $\ln \gamma_1^S$ at 0·1 segment fraction intervals as well as those extrapolated to infinite dilution for comparison with GLC studies. The experimental measurements were all made at a concentration less than $\psi_1 = 0{\cdot}25$ so that it was invalid to extrapolate the results above $\psi_1 = 0{\cdot}5$. Also, in this range, the calculated values become rather small when compared with experimental error and would be rather dubious.

The experimental results over the temperature range studied are shown in Figure 5-3 for hexane and Figure 5-5 for benzene as plots of

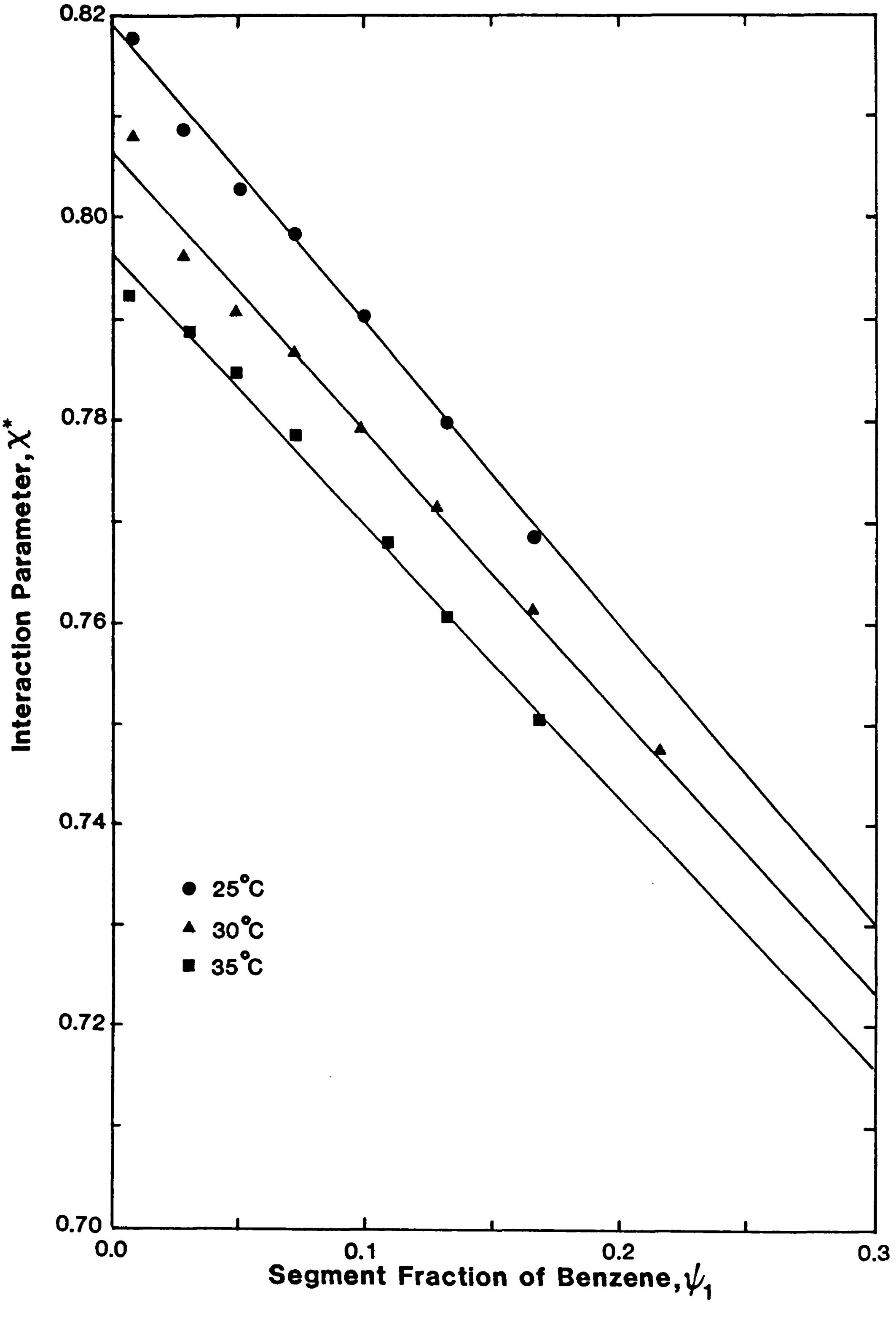

FIGURE 5-5: TEMPERATURE VARIATION OF BENZENE INTERACTION PARAMETER IN PDMS

χ^* *versus* ψ_1 and the smoothed (best fit) values shown in Tables 5-1 and 5-2. Consideration of the results showed that, as expected, calculations involving $\ln\gamma_1^S$ or χ^* lead to the same values for $\overline{\Delta H}_1^M$; hence only the former are listed.

TABLE 5-1: BEST FIT VALUES FOR HEXANE IN PDMS

SEGMENT FRACTION	$\ln\gamma_1^S$ 25°C	$\ln\gamma_1^S$ 30°C	$\ln\gamma_1^S$ 35°C	χ^* 30°C
0•0	1•4752	1•4720	1•4697	0•4734
0•1	1•2742	1•2725	1•2696	0•4614
0•2	1•0872	1•0855	1•0834	0•4494
0•3	0•9134	0•9124	0•9104	0•4374
0•4	0•7519	0•7513	0•7497	0•4254
0•5	0•6021	0•6017	0•6005	0•4134

The partial molar enthalpies of mixing were calculated using equation (5.2) and are shown in Table 5-3. Also shown are the enthalpic contributions to the interaction parameters χ_H calculated from equation (1.33),

TABLE 5-2: BEST FIT VALUES FOR BENZENE IN PDMS

SEGMENT FRACTION	$\ln\gamma_1^S$ 25°C	$\ln\gamma_1^S$ 30°C	$\ln\gamma_1^S$ 35°C	χ^* 30°C
0•0	1•8179	1•8054	1•7954	0•8064
0•1	1•5382	1•5299	1•5225	0•7787
0•2	1•2850	1•2799	1•2746	0•7510
0•3	1•0565	1•0538	1•0501	0•7234
0•4	0•8511	0•8499	0•8475	0•6957
0•5	0•6668	0•6666	0•6651	0•6681

$$\chi_H = \overline{\Delta H_1^M} / RT\psi_2^2$$

and the entropic contribution calculated from equation (1.34)

$$\chi^* = \chi_H + \chi_S$$

TABLE 5-3: PARTIAL MOLAR QUANTITIES FOR PDMS SOLUTIONS AT 30°C

SEGMENT FRACTION	HEXANE			BENZENE		
	$\overline{\Delta H_1^M}$ (J mol^{-1})	χ_H	χ_S	$\overline{\Delta H_1^M}$ (J mol^{-1})	χ_H	χ_S
0·0	419·9	0·167	0·306	1717·8	0·682	0·124
0·1	351·2	0·172	0·289	1198·6	0·587	0·192
0·2	290·1	0·180	0·269	794·0	0·492	0·259
0·3	229·0	0·185	0·252	488·6	0·396	0·327
0·4	168·0	0·185	0·240	274·8	0·303	0·393
0·5	122·0	0·194	0·219	129·8	0·206	0·462

It should be noted that the 30°C isotherms were measured at an actual temperature of 29·84°C whereas the average of the 25°C and 35°C temperatures is 29·93°C. However, consideration of the values suggests that the 0·09°C difference would have a negligible effect on the results. The accuracy of the χ^* and $\ln\gamma_1^S$ results leads to uncertainties of ~200 J mol^{-1} in $\overline{\Delta H_1^M}$ or ~0·07 in χ_H.

The values of $\overline{\Delta H_1^M}$ for hexane at infinite dilution may be compared with those of Hammers *et al.* who obtain a value of 485 ± 210 J mol^{-1} at 30°C[163] and χ_H = 0·23 ± 0·06 at 20°C[164] for a polymer of molecular weight 30000. In view of the large experimental error of the methods, this represents reasonable agreement.

A more accurate method of determining heats of mixing is the technique of direct calorimetry. Patterson and co-workers[159] have applied this to the systems studied here and have used their results to derive χ_H values accurate to 0·02 - 0·05 depending on the system and the concentration. Their values and that from the present work are compared in Figure 5-6, though the values from the work of Patterson *et al.* are read from a graph having rather a small scale and so carry greater uncertainty than implied by Figure 5-6. It may be seen that, as infinite dilution is approached, the values for hexane agree reasonably well but that the concentration variation is poorly predicted by the microbalance work. For the benzene system, the concentration variation is predicted reasonably well but the values from the present work are ~0·2 lower across the range, this being outside the experimental error of the methods. Values of χ_S are not plotted but, in view of the reasonable agreement of χ^* these will be similarly divergent between the two works.

CONCLUSIONS

The Magnetic Suspension vacuum microbalance has been shown to be capable of giving accurate results for activity coefficients and interaction parameters over a wide range of concentrations with a considerably greater precision than the McBain-Bakr microbalances usually employed for this work.

It has also been shown that meaningful values of partial molar enthalpies of mixing can be measured with an accuracy commensurate with that of similar GLC techniques but that the method lacks the precision of, for example, direct calorimetric determinations. However, the values of $\overline{\Delta H_1^M}$ in the systems involved in this study are fairly small and, for systems with greater heats of mixing, the method could be useful.

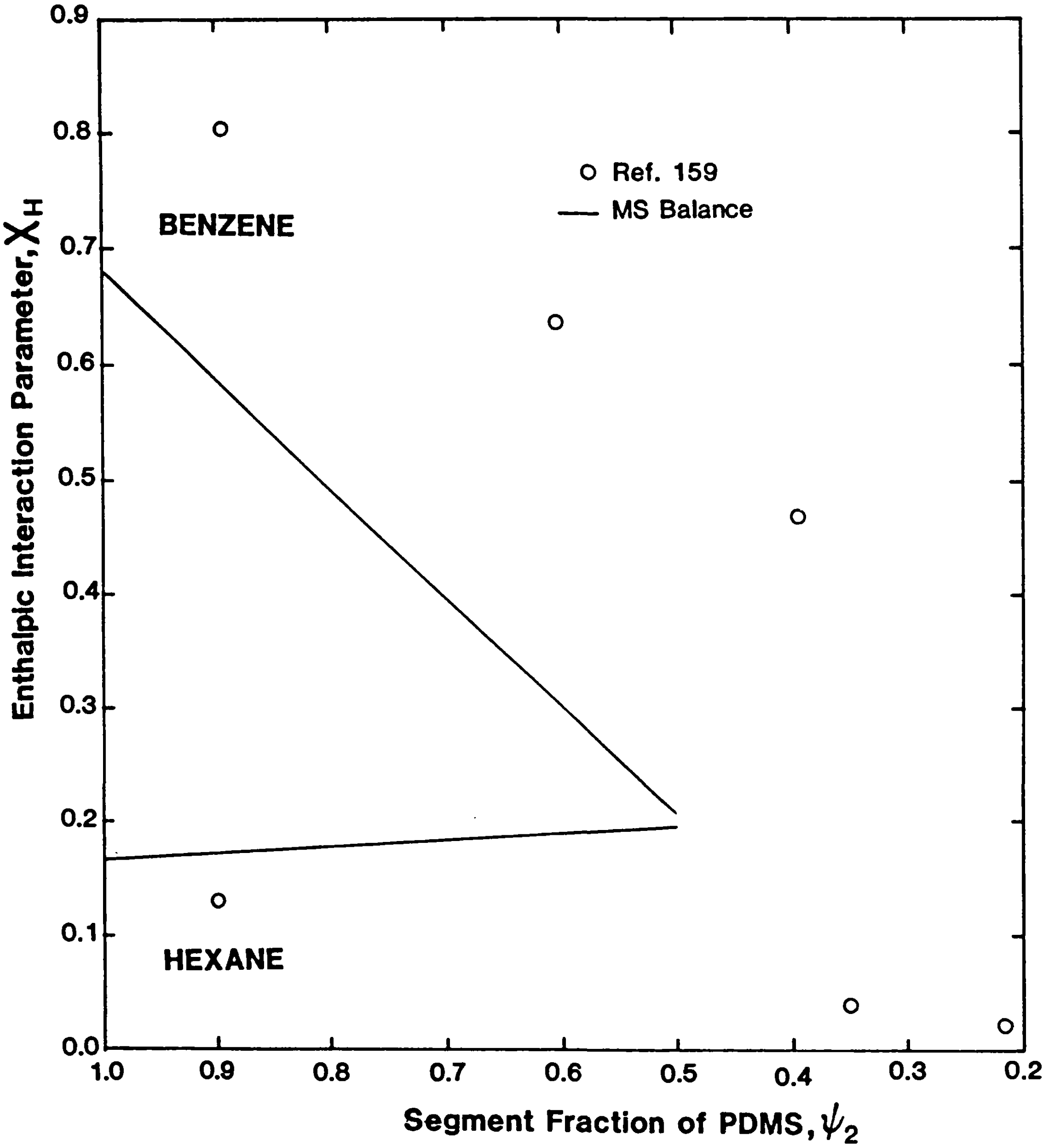

FIGURE 5-6: THE ENTHALPY CONTRIBUTION TO INTERACTION PARAMETERS FOR BENZENE AND HEXANE IN PDMS AT 30°C

Chapter 6

Interaction Parameters and Miscibility Limits in Mixtures of PDMS with DNP or Squalane

The use of polymers and plastics in industry has grown enormously over the past twenty-five years and is projected to continue to do so despite the World's "oil crisis" which has increased the cost of many raw materials. Despite this, in 1975 some eighty-five per cent of World production consisted of just four polymers - polyethylene, polystyrene, poly(vinyl chloride) and polypropylene - and very few of the thousands of new polymers synthesised each year find their way into major commercial use.[177] Thus it is important for economic reasons to manufacture new materials by modification of existing materials by, for example, the formation of co-polymers and polymer blends or by the inclusion of fillers, plasticisers etc.

A large number of studies of polymer mixtures has been made and most have been found to be immiscible[178] although more miscible polymer blends have been found recently.[179] However, perhaps a more usual method of altering the properties of a polymer is by the inclusion of a plasticiser, a common example being the widely differing properties of PVC. The materials used as plasticisers are often monomeric compounds of a moderately high molecular weight in the range 150-1000 and relatively few thermodynamic studies have been carried out on mixtures of this type of material with a polymer, although interactions in n-tetracosane-PDMS[172] and dioctyl phthalate-PVC[180] systems have been studied by Patterson and co-workers. Again, the miscibility of the system is important since if the plasticiser is immiscible with the polymer it is easily lost and the polymer properties altered. Thus it is of practical importance to study interactions in these systems and the ability to predict their partial miscibility would be useful in an industrial context.

By their nature, polymers and plasticisers are involatile compounds and the direct study of their interaction is very difficult, if not impossible, by traditional methods. Interaction parameters in such systems have usually been determined from miscibility studies or by the effect of additives on some property of the polymer such as the glass transition temperature, although the newer light and neutron scattering techniques have provided other methods[181] for this type of study. However, as previously discussed, the use of a volatile component as a probe to obtain information in polymer mixtures is now common in GLC techniques, having been employed by Patterson *et al.* for the work referred to above, and has also been used in static methods.

The use of a probe molecule as the absorbate has been used on the microbalance apparatus with the binary polymer-monomeric component mixture being used as the absorbent. Two systems were studied, both employing PDMS as the polymer. The monomeric components used were squalane and dinonyl phthalate, the latter being appropriate in view of the use of alkyl phthalates as commercial plasticisers. The same technique has been used by Ashworth and co-workers[112-114] to study interactions in SQ-DNP mixtures and that work, together with work described earlier in this Thesis, has shown hexane to be suitable as a probe molecule for this study. The effect of polymer molecular weight on the solution interactions was investigated and the calculated interaction parameters were used to predict the miscibility limits of the mixtures for comparison with the experimentally determined values.

6.1. INTERACTION PARAMETERS

The experimental techniques described in Chapter 2 were employed on the QB balance apparatus to record absorption isotherms for hexane in the binary absorbent samples at 30°C. The samples were prepared to ensure a miscible mixture and were in the region of ~90% by weight of polymer for PDMS-SQ mixtures and ~95% by weight for those containing

DNP. The measured isotherms are listed in Tables AI-9 and AI-10 of Appendix I.

The results for the two separate components and those for mixture in each system were analysed as described in Chapter 3 to find the best fit values of χ°_{AB}, χ'_{AB}, χ°_{AC}, χ'_{AC}, accounting for the interaction of hexane with each component and the concentration dependences, and χ_{BC} for the interaction between the two involatile components. In the following discussion, A refers to hexane, B to SQ or DNP and C to the polymer as appropriate. The calculated values are shown in Table 6-1 together with the RMSD of the fit calculated using equation (3.9) which gives an indication of the fit of the results to the Flory-Huggins theory.

TABLE 6-1: BEST FIT INTERACTION PARAMETERS OF HEXANE IN PDMS-DNP AND PDMS-SQ MIXTURES AT 30°C

SYSTEM	χ°_{AB}	χ'_{AB}	χ°_{AC}	χ'_{AC}	χ_{BC}	10^3 RMSD
DNP-PDMS I	5·171	0·221	2·802	-0·598	3·524	0·79
DNP-PDMS II	5·172	0·211	2·857	-0·772	3·534	0·89
DNP-PDMS III	5·172	0·210	2·938	-0·769	3·599	0·90
DNP-PDMS IV	5.170	0·225	2·957	-0·675	3·853	0·83
DNP-PDMS V	5·165	0·286	3·005	-0·467	4·145	1·55
SQ-PDMS I	1·459	0·220	2·797	-0·547	2·663	0·80
SQ-PDMS II	1·457	0·238	2·842	-0·618	2·795	0·68
SQ-PDMS III	1·456	0·254	2·914	-0·506	3·045	1·14
SQ-PDMS IV	1·456	0·253	2·946	-0·556	3·495	1·21
SQ-PDMS V	1·459	0·215	3·005	-0·470	3·882	1·42

The values quoted are equivalent to χ_{FH}/V°_{A} where χ_{FH} is the interaction parameter as defined by Flory and Huggins, this quantity being quoted in order to obtain results that are independent of the probe used. The same results have been calculated on the basis of segment fraction concentrations and are shown in Table 6-2.

TABLE 6-2: BEST FIT SEGMENT FRACTION INTERACTION PARAMETERS OF HEXANE IN PDMS-DNP AND PDMS-SQ MIXTURES AT 30°C

SYSTEM	$\chi^{*\circ}_{AB}$	$\chi^{*\prime}_{AB}$	$\chi^{*\circ}_{AC}$	$\chi^{*\prime}_{AC}$	χ^{*}_{BC}	10^3 RMSD
DNP-PDMS I	7·647	-1·273	4·406	-1·225	3·677	1·04
DNP-PDMS II	7·650	-1·309	4·517	-1·565	3·559	0·59
DNP-PDMS III	7·652	-1·318	4·647	-1·596	3·595	0·73
DNP-PDMS IV	7·649	-1·290	4·679	-1·464	3·922	1·23
DNP-PDMS V	7·648	-1·196	4·756	-1·149	4·463	1·95
SQ-PDMS I	2·678	-0·105	4·409	-1·238	3·131	0·85
SQ-PDMS II	2.675	-0·008	4·499	-1·366	3·304	0·97
SQ-PDMS III	2·673	-0·005	4·615	-1·299	3·640	1·51
SQ-PDMS IV	2·672	-0·005	4·663	-1·289	4·226	1·54
SQ-PDMS V	2·683	-0·125	4·759	-1·227	4·404	1·41

The tables show that the interaction parameters calculated on a segment fraction basis are larger than those based on volume fractions, as has generally been found.[39] The fit of the results to the Flory-Huggins equation is shown to be good by the small values of the RMSD, which are all well within the experimental error of the method, the volume fraction treatment generally producing a slightly better fit.

The results show a high degree of consistency. The χ and χ^* values should be accurate to 0·2 to 0·4 since they are the values considered in Section 3.6 divided by V_A° which is ~0·1 mol dm^{-3}. The results for hexane-SQ and hexane-DNP in the second columns of the Tables and those for each pair of results for each polymer in the fourth column agree to well within these limits confirming the analysis used. With the exception of DNP-PDMS I, the interaction parameters increase with increasing molecular weight, the increase being greater with squalane than with DNP but not particularly large in either case.

The increase of the χ_A° values from SQ to PDMS to DNP reflects the increasingly poor solvency of hexane for these compounds, larger values of interaction parameter generally being an indication of lower compatibility of the components. The low value shows squalane to be a good solvent for hexane as would be expected from the chemical similarity of the compounds. DNP is shown to be much less compatible by the higher value of χ as might be expected since its slightly polar nature would be disrupted on absorbing hexane. The PDMS structure has flanking methyl groups around a more polar siloxane backbone and so might be expected to show behaviour between that of DNP and SQ and this was observed experimentally. Similar behaviour was found by Patterson *et al.* for the n-tetracoasane-dioctylphthalate-PDMS systems.[172]

The interaction parameters between the involatile components are positive and quite large indicating that the two sets of components are not very compatible and this will be seen in the next Section when the partial miscibility of the systems is examined. In the analysis used above and in the following Section, this interaction parameter is assumed to be independent of concentration. This has clearly been demonstrated not to be valid for polymers in low molecular weight studies and there is ample evidence to doubt its validity for polymer mixtures. Hooker[182] has shown that inclusion of an extra parameter in the least squares fit procedure to account for any concentration dependence of χ_{BC} or χ_{BC}^* does not significantly improve the results for the SQ-DNP systems and, as will be seen in the next Section, the available range of miscible compositions is, with the possible exception of the lowest molecular weight polymer systems, rather small to accurately quantify any change in χ_{BC}. Intuitively perhaps this parameter would not be expected to remain constant. The validity of equation (3.12) for a ternary system lies on the assumption in the Flory-Huggins theory of random mixing. The χ_{AB} and χ_{AC} parameters show that hexane is much more compatible with SQ than with PDMS so that, on absorption of hexane, contacts between PDMS molecules would be broken in preference to those between SQ molecules and the extent to which this would happen would clearly depend on the PDMS-SQ composition. The same argument can be applied (in reverse) to the PDMS-DNP system and has been used by Patterson *et al.*[180] to explain the observed large concentration dependence in the PVC-dioctyl phthalate system. These two compounds have a negative χ_{BC} value for much of the composition range and are much more compatible than the systems involved in the present work. Dioctyl phthalate is a common commercial plasticiser for PVC and might be expected to show a greater concentration dependence.

6.2. PREDICTION OF MISCIBILITY LIMITS

As was shown in Section 1.5. it is possible in principle to derive the compositions of the conjugate solutions of a partially miscible mixture if an expression for the free energy of mixing of the system is available. Flory-Huggins theory leads to equation (1.24) for the molar free energy of mixing as a function, G, of concentration, x.

$$G(x) = \Delta G^M/RT = x_1 \ln \phi_1 + x_2 \ln \phi_2 + (x_1+rx_2)\,\phi_1\,\phi_2\,\chi_{12}$$

the terms having been described previously. Here only the PDMS-SQ or PDMS-DNP systems are being considered so that χ_{12} represents the χ_{BC} parameter from the previous section. Properties for hexane are not involved, it having been used solely as a 'probe' to determine the interactions between the involatile components.

Using the above expression, equation (1.25) was derived for the chemical potential of mixing of the solvent. Expansion of the logarithm term in the equation combined with the requirement for a negative value for miscibility, may be used to show that the maximum value for χ for complete miscibility of the components, χ_c, is given by

$$\chi_c = 0{\cdot}5[V_1^{\circ-\frac{1}{2}} + V_2^{\circ-\frac{1}{2}}] = 0{\cdot}5(1 + r^{-\frac{1}{2}})^2 \qquad (6.1)$$

Application of equation (6.1) to the systems studied here leads to the values listed in Table 6-3.

TABLE 6-3: MAXIMUM VALUES OF INTERACTION PARAMETER FOR COMPLETE MISCIBILITY IN PDMS-DNP AND PDMS-SQ SYSTEMS AT 30°C

	$0{\cdot}5(1+r^{-\frac{1}{2}})^2$	
	DNP	SQ
PDMS I	2·10	1·82
PDMS II	1·80	1·55
PDMS III	1·56	1·32
PDMS IV	1·46	1·23
PDMS V	1·31	1·10

Comparison of these values with the experimentally determined values listed in Table 6-1 shows that partial miscibility is to be expected in the systems.

In a similar manner to equation (1.25), the chemical potential of mixing of the polymer may be given by

$$\Delta\mu_2 = \ln(1-\phi_1) + (r-1)\phi_1 + r\,\chi\,\phi_1^2 \qquad (6.2)$$

Combining these expressions with the requirement of the equality of chemical potentials in each phase (equation (1.15)) and performing a mass balance on the system, that is, relating the amounts of each component in each phase to the total amount present, it is possible to calculate the compositions of each phase. This was the original method used by Flory[183,184] who needed to introduce approximations since the form of the expressions does not allow explicit solution of the resulting equations. Since then the development of high speed computers has allowed their solution to a reasonable degree of accuracy using numerical methods.

An alternative way of finding the compositions is to use the double tangent construction outlined in Section 1.5. The gradient of the G(x) curve, denoted by G'(x), is given by the differential of equation (1.24), leading to

$$G'(x) = \partial(\Delta G^M/RT)/\partial x_1 = \left[(1-2x_1) - \frac{(x_1-x_1^2)(V_1^\circ-V_2^\circ)}{x_1V_1^\circ + (1-x_1)V_2^\circ}\right]\frac{V_1^\circ\,V_2^\circ\,\chi_{12}}{x_1V_1^\circ+(1-x_1)V_2^\circ} + \ln\left[\frac{x_1V_1^\circ}{(1-x_1)V_2^\circ}\right] - \frac{V_1^\circ - V_2^\circ}{x_1V_1^\circ+(1-x_1)V_2^\circ} \qquad (6.3)$$

Again the form of the equations does not allow an analytic solution for the concentration but, knowing values of V_1° and V_2° and having measured values of χ_{12}, G'(x) can be evaluated at a series of concentrations and a numerical construction of the double tangent made.

The interaction parameters shown for the systems in Tables 6-1 and 6-2 were used in equation (6.3) to generate a series of G(x) curves. These were of the form shown in Figure 6-1 showing only one minimum, heavily skewed toward the polymer rich end of the concentration range, rather than the two minima usually shown by a partially miscible system as in Figure 1-2. In most cases, in addition to there being no minimum at the low polymer range, the G(x) curve started in the positive direction implying no mixing of the components in this region.

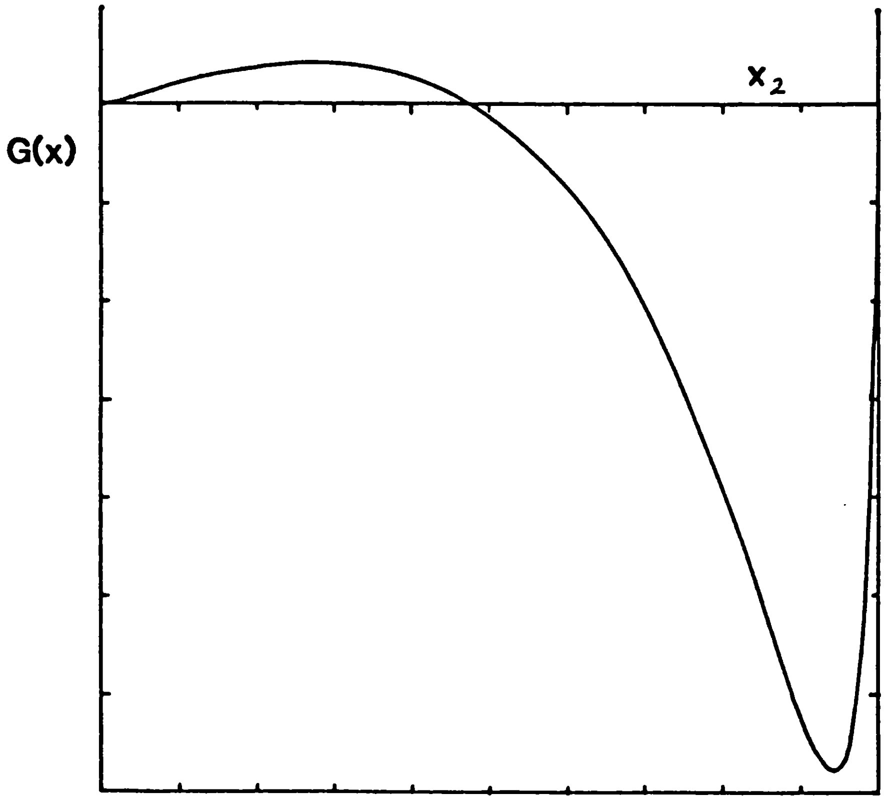

FIGURE 6-1: TYPICAL FREE ENERGY OF MIXING VERSUS COMPOSITION CURVE

Using Flory's original method of equating chemical potentials, Tompa[183] has shown that the concentration of polymer in one phase becomes vanishingly small as values of r and χ increase. This is to be expected since it can be shown that, at low polymer concentrations, equation (6.3) may be simplified to

$$\lim_{x_2 \to 0} G'(x) = \ln(V_1^\circ/V_2^\circ) + (V_2^\circ/V_1^\circ) - 1 - \ln x_2 - V_2^\circ \chi_{12} \qquad (6.4)$$

Equating G'(x) to zero in this expression allowed estimation of any minimum in the G(x) curve at low polymer concentrations. Insertion of the appropriate values in equation (6.4) for the PDMS V - DNP system (the first system that was studied) led to the prediction of a minimum at a polymer mole fraction $x_2 \approx 10^{-70}$ so that it effectively lay at zero.

The predicted minimum lying at highest concentration by this method was $x_2 \approx 3{\cdot}7 \times 10^{-3}$ for the PDMS I - SQ system so that the estimated minimum in each system was close to zero. Therefore in predicting the miscibility limits at the polymer rich end of the concentration range, it was assumed that there was zero solubility of polymer in the other component and that negligible error was caused by locating one end of the tangent to the G(x) curve at the origin. The point of contact of this tangent to the curve was then found to represent the miscibility limit.

This 'Tangent through the Origin' treatment was first tested against the data given by Tompa[184] and was found to give excellent agreement with the method of Flory. It was then applied to the systems studied in this work using the computer program described in Appendix II.

6.3. COMPARISON OF EXPERIMENTAL AND PREDICTED MISCIBILITY LIMITS

The predicted miscibility limits for both concentration bases are shown in Table 6-4 along with the experimental values measured in Section 2.10. by determining the cloud points of the mixtures and the phase compositions as determined by nmr spectroscopy (Section 2.11.). The values are shown as weight percentages of polymer in the mixtures.

Inspection of the Table shows that in all cases the phase concentrations calculated by nmr were less than the cloud points. The latter were measured to ±0·1 wt% while the spectroscopic analyses are expected to be accurate to, at best, ±2%, but the observed differences were outside any expected experimental errors. This may be explained since the systems have been treated as 'pseudo-binary' solutions, i.e. the polymer has been treated as a single component, its polydisperse nature having been ignored, and its properties represented by their average values. Koningsveld and Staverman[185] have shown that only in

TABLE 6-4: MISCIBILITY LIMITS (WT% POLYMER) FOR PDMS-DNP AND PDMS-SQ SYSTEMS AT 30°C

SYSTEM	PREDICTED		EXPERIMENTAL	
	VOL. FRAC.	SEG. FRAC.	CLOUD POINT	NMR
DNP-PDMS I	83·6	77·2	87·0	78·1
DNP-PDMS II	85·4	78·7	89·4	79·9
DNP-PDMS III	86·8	80·8	90·1	82·9
DNP-PDMS IV	88·9	84·5	90·8	83·9
DNP-PDMS V	90·8	88·7	92·2*	-
SQ-PDMS I	75·1	79·8	67·5	61·9
SQ-PDMS II	80·8	85·2	78·3	70·2
SQ-PDMS III	85·3	89·2	83·5	76·2
SQ-PDMS IV	89·5	92·7	87·8	82·4
SQ-PDMS V	92·1	93·6	90·3	-

*Measured by D.M. Hooker[131]

strictly binary solutions do the cloud points and phase concentrations exactly coincide and that neglect of polydispersity can cause appreciable differences between the two values. Using the method employed, the phase concentration given by the nmr results was the average polymer concentration in the solution, i.e. the concentration of polymer as if all polymer species were the average size. However the cloud point represents a limiting solubility of one component in the other - another name for it being the 'precipitation threshold'. Clearly the least soluble species would precipitate from solution first once saturation is reached, making the apparent concentration of polymer greater than the true or average concentration. If addition of further polymer to an immiscible mixture is considered the higher molecular weight fractions would be expected to dissolve last on approaching the miscibility limit, leading to the same conclusion. These comments apply only to the polymer rich phase. The same considerations applied to the polymer dilute phase would lead to the opposite conclusion, that the cloud point would be at a lower polymer concentration than the average. Effectively then, the cloud point is a limiting phase composition which is virtually equivalent to the phase concentration of the highest molecular weight species in a polydisperse polymer.

Comparisons of the predictions with the experimental values is facilitated by the graphs of miscibility limit versus molecular weight in Figures 6-2 and 6-3. The logarithmic plot is not meant to imply a particular relationship but was used to give a more convenient scale.

Figure 6-2 shows the results for the PDMS-DNP systems. It may be seen that the predictions on the basis of segment fractions estimate the phase compositions to within ~2 wt% across the molecular weight range studied. The volume fraction predictions lie some 2-6 wt% higher but predict the cloud points to within, on average, 4 wt%. However, as can be seen from Figure 6-3, the volume fraction predictions in the PDMS-SQ systems are some 3-5 wt% lower than those based on segment fractions. The volume fraction treatment overestimates the cloud points by 2-8 wt% with the segment fraction values correspondingly higher. The nmr concentrations, as expected, are lower than the cloud points but are not predicted well by the treatments used.

A notable point is that in each case the values for systems containing PDMS III lie away from a smooth curve drawn through the other four points. This suggests that the wrong molecular weight has been used. However, to bring the values onto the curves needs a value of ~12500 compared to the measured value of 15650 and this difference is

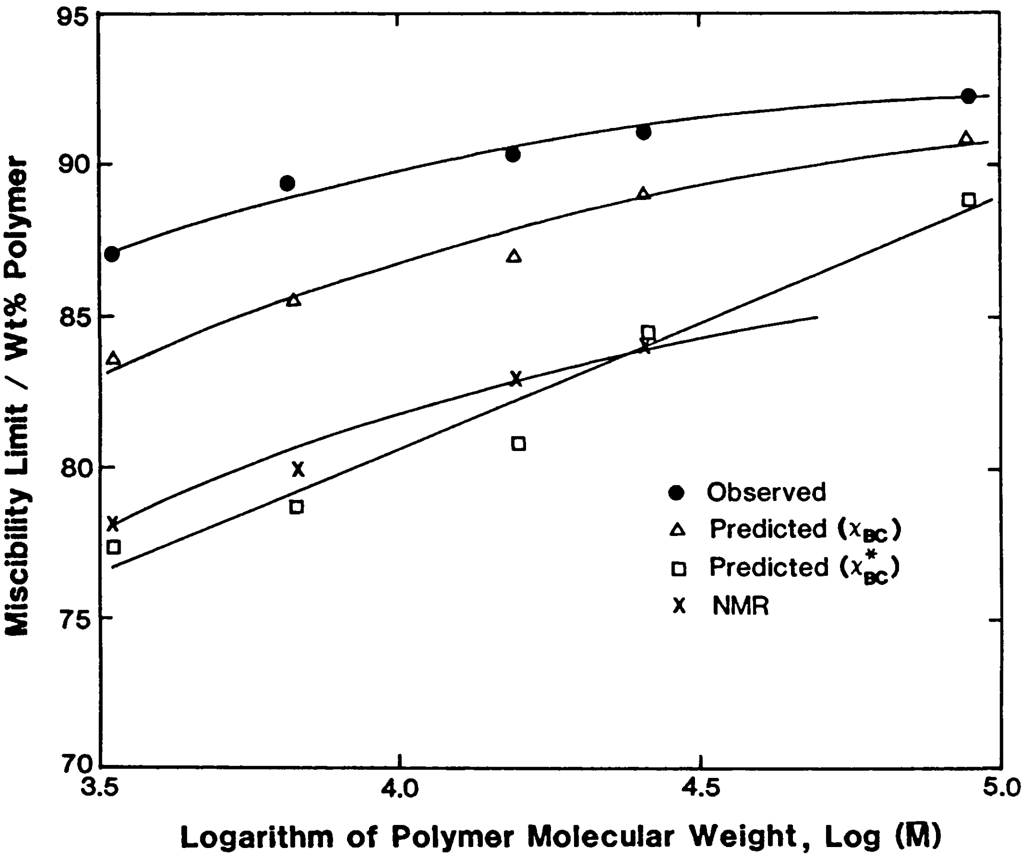

FIGURE 6-2: DEPENDENCE OF MISCIBILITY LIMIT ON POLYMER MOLECULAR WEIGHT FOR PDMS-DNP MIXTURES AT 30°C

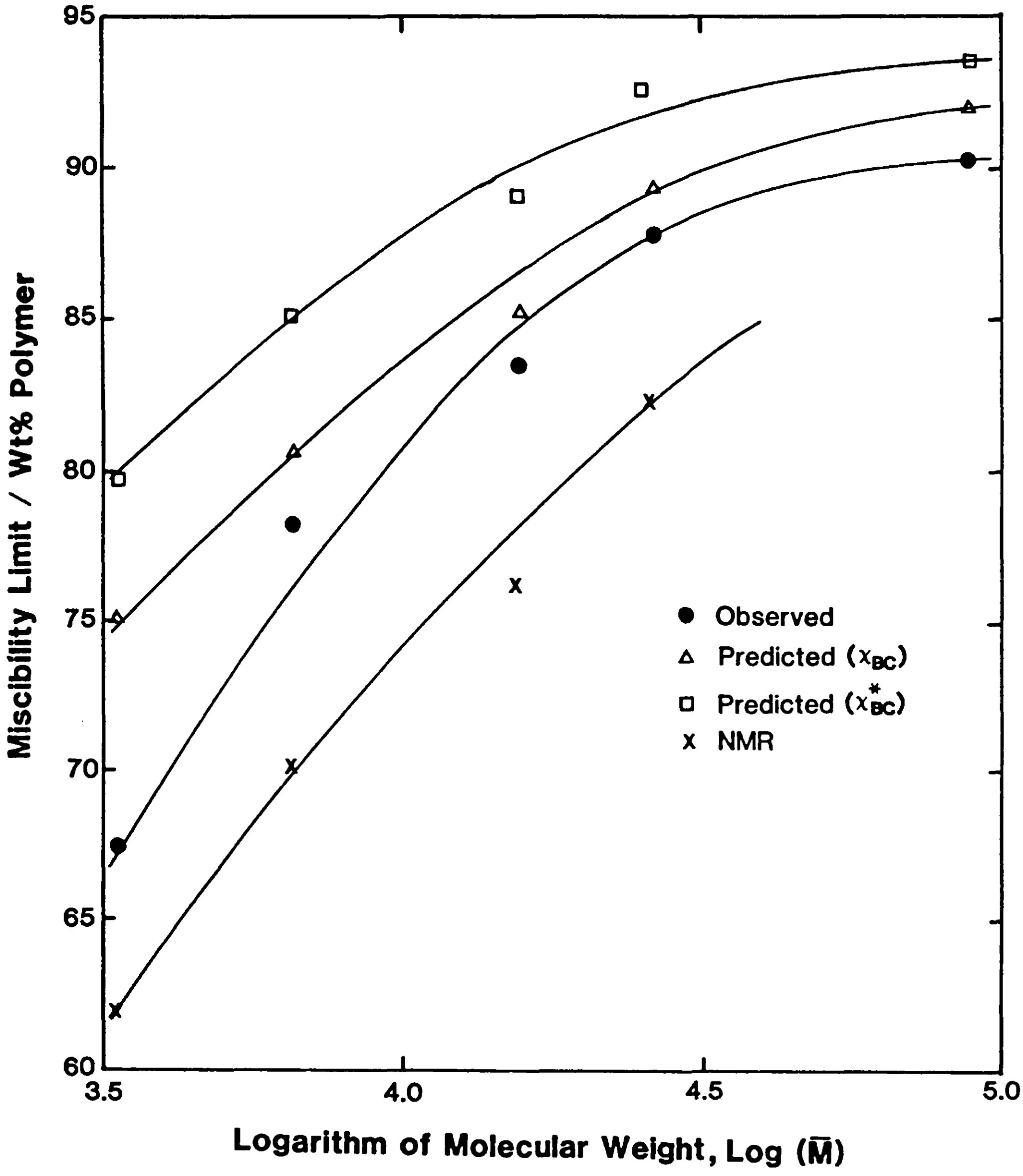

FIGURE 6-3: DEPENDENCE OF MISCIBILITY ON POLYMER MOLECULAR WEIGHT FOR PDMS-SQUALANE MIXTURES AT 30°C

well outside any error occurring in the determination of the molecular weight as described in Chapter 2.

6.4. DISCUSSION

It should be emphasised that the predicted miscibility limits can only be considered as estimations, as the treatments used contain a number of approximations and simplifications. The deficiencies involved in the use of the Flory-Huggins theory have been discussed in Chapter 1 and the neglect of polydispersity and the assumption of a concentration independent interaction parameter have also been mentioned in this Chapter.

The major approximation involved in the treatment of partial miscibility was the use of the 'Tangent through the Origin' method to estimate the miscibility limit which assumed zero solubility of polymer in DNP or SQ. The only system which showed any noted solubility was the PDMS I-SQ system which also showed a cloud point around 1 - 1·5 wt% of polymer. This is equivalent to a mole fraction of $\sim 1{\cdot}9 \times 10^{-3}$ so that the assumption that $x_2 = 0$ is not unreasonable, but does explain why this system shows the greatest difference between the observed and predicted limits and that the predictions generally improve with increasing molecular weight as the approximations become less serious.

As a check on the validity of this treatment an alternative method of predicting the phase limits was used. This involved finding the phase compositions that gave the minimum total free energy of the systems as a whole and was done using a computer program written by Dr. P.F. Tiley of the University of Bath. The program set up an expression for the system free energy by summing the free energies of the two phases using the expressions above. It was then minimised subject to a material balance over the whole system using the Nelder-Mead 'Simplex' non-derivative minimisation technique.[186]

The computed results are shown in Table 6-5 and show excellent agreement between the two methods of predicting the miscibility limits. The only systems that show differences are those involving the lowest molecular weight polymer as would be expected from the foregoing discussion. With the exception of these systems the predicted limit in the polymer dilute phase was at an unmeasurably small concentration, as was found experimentally. This shows that, for the systems studied, the 'Tangent through the Origin' treatment introduces negligible error and so is valid except where the lowest molecular weight polymer was used.

TABLE 6-5: COMPARISON OF PREDICTED MISCIBILITY LIMITS (WT% POLYMER)

SYSTEM	POLYMER RICH PHASE		DILUTE PHASE
	TANGENT	SIMPLEX	SIMPLEX
DNP-PDMS I	83·6	83·5	$1{\cdot}8 \times 10^{-3}$
DNP-PDMS II	85·4	85·4	$1{\cdot}3 \times 10^{-5}$
DNP-PDMS III	86·8	86·8	$8{\cdot}5 \times 10^{-12}$
DNP-PDMS IV	88·9	88·9	$5{\cdot}5 \times 10^{-14}$
DNP-PDMS V	90·8	90·8	$5{\cdot}7 \times 10^{-14}$
SQ-PDMS I	75·1	75·2	$8{\cdot}4 \times 10^{-3}$
SQ-PDMS II	80·8	80·8	$1{\cdot}2 \times 10^{-4}$
SQ-PDMS III	85·3	85·3	$2{\cdot}9 \times 10^{-12}$
SQ-PDMS IV	89·5	89·5	$4{\cdot}0 \times 10^{-11}$
SQ-PDMS V	92·1	92·1	$2{\cdot}4 \times 10^{-12}$

TANGENT : Predicted by the 'Tangent through the Origin' method

SIMPLEX : Predicted by the Simplex minimisation of free energy

6.5. CONCLUSIONS

The use of hexane as a 'probe' molecule has been shown to enable the calculation of consistent values for the interaction parameter between a polymer and a large monomeric component of the type commonly used as plasticisers and that reasonable estimates of the miscibility limits in the systems can be found using classical Flory-Huggins theory.

Although calculation of phase compositions is interesting from a thermodynamic standpoint, the cloud point represents, perhaps, a more important quantity in an industrial context for polymer processing. This work has shown that Flory-Huggins theory using volume fractions gives a better estimate of this than that using segment fractions and that, for high molecular weight polymers, the use of the 'Tangent through the Origin' treatment allows good estimates of the cloud points to be made. Despite being considerably more mathematically complex, the estimation of the miscibility limits by direct minimisation of the free energy of the system does not produce significantly better results.

Chapter 7

Application of Solution Theories to PDMS-Solvent Systems

7.1. APPLICATION OF SOLUBILITY PARAMETER THEORY TO PDMS SYSTEMS

As noted in the Introduction to the Thesis, the solubility parameter has proved to be a useful, if limited, concept and has been extensively used in practical applications of polymer chemistry.[14,195] However, the definition of δ in terms of an energy of vapourisation per unit volume is inappropriate for application to polymers since they are generally involatile and the molar volumes are often uncertain. Thus there is no direct way of measuring the polymer solubility parameter, δ_2, and indirect methods such as swelling or solubility studies have usually been used to obtain an estimate.[43] However, Di Paola-Baranyi and Guillet have developed a method to measure δ_2 using GLC results[187] finding good agreement with literature values for polystyrene and poly(ethyl acrylate) and this has been applied by Guillet and co-workers to a number of polymer systems.[188,189]

If the solubility parameter treatment is considered to account for enthalpic contributions to the interaction parameter, then combining equations (1.34) and (1.37) leads to

$$\chi = (V_1^\circ/RT)(\delta_1-\delta_2)^2 + \chi_S \qquad (7.1)$$

Expanding the solubility parameter term and rearranging leads to

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1^\circ}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S}{V_1^\circ}\right) \qquad (7.2)$$

so that if the expression on the left-hand side of equation (7.2) is plotted against δ_1, the solubility parameter of the volatile component for a number of such 'probes', then a straight line of slope $(2\delta_2/RT)$ should be obtained, allowing δ_2 to be calculated.

The results for the seven probes used in PDMS are shown Table 7-1 and the plot as described appears as Figure 7-1.

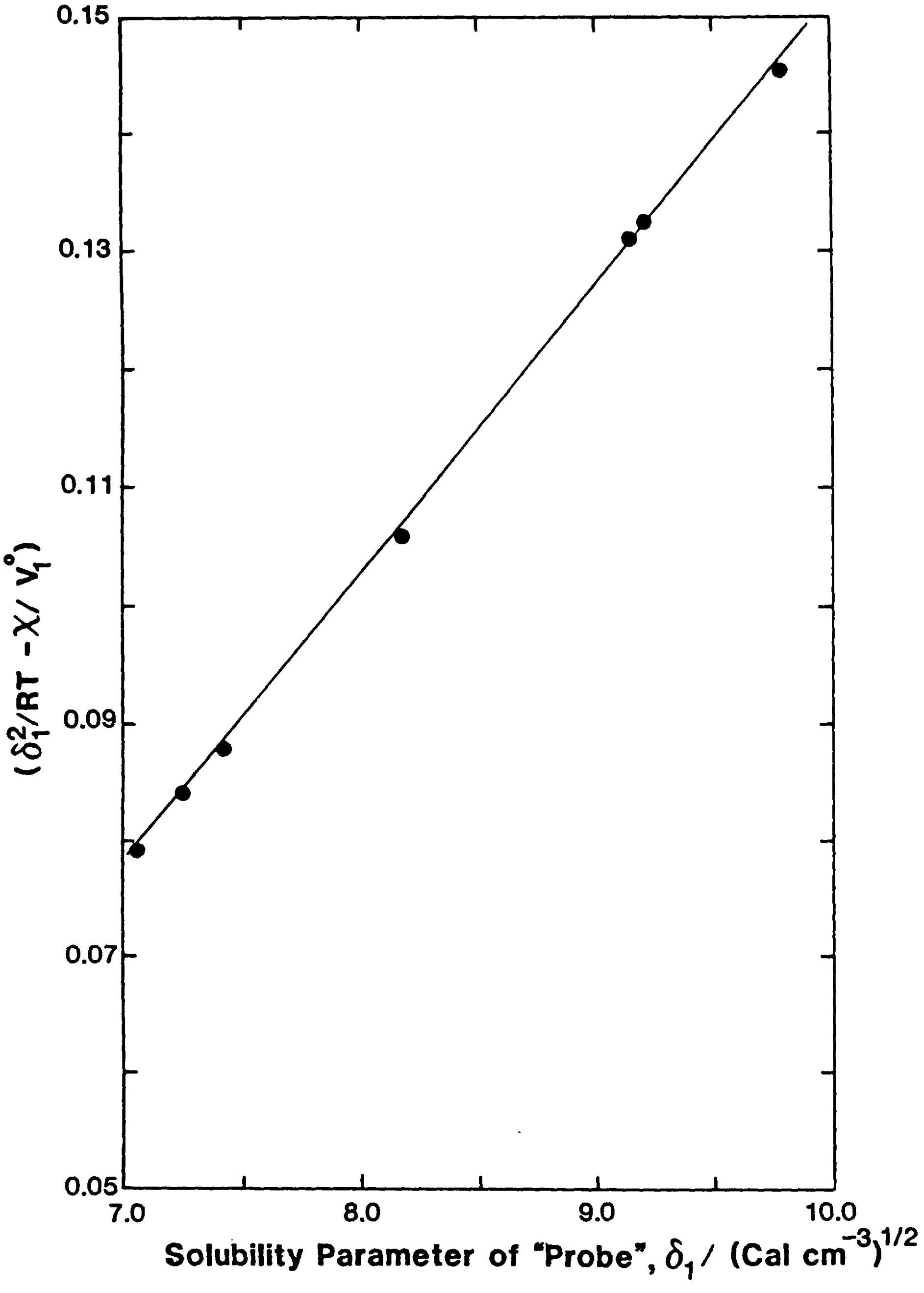

FIGURE 7-1: CALCULATION OF PDMS SOLUBILITY PARAMETER AT 30°C

TABLE 7-1: RESULTS FOR THE DETERMINATION OF THE SOLUBILITY PARAMETER OF PDMS V AT 30°C

PROBE	χ	δ_1(cal cm^{-3})$^{\frac{1}{2}}$	$\delta_1^2/RT-\chi/V°$	χ_H	χ_S
n-Pentane	0·3580	7·04	0·0792	0·020	0·369
n-Hexane	0·3965	7·25	0·0840	0·003	0·418
n-Heptane	0·4569	7·41	0·0880	0·001	0·468
Benzene	0·7588	9·14	0·1311	0·473	0·284
Cyclohexane	0·4758	8·18	0·1058	0·122	0·345
Chloroform	0·6515	9·20	0·1327	0·456	0·256
Dichloromethane	0·9081	9·80	0·1454	0·642	0·205

The units of (cal cm^{-3})$^{\frac{1}{2}}$ are conventionally used for solubility parameters and have been retained for use here. The δ_1 values for the probes were calculated from heat of vapourisation data for the hydrocarbons[190] and taken from literature sources for the chlorinated compounds.[15] They are quoted at 25°C but are not very dependent on temperature and so have not been adjusted to 30°C.

The plot in Figure 7-1 can be seen to give the linear relationship predicted by equation (7.2) supporting the analysis used. A least squares fit of the data gave a slope of 0·0244 with a correlation coefficient of 0·9996 and, as Guillet and Lipson have found,[189] the same correlation held for the more polar probes as well as the non-polar hydrocarbons. From this slope, the value of δ_2 was calculated to be 7·36 (cal cm^{-3})$^{\frac{1}{2}}$. This may be compared with literature values of 7·61 (cal cm^{-3})$^{\frac{1}{2}}$ calculated from measurements of thermal pressure coefficients,[191] 7·3 - 7·7 calculated by Bianchi *et al.*[192] and 7·3 - 7·6 measured by various methods.[43] In making this comparison it should perhaps be noted that the value measured here is at infinite dilution of the probe component. Guillet has used the symbol δ_2^∞ to designate this. Other techniques often involve measuring δ_2 at quite large solvent (probe) concentrations and it is not clear[187] how these are related although there seems to be no reason to suspect any differences.

The χ_H values listed in Table 7-1 are calculated using equation (1.37)

$$\chi_H = V_1^\circ (\delta_1 - \delta_2)^2/RT$$

and illustrate the error that would be involved if, as in the original formulation of the theory, the solubility parameter differences were taken as the whole contribution to χ. The final column of the Table shows the values of the entropic contribution to the interaction parameter predicted by this method and were calculated from the intercept of the slope which represents the final bracketed term in equation (7.2), assuming $\delta_2 = 7{\cdot}36\ (\text{cal cm}^{-3})^{\frac{1}{2}}$. The values for benzene and hexane may be compared with those in Table 5-3.

Solubility parameter theory may be seen to give qualitative agreement in that χ_H (at infinite dilution) is larger and χ_S lower for benzene than hexane as is found experimentally but, as might be expected, the quantitative agreement is not good, especially when it is remembered that calorimetric determinations of χ_H generally lead to values higher than those found in Chapter 5. The present treatment underestimates the enthalpic effects in the systems considered and so suggests the entropic effects to be more important than is found experimentally. This underestimation cannot be explained by an erroneous value of χ_H since, as δ_2 lies between the δ_1 values for the two systems, any change to improve one system must necessarily worsen the agreement in the other.

Results for hexane and benzene were also obtained for PDMS covering a range of molecular weights as described in Chapter 4. Although two values are a rather small sample on which to base a conclusion the above treatment was applied and the calculated values are shown in Table 7-2.

TABLE 7-2: VALUES FOR THE DETERMINATION OF δ_2 FOR PDMS AT 30°C

POLYMER MOL. WT.	$\delta_1^2/RT - \chi^{\infty}/V_1^{\circ}$	
	HEXANE	BENZENE
3350	0·0842	0·1312
6550	0·0843	0·1313
15650	0·0844	0·1314
26000	0·0844	0·1314

Inspection of the tables shows that each polymer sample will give an identical value of the slope when plotted against δ_1, the value of which leads to $\delta = 7{\cdot}33$ (cal cm^{-3})$^{\frac{1}{2}}$, which is negligibly different to that obtained for the highest molecular weight polymer. Thus it may be concluded that the solubility parameter is independent of molecular weight for values above ~3000 and is thus incapable of predicting any variation of χ with either concentration or molecular weight.

To determine how well the solubility parameters would predict the interaction parameters found in Chapter 6, equation (1.34) was applied to the systems. From data on several solutes, Perry and Tiley[110] estimate the solubility parameter of DNP to be 8·41 (cal cm^{-3})$^{\frac{1}{2}}$. Application of equation (1.34) with PDMS V leads to a value of χ^{∞} = 0·729. No data could be found for the solubility parameter of squalane. The group contribution method of Small[193] leads to a value of $\delta_2 = 7{\cdot}62\ (\text{cal cm}^{-3})^{\frac{1}{2}}$. Alternatively, Gee *et al.*[194] use compressibility results to calculate the internal pressure of squalane to be 73·9 cal cm^{-3}. They relate this to the cohesive energy density (δ^2) by a factor, n, which they estimate to be ~1·2 for n-alkanes and ~1·3 for poly(alkanes) and these lead to $\delta_2 = 7{\cdot}53 - 7{\cdot}85\ (\text{cal cm}^{-3})^{\frac{1}{2}}$. Using an intermediate of these two values in equation (1.34) gives $\chi^{\infty} = 0{\cdot}08$ for SQ with PDMS V.

Converting these values to the basis of per unit volume of hexane ($\chi^{\infty}/V_1^{\circ}$) as used in Chapter 6 yields 5·5 mol dm^{-3} and 0·61 mol dm^{-3} for DNP and SQ respectively. These may be compared to the results of 3·5 - 4·1 for DNP and 2·7 - 3·9 for SQ found in Chapter 6. The use of the highest value for δ_2 from the results for squalane above gives $\chi^{\infty}/V_1^{\circ}$ = 1·26. Therefore, although the qualitative agreement is reasonable for DNP with PDMS in that the values are higher than the critical values needed to predict partial miscibility, this is not so for SQ with PDMS and overall the quantitative agreement is not good.

7.2. APPLICATION OF THE FLORY 'EQUATION OF STATE' THEORY TO PDMS SOLUTIONS

Flory's 'equation of state theory' as outlined in Section 1.10.(iii) has been applied to solutions of PDMS in a number of solvents.[159,174,153] However, the dependence of interaction parameter on molecular weight has largely been ignored, although Muramoto,[153] while finding that the theory correctly predicted the concentration dependence of χ, reported that the observed variation with molecular weight was negligible for solutions of PDMS in methyl ethyl ketone. The theory has here been applied to the results for benzene and hexane described in Chapter 5. Since the theory predicts χ^*, these have been recalculated on the basis of segment fractions.

The energy interchange parameter X_{12} is usually calculated from a single determination of one thermodynamic quantity. The enthalpy of mixing at infinite dilution has often been used but since interaction parameters have been calculated in the present work and the fit of the theory to results was only considered over a small range at polymer concentrations, the most convenient quantity to use was the infinite dilution interaction parameter. Equation (1.45) may be simplified since $\psi = \theta_2 = 1$ at infinite dilution. Hence

$$RT\ \chi^{*\infty} = p^*V_1^*\{3\tilde{T}_1 \ln[(\tilde{v}_1^{\frac{1}{3}}-1)/(\tilde{v}_2^{\frac{1}{3}}-1)] + (\tilde{v}_1^{-1}-\tilde{v}_2^{-1})\} + X_{12}\ V_1^*/\tilde{v}_2 \tag{7.3}$$

where V_1^* is the molar characteristic volume of the solvent. Applying this to the values of $\chi^{*\infty}$ extrapolated from the results in Chapter 4, the X_{12} value shown in Table 7-3 were calculated.

TABLE 7-3: INTERACTION PARAMETERS FOR HEXANE AND BENZENE AT 30°C

POLYMER	HEXANE		BENZENE	
	$\chi^{*\infty}$	X_{12}/J cm^{-3}	$\chi^{*\infty}$	X_{12}/J cm^{-3}
PDMS I	0·4401	10·61	0·7865	33·45
PDMS II	0·4509	10·74	0·7934	33·51
PDMS III	0·4606	10·95	0·8020	33·72
PDMS IV	0·4696	11·10	0·8074	33·87
PDMS V	0·4731	11·15	0·8142	34·15

Application of equation (1.45) to find the concentration variation of χ^* by the theory requires the specification of one other parameter, the ratio of the surface to volume ratios of the components s_1/s_2. This has been calculated by some workers from consideration of the geometries of the components while others have used the group contribution method of Bondi.[54]

7.2.(i) HEXANE-PDMS SYSTEMS

The data tabulation of Bondi leads to a value of $s_1/s_2 = 1{\cdot}44$ although this is considerably smaller than the value of 2·1 used by Patterson *et al.*[159] which they derived from molecular geometries. The prediction of X^* according to this theory with $s_1/s_2 = 1{\cdot}44$ is shown by Curve I_A in Figure 7-2 for hexane in PDMS V. The curves in the Figure were calculated using the computer program listed in Appendix II and the appropriate pure component data from Chapter 3, with the other characteristic parameters being derived using the expressions in Section 1.10.(iii).

It may be seen that these conditions lead to a poor prediction of the concentration dependence. In many systems, Flory and co-workers have introduced an extra parameter, Q_{12} to account for an entropy contribution such that

$$X_{12} = X_{12}' - \tilde{V}\, T\, Q_{12}$$

where X_{12}' represents the enthalpic contribution to the energy interchange parameter. Patterson *et al.* found a value of $X_{12} = 4{\cdot}6$ J cm^{-3} from a calorimetric determination of the heat of mixing which leads to a value of $Q_{12} = -0{\cdot}018$ J cm^{-3} K^{-1}. This slightly improves the fit to the data as shown by Curve I_B in Figure 7-2, but it is still not very good and it was found that no reasonable values of X_{12}' and Q_{12} led to a good fit with this value of s_1/s_2. A similar effect is shown by the lowest molecular weight polymer as shown by Curves III_A and III_B.

Higher values of s_1/s_2 as suggested by the molecular geometries lead to a considerably worse fit of the theory to the concentration dependence. However, Flory and Shih[174] have to a certain extent used s_1/s_2 as another adjustable parameter. On this basis, a series of curves was generated using a range of s_1/s_2 values and, with

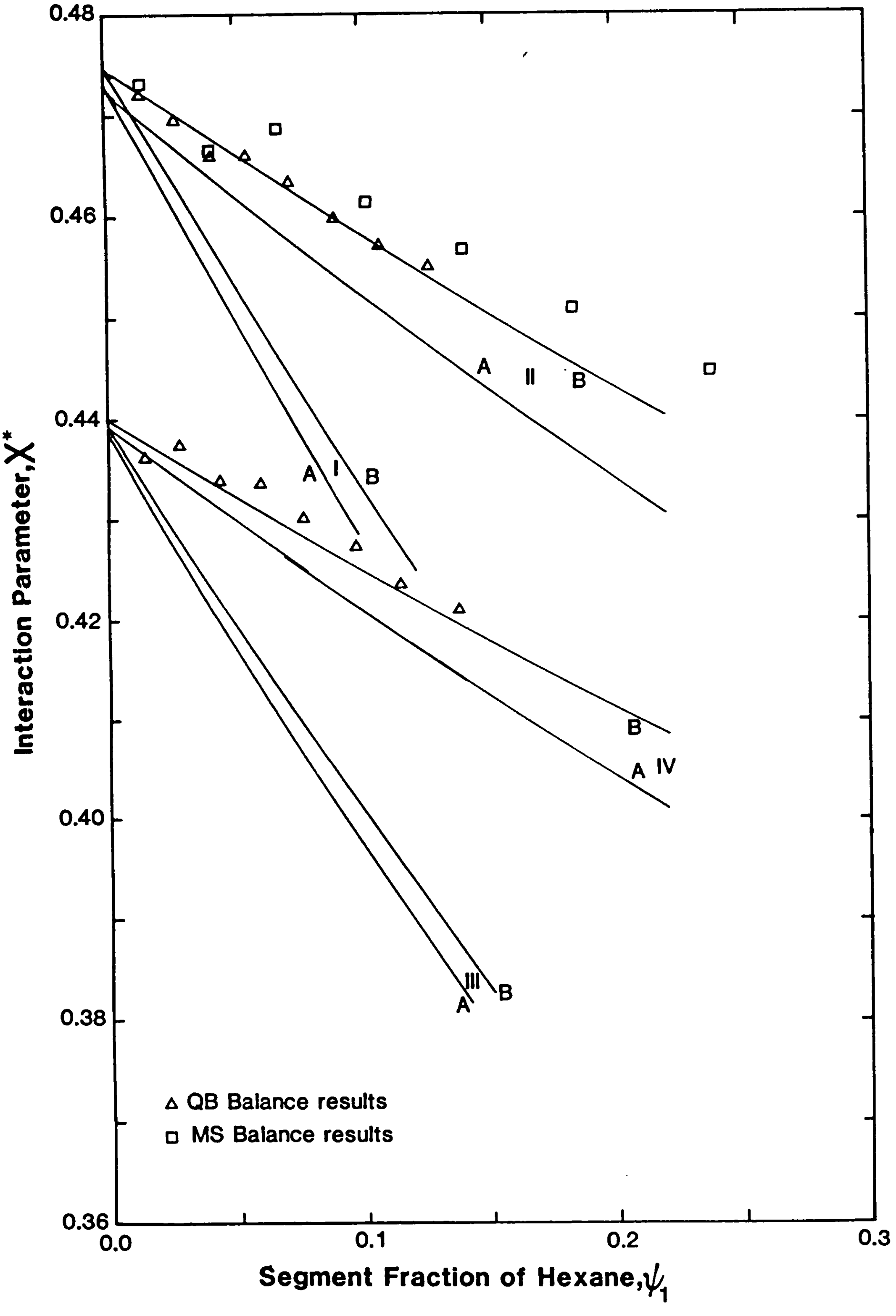

FIGURE 7-2: PREDICTION OF INTERACTION PARAMETERS BY FLORY 'EQUATION OF STATE' THEORY FOR HEXANE IN PDMS AT 30°C

Experimental results from Chapters 4 and 5.

For explanation of curves, see text.

$X_{12} = 11{\cdot}15$ J cm^{-3}, an s_1/s_2 value of less than 1 is needed to give a reasonable fit. Introduction of the Q_{12} parameter as above allows a reasonable fit with $s_1/s_2 = 1{\cdot}05$ as shown by Curve II_B. These values also lead to a good fit with the lowest molecular weight polymer as shown by Curve IV_B.

Therefore, to judge the fit of the theory to the different molecular weight samples, the concentration dependence of X^* for PDMS in hexane was calculated with $s_1/s_2 = 1{\cdot}05$. The value of X'_{12} has been taken as $4{\cdot}6$ J cm^{-3} in each case and the value of Q_{12} adjusted to bring the value of X_{12} to that in Table 7-3. An alternative procedure would have been to keep Q_{12} constant and vary X'_{12} but there seems to be no reason to suggest that this would lead to significantly different results.

The computed curves are shown in Figure 7-3 along with the experimentally measured X^* values, the Q_{12} values used being indicated in the Figure. As can be seen, assumption of these values leads to a very good fit of the theory to the experimental data.

7.2.(ii) BENZENE-PDMS SYSTEMS

Flory and Shih[174] have applied the 'equation of state' theory to X^* results for the benzene-PDMS system obtained both by osmotic pressure measurements on dilute solutions and by vapour sorption at higher polymer concentrations. Their estimation of the s_1/s_2 ratio by consideration of the molecular geometries was $1{\cdot}67$ while the tabulated data of Bondi leads to $1{\cdot}14$. However, they found that an intermediate value of $1{\cdot}32$ best fitted the interaction parameter values across the whole concentration range but, significantly for the present work, found the greatest difference between theoretical predictions and experimental values as infinite dilution of solvent was approached. They also found it necessary to introduce the Q_{12} parameter and used

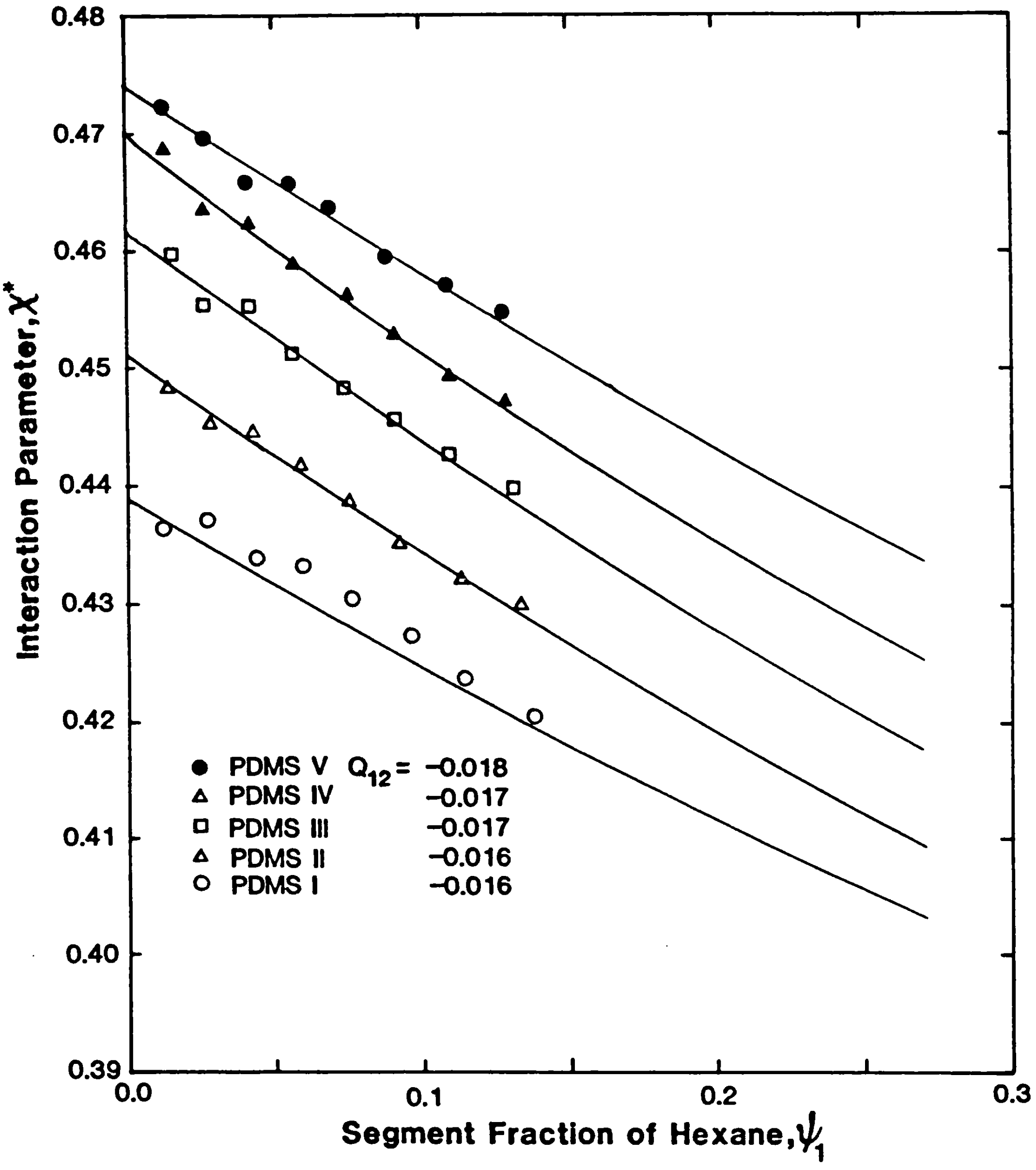

FIGURE 7-3: INTERACTION PARAMETERS FOR HEXANE IN PDMS AT 30°C

Experimental Points from Chapter 4.

Solid lines: Flory theory with X'_{12} = 4·6 J cm^{-3},

s_1/s_2 = 1·05 and Q_{12} values as indicated.

the enthalpy measurements of Delmas *et al.*[196] to calculate $X_{12}' = 22{\cdot}0\ \mathrm{J\ cm^{-3}}$.

The effect of adopting the s_1/s_2 values above along with the X_{12} parameters shown in Table 7-3 can be seen in Figure 7-4. Assumption of $s_1/s_2 = 1{\cdot}32$ leads to a poor prediction of the concentration dependence and even if a value of 1·14 is used the agreement with experimental data is not greatly improved, even on introduction of the Q_{12} parameter, as can be seen from Curves I and II for the highest molecular weight polymer in Figure 7-4. A reasonable fit can be seen with Curve $\mathrm{III_B}$ which employs $X_{12}' = 22{\cdot}0\ \mathrm{J\ cm^{-3}}$, $Q_{12} = -0{\cdot}0325\ \mathrm{J\ cm^{-3}K^{-1}}$ and $s_1/s_2 = 1{\cdot}05$. A similar situation exists for the lowest molecular weight polymer as shown by Curves IV - VI in Figure 7-4.

These values of X_{12}' and s_1/s_2 were used to calculate a set of curves to represent X^* for each polymer sample considered with Q_{12} again being adjusted to give agreement with Table 7-3 and the generated curves are shown in Figure 7-5 together with the experimental results. As can be seen, the fit using these parameters is quite good. It could be improved by slight alterations to the Q_{12} parameters, for which no justification could be seen, or by adopting an s_1/s_2 value that varies slightly with molecular weight which also seems unlikely, Muramoto[153] having shown that, to the level of accuracy used here, there is no change in s_1/s_2 over a wide range of molecular weights.

7.2.(iii) DISCUSSION

As found by previous workers, PDMS solutions have been found to fit the 'equation of state' theory to a lesser degree than some other polymers,[39] particularly when the theory is used in its original formulation with s_1/s_2 representing the ratio of the surface to volume ratios of the components. Adoption of this as an adjustable parameter can allow better prediction of interaction parameters across a wide

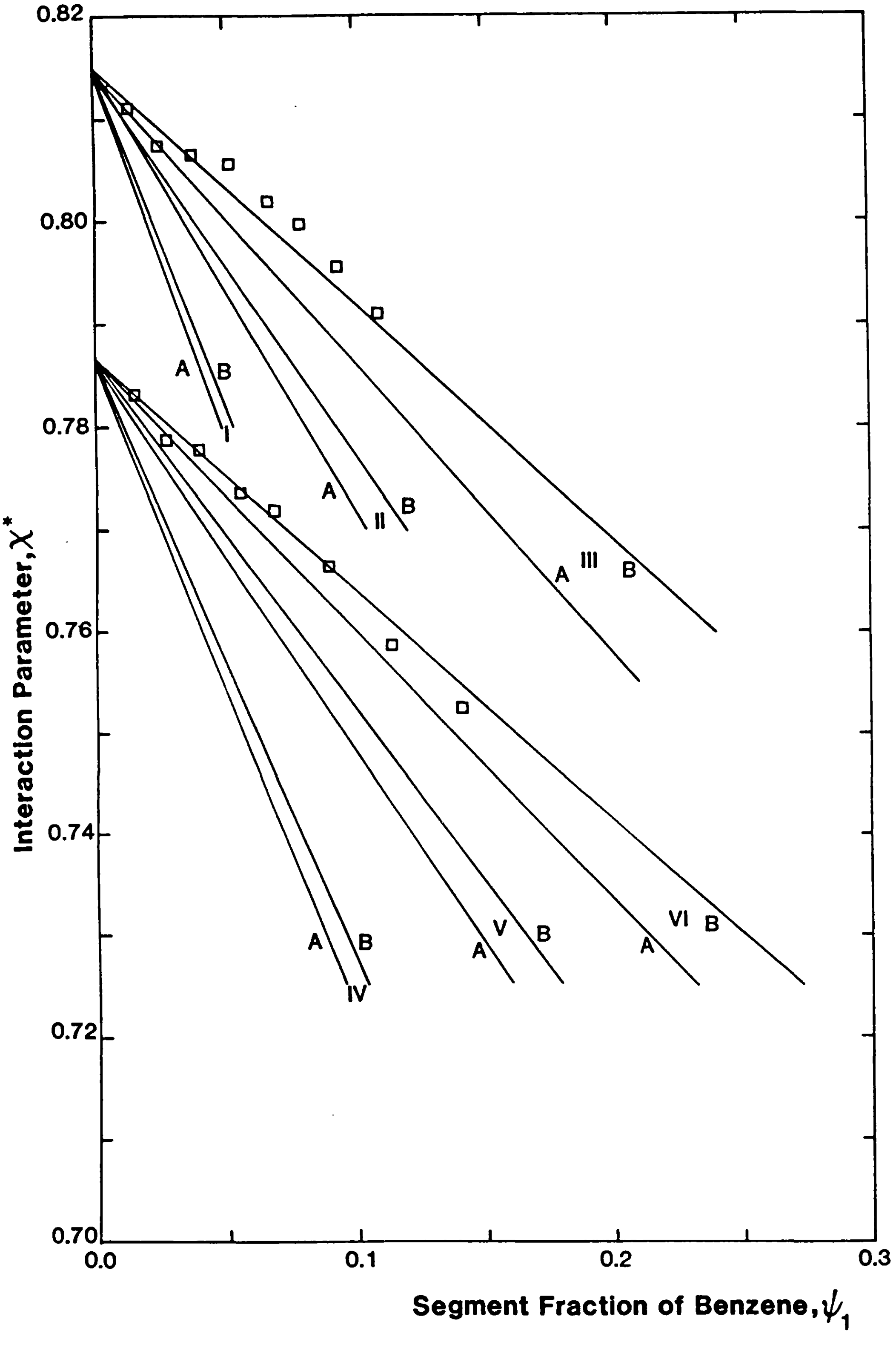

FIGURE 7-4: PREDICTION OF INTERACTION PARAMETERS BY FLORY'S 'EQUATION OF STATE' THEORY FOR BENZENE IN PDMS AT 30°C

Experimental points from Chapter 4.

For explanation of curves, see text.

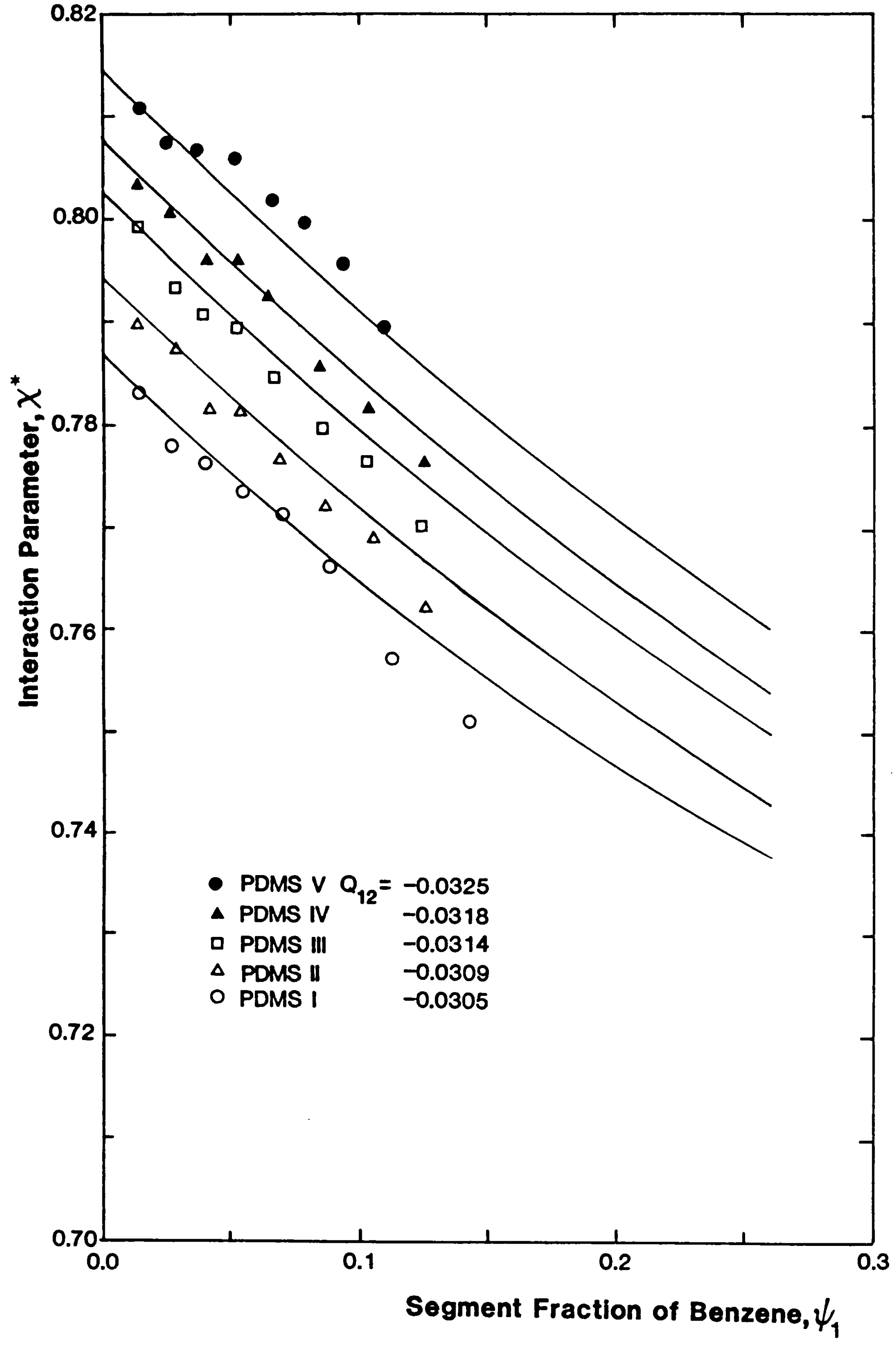

FIGURE 7-5: INTERACTION PARAMETERS FOR BENZENE AT 30°C

Experimental points from Chapter 4.

Solid curves: Flory's theory with $X_{12}' = 22{\cdot}0$ J cm^{-3}, $s_1/s_2 = 1{\cdot}05$ and Q_{12} values as indicated.

range of concentrations but to achieve a satisfactory fit to experimental results at high polymer concentrations physically unreasonable values of s_1/s_2 have to be adopted. The value of 1·05 found to best fit the experimental results in the systems studied here is not predictable from pure component parameters.

The reasons for this disagreement have been discussed by many workers, notably by Patterson *et al.*[159] They found poor agreement of theoretical predictions of χ^* and χ_S for a number of systems, although they did not use s_1/s_2 as an adjustable parameter, and found that other intermolecular force models within the basic outlines of the theory did not significantly improve the agreement. They also cast doubt on the physical significance of the Q_{12} parameter and found that this did not greatly improve the theory.

A likely explanation for non-agreement of the theory lies in the adoption of the Flory-Huggins expression for the combinatorial entropy (equation (1.21)). Since χ^* is calculated by subtraction of the $\overline{\Delta S_1^{comb}}$ term from the experimentally measured change in chemical potentials on mixing, the value is clearly dependent on the model chosen for ΔS^{comb} so that deficiencies in equation (1.21) would lead to poor prediction of χ^*. Scott[197] has suggested that, since the cross section of the PDMS chain is greater than that of most solvents, the F-H expression would not be the best one to use. However, Patterson *et al.*[159] pointed out that its chain diameter is not that much greater than other polymers which seem to fit the theory quite well. Also the experimental results for siloxane oligomers show similar departures from theory despite having, presumably, very similar chain diameters. It had been suggested that the Q_{12} parameter, as the χ_S parameter, reflected an overestimation by the F-H expression of ΔS^{comb} but, as Flory has pointed out, the values found are too large to be considered a correction term. More recently, Lichtenthaler[198] has recalculated χ^* using his expression for ΔS^{comb} as mentioned in Section 1.1.(x) and claims much better agreements with the 'equation of state' theory.

Another possible source of explanation for the non-agreement of PDMS solutions with the theory is that PDMS has a considerably larger coefficient of expansion[134] than most polymers, a value close to that of many solvents. This means that 'equation of state' effects, which this theory emphasises, are small and deficiencies in the other parts of the theory may be more apparent than when considering other polymers with much greater 'equation of state' contributions to χ^*.

Muramoto[153] found that the Flory theory fitted his results for PDMS in MEK to within at most 10%. However, these were obtained around the middle of the concentration range ($\phi_2 \approx 0{\cdot}3 - 0{\cdot}7$) and from his results considerably greater deviations would be expected outside this range. Also, he found no significant change of χ^* for polymers with differing molecular weights above 4600. He has calculated χ^* from vapour pressure lowering measurements in a similar manner to the calculations in this Thesis, except that he retained r as the ratio of the molar volumes of the components despite calculating ΔS^{comb} on the basis of segment fractions, and the results should be of sufficient accuracy to show changes of the order noticed during this work. It may be that differences due to molecular weight are accentuated at very high polymer concentrations and so may not be so noticeable at lower concentrations. The molecular weight variation found in the present work may be described reasonably well by the 'equation of state' theory as long as the X_{12} (or Q_{12}) parameter is allowed to vary slightly. It is not clear whether or not this variation is to be expected but since X_{12} is an energy density, with units of J cm^{-3}, a small effect might be expected due to the density of the solution or, at infinite dilution, the density of the polymer. The density would increase with rising molecular weight and so would explain the trends found in Table 7-3.

7.3. APPLICATION OF THE UNIFAC METHOD TO PDMS-SOLVENT SYSTEMS

The UNIFAC method was applied to polymer solutions by Oishi and Prausnitz[76] and, by including a correction for 'free volume' effects they found that, for a number of polymer systems including poly(isobutylene), polystyrene and poly(vinyl acetate), prediction of solvent activities could be made to, at worst, 11% and in most cases considerably better. Teng and Lloyd[199] reported that for polystyrene solutions, UNIFAC predicted the activity but not the interaction parameter. Gottlieb and Herskowitz[200] applied the method to PDMS solutions in a number of solvents including pentane, heptane and benzene and found agreement of the interaction parameter with experimental measurements to within 10%. They suggest, as might be expected, that the free volume corrections are small for these systems and with n-alkanes lead to a worsening of the prediction of solution properties. In general they found that the concentration dependence was predicted reasonably well but that the method overestimated χ in n-alkane-PDMS systems and underestimated it in others but found that agreement[201] could be improved by varying the $3c_1$ parameter (see Section 1.11.(i)), but in most cases unreasonable values were needed. Prausnitz[201] stressed the fact that UNIFAC is only an estimation method and rejected this approach. It is of limited use since there is no way to predict the value required for any particular system. The greatest differences between the predictions and experimental values were, in general, found as the concentration of solvent decreased, particularly in the case of benzene. Since this is the concentration region concerned in most of the work covered in this

Thesis and is of considerable practical importance, it would be useful if the fit in this region could be improved.

As discussed in Section 1.11.(ii) the method is necessarily approximate. Suggestions for possible improvements have included accounting for the temperature dependence of the UNIFAC parameters.[203] An additional complication arises when using the method with PDMS since the parameters for silicone type compounds published by Gottlieb and Herskowitz[204] are based on a relatively small data set.

The residual part of the solution activity will be mainly that due to exchange interactions, i.e. that part covered by χ_H or X'_{12} in the solution theories previously discussed. There is no account of any entropic contribution, the counterpart of which would be χ_S or Q_{12}. The configurational part of the activity may also be in error as was discussed in Section 1.8. It is not clear whether any or all of these effects are in operation.

The great advantage of the UNIFAC method is that it needs no experimental data. It is difficult to see how the theory could be improved in terms of the problems discussed in the preceding paragraph, except perhaps by modification of the expression for a^{comb}. However, it was interesting to determine whether a single value of one experimentally measurable property would allow a better prediction of solution properties across the range. As was shown in Chapter 4, GLC provides a quick and convenient method of determining solution properties and this leads to values at infinite dilution. Therefore, the χ^{∞} value was used in conjunction with the UNIFAC method as described by Oishi and Prausnitz to attempt to improve the fit to experimental results.

A computer program was written to apply UNIFAC to polymer solutions and is reproduced and discussed in Appendix II. It may also be used to predict results in terms of volume or segment fractions but for the discussion in this Chapter, only the former has been used. Initially it was applied to the results described in Chapter 5 for benzene, cyclohexane and hexane at 25°C and the results are shown as the broken curves in Figure 7-6. The UNIFAC parameters needed for the calculations were taken from literature sources.[75,204] Also shown are the experimental measurements from Chapter 5 and the predicted values from two modified versions of the theory. If χ^{∞} is the experimentally determined interaction parameter at infinite dilution and χ_{UNI} that predicted by the UNIFAC method, then to obtain agreement χ_{UNI} needs to be adjusted by a factor χ_A such that

$$\chi_A = \chi^{\infty} - \chi_{UNI} \tag{7.4}$$

The value of χ_A may be assumed to account for deficiencies in the entropic contribution to the theory or any other deficiences not previously accounted for. The simplest adjustment is simply to add this value to χ_{UNI} across the concentration range to give a series of values which will be denoted by $\chi_{UNI(1)}$. In view of the observation in the work of Gottlieb and Herskowitz cited above that the method led to better predictions at higher solvent concentrations in some systems, an alternative adjustment was tried whereby it was multiplied by the polymer volume fraction so that a smaller correction was applied at higher solvent concentrations. This is denoted by $\chi_{UNI(2)}$. Thus the two adjusted versions of χ_{UNI} shown in Figure 7-6 are given by

$$\chi_{UNI(1)} = \chi_{UNI} + \chi_A \tag{7.5}$$

and

$$\chi_{UNI(2)} = \chi_{UNI} + \chi_A(\phi_2) \tag{7.6}$$

To quantify the fit of these treatments, the percentage deviation of each UNIFAC treatment from the experimental results (assumed to be given by the linear relations described in Chapter 5)

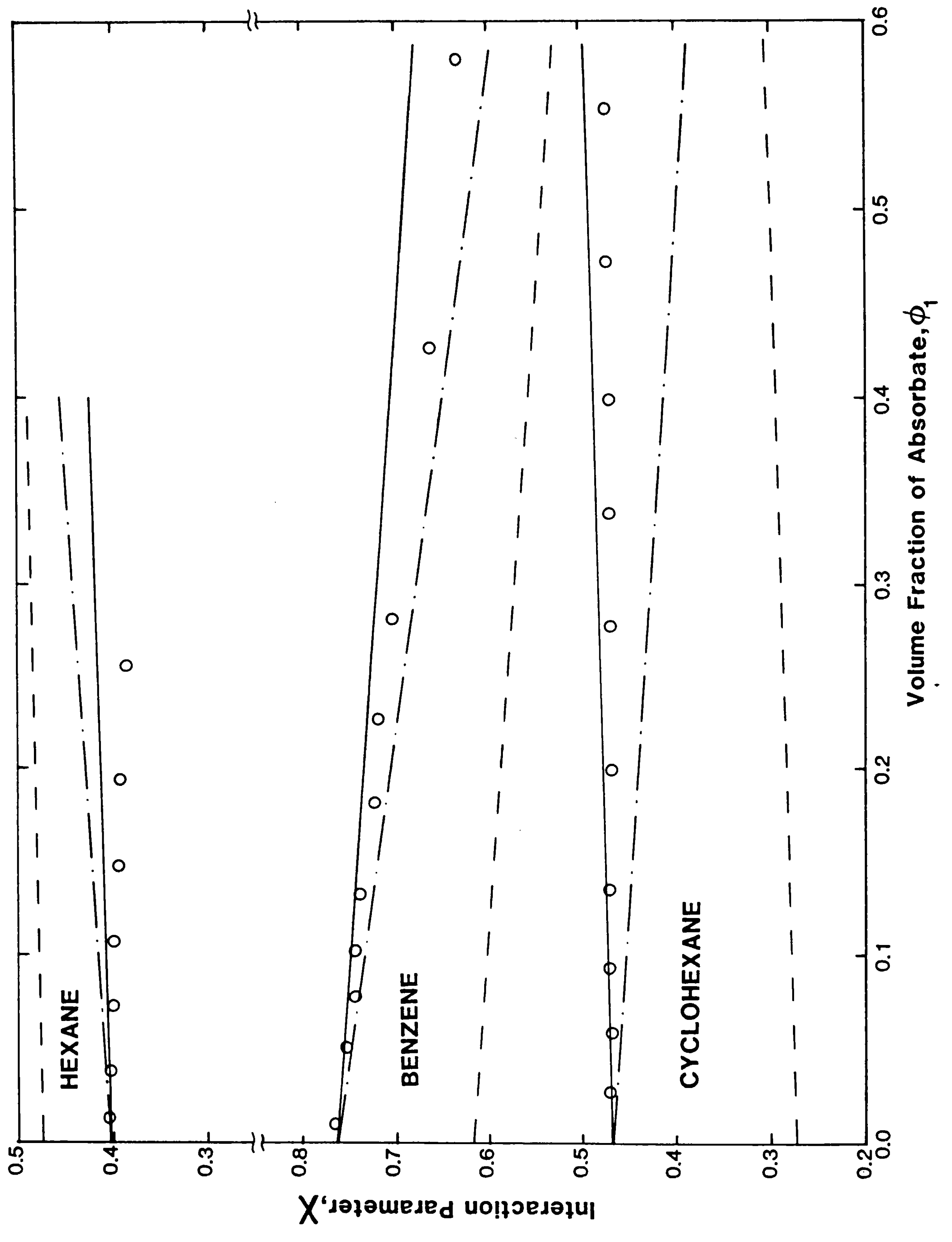

FIGURE 7-6: PREDICTION OF INTERACTION PARAMETERS BY THE UNIFAC METHOD

Experimental points from Chapter 5.

— — — χ_{UNI}; —— · —— · — $\chi_{UNI(2)}$; ———— $\chi_{UNI(1)}$.

was calculated at solvent volume fractions of 0, 0•2 and 0•5. Clearly the form of the adjustments made must lead to exact agreement at infinite dilution. The results are shown in Table 7-4, negative values indicating that the prediction underestimates the results.

TABLE 7-4: PERCENTAGE DEVIATION OF UNIFAC TREATMENTS FOR PDMS INTERACTION PARAMETERS AT 30°C

SOLVENT	CYCLOHEXANE			BENZENE			HEXANE		
VOL. FRAC	0•0	0•2	0•5	0•0	0•2	0•5	0•0	0•2	0•5
UNIFAC	-41•4	-39•6	-36•3	-19•7	-19•3	-17•4	17•8	24•3	36•4
UNI(1)	0	1•7	2•3	0	1•7	5•8	0	5•9	17•0
UNI(2)	0	-6•6	-7•4	0	-2•5	-5•8	0	9•6	26•7

Inspection of Figure 7-6 and Table 7-4 shows that for both hexane and cyclohexane the best fit is given by the adjustment in equation (7.5). For hexane a larger adjustment would be needed to give complete agreement with experiment while a smaller adjustment would be needed in the cyclohexane system. For benzene, the concentration dependent adjustment gave a slightly better fit. In every case though the introduction of one experimental measurement allows a vastly improved prediction of solution properties across the concentration range.

Since the treatment given by equation (7.5) gave the best fit for two of the systems and was not significantly worse than the other treatment at low concentrations of benzene, it was applied to the five hydrocarbon-PDMS systems at 30°C described in Chapter 4. No literature values for the interaction constants for the chlorinated hydrocarbon-siloxane compounds could be found so that these systems were not included in this discussion. The results are shown in Figure 7-7. In a similar manner to above the percentage deviation is shown in Table 7-5.

TABLE 7-5: PERCENTAGE DIFFERENCES OF UNIFAC TREATMENTS FOR PDMS INTERACTION PARAMETERS AT 30°C

SYSTEM	PENTANE		HEXANE		HEPTANE		BENZENE		CYCLOHEXANE	
VOL. FRAC	0·0	0·2	0·0	0·2	0·0	0·2	0·0	0·2	0·0	0·2
UNIFAC	19·6	27·9	17·9	25·2	10·9	22·2	-20·3	-20·9	-49·5	-39·5
UNI(1)	0	2·4	0	6·6	0	10·5	0	0·5	0	-1·5

As was noted with the results at 25°C the adjustment is insufficient to give exact agreement with the n-alkane systems, especially n-heptane, and slightly overestimates the differences for benzene and cyclohexane.

Finally, the ability of the UNIFAC method to predict the molecular weight variation of the interaction parameters as found in Chapter 4 was examined. Teng and Lloyd[199] have recently studied this for polystyrene solutions but since no significant variation of solution property with molecular weight was found no conclusion was reached. The basic UNIFAC method and that adjusted using equation (7.5) was applied to the five PDMS samples studied in hexane and benzene at 30°C and may be compared with the experimental results from Chapter 4 in Figure 7-8 where, for clarity, only the experimental values for three polymers (PDMS I, PDMS III and PDMS V) are shown. The basis of UNIFAC is that group parameters are independent of the molecule in which the group occurs and so no adjustment of these values was needed for application of the method.

It may be seen that in both solvents a variation of χ_{UNI} with

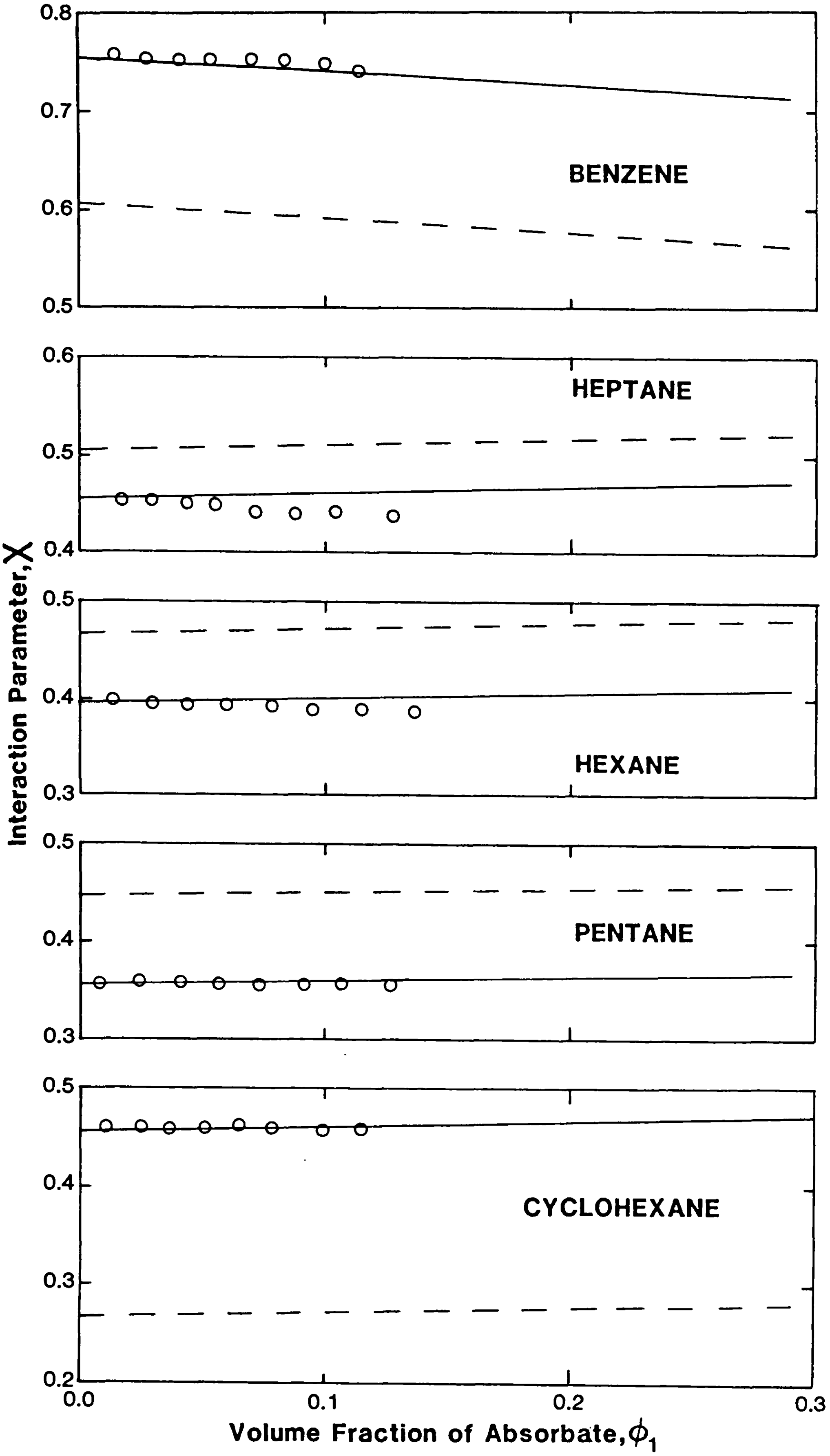

FIGURE 7-7: INTERACTION PARAMETERS PREDICTED BY THE UNIFAC METHOD

χ_{UNI} — — — — $\chi_{UNI(1)}$ ————

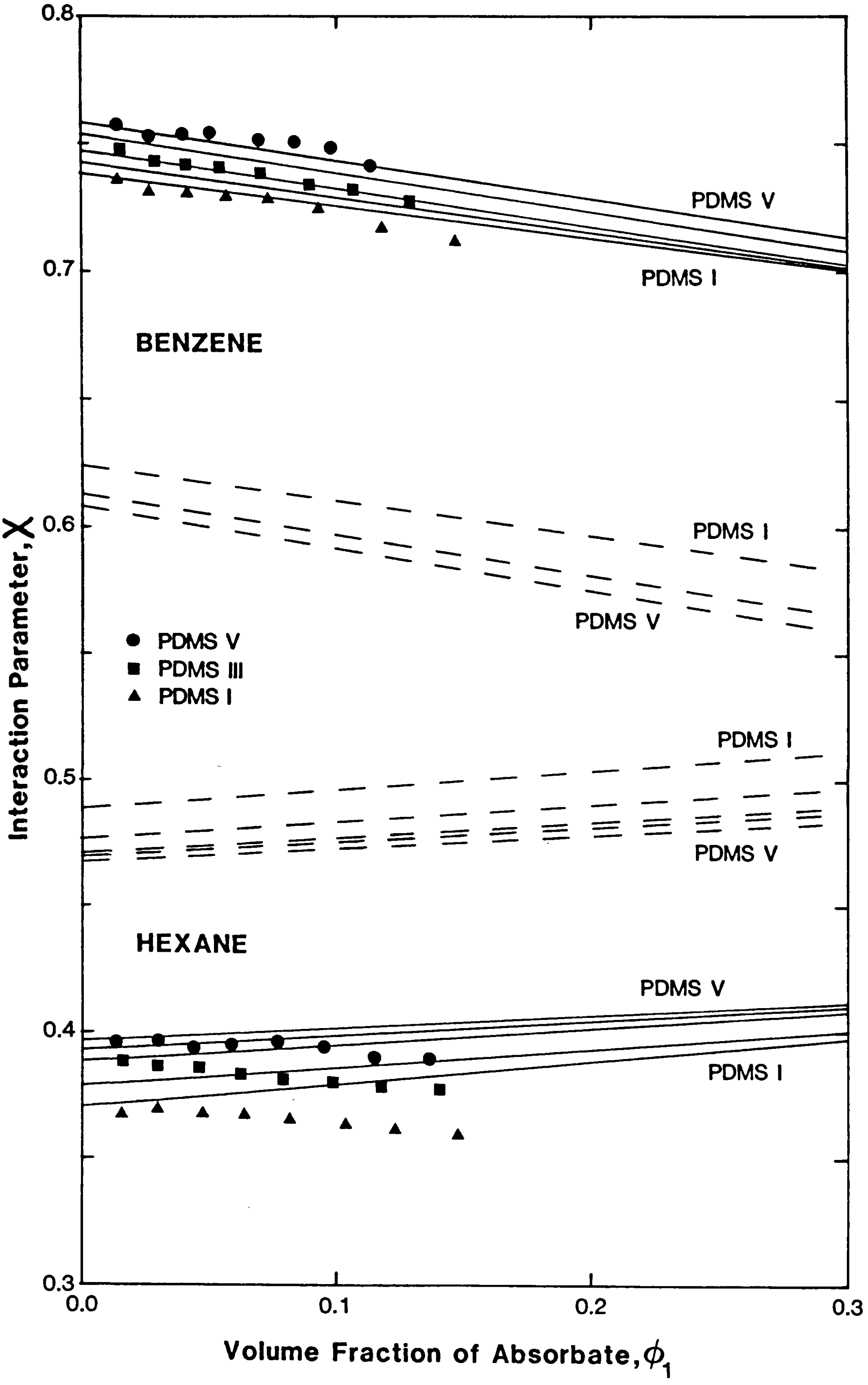

FIGURE 7-8: PREDICTION OF INTERACTION PARAMETERS FOR VARIOUS MOLECULAR WEIGHT PDMS AT 30°C BY THE UNIFAC METHOD

χ_{UNI} — — — —　　　$\chi_{UNI(1)}$ ————

molecular weight is predicted although the values for the three higher molecular weight polymers in benzene are indistinguishable on the scale used in Figure 7-8. However, in both cases the direction of the variation is wrongly predicted, the experimental values having χ increasing with molecular weight while the opposite trend is predicted by UNIFAC. If the UNIFAC results are recalculated on the basis of the adjustments outlined above then the experimentally observed trend is reproduced. However, it is clear, particularly with hexane as solvent, that even when using this proposed adjusted method the agreement with experimental is not as good with the lower molecular weight polymers.

7.4. CONCLUSIONS

It has been shown that absorption results, extrapolated to infinite dilution can be used to obtain a reasonable estimate of the solubility parameter of a polymer. Although the solubility parameter is still used for many applications and has the great advantage of simplicity, its use in polymer solution thermodynamics is severely limited as has been shown in the present work in attempting to predict interactions in PDMS solutions. The qualitative prediction is quite good in many cases but the treatment gives poor prediction of the χ values. Even if the solubility parameters are assumed to give χ_H, the treatment has limited predictive value since there is no way to adequately predict χ_S at present.

The Flory 'equation of state' polymer solution theory as originally formulated has been shown to lead to a poor prediction of the benzene and hexane interaction parameters in PDMS as infinite dilution is approached. The agreement with experimental results can be improved by treating the s_1/s_2 value as an adjustable parameter but, while other workers find good agreement at higher concentrations, physically unreasonable values have to be adopted to obtain a satisfactory fit to the small concentration dependences found near infinite dilution. This may mean that, as the polymer concentration becomes large, other effects not completely accounted for by the theory, such as the packing of polymer chains when in close proximity to each other, come into play.

As reported by other workers, the UNIFAC method has been found to give reasonable estimates of interaction parameters for PDMS solutions. It is particularly valuable in systems where no experimental data is available but the present work has shown that if one experimental measurement is available the predictions of the method can be vastly improved. The measurement used here is that of an infinite dilution interaction parameter but there appears to be no reason why values of other measurements or at other concentrations should not be used, although the form of the adjustments might have to be altered accordingly.

Chapter 8

Concurrent Retention Phenomena during Absorption

As described in the Introduction to this Thesis, vacuum microbalance techniques such as those employed here have often been used to confirm the validity of GLC results. Previous work by Ashworth and co-workers,[112-114] including the present author, has described this and, in particular, has investigated the retention behaviour of mixtures of DNP and squalane using a number of absorbates. It was desirable to extend this study to more polar absorbates but in these cases adsorption effects are known to complicate results, as mentioned in Section 1.13. It was established during early work[87] that spreading the liquids onto a solid support did not affect results using non-polar solutes but, with the moderately polar diethyl ether appreciable variation of activity coefficients with liquid loading was found.[114] Three more polar solutes: chloroform, dichloromethane and ethyl acetate have been used to extend the study of mixed solvents and the results are reported in Chapter 9. However, it was important to check that true equilibrium properties were being measured and that adsorption processes had no effect on the results.

Freeguard and Stock[205] studied the absorption of chloromethanes by DNP and by squalane using a McBain-Bakr microbalance and found no adsorption effects for liquid loadings of around 30%. As previously in this Thesis, liquid loadings are quoted as percentages by weight of the absorbent sample. In a GLC study, Nitta *et al.*[206] found significant effects with loadings as high as 40% although they claimed that adsorption effects occurred with non-polar solutes such as hexane which had not been detected by other workers. Thus, absorption isotherms were recorded for loadings of (nominally) 20% and 30% for the chloromethanes to confirm that true bulk sorption results were being measured. Ethyl acetate presented an additional problem in that it was found to interact strongly with components of the QB microbalance making measurement of equilibrium properties difficult. These interactions are not possible with the MS balance, as was described in Chapter 2, and so this balance was used for the study of ethyl acetate. In view of the results of Nitta *et al.* adsorption effects were expected to be more pronounced in this system and so isotherms were recorded over a wider range of loadings as well as for the bulk liquids. The absorption isotherms are listed in Tables AI-11 to AI-14 in Appendix I.

8.1. ACTIVITY COEFFICIENTS

The results for the two chloromethanes are shown in Figure 8-1 for squalane and Figure 8-2 for DNP as plots of logarithm of activity coefficient versus mole fraction of absorbate.

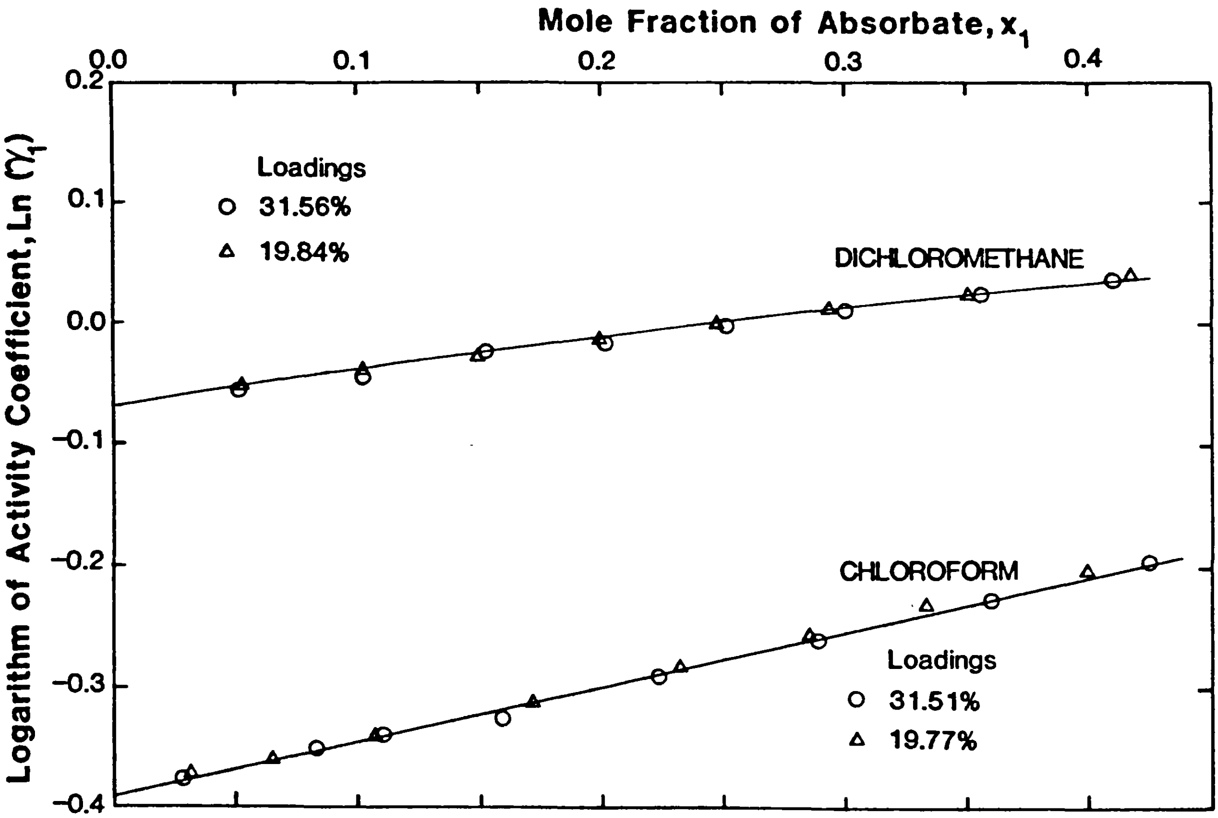

FIGURE 8-1: ABSORPTION ISOTHERMS FOR CHLOROFORM AND DICHLOROMETHANE IN SQUALANE AT 30°C

The isotherms at different loadings are indistinguishable on the scale used in the Figures and are well within experimental error, showing that bulk solution is the major contribution to absorption and that adsorption processes are not significant at loadings greater than 20%.

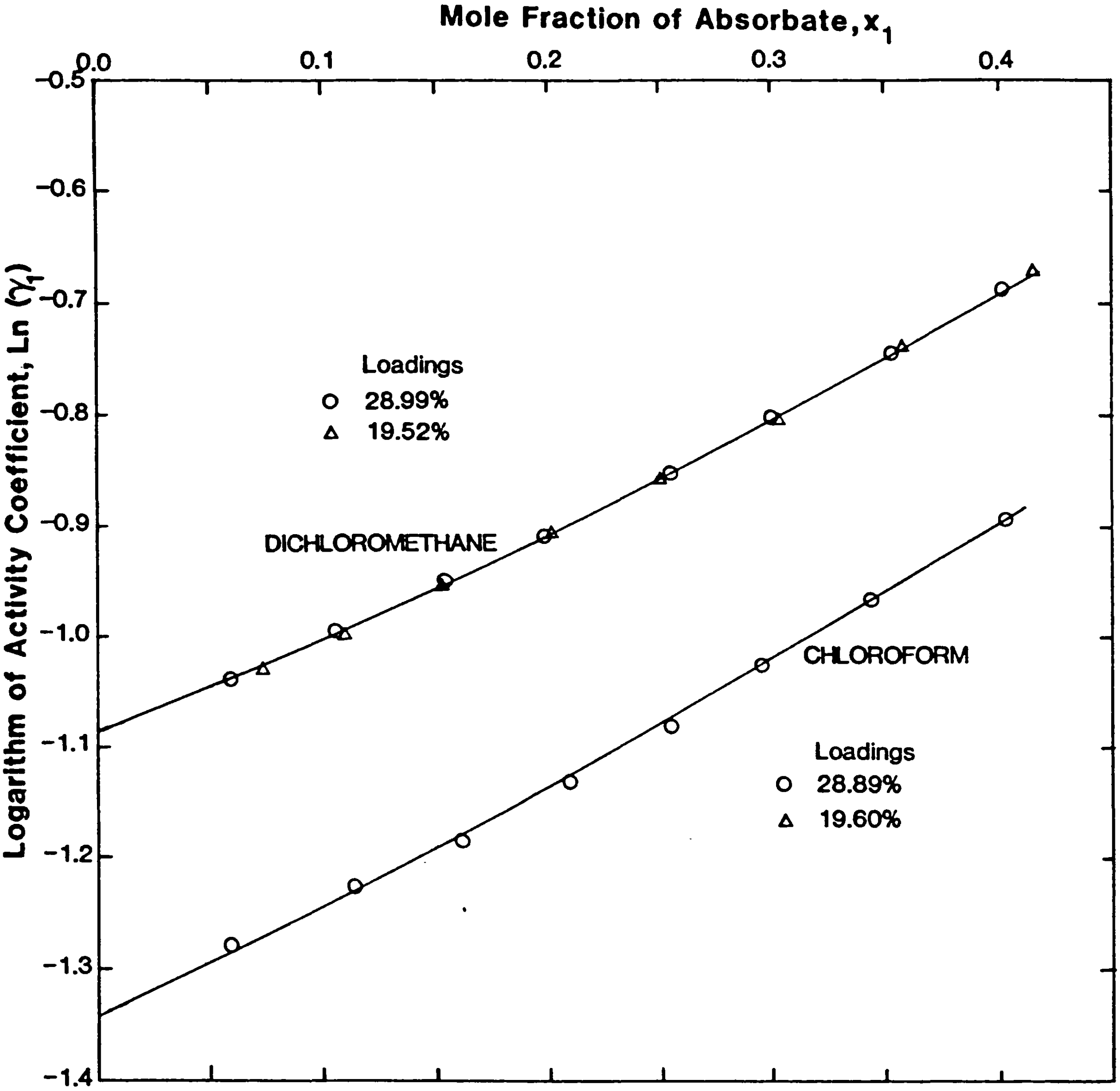

FIGURE 8-2: ABSORPTION ISOTHERMS FOR CHLOROFORM AND DICHLOROMETHANE IN DNP AT 30°C

The same plots for ethyl acetate in the two absorbents are shown in Figures 8-3 and 8-4 and clearly show the effect of liquid loading on the activity coefficients.

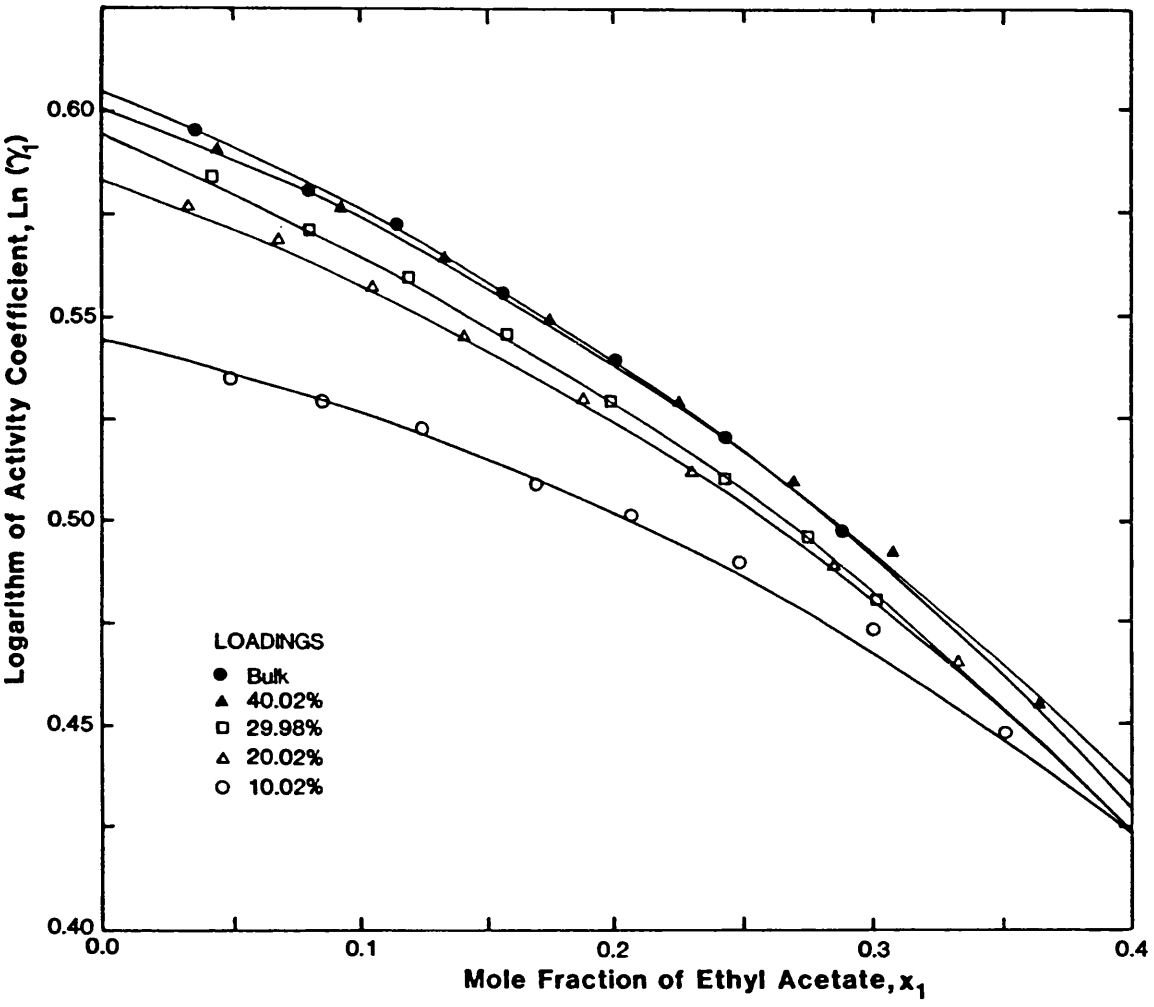

FIGURE 8-3: EFFECT OF LIQUID LOADING ON THE ABSORPTION OF ETHYL ACETATE BY SQUALANE AT 30°C

The plots follow the trend of lower values of activity coefficient at lower loadings as was found with the benzene-PDMS systems discussed in Chapter 4. The results for the bulk liquids and the 40% loaded samples agree within experimental error, although the former are

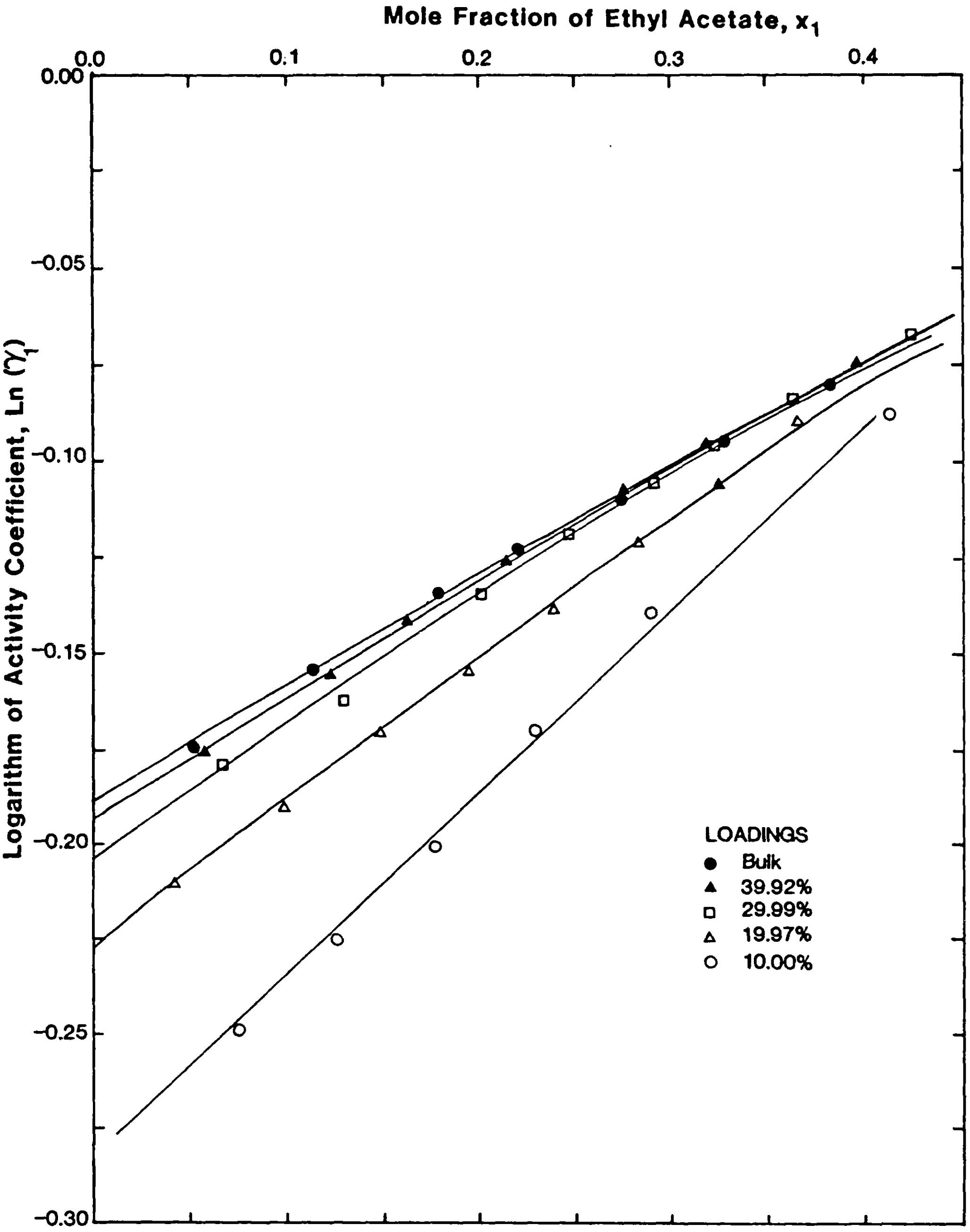

FIGURE 8-4: EFFECT OF LIQUID LOADING ON THE ABSORPTION OF ETHYL ACETATE BY DNP AT 30°C

slightly higher, but there is a large variation at lower loadings.

Ashworth and Everett[87] showed that the activity coefficient for systems such as those studied here could be represented by the sum of two contributions,

$$\ln \gamma_1 = \ln \gamma_1^{ath} + \ln \gamma_1^{th}$$

where γ_1^{ath} accounts for the athermal or configurational effects and γ^{th} for those due to thermal or energetic effects. They, and other workers, tried several forms for these contributions but showed that they could be adequately accounted for by the Flory-Huggins expressions outlined in Section 1.7. The theory was applied to the systems here by assuming a linear variation of interaction parameter with volume fraction (see Section 3.2.) and this was justified by the correlation coefficients of $>0{\cdot}999$ for each isotherm with the exception of the lowest loaded samples with ethyl acetate. The fit to the theory was again judged by calculation of an RMSD using equation (3. 9) and these were $<3 \times 10^{-3}$ in each case which was within experimental error. This was perhaps slightly surprising since the presence of polar components might be expected to invalidate some of the assumptions involved in F-H theory. However, the theory was shown to fit the results well over the limited concentration range studied and so was retained for use as the basis for extrapolation to infinite dilution. The true equilibrium properties were assumed to be given by the 30% loaded samples with the chloromethanes and by the bulk liquids with ethyl acetate. The results extrapolated to infinite dilution are summarised in Table 8-1.

The γ^{∞} values determined by Freeguard and Stock[205] for chloroform and dichloromethane were 0·653 and 1·076 in squalane and 0·251 and 0·379 in DNP respectively, showing reasonable agreement between the studies when the experimental errors of their results are taken into account.

TABLE 8-1: INFINITE DILUTION PROPERTIES OF ABSORBATES IN DNP AND SQUALANE AT 30°C

	DNP			SQUALANE		
	$\ln \gamma_1^\infty$	γ_1^∞	χ^∞	$\ln \gamma_1^\infty$	γ_1^∞	χ^∞
CHLOROFORM	-1·3412	0·2615	-0·4765	-0·3928	0·6752	0·6324
DICHLOROMETHANE	-1·0934	0·3350	-0·0434	-0·0733	0·9256	1·1398
ETHYL ACETATE	-0·1884	0·8283	0·5169	0·6054	1·8320	1·4640

Similar agreement was found with the GLC results of Sewell and Stock.[91] Nitta *et al.*[206] measured a value of $\gamma^\infty = 1{\cdot}96$ for ethyl acetate in squalane using GLC which is somewhat higher than the value of 1·832 found in the present work.

8.2. DEVIATIONS FROM SOLUTION IDEALITY

Ideal behaviour implies that the intermolecular forces in a solution are the same as those in the pure components. However, in most solutions those in solution are weaker than those in the pure liquids so that, on a simple model, molecules may escape into the vapour phase more readily. This results in a vapour pressure greater than the ideal value or, from equation (1.2), an activity coefficient greater than unity ($\gamma > 1$, $\ln \gamma > 0$). These are classified as 'Positive deviations' from Raoult's Law and are exhibited by most solutions.

In some cases solution forces can be greater than those in the pure components. This usually occurs when specific interactions such as hydrogen bonding, which are not possible in the pure components, exist in the solution. These forces reduce the tendency for molecules to move into the vapour phase and lead to a vapour pressure lower than the ideal value resulting in an activity coefficient less than unity ($\gamma < 1$, $\ln \gamma < 0$). These are classified as 'Negative deviations' from

TABLE 8-1: INFINITE DILUTION PROPERTIES OF ABSORBATES IN DNP AND SQUALANE AT 30°C

	DNP			SQUALANE		
	$\ln \gamma_1^\infty$	γ_1^∞	X^∞	$\ln \gamma_1^\infty$	γ_1^∞	X^∞
CHLOROFORM	-1·3412	0·2615	-0·4765	-0·3928	0·6752	0·6324
DICHLOROMETHANE	-1·0934	0·3350	-0·0434	-0·0733	0·9256	1·1398
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Raoult's Law.

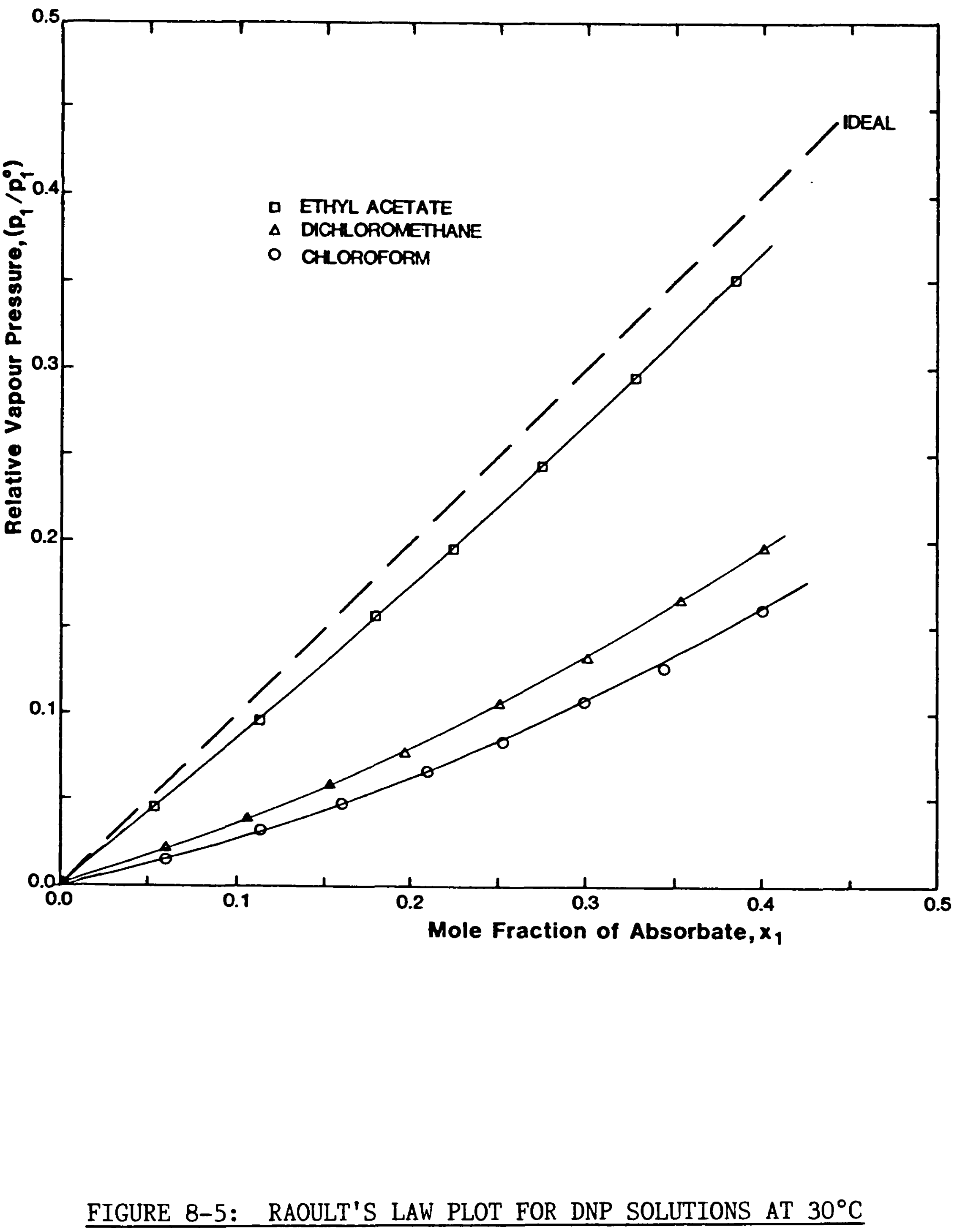


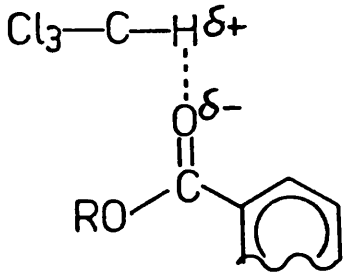
FIGURE 8-5: RAOULT'S LAW PLOT FOR DNP SOLUTIONS AT 30°C

The other contribution to solution non-ideality arises from the combinatorial effects due to size and shape differences between the components. These always give rise to negative deviations from

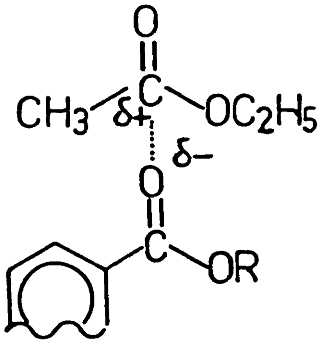
Raoult's Law and are usually smaller than the energetic effects. However, there are considerable size differences between the components in the system studied here and so these effects may be of importance.

Interpretation of the results is assisted by the Raoult's Law plots of relative pressure versus mole fraction shown in Figures 8-5 and 8-6 for DNP and squalane respectively.

Figure 8-5 shows that the three solutions in DNP exhibited negative deviations ($\gamma < 1$) indicative of combinatorial effects but also suggesting the presence of specific interactions in the solutions. Chloroform, dichloromethane and ethyl acetate are fairly polar compounds having dipole moments of 1·10, 1·60 and 1·78 Debye respectively.[207] No value could be found for DNP but the two carboxylic ester groups would impart slight polarity to the molecule. The oxygen atom of a carbonyl group is more electronegative (i.e. has a greater affinity for electrons) than the carbon atom leading to a polarisation of the carbonyl bonds. Similarly in the chloromethanes, the electronegative chlorine atoms would polarise the carbon-hydrogen bonds leaving the hydrogen atoms electron deficient. Thus, in solutions of these compounds, a weak chemical bond can form between the hydrogen atom and the carbonyl oxygen.



This type of 'Hydrogen bonding' has been shown to exist[208] in solutions of chloroform in ketones such as acetone and cyclohexanone and in esters by methods such as infra-red spectroscopy. The marked deviation of the DNP-chloromethane solutions from ideal behaviour can be explained in this way. Chloroform, as observed, would be expected to show greater deviations since, although it is a less polar molecule, the single carbon-hydrogen bond will be more polarised due to the three chlorine atoms and so will have a greater propensity to form hydrogen bonds. Specific interactions would also be expected in solutions of DNP and ethyl acetate since the polarisation of the carbonyl group is effective in both compounds so that alignment of dipoles can occur.



However, dipole interactions operate over only a short range and steric effects between groups around the dipoles can interfere. They are also weaker than hydrogen bonds and so the ethyl acetate solution shows smaller deviations from ideal behaviour.

The Raoult's Law plots for squalane in Figure 8-6 show a wider range of behaviour. Ethyl acetate shows positive deviations, chloroform negative and dichloromethane exhibits almost ideal behaviour. The results for ethyl acetate can be attributed to the relative weaknesses of the intermolecular forces. It is difficult to see how any specific interactions of chloroform and squalane could

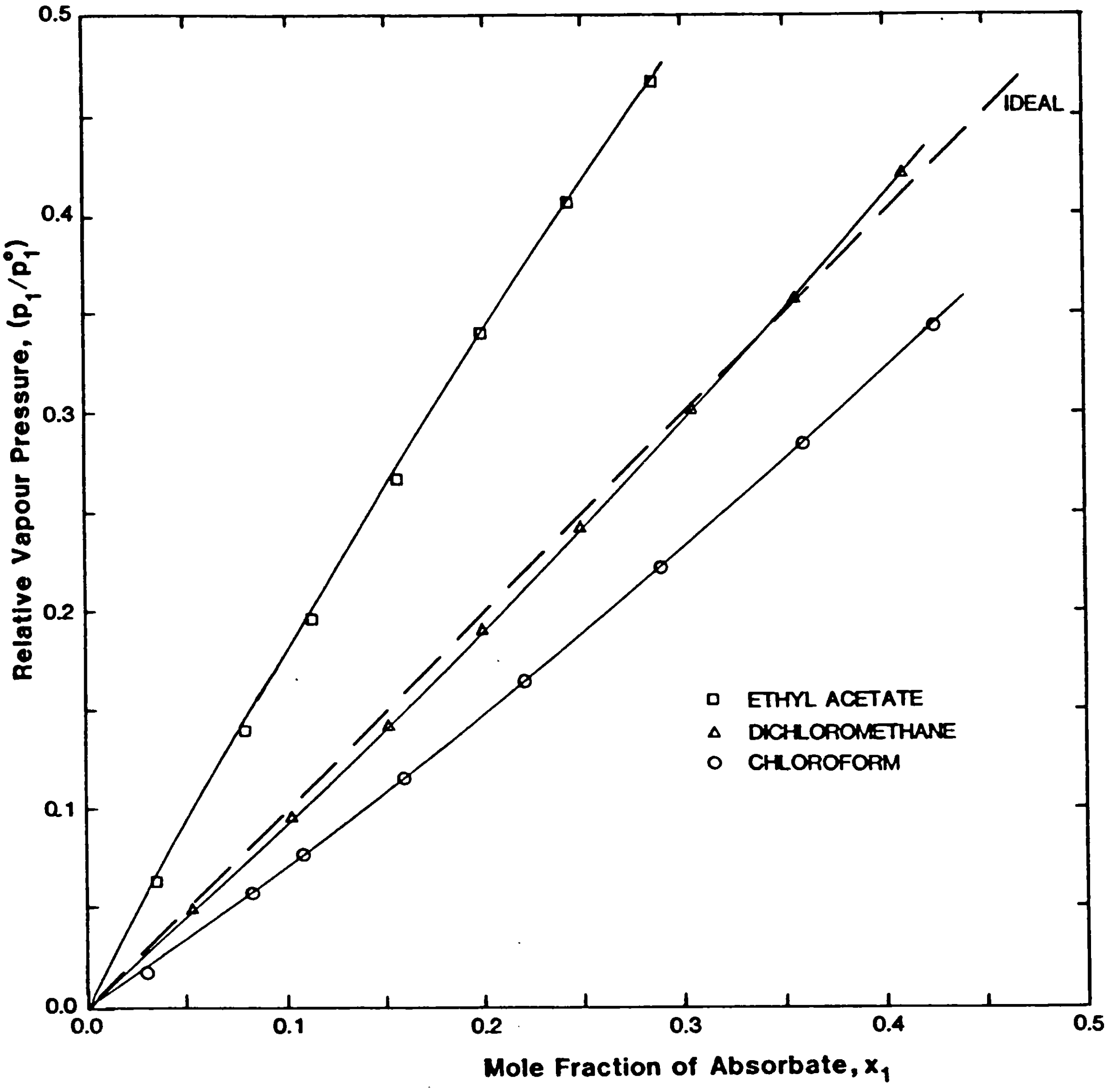


FIGURE 8-6: RAOULT'S LAW PLOT FOR SQUALANE SOLUTIONS AT 30°C

occur since the latter has no polarity and no capacity for hydrogen bonding so the deviation from ideality may have been due simply to the differing size and shape of the compounds. It is difficult to envisage squalane and dichloromethane forming an ideal solution and the results are probably best explained by assuming the cancellation of combinatorial and energetic effects. However, it should perhaps be noted that since dichloromethane is a smaller molecule than chloroform the combinatorial effects with the latter absorbate might be expected to be smaller.

8.3. ADSORPTION EFFECTS

It is clear from Figures 8-1 to 8-4 that no significant adsorption effects occurred with the chloromethanes with DNP or squalane at loadings above ~20%. However, such effects were noticeable for ethyl acetate at loadings up to ~40%. This may be compared to previous work on diethyl ether where the effects became negligible at >27-28% loadings.

As discussed in Chapter 1, interfacial adsorption can arise from three sources: gas-liquid, gas-solid and liquid-solid, although the last two of these are often difficult to separate. Treatments of the effects have occasionally been considered at finite concentrations[209] but the treatment is simpler when infinite dilution results are considered. Most quantitative work of this kind has been done on GLC results at infinite dilution and so the results from the adsorption isotherms for ethyl acetate extrapolated to infinite dilution have been treated in a similar manner. Table 8-2 shows the variation of γ^{∞} with liquid loading.

It may be seen that serious errors could be caused by assuming that, for this system, true bulk liquid activity coefficients were measured using samples of low liquid loadings. The differences between the results from the 10% loaded samples and the bulk liquids are 0·076 (9·1%) for DNP and 0·11 (6·0%) for squalane, considerably higher than were found with the polymer systems in Chapter 4 where differences of 1 - 1·5% were observed.

Martin[93] proposed equation (1.68) to account for the various

TABLE 8-2: VARIATION OF INFINITE DILUTION ACTIVITY COEFFICIENT WITH LIQUID LOADING FOR ETHYL ACETATE IN DNP AND SQUALANE AT 30°C

DNP		SQUALANE	
LOADING/wt%	γ_1^∞	LOADING/wt%	γ_1^∞
BULK	0·8283	BULK	1·8320
39·92	0·8237	40·02	1·8220
29·99	0·8167	29·98	1·8107
19·97	0·7964	20·02	1·7928
10·00	0·7524	10·02	1·7224

contributions to retention,

$$V_N = KV_L + K_IA_I + K_SA_S$$

where the symbols were defined in Section 1.13. This equation is only valid at infinite dilution and also only if the three contributions are independent, a condition usually fulfilled at the liquid loadings employed in the present work.[210]

Dividing each term in equation (1.68) by w_L, the weight of absorbent or stationary phase used gives V_g, the specific retention volume

$$V_N/w_L = V_g = K/\rho_L + K_IA_I/w_L + K_SA_S/w_L \qquad (8.1)$$

If a quantity W is introduced as the ratio of the weights of liquid to solid (i.e. $W = w_L/w_S$), then equation (8.1) may be written as

$$V_g = K/\rho_L + (K_SA_S/w_SW) + K_IA_I/w_L \qquad (8.2)$$

Since from equation (1.62)

$$V_g = 273\ R / \gamma_1^{\infty}\ \rho_1^{\circ}\ M_L = A/\gamma_1^{\infty}$$

where A is a constant term, γ_1^{∞} is inversely proportional to V_g so that

$$A(1/\gamma_1^{\infty}) = K/\rho_L + (K_SA_S/w_S)(1/W) + (K_IA_I/w_L) \qquad (8.3)$$

Thus, if only bulk partitioning occurred in the systems studied, there would have been no variation of γ_1^{∞} with loading. A linear plot of $(1/\gamma_1^{\infty})$ versus $(1/W)$ would be indicative of adsorption onto the solid and negligible contribution from gas-liquid interfacial adsorption which is accounted for by the final term of equation (8.3). The solid support used was a white diatomaceous earth which was a porous, irregular solid. Thus it was difficult to formulate an expression for the variation of interfacial area, A_I, with the amount of liquid so that the effect of the last term in equation (8.3) cannot be predicted. However, it would not in other than exceptional circumstances be a linear variation and so would have caused the plots to deviate from linearity.

The plots for the results for ethyl acetate with DNP and with squalane are shown in Figures 8-7 and 8-8. Also shown in Figure 8-9 is the corresponding plot for the benzene-PDMS systems investigated in Chapter 4. The same plot is valid when using volume fraction based activity coefficients except that the constant term, A, in equation (8.3) needs to be redefined.

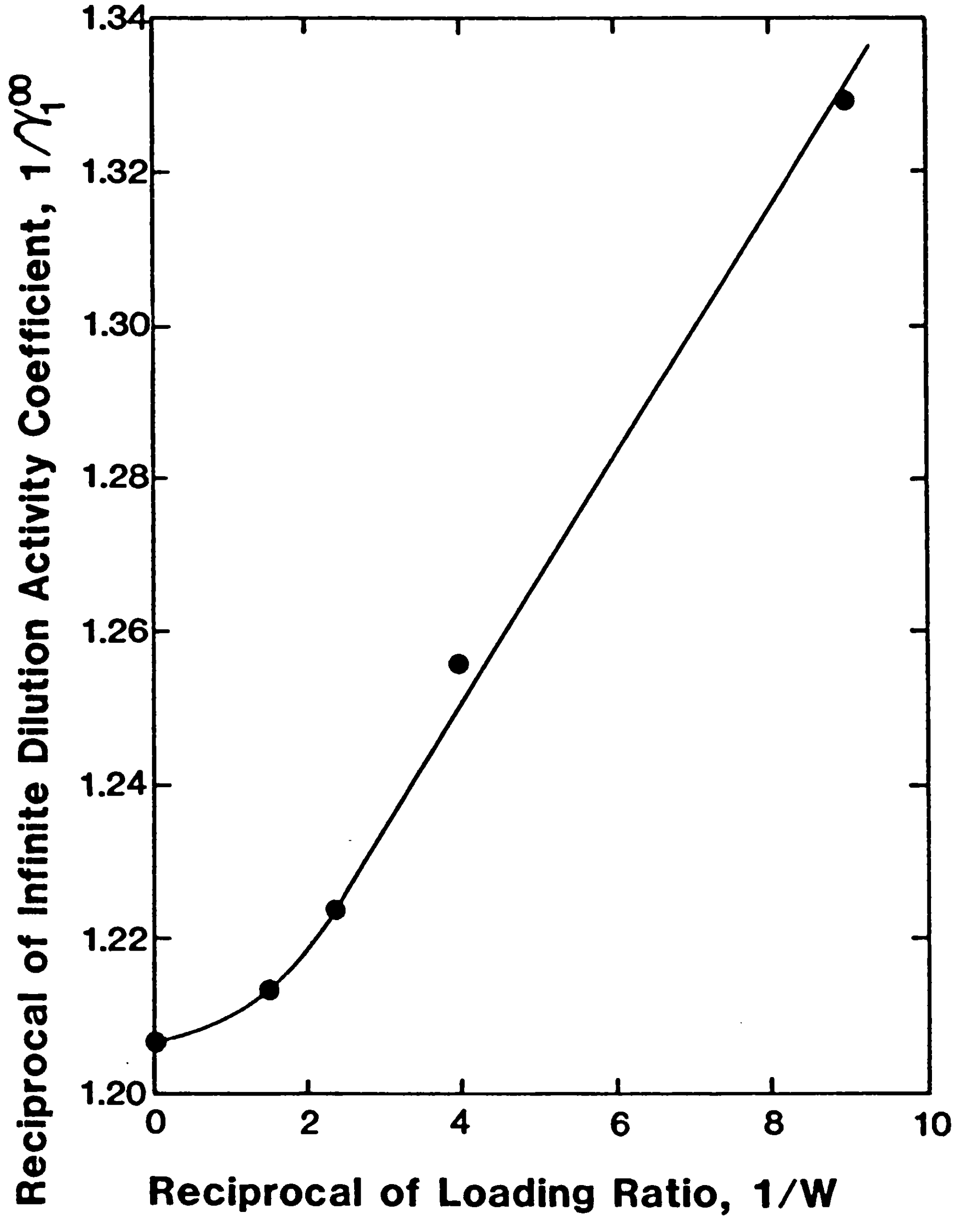


FIGURE 8-7: VARIATION OF $(1/\gamma_1^\infty)$ WITH (1/W) FOR ETHYL ACETATE IN DNP AT 30°C

The plots for the ethyl acetate solutions seem to be linear at low loadings (high W^{-1}) but there are too few results in this region to confirm this. There are, though, definite deviations from linearity suggesting that more than one adsorption process was in operation.

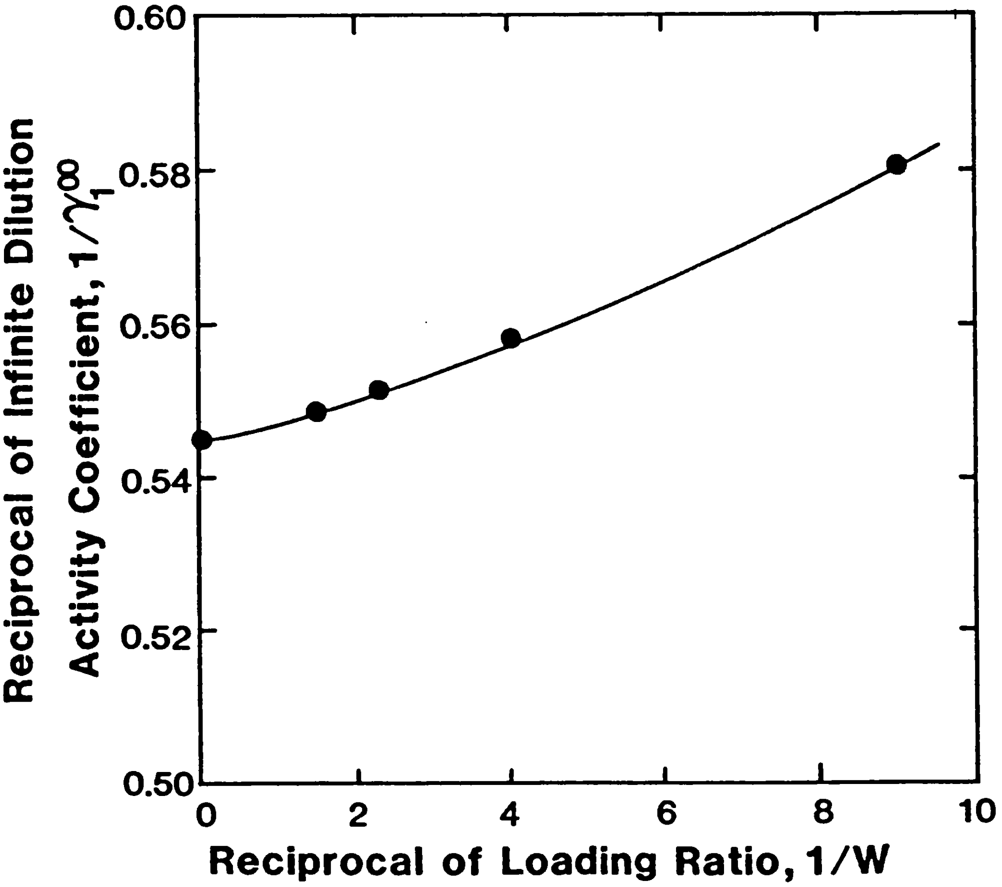


FIGURE 8-8: VARIATION OF $(1/\gamma_1^\infty)$ WITH (1/W) FOR ETHYL ACETATE IN SQUALANE AT 30°C

There is definite curvature in the plots for the PDMS-benzene systems but the effect of the adsorption processes is very much smaller than in the ethyl acetate solutions.

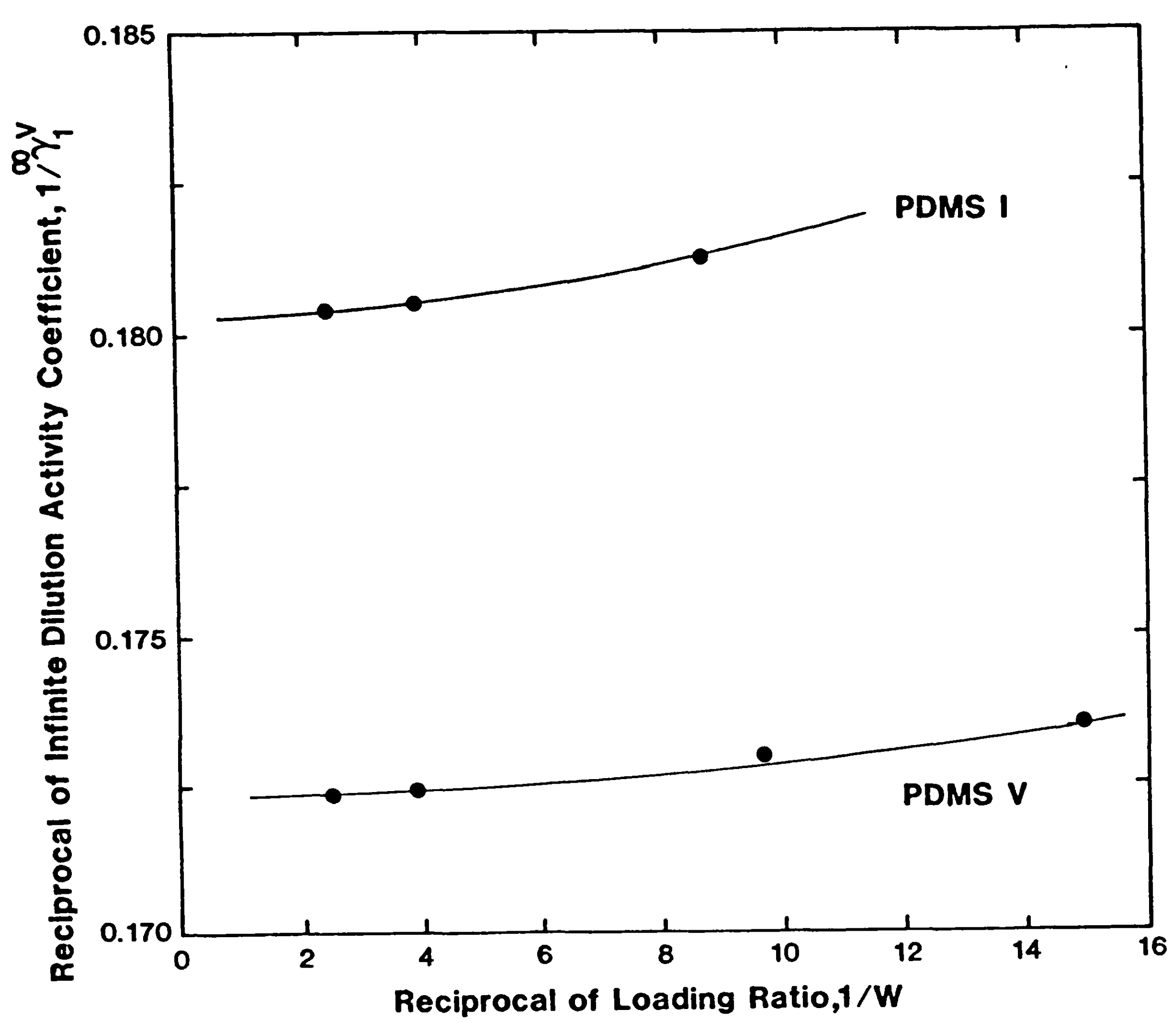


FIGURE 8-9: VARIATION OF $(1/{}^{\infty}\gamma_1^V)$ WITH (1/W) FOR BENZENE-PDMS SOLUTIONS AT 30°C

8.4. RETENTION PROCESSES

It was originally thought that adsorption at the gas-liquid interface would only occur with polar stationary phases. For instance, Littlewood and Wilmott[109] found significant adsorption effects with polar solutes in squalane but attributed these solely to solid support interactions. Parcher and Hussey[211] and Urone and co-workers[212] reached the same conclusion with other stationary phases. However, it was subsequently shown by Pecsok and Gump[97] and others[213,214] that these effects were possible when using polar absorbates in non-polar phases such as squalane or hexadecane so that some effect might be expected in the systems studied here. Gas-liquid interfacial adsorption can be related to differences in the surface tensions, σ, of the components of a solution. The surface tension is the result of a free energy at a liquid interface due to a net attraction of surface molecules into the liquid and can be used to explain many common properties of liquids.

The liquid surface partition coefficient, K_I, in equation (8.3) may be written as

$$K_I = \Gamma_1/c$$

where c is the concentration of absorbate in the vapour phase and Γ_1 its excess surface concentration over that in the bulk solution. This can be related to the surface tension via the Gibbs adsorption equation and it may be shown that (see Section 1.13.(i)).

$$\Gamma_1 = -(x_1/RT)(d\sigma/dx_1)$$

Thus it may be seen that if a solution has a different surface tension to the absorbent then an excess surface concentration should arise, although it is important to note that it is the rate of change of σ with concentration that is important rather than the absolute values. For solutions of acetone and methanol in squalane, Pecsok and Gump[97] found that there was a large change in surface tension of a solution at low absorbate concentrations ($x_1 < \sim 0{\cdot}02$) but that above this the change was fairly small so that adsorption at the gas-liquid interface would be most important at concentrations lower than those studied during the recording of the absorption isotherms in the present work. However, this does partly explain why in all cases the disparity between results obtained at different loadings decreases at higher concentrations.

To gain an idea of the amount of adsorption onto the solid support that might be expected, adsorption isotherms were recorded using bare Celite. The results are recorded in Table AI-15 of Appendix I and are shown in Figure 8-10 in the form of weight of vapour absorbed per gram of Celite versus relative pressure. As would be expected, the increase in adsorption decreases at higher pressures, as the active sites on the solid are used up. The surface of the Celite is likely to contain two types of active site;[4] polar siloxane groups and exposed silanol groups that can form hydrogen bonds. Ethyl acetate has less capacity for polar interactions and is also a larger molecule and so excluded from the smaller pores of the solid. Thus it is retained least of the three solutes while chloroform which readily forms hydrogen bonds is adsorbed to the greatest extent.

The 30% loaded samples used for the chloromethanes contained ~1·1 g of Celite so the maximum adsorption at $p/p^\circ = 0.5$ could have been ~1·3 mg and 0·99 mg for chloroform and dichloromethane respectively compared to total vapour uptakes in the range 85–100 mg and 60–70 mg so that adsorption onto the solid could represent at most 1 - 1·5% of the total absorption. For the 40% and 10% loaded samples used with ethyl acetate there could have been adsorptions onto the solid of ~2·4 mg and ~5·4 mg compared to vapour uptakes of ~1 g and 200–300 mg. Thus the contribution to absorption could be about 0·2% for the 40% sample but 2–3% for the 10% loaded sample. However, these represent maximum values for adsorption. Freeguard and Stock[215] studied the absorption in these systems using a McBain-Bakr microbalance and found Celite to be "virtually inert" but firebrick (a pink diatomaceous solid) was quite "active". However, interestingly, a 5% sample on this

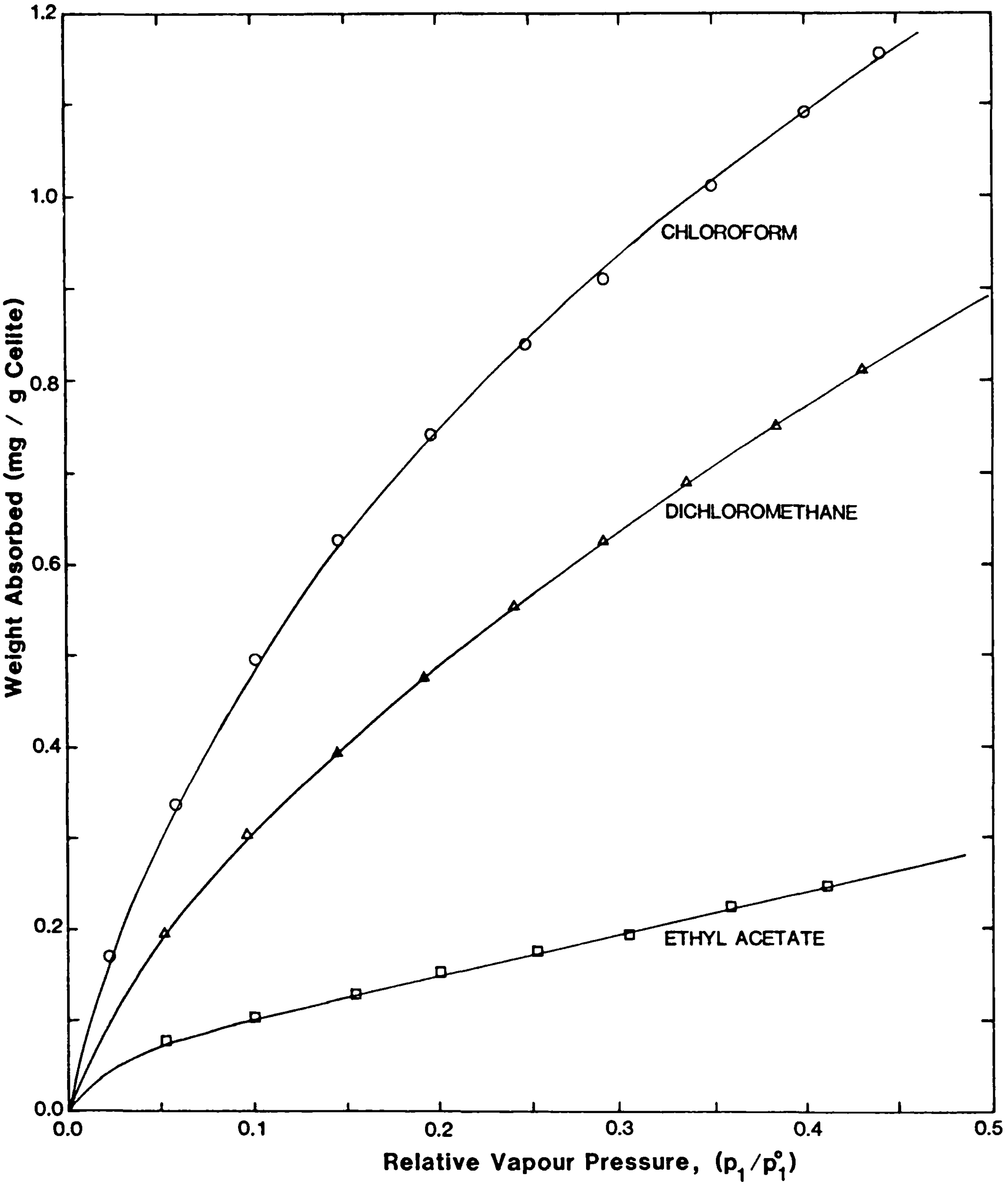


FIGURE 8-10: ADSORPTION OF SOLUTES BY 'CELITE' AT 30°C

latter support had a vapour uptake less than that of the bare support showing that the absorbent liquid had a deactivating effect. The same type of effect would be expected with Celite, particularly with DNP which would cover some polar sites on the solid, and so the above calculations almost certainly overestimate the effect of adsorption onto the solid support.

If bulk solubility were the only retention process in operation, the same vapour uptake per unit weight of liquid absorbent would be expected at the same pressure irrespective of loading. That this is not so is further illustrated for the ethyl acetate solutions by Figures 8-11 and 8-12. The Figures show that the absorptions were virtually identical for the 30% samples and the bulk liquids but that the 10% loaded samples absorbed significantly higher amounts of vapour. For the bulk squalane solution there was an approximate uptake of 93 mg g^{-1} at $p/p^\circ = 0{\cdot}5$ while the value for the 10% sample was 97 mg g^{-1}. Thus for a total weight of 1·96 g, there was an 'excess absorption' of approximately 7·8 mg. From the above discussion the maximum adsorption onto the solid could have been ~5·4 mg so that adsorption at the gas-liquid interface must have been taking place to some extent. The DNP samples showed solubilities of ~103 mg g^{-1} for bulk liquid and ~107 mg g^{-1} for the 10% loaded sample, giving an 'excess absorption' of about 8·0 mg while the 18 g of solid would only account for at most 3·6 mg (the adsorption onto the solid was ~0·2 mg g^{-1} at $p/p^\circ = 0{\cdot}3$). Thus adsorption at the liquid surface is also indicated in this system but the effect was greater with the slightly polar DNP. These results seem to confirm the previous suggestions of gas-liquid interfacial adsorption with non- or slightly polar absorbents.

This calculation can also be applied to the benzene-PDMS systems.

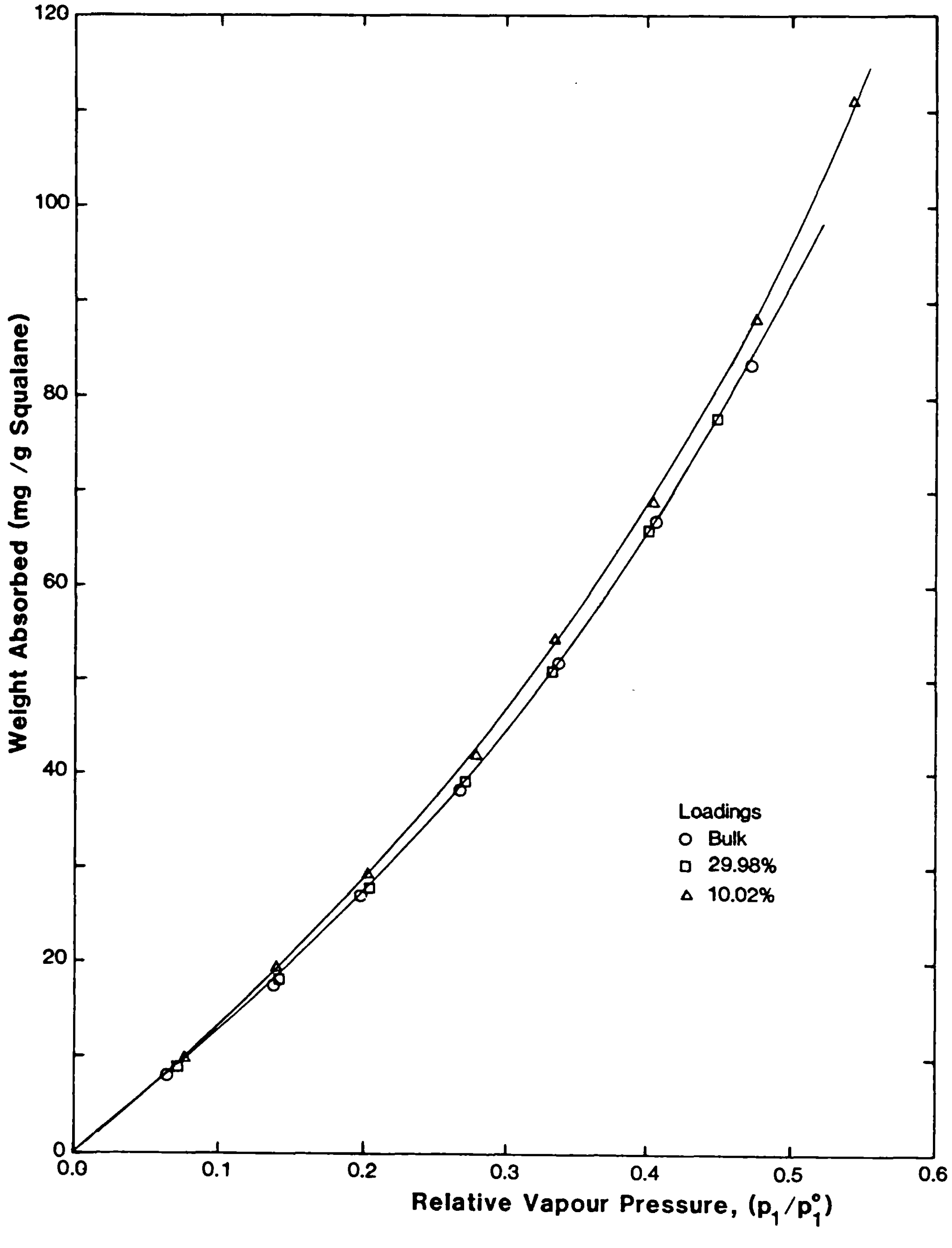


FIGURE 8-11: VARIATION OF ABSORPTION OF ETHYL ACETATE BY SQUALANE WITH LIQUID LOADING AT 30°C

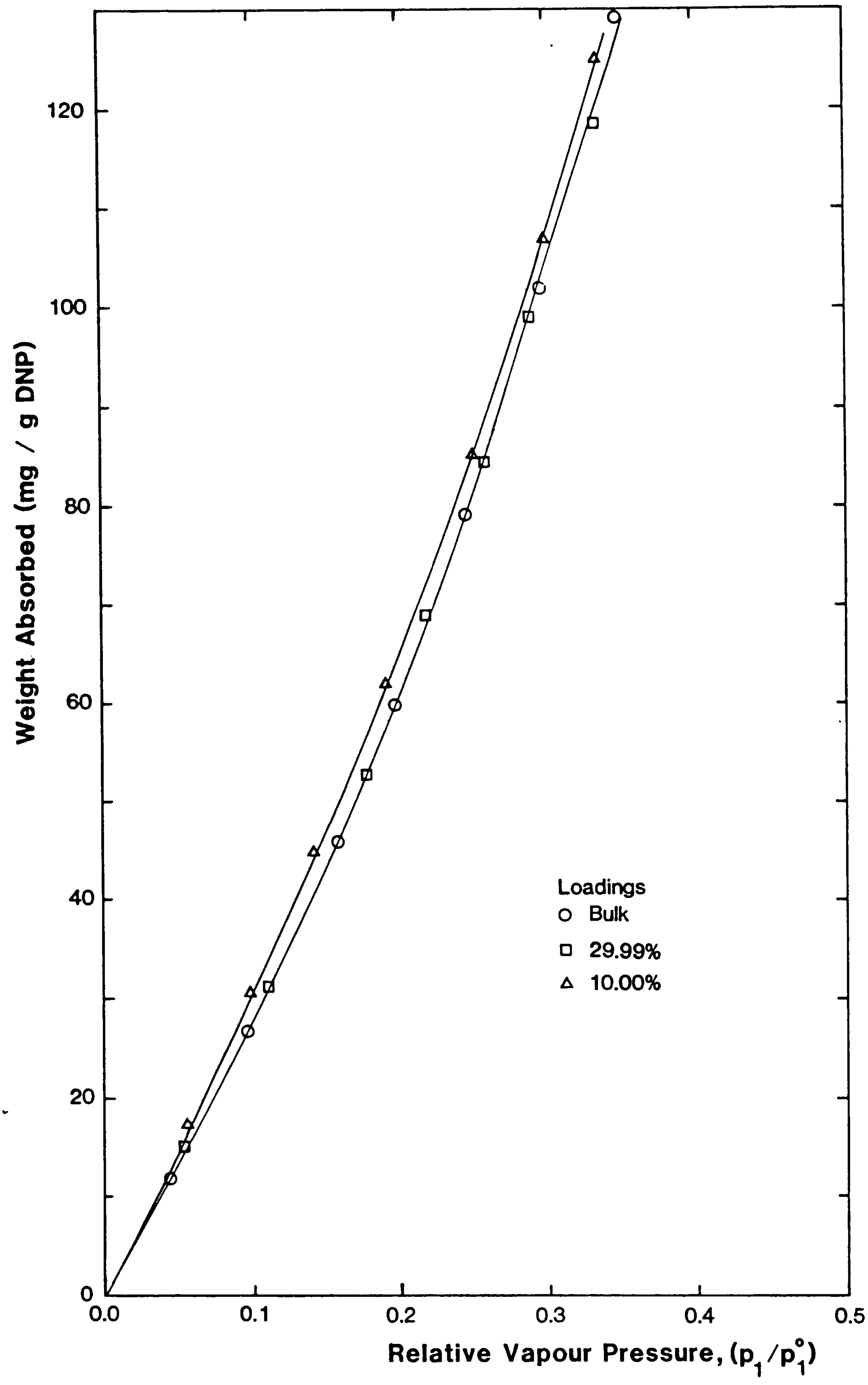


FIGURE 8-12: VARIATION OF ABSORPTION OF ETHYL ACETATE BY DNP WITH LIQUID LOADING AT 30°C

As an example, at a relative pressure of 0·53, the solubility of benzene in PDMS I at 30% loading was 138 mg g^{-1} while it was 146·5 mg g^{-1} for a 10% loaded sample. For the amounts of material used this leads to an 'excess absorption' of about 1·3 mg while the solid support would be expected to absorb less than 0·5 mg. This latter value was calculated using 0·28 mg g^{-1} for the adsorption of benzene by Celite as found by Ashworth.[129] However, while this appears to suggest that liquid surface adsorption is taking place, this conclusion should be treated carefully since the adsorption effects are much smaller than those found in the other systems and these values are close to the expected experimental error.

8.5. DISCUSSION

Summers *et al.*[158] found changes in retention to be important for PDMS-hydrocarbon systems only at loadings below 7% and attributed these effects to adsorption on bare, uncovered solid support. However, the precision of the GLC results was such that it would not show the variation found in the present work for loadings up to 20% and the present work also suggests that the support would adsorb insufficient solute to account for the observed effects. Indeed no significant retention was detected for benzene on the bare support in their GLC study. Thus, although the bare support may play a part at low loadings, the observed variation appears to be better explained by assuming a combination of adsorption onto the support (whether covered or uncovered) and at the gas-liquid interface. Braun and Guillet[216,217] have shown that surface effects can be important when using polymeric stationary phases. Naito and Takei[218] have also considered retention in polymeric stationary phases, including PDMS, and find considerable effects although the modified alumina support that was used was designed to maximise solid support effects and so liquid surface effects may not have been noticed.

The surface tension of squalane at 30°C was measured by Pecsok and Gump[97] and found to be 26·9 mN m^{-1}. The corresponding values for chloroform and dichloromethane are 26·4 and 25·8 mN m^{-1} respectively[147] so that the lowering of the surface tension of their solutions in squalane and the surface excess concentrations would be small. Solid support effects are also comparatively small in these systems and so large adsorption effects would not be expected and this is in accord wtih the observed results. Even though the solid support effects are smaller with ethyl acetate, the surface tension is considerably lower at 22·6 mN m^{-1} (interpolated from results over a range of temperatures[130]) so a greater liquid surface adsorption would be expected. Also, ethyl acetate is less soluble than the chloromethanes so that a surface excess concentration would be more apparent. Unfortunately no value for the surface tension of DNP could be found so that no further discussion of these systems in these terms can take place. Legrand and Gaines[219] have given a relationship from which the surface tension of PDMS polymers can be calculated and this leads to values of 19·9 mN m^{-1} and 20·57 mN m^{-1} for PDMS I and PDMS V at 30°C. Comparing the value of 27·5 mN m^{-1} for benzene it may be seen that some adsorption at the liquid surface would be expected. However, it should be stressed that discussion in these terms must necessarily be approximate since, as previously mentioned, it is the $(d\sigma/dx)$ value that determines Γ_1 and not merely differences between the surface tensions of the components.

A common method of reducing solid support interactions is to employ a silanised support. This type of support has active hydroxyl and other sites replaced by inert organosilane groups and the treatment has been shown to reduce the absorptivity of some supports by up to 70 per cent.[220] The absorption of diethyl ether by squalane showed that a 20% loaded sample supported on Celite or on a silanised (hexamethyl disilazane treated) support produced identical results and solid support effects were therefore assumed to be negligible. Thus it might be felt that use of a silanised support for the present systems would eliminate support effects and enable the liquid surface effects to be studied in isolation. However, in using silanised supports there is an additional factor to be considered. An untreated support has a relatively high surface energy (analogous to the surface tension of a liquid) but this is considerably reduced on silanising. Serpinet[221] has estimated the surface energy of a silanised solid to be ~24 mN m^{-1}.

This means that a liquid with a higher surface tension, such as squalane, will spread across the surface of an untreated support but will not wet a silanised solid. In this latter case, the liquid would lie in pools in pores and capillaries or in droplets at the surface, leading to a considerably reduced gas-liquid interfacial area and consequent reduction of adsorption effects. These considerations have led Serpinet[221] and Conder and Young[4] to suggest that silanised supports should not be used for physicochemical measurements. Thus there would be ambiguity if silanised supports were used with the present system even though the type of support appeared to have little influence on results in the diethyl ether - squalane system. This may be explained since, as it is a less polar molecule than ethyl acetate, diethyl ether (dipole moment = 1·25 Debye[206]) would interact to a lesser extent with the solid. Also, because it has a considerably lower surface tension[130] (15·8 mN m^{-1}) much larger gas-liquid interfacial effects would be expected with diethyl ether.

8.6. CONCLUSIONS

It has been shown that the effect on the absorption of benzene by poly(dimethyl siloxane) of spreading the polymer onto a solid support is probably due to a combination of adsorption at the gas-liquid and solid-liquid interfaces as well as, at very low loadings, on the bare support rather than simply due to the last of these effects as had been previously suggested. The effects, though, can be eliminated by using liquid loadings greater than 20%.

The suggestion of previous workers that adsorption at the gas-liquid interface could occur in non-polar stationary phases with polar absorbates has been confirmed for the ethyl acetate - squalane system since the (presumed) maximum measured adsorption onto the solid support was insufficient to account for the variations noticed. A similar effect was found with the slightly polar DNP. In these systems adsorption effects are important even for loadings as high as 40%. However, when chloroform and dichloromethane are used with these absorbents, loadings of 20-30% are sufficient to ensure that bulk sorption is the main retention process.

Conder and Purnell[210] have discussed concurrent retention mechanisms and concluded that "only bulk liquid partition can be determined by chromatography alone". To separate and quantify the adsorption effects, other measurements such as the surface area of the solid or the liquid interfacial areas, would be necessary as in the treatments of Conder and co-workers[4,210] and Berezkin.[222] There are other effects possible in chromatographic systems, such as the reduction of vapour pressure due to the Kelvin effect in capillaries, but, although these cannot be quantified, they are expected to be very small in the systems studied here.

Chapter 9

Partition Coefficients in Mixed Absorbents

The study of mixed stationary phases in gas-liquid chromatography has been used to provide information in two main areas.[223] One of these is the prediction of retention behaviour to assist in the selection of appropriate phases for analytical purposes. The other involves the study of the interaction of mixed components in terms of the formation of molecular complexes. The work to be described in this Chapter is exclusively concerned with the former of these applications.

The ability to design a stationary phase with known retention characteristics from mixtures of relatively few components rather than the use of a large number of single phases would obviously be an advantage. This, though, requires knowledge of the behaviour of the mixed phase in terms of that of the pure components and this has been considered by a number of workers as discussed in Section 1.14. In 1975, Purnell and Vargas de Andrade[106] published a study of the retention of a selection of compounds into mixtures of di n-octyl phthalate with n-heptadecane and dibutyl tetrachlorophthalate with squalane and concluded that the partition coefficient for the mixture was a linear function of composition by volume of the mixed phase and proposed equation (1.70).

$$K_{12} = \phi_1 K_1 + \phi_2 K_2$$

where the symbols have the meanings assigned in Section 1.14. The following year Laub and Purnell[107,108] used their results and others taken from the literature to extend the study to a large number of systems and found that equation (1.70) satisfactorily described the mixed solvent behaviour irrespective of the nature of the components involved. This relation is purely empirical and cannot be derived from conventional non-electrolyte solution theory except for ideal solutions or immiscible mixtures. On the basis of their results, Purnell and co-workers[224] suggested that there might be "the prospect of a coherent theory of solutions of a generality not hitherto visualised". Laub and Purnell proposed a 'Micropartitioning' theory of solutions[108,224] where the components do not mix on a microscopic scale. They named these solutions 'diachoric'.

Using conventional Regular Solution and Flory-Huggins theories, Tiley and Perry[110] derived an alternative to the Purnell-Andrade relation, equation (1.71) which includes a term containing the F-H interaction parameter to account for any interactions between the components comprising the mixture

$$\ln K_{12} = \phi_1 \ln K_1 + \phi_2 \ln K_2 + \phi_1 \phi_2 \chi_{12}$$

Tiley subsequently showed[225] that this relation accounted for the behaviour of many systems. Ashworth and co-workers, including the present author [112–114] have applied equations (1.70) and (1.71) to results for several solutes in mixtures of DNP and squalane determined by vacuum microbalance techniques. They showed that the Tiley-Perry (TP) relation predicted the results to within 1% while that of Purnell *et al.* (PA) showed deviations of up to 8%. Laub and Chien[226] and Harbison *et al.*[111] also found similar deviations in these systems using GLC. The latter work showed excellent agreement with the static results giving further validity to GLC studies of this type.

To extend the vacuum microbalance study, the absorption of chloroform, dichloromethane and ethyl acetate by mixtures of DNP and squalane has been studied. Three mixtures of approximately 25, 50 and 75 mole per cent were used. The liquid loadings employed were ~30% for the chloromethanes and ≥40% for ethyl acetate to eliminate adsorption effects as described in the previous Chapter. The study using ethyl acetate was performed using the MS microbalance for the reasons outlined previously. The absorption isotherms are listed in Tables AI-16 to AI-18 in Appendix I.

9.1. ACTIVITY COEFFICIENTS

The isotherms are shown as plots of ln γ_A versus mole fraction of absorbate for each of the systems studied in Figures 9-1 to 9-3. For each mixture, the isotherms lie between those for the pure components as has usually been found, although with tetrachloromethane[113] the activity coefficients for the mixtures lay outside those of the pure components for a large part of the composition range. Due to the greater solubility of each component in DNP, the isotherms lay nearer to that for DNP than might be expected.

The results were initially analysed by treating the ternary systems (absorbate + 2 absorbents) in terms of the Flory-Huggins equation for a pseudo-binary system as outlined in Section 3.3. The molar volumes of the mixtures were taken as the molar average of the pure components, it having been shown[111] that there is negligible volume change on mixing DNP and squalane. The fit of the F-H equations was good, as may be judged from the low RMSD values listed in Appendix I and the fit of the results to the solid lines in Figures 9-1 to 9-3. This is perhaps surprising since the assumptions of random mixing involved in Flory-Huggins theory would be invalid as was shown in the previous Chapter. However, the treatment of Section 3.3. was clearly valid and was used to extrapolate the results to infinite dilution although, as may be seen from the Figures, essentially the same values would be obtained by simple extrapolation of the experimental results.

In the following discussion it will be convenient to change the subscripts of symbols so that A will refer to the absorbate, B to squalane and C to DNP. The infinite dilution activity coefficients, γ_A^{∞}, were used to calculate partition coefficients for the mixtures using equation (1.60). The results are summarised in Table 9-1.

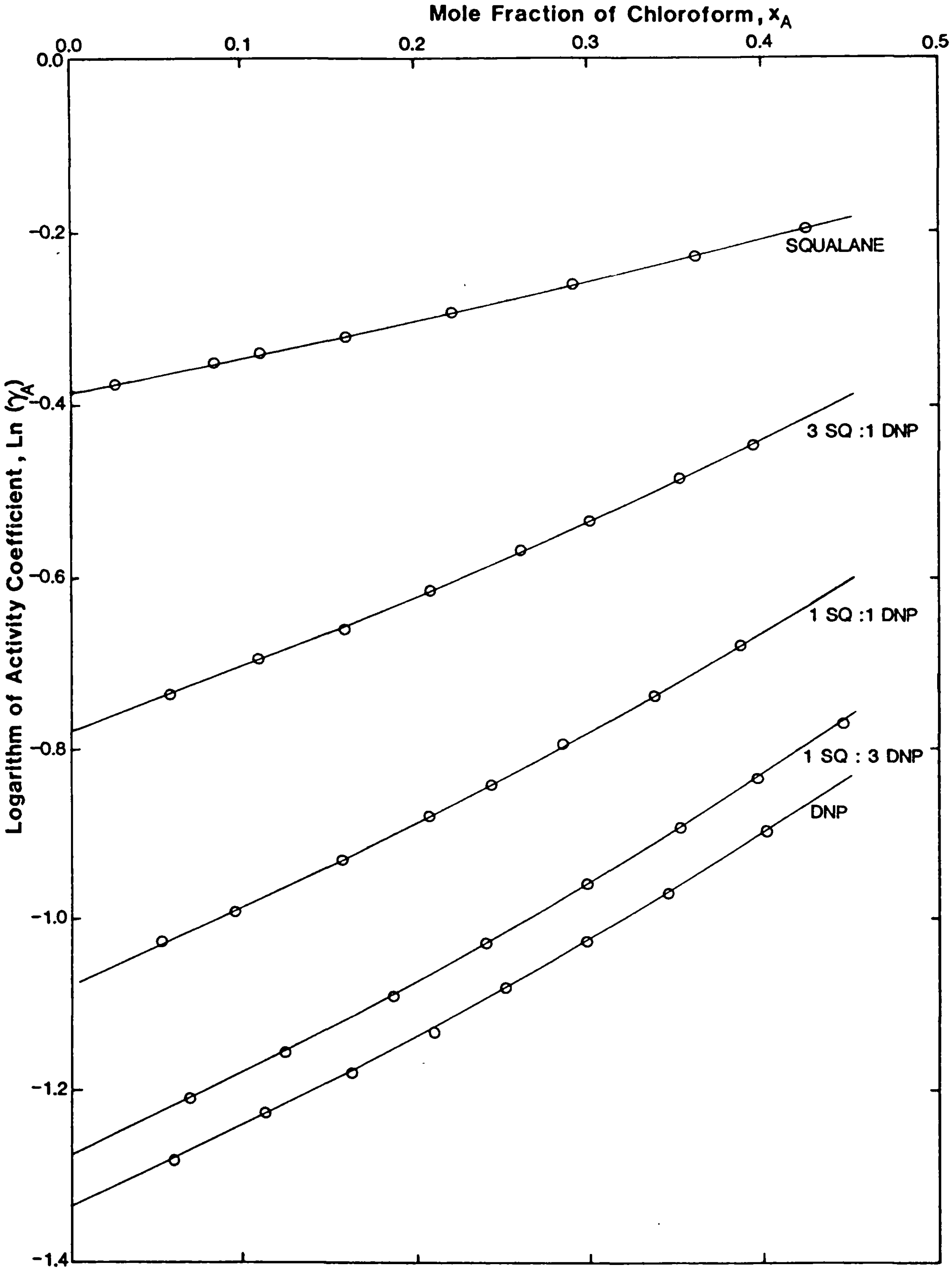


FIGURE 9-1: ACTIVITY COEFFICIENTS FOR CHLOROFORM IN SQUALANE-DNP MIXTURES AT 30°C

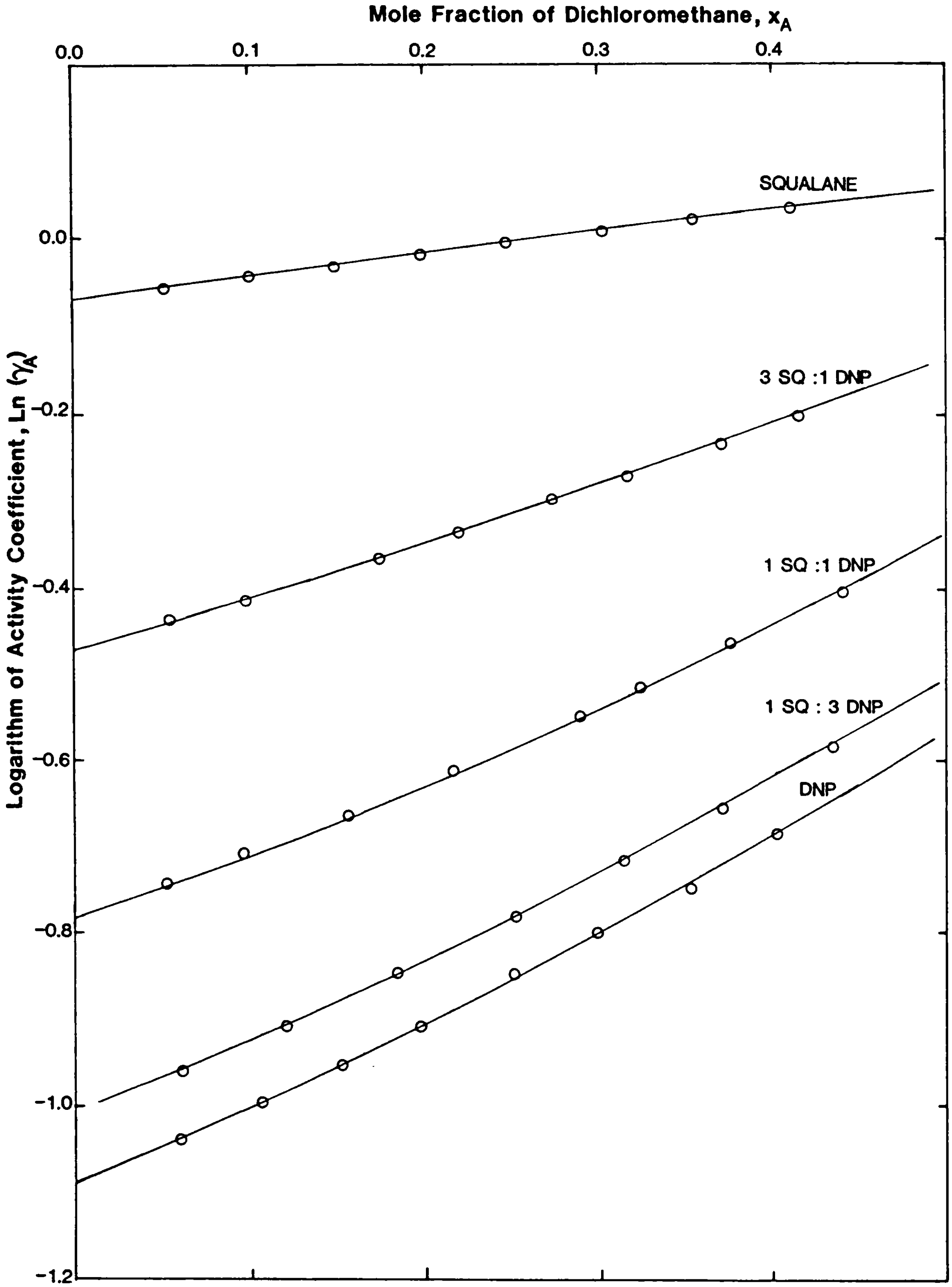


FIGURE 9-2: ACTIVITY COEFFICIENTS FOR DICHLOROMETHANE IN SQUALANE-DNP MIXTURES AT 30°C

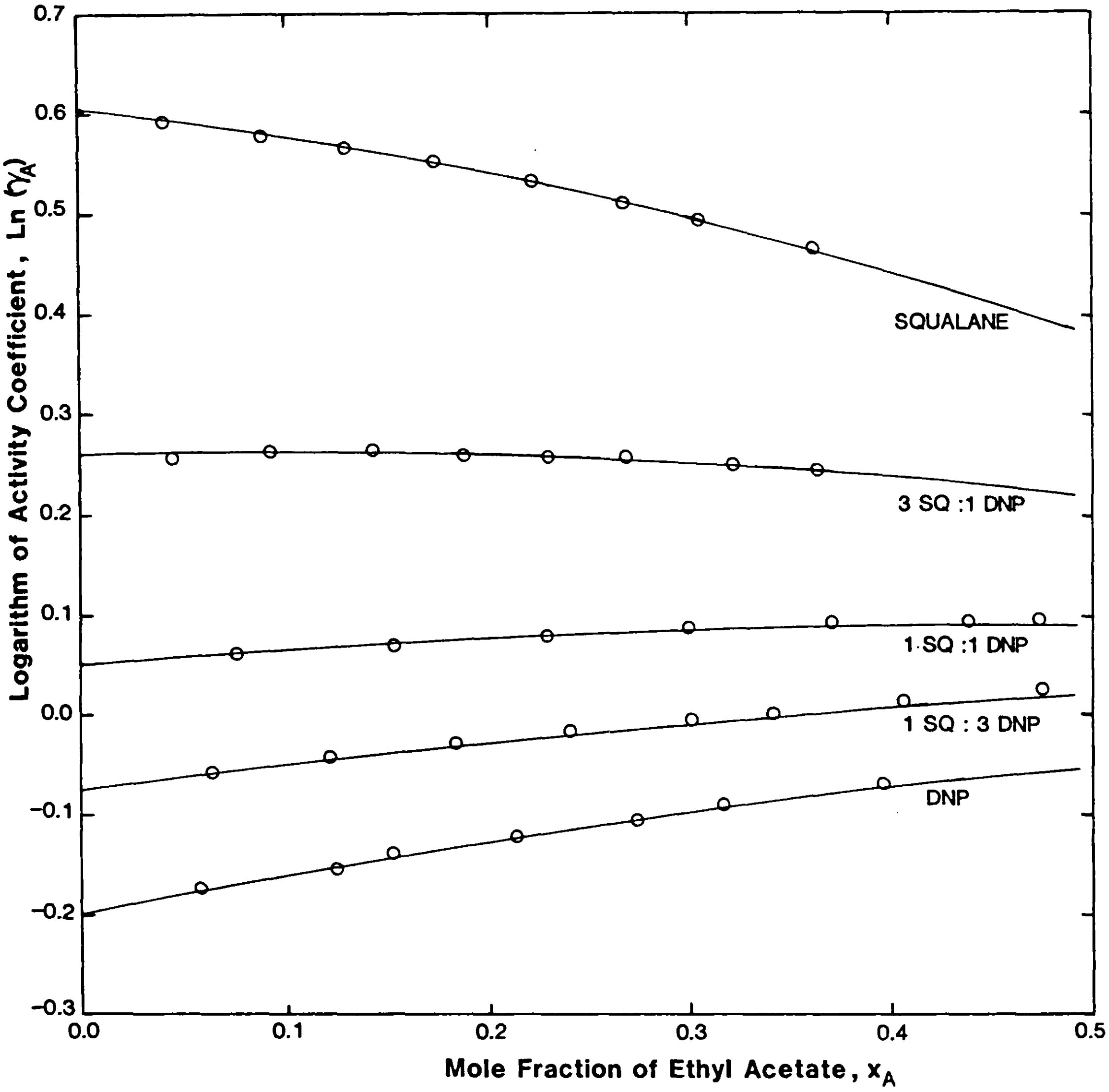


FIGURE 9-3: ACTIVITY COEFFICIENTS FOR ETHYL ACETATE IN SQUALANE-DNP MIXTURES AT 30°C

TABLE 9-1: INFINITE DILUTION ACTIVITY COEFFICIENTS AND PARTITION COEFFICIENTS FOR MIXTURES OF SQUALANE(B) AND DNP(C) AT 30°C

		$n_B : n_C$*				
		1:0	3:1	1:1	1:3	0:1
CHLOROFORM	γ_A^∞	0·6752	0·4573	0·3409	0·2795	0·2615
	K	223·9	346·2	487·1	621·7	701·3
DICHLOROMETHANE	γ_A^∞	0·9256	0·6236	0·4559	0·3636	0·3350
	K	76.3	118·4	170·4	224·1	255·7
ETHYL ACETATE	γ_A^∞	1·8218	1·2953	1·0488	0·9290	0·8238
	K	167·3	245·6	318·7	377·8	448·9

*$n_B : n_C$ = approximate mole ratio of absorbents

9.2. INTERACTION PARAMETERS

In order to apply the Tiley-Perry relationship, a value of χ_{BC}, the intersolvent interaction parameter, was needed. This, and the interaction parameters between the absorbate and each absorbent were calculated by applying the least squares fit to the Flory-Huggins equation for a ternary system as described in Chapter 3. This found the best fit values of χ over all the results from the isotherms for the mixtures and the pure components. The calculated values are shown in Table 9-2, along with the RMSD calculated using equation (3.9) which described the fit of the ternary equation to the experimental activity coefficients.

The greater affinity of each absorbate for DNP rather than squalane is shown by the value of χ_{AC}° being smaller than χ_{AB}° in each case. The negative values of χ_{AC}° for the chloromethanes are indicative of the specific solution interactions described in Chapter 8. An

TABLE 9-2: INTERACTION PARAMETERS FOR ABSORBATES (A) IN MIXTURES OF SQUALANE (B) AND DNP (C) AT 30°C

	χ°_{AB}	χ'_{AB}	χ°_{AC}	χ'_{AC}	χ_{BC}	χ_{BC}/V°_A (mol dm^{-3})	RMSD
CHLOROFORM	0·613	-0·185	-0·505	0·882	0·888	10·94	0·009
DICHLOROMETHANE	1·097	-0·658	-0·058	1·070	0·807	12·42	0·014
ETHYL ACETATE	1·369	-0·439	0·531	0·234	0·583	5·88	0·027

interesting point is that the concentration dependences shown by χ'_{AB} and χ'_{AC} with these polar solutes are considerably larger than those with tetrachloromethane or the hydrocarbons found in previous work. This is presumably due to the greater disruption of solution intermolecular forces on adding polar absorbates compared to the purely dispersion forces involved with the non-polar compounds.

The RMSD values are larger for the ternary fit than the binary and show that the ternary equation does not fit the systems to within experimental error. If the Flory-Huggins theory is to describe the results successfully then the intersolvent interaction parameter per unit volume of absorbate, χ_{BC}/V°_A should be independent of the absorbate used. This is clearly not the case in the current work. Using alkane absorbates[112] consistent values of 2·70 ± 0·6 mol dm^{-3} were found while tetrachloromethane[113] gave a value of 3·13 mol dm^{-3}. The use of benzene[112] yielded a value of 3·80 mol dm^{-3} and the difference was attributed to the possibility of complexing between the aromatic components. Ethyl acetate would have been involved in dipole interactions with DNP and this is reflected by the higher value as shown in Table 9-2. Predictably the chloromethanes show even higher values as they would have been involved in stronger solution interactions, although if this were the sole criterion determining the value of χ_{BC}/V°_A, the value for chloroform would be expected to be higher than that for dichloromethane since it interacts more strongly. The value of 2·53 mol dm^{-3} obtained using diethyl ether[114] appears to be anomalous as it is lower than that obtained using the alkanes.

It is not surprising that the Flory-Huggins ternary equation did not give a good description of these systems since the presence of polar components invalidates some of its assumptions. Also, since the absorbates are much more compatible with DNP than with squalane, the absorbent composition may have had a greater effect on absorption. This would lead to a greater dependence of χ_{BC} on composition than when using hydrocarbon absorbates where neglect of this was found to only slightly worsen the fit to the results.[122] For solvent mixtures of DNP and trinitrotoluene Tiley and Perry[110] suggested that χ_{BC} was linearly dependent on composition.

9.3. PARTITION COEFFICIENTS IN MIXED ABSORBENTS

Table 9-3 lists the experimental results for the partition coefficients of the mixed solvents together with those predicted by the Purnell-Andrade equation, K(PA), and the Tiley-Perry relationship, K(TP). Also listed is the percentage deviation, D, of the partition coefficients predicted by each relation from their experimental values. This is also shown graphically in Figures 9-4 to 9-6.

The Purnell-Andrade equation predicts the partition coefficients to within an average of 7·9%, 5·6% and 6·0% respectively for chloroform, dichloromethane and ethyl acetate respectively. The corresponding values for the Tiley-Perry equation are 4·1%, 3·1% and 3·9%. Thus, as has been found in previous work, the latter equation gave a better prediction of mixed absorbent or stationary phase behaviour than the simpler linear relationship. The deviation of the K(PA) values of

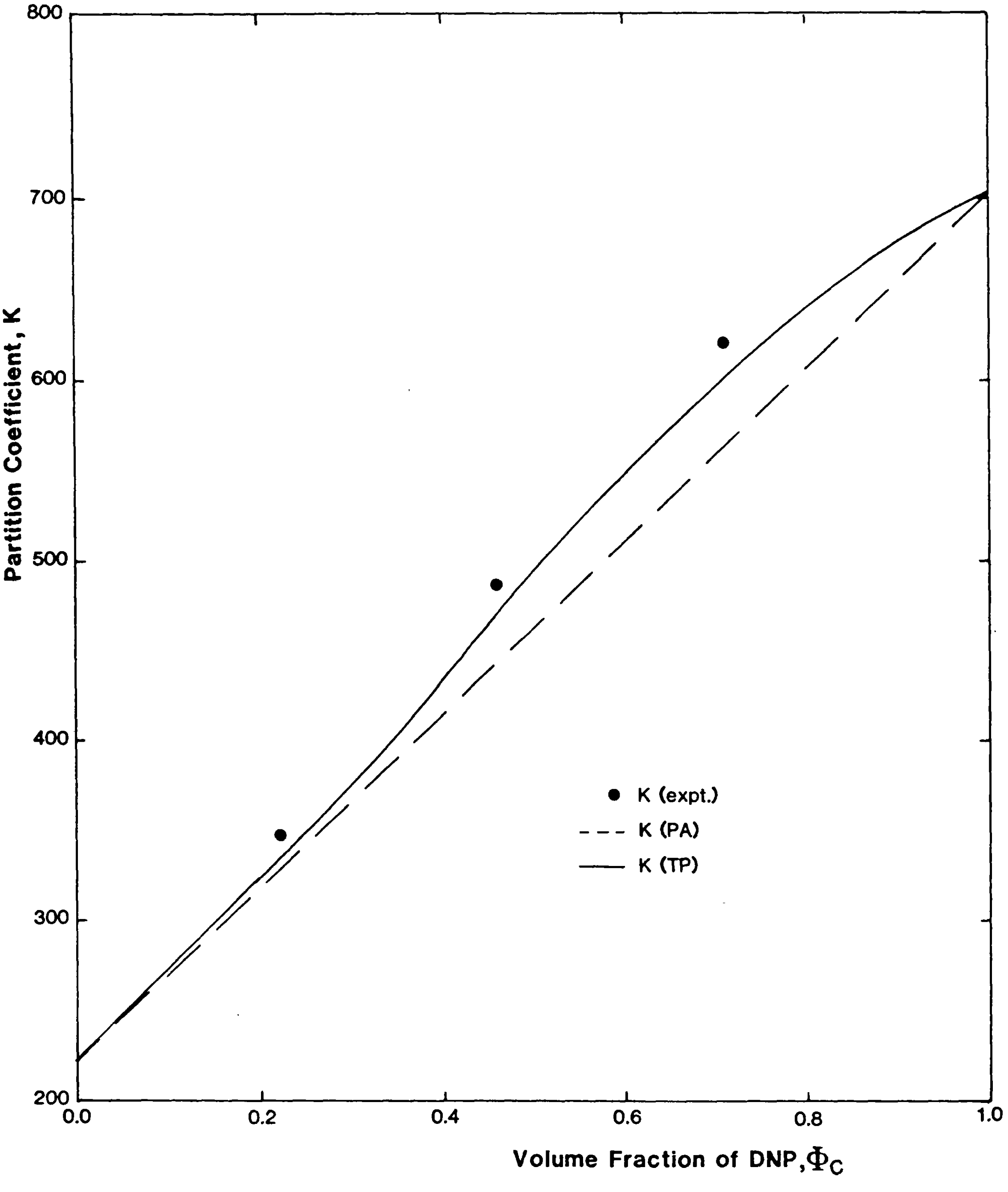


FIGURE 9-4: PARTITION COEFFICIENTS FOR CHLOROFORM IN SQUALANE-DNP MIXTURES AT 30°C

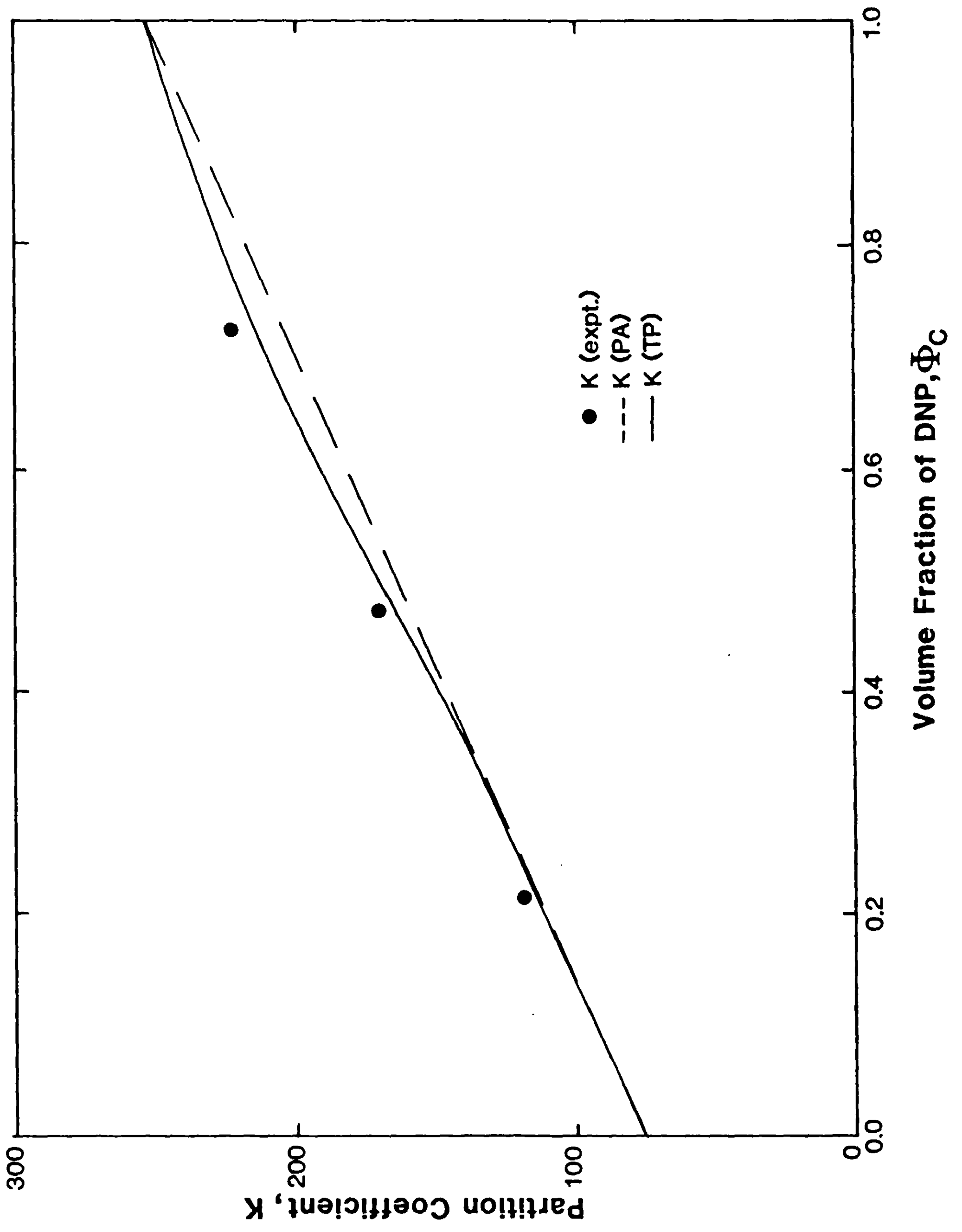


FIGURE 9-5: PARTITION COEFFICIENTS FOR DICHLOROMETHANE IN SQUALANE-DNP MIXTURES AT 30°C

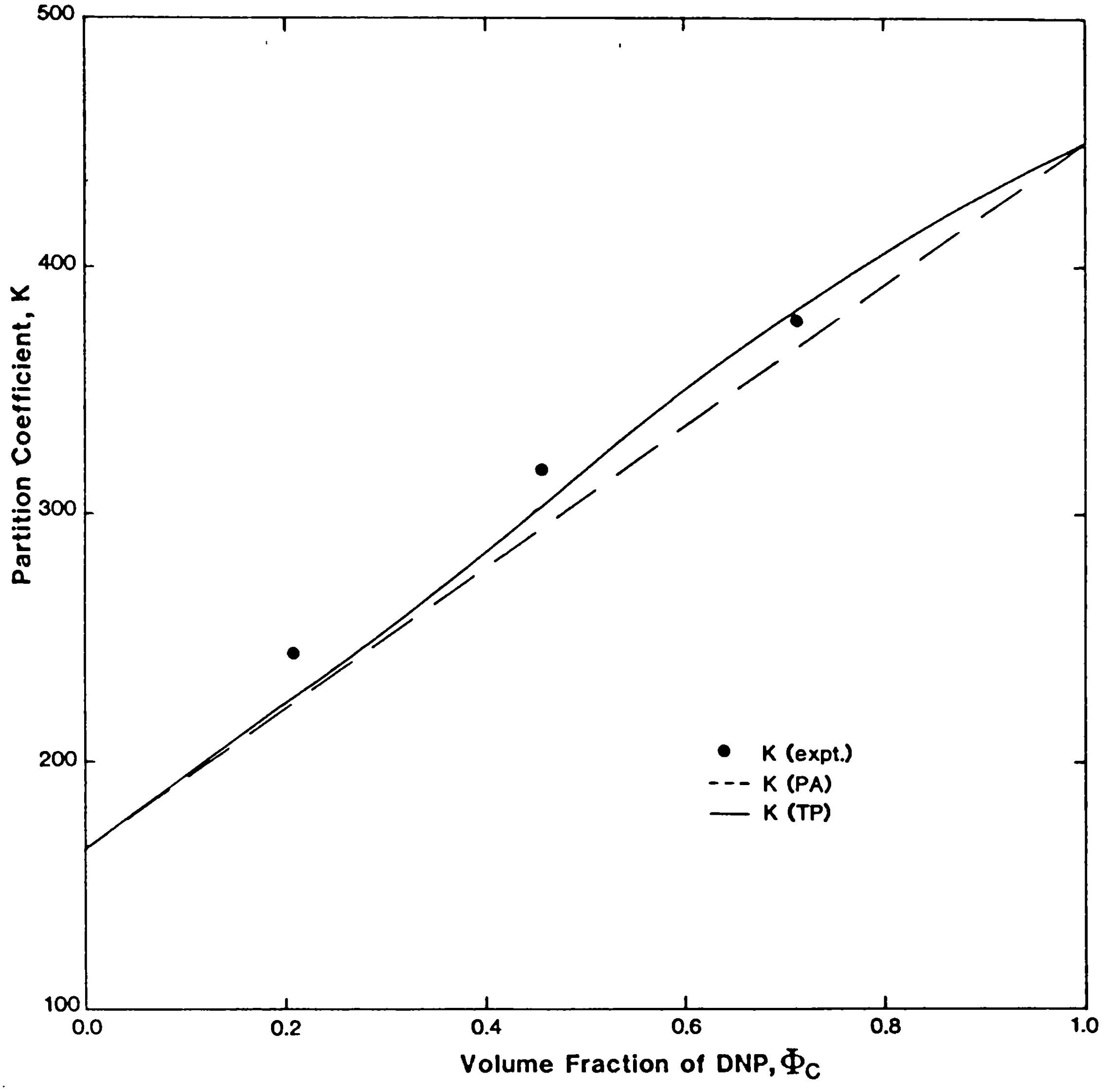


FIGURE 9-6: PARTITION COEFFICIENTS FOR ETHYL ACETATE IN SQUALANE-DNP MIXTURES AT 30°C

TABLE 9-3: PARTITION COEFFICIENTS FOR ABSORBATES IN MIXTURES OF SQUALANE (B) AND DNP (C) AT 30°C

	$n_B:n_C$	ϕ_B	K	K(PA)	D/%	K(TP)	D/%
CHLOROFORM	3:1	0·7785	346·2	329·6	4·8	336·1	2·9
	1:1	0·5389	487·1	444·0	8·8	472·7	3·0
	1:3	0·2983	621·7	558·9	10·1	600·8	3·4
DICHLOROMETHANE	3:1	0·7861	118·4	114·7	3·1	113·2	4·4
	1:1	0·5287	170·4	160·9	5·6	165·0	3·2
	1:3	0·2784	224·0	205·8	8·1	214·7	4·2
ETHYL ACETATE	3:1	0·7934	245·6	225·5	8·2	225·7	8·1
	1:1	0·5457	318·6	295·2	7·3	302·7	5·0
	1:3	0·2881	377·8	367·8	2·6	380·7	-0·8

2·6 - 10·1% is similar to that found in previous work. However, in that work K(TP) values agreed with experimental values to within 1%. Based as it was on Flory-Huggins theory, the Tiley-Perry equation would not be expected to give as good a prediction when using polar absorbates and this is shown by the deviations of, on average 3-4% observed in the systems studied here.

The graphs show that for mixed absorbents containing large amounts of squalane, the two relationships lead to similar predictions of partition coefficients whereas the predictions differ to a larger extent at higher DNP compositions. This is a consequence of the values predicted by the Tiley-Perry equation shown by the solid lines in Figures 9-4 to 9-6 showing points of inflexion rather than being concave to the composition axis throughout as was observed with, for example, tetrachloromethane and the alkanes. Tiley[115] has shown that in cases such as these the average deviation of the two relationships can be similar so that misleading conclusions could easily be reached. Indeed, calculation of the correlation coefficients of regression for the K(TP)-ϕ_C results yielded values of 0·9954, 0·9985 and 0·9988 for the three systems which are very close to 1·0 for a linear function. Thus, without closer examination, the results might well be assumed to conform to a linear relationship.

The equation of Tiley and Perry is similar to that proposed some years ago by Waksmundzki and Suprynowicz[103] and also suggested by Harbison *et al.*[111] More recently, Acree and Bertrand[104] have adapted their "Nearly Ideal Binary Solvent" approach which they have used successfully for several applications to the study of mixed stationary phases in GLC. They used it to demonstrate that the Purnell-Andrade equation is a non-general thermodynamic relation which can only hold approximately in certain circumstances. Tiley[115] has also pointed out that equations (1.70) and (1.71) can only give similar results where $K_B \approx K_C$ and $\chi_{BC} \approx 0$. Acree and Bertrand used their approach to derive equation (9.1) for the behaviour of a mixed phase,

$$\ln K_{BC} = \phi_B \ln K_B + \phi_C \ln K_C + V_A^\circ \overline{\Delta G}_{BC}/RT\, V_M^\circ \qquad (9.1)$$

where the symbols have the same meaning as previously, V_M° being the molar volume of the mixture. $\overline{\Delta G}_{BC}$ is the excess Gibbs free energy per mole of solvent mixture. This equation can be shown to be identical to that of Tiley and Perry since it is this latter quantity that χ_{BC} represents. Acree and Bertrand define $\overline{\Delta G}_{BC}$ as (adapting their expression to a binary solvent mixture)

$$\overline{\Delta G}_{BC} = RTV_M^\circ\, \phi_B\, \phi_C\, A_{BC} \qquad (9.2)$$

where A_{BC} is a constant for a particular pair of compounds. Combining equations (9.1) and (9.2),

$$\ln K_{BC} = \phi_B \ln K_B + \phi_C \ln K_C + (V_A^\circ A_{BC})\, \phi_B\, \phi_C \qquad (9.3)$$

it may be clearly seen that equations (9.3) and (1.71) are identical and are simply derived from slightly different solution models with the constant A_{BC} identified as a Flory-Huggins interaction parameter in the Tiley-Perry equation.

As discussed above for the Tiley-Perry relation, if equation (9.3) is to satisfactorily account for mixed solvent behaviour then a consistent value of A_{BC} should be obtained irrespective of the absorbate. To determine whether this more general treatment was more successful than assumption of Flory-Huggins theory, the experimental values of K_B, K_C and K_{BC} were used to calculate A_{BC} values for the three mixtures in each of the ten systems studied.[112-114] The values are shown in Table 9-4.

TABLE 9-4: A_{BC} VALUES FOR ACREE-BERTRAND TREATMENT OF MIXTURES OF SQUALANE (B) AND DNP (C) AT 30°C

$n_B:n_C$	PENTANE	HEXANE	HEPTANE	CYCLOHEXANE	BENZENE
3:1	2·7	2·4	2.8	2·3	4·4
1:1	2·6	2·5	2·6	2·4	3·7
1:3	2·7	2·8	2·8	2·4	3·5
	ETHER	CCl_4	$CHCl_3$	CH_2Cl_2	EtOAc
3:1	3·5	3·2	13·1	16·5	11·1
1:1	2·5	3·1	12·4	14·4	8·1
1:3	2·2	3·1	11·9	13·7	5·6

It may be seen that for the alkanes consistent values of 2·6 ± 0·2 dm^3 mol^{-1} were found, in excellent agreement with the χ_{BC} values found, as were those for benzene and tetrachloromethane. The values for the three absorbates studied in the present work are well removed from these showing that the treatment assuming simply a constant rather than specifying a F-H interaction parameter does not produce more consistent results. This may be taken as further evidence of the contention of several workers[225] that a single parameter cannot account for the excess free energy of a solution. A further interesting point arising from Table 9-4 is that with the more polar absorbates there is a considerable variation of A_{BC} with the composition of the mixture. This also suggests the neglect of the concentration variation of the X_{BC} in the Tiley-Perry equation to be a source of error.

9.4. PARTITION COEFFICIENTS IN PDMS-SQUALANE AND PDMS-DNP SYSTEMS

The results for the absorption of hexane by mixtures of PDMS with squalane and with DNP that were presented in Chapter 6 were also analysed in the Purnell-Andrade and Perry-Tiley equations. Partition coefficients for hexane of 304·7 and 196·8 for squalane and DNP respectively were calculated from the data of Ashworth[89] while values of 202·4, 201·0, 196·5, 195·0 and 193·8 were obtained for PDMS I - PDMS V. These latter values were calculated from results in Chapter 4 using equation (1.60) modified to take account of the use of volume fraction rather than mole fraction based activity coefficients. This was also done for each mixture that was studied and the calculated results are shown in Table 9-5.

The Purnell-Andrade equation predicts partition coefficients to within an average of 2·9% for mixtures containing DNP and 4.5% for those with squalane. The mixtures with the lowest molecular weight polymer show significantly larger deviations than any of the other systems. Since these systems were shown in Chapter 6 to be well described by the Flory-Huggins theory it was expected that the Tiley-Perry equation would give good predictions and this is observed. With the exception of mixtures containing PDMS I, the K(TP) values are within 0·5% of the

TABLE 9-5: PARTITION COEFFICIENTS FOR PDMS-SQUALANE AND PDMS-DNP MIXTURES AT 30°C

SYSTEM	ϕ_B	$\chi_{BC}^{\neq}$	K	K(PA)	D/%	K(TP)	D/%
DNP-PDMS I	0·075	0·467	212·1	202·0	4·8	208·6	1·7
DNP-PDMS II	0·053	0·468	205·0	200·8	2·1	205·6	-0·3
DNP-PDMS III	0·045	0·477	200·2	196·6	1·8	200·7	-0·2
DNP-PDMS IV	0·046	0·511	200·1	195·1	2·5	199·6	0·3
DNP-PDMS V	0·063	0·549	200·2	194·0	3·1	200·4	-0·1
SQ-PDMS I	0·107	0·353	224·5	213·4	8·9	218·7	2·6
SQ-PDMS II	0·103	0·370	217·5	211·7	2·7	217·1	0·2
SQ-PDMS III	0·120	0·404	217·1	209·6	3·5	216·2	0·4
SQ-PDMS IV	0·117	0·463	216·2	207·8	3·9	215·5	0·4
SQ-PDMS V	0·105	0·514	212·6	205·4	3·4	213·3	-0·3

$\neq$ calculated from χ_{BC}/V_A° values in Chapter 6

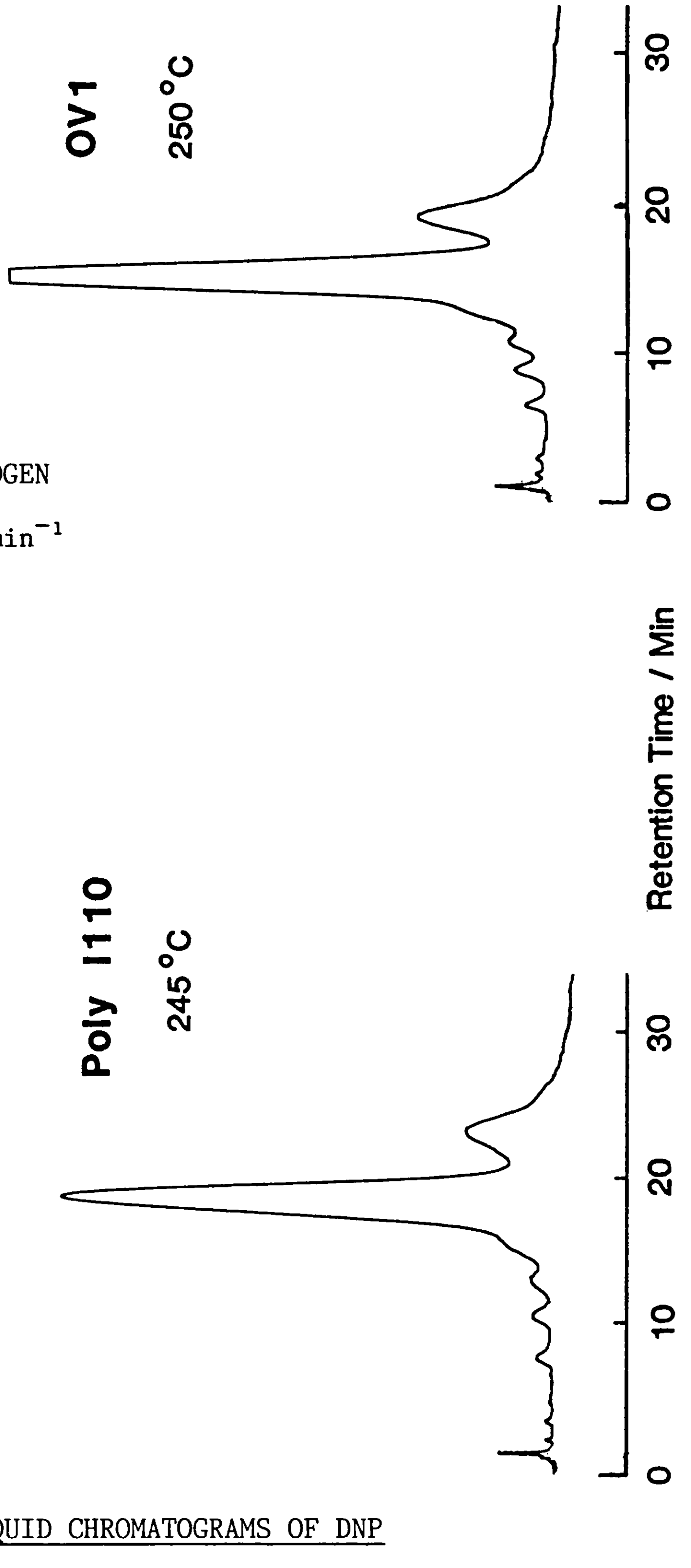
experimental results, a figure well inside the experimental error of the method. It should perhaps be stressed that these results were obtained on a single mixture containing a large proportion of polymer. For solutions containing larger amounts of the lower molecular weight component, greater deviations of the K(TP) values from the experimental results would be expected provided that the mixture was miscible at that composition. Patterson and co-workers[172] used GLC to study a mixture of PDMS with n-tetracosane with a number of solutes and found results 5-10% higher than would be expected from a linear relationship such as the Purnell-Andrade equation. An alternative version of equation (1.70) has been used to explain retention in mixed polymer stationary phases. Klein and Widdecke[227] showed there to be a linear variation with composition for both 'mixed-bed' and 'mixed-solvent' columns containing polystyrene and polybutadiene. In addition they showed that block and graft co-polymers of the same composition also showed no difference in behaviour. Similarly, Lynch *et al.*[228] found the properties of phenylmethylsilicone co-polymer stationary phases to be identical to those of mixed dimethylsilicone and diphenylsilicone absorbents.

9.5. THE PURITY OF DNP

It is known that the DNP used in the work described in this Thesis is not a pure compound.[121,228] It is sold as a reagent for chromatographic analysis and is purported to be the bis(3,5,5-trimethyl hexyl) isomer. Harbison *et al.*[111] claimed that the "diachoric solution hypothesis cannot be dismissed on the grounds of the currently observed deviations until the molecular state of DNP is better defined". However, despite the questionable composition of the DNP, excellent agreement was found between static and GLC determinations on infinite dilution activity coefficients and other properties on single components and mixtures containing commercially available DNP samples. Harbison *et al.* pointed out that the presence of a number of isomers would not affect the validity of equation (1.70) since each should act independently. Since the Flory-Huggins binary equation has been shown to describe DNP-absorbate interactions well, there is no reason to suppose that treating the DNP as a single component in deriving χ_{BC} for use in equation (1.70) would invalidate any conclusions. To check this it would have been desirable to obtain a pure sample of one isomer and to measure absorption isotherms on mixtures containing this compound.

The problem of separation and identification of phthalate esters has been approached by a number of workers[230] because of their commercial importance as plasticisers. Using high temperature GLC, Harbison *et al.*[111] found their DNP sample to have a purity of ~70%. the remainder of the sample being a mixture of up to ten other alkyl isomers. Grenier-Loustalot[229] found a somewhat lower purity. Following some methods of previous workers, the DNP employed in the present work was analysed using GLC. The chromatograms on two stationary phases, OV101 and POLY I110 are shown in Figure 9-7. The conditions used were as listed. Integration of the peaks suggests the major component to comprise around 74% of the sample while the second largest component was around 20%. The presence of four or five other compounds was also indicated. However, these results were difficult to reproduce and, due to the high temperatures, long retention times and amount of material needed these analyses were felt to be unsuitable for preparative purposes. Thus the technique of high performance liquid chromatography, HPLC was tried.

The solvent system 95% hexane : 5% ethyl acetate on 5 μm 'Spherisorb' silica gave the chromatogram in Figure 9-8. This again suggested the presence of four components with two comprising ~70% and ~20%. These conditions were used on a Waters 500A preparative HPLC system. Five fractions were collected but when the major sample was analysed using the above conditions it was found to be more impure than the starting material. This may have been due to lower resolution of a preparative column so that incomplete separation was achieved. However, the possibility was suggested that the above solvent system was inappropriate since the silica may have acted as a transesterification catalyst for the DNP and the ester in the solvent. Alternative solvent systems were tried (combinations of chloroform, acetone and acetonitrile in hexane) and the best result is shown in



CARRIER GAS : NITROGEN

FLOW RATE : 28 ml min^{-1}

SAMPLE SIZE : 2 µl

FIGURE 9-7: GAS-LIQUID CHROMATOGRAMS OF DNP

SOLVENT : 95:5 Hexane:Ethyl Acetate

FLOW RATE : 1·5 cm^3 min^{-1}

INJECTION : 20 µl of 5% solution

STATIONARY PHASE : 20 cm 'Spherisorb' 55W

5 µ Silica

Differential Refractometer Detector

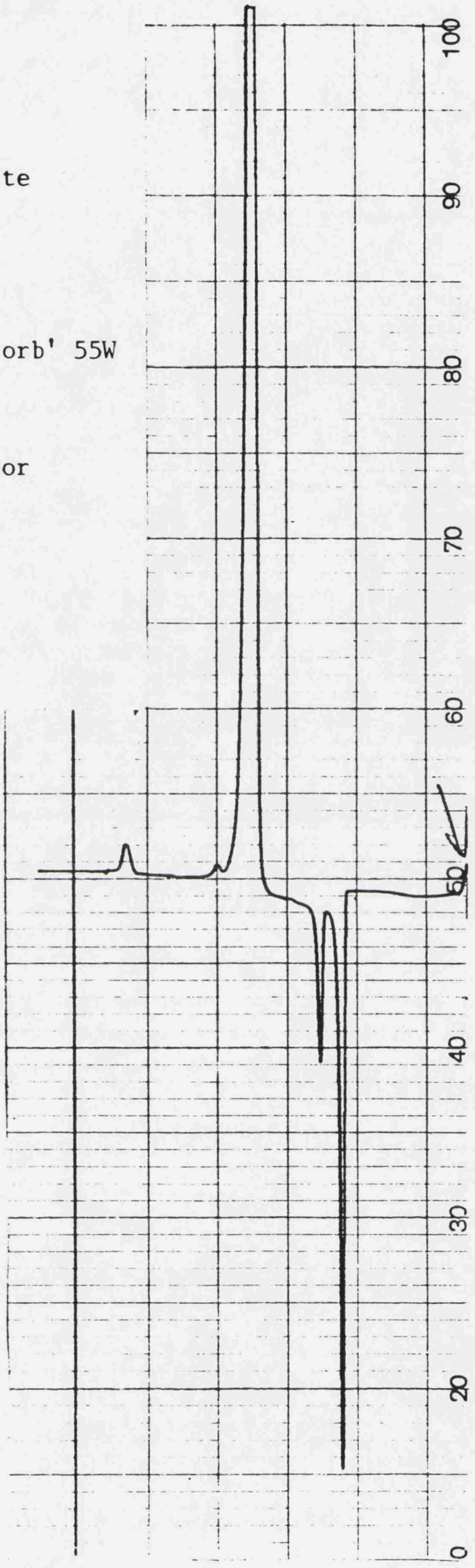


FIGURE 9-8: HPLC CHROMATOGRAM OF DNP

SOLVENT 94:4:2 Hexane:Acetone:$CHCl_3$

CONDITIONS : As Figure 9-8

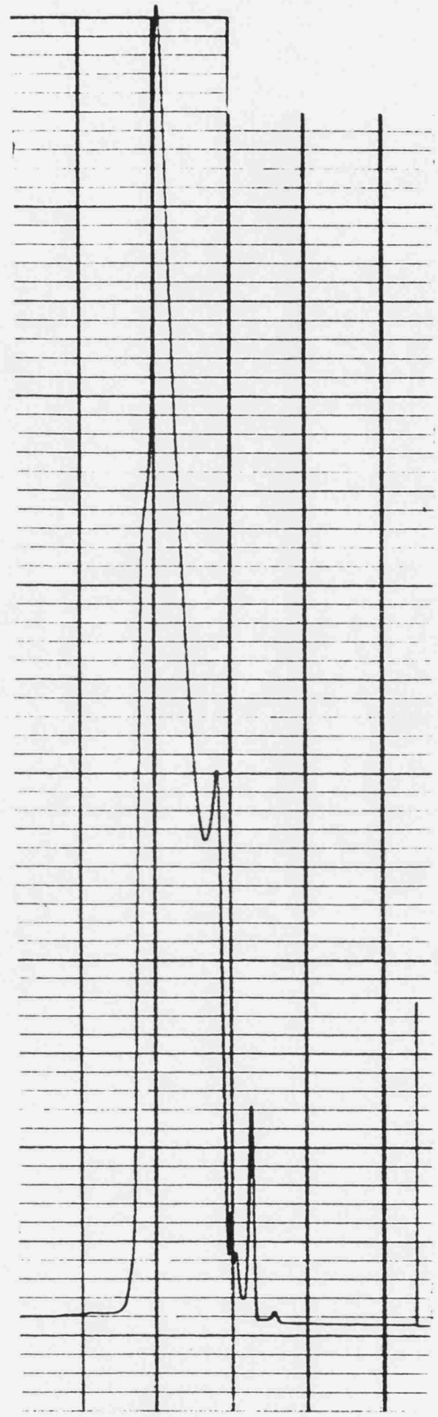


FIGURE 9-9: HPLC CHROMATOGRAM OF DNP

Figure 9-9 using 94% hexane : 4% acetone : 2% chloroform. However, even though the presence of four or five components is again indicated, the resolution was too low for use on a preparative system.

9.6. CONCLUSIONS

As has been found in previous work on solvent mixtures of squalane and DNP, partition coefficients calculated on the basis of the Purnell-Andrade equation have been shown to deviate by up to 10% from experimental values. However, the Tiley-Perry relation, which had previously been used to predict mixed solvent behaviour to within 1%, has been shown to predict partition coefficients to within, on average, 3-4% for the polar compounds chloroform, dichloromethane and ethyl acetate. Since the Tiley-Perry relation is based on Flory-Huggins theory its use with these polar compounds would not be expected to be as accurate as with the hydrocarbons which conform to the theory. This is also indicated by the excellent prediction of the behaviour of mixtures of PDMS with squalane and with DNP which were shown to be well fitted by Flory-Huggins theory.

A 'mixed-bed' stationary phase would certainly obey a linear relation and so may be preferable for analytical purposes since its retention properties should be accurately predictable. The Purnell-Andrade equation gives a reasonable prediction for the behaviour of 'mixed-solvent' stationary phases in some cases and has been used with some success by Purnell and co-workers to produce a "Window Diagram" strategy for the selection of conditions for particular analyses.[231,232] However, reliance on this relationship alone could in many instances produce misleading results. The Tiley-Perry equation would give better predictions but this requires a value of X_{BC} which may well not be available and may be difficult to predict from theoretical parameters.

The 'diachoric' solution hypothesis with its concept of micropartitioning is the opposite of the random mixing basis of Flory-Huggins theory to which the systems studied here conform better. Indeed, as Tiley[225] has pointed out, the treatments of Eon *et al.*[233] and of Martire and co-workers[234] lead to an approximately linear variation of partition coefficient on composition. These treatments are based on the assumption of the formation of molecular complexes so that the conclusions of Purnell *et al.* could be equally well explained by complex formation which is much more likely than micropartitioning.

Chapter 10

Concluding Remarks and Recommendations for Future Work

Various aspects of the measurement of non-electrolyte solution properties using two vacuum microbalances have been described in this Thesis as detailed by the conclusions of Chapters 4-9. All of the systems studied were found to be fitted satisfactorily by the Flory-Huggins theory over the limited concentration ranges studied with the assumption of a concentration dependent interaction parameter. A linear variation of the interaction parameter with volume or segment fraction was adopted and was justified in that regression correlation coefficients in excess of 0·99 were calculated for each system studied.

A useful scientific investigation should produce results that advance knowledge in the area under study but should also suggest topics for further study. The results from the comparison with GLC work described in Chapter 4 have been published in *Macromolecules*[168] and, in the near future, it is hoped to submit a paper for publication on the variation of solution properties with polymer molecular weight and liquid to solid support ratio that was found. The work described in Chapter 5 using the magnetic suspension microbalance was presented to the 20th International Vacuum Microbalance Techniques Conference in September 1983 and will be published in the forthcoming edition of *Thermochimica Acta*. A paper on the partial miscibility study in Chapter 6 was presented at a meeting of the 'Statistical Mechanics and Thermodynamics' Group of the Faraday Division of the Royal Society of Chemistry entitled 'The Thermodynamics of Mixed Polymer Systems' at Sheffield in April 1984 and has been submitted for publication. It is also hoped to publish the studies of adsorption effects and mixed solvent behaviour described in Chapters 8 and 9.

A number of possibilities for future studies are suggested by the work in this Thesis. The results presented in Chapter 4 were used to show good agreement between static and GLC measurements. However, this can only be claimed for one polymer-PDMS, which is known to be amenable to study by these methods. Extension of the study to other polymers would be desirable, particularly those of a more polar nature. This would also give a further opportunity to study adsorption effects in polymeric systems. The magnetic suspension microbalance was shown to be suitable for the study of polymer solutions. An interesting extension of this work would be the study of diffusion/solution phenomena in solid polymers since the design of the apparatus eliminates some of the problems associated with the long experiment times encountered with these systems.

The methods developed for the prediction of partial miscibility in systems such as those described in Chapter 6 could be further tested if a more compatible system was found, particularly one that contained a higher proportion of the smaller component in the polymer rich phase. Although the 'Tangent through the Origin' treatment would be inappropriate, it would be interesting to see how well the miscibility limits were predicted using the F-H interaction parameters. Also of interest would be the prediction of properties in terms of the X_{12} parameter and Flory's 'Equation of State' theory or the use of a concentration dependent χ_{12} parameter in the Flory-Huggins theory to determine whether the agreement with experiment could be improved. The three solution theories applied to PDMS-solvent systems in Chapter 7 did not give a satisfactory fit to experimental results at high polymer concentrations and it would be interesting to apply some of the newer theories such as that of Sanchez and Lacombe to these results.

The adsorption study using DNP and squalane could be extended by measuring the surface tensions of solutions and using the Gibbs adsorption isotherm to account for the effects and by measuring surface and interfacial areas to determine the individual contributions to retention. This second area of study would be particularly interesting, although differing techniques used by a number of other workers have often given conflicting results. The study of more polar compounds such as aliphatic ketones or alcohols which give larger adsorption effects would also be desirable. The study of mixed solvent behaviour using a number of other probes to determine any trend in χ_{BC} values with probe polarity or size etc. would be interesting. The use of a series of isomeric absorbates, e.g. the three xylenes, might be useful. Calculation of results in terms of a concentration dependent χ_{BC} and also in terms of the 'Equation of State' theory to determine whether more consistent values of χ_{BC} could be obtained would be of interest. Finally, calculation in terms of complexing systems and/or study of systems in which complexing between the absorbents was known to occur might also be profitable.

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Appendix 1

The Absorption Isotherms

The recorded absorption isotherms are tabulated in the following pages in the order in which they were discussed in Chapters 4-9 of this Thesis.

The symbols in the tables have the following meanings:

w_1	weight of vapour absorbed (mg).
p_1	absorbate vapour pressure (torr).
x_1	mole fraction of absorbate in solution.
ϕ_1	volume fraction of absorbate in solution.
ψ_1	segment fraction of absorbate in solution.
γ_1	activity coefficient of absorbate based on mole fraction.
γ_1^V	activity coefficient of absorbate based on volume fraction.
γ_1^S	activity coefficient of absorbate based on segment fraction.
χ	Flory-Huggins interaction parameter based on volume fraction.
χ^*	Flory-Huggins interaction parameter based on segment fraction.
w_2, w_B, w_C	weight of absorbent (mg).
r	correlation coefficient of regression
Δ	10^3 RMSD.

TABLE AI-1: ABSORPTION OF SOLUTES BY PDMS V AT 30°C

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
n-HEPTANE	1·81	20·07	0·0089	1·3428	0·3594
	4·93	52·53	0·0239	1·3160	0·3581
w_2 = 315·3	8·75	88·90	0·0416	1·2843	0·3563
	12·18	118·95	0·0570	1·2589	0·3567
r = 0·9992	15·83	148·18	0·0729	1·2315	0·3556
	20·09	179·65	0·0907	1·2031	0·3568
Δ = 0·8	24·27	207·66	0·1076	1·1758	0·3572
	29·11	203·94	0·1263	1·1451	0·3570
n-HEXANE	2·89	10·22	0·0142	1·3696	0·3964
	6·04	20·47	0·0292	1·3414	0·3948
w_2 = 297·7	9·22	29·89	0·0440	1·3113	0·3902
	12·74	39·66	0·0597	1·2863	0·3930
r = 0·9994	16·77	49·70	0·0772	1·2548	0·3915
	21·09	59·36	0·0952	1·2219	0·3890
Δ = 1·1	26·08	69·40	0·1151	1·1871	0·3876
	31·51	79·12	0·1358	1·1517	0·3867
n-HEPTANE	3·77	4·19	0·0176	1·4192	0·4543
	6·34	6·81	0·0292	1·3966	0·4536
w_2 = 300·9	9·62	9·87	0·0437	1·3653	0·4490
	12·42	12·31	0·0557	1·3430	0·4490
r = 0·9997	16·09	15·20	0·0710	1·3109	0·4440
	20·23	18·12	0·0877	1·2751	0·4377
Δ = 1·7	24·45	20·95	0·1041	1·2487	0·4413
	30·08	24·59	0·1277	1·2038	0·4376

/continued

TABLE AI-1 continued

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
BENZENE	3·92	9·48	0·0144	1·7195	0·7566
	7·25	16·76	0·0264	1·6860	0·7525
w_2 = 297·6	11·09	24·52	0·0398	1·6547	0·7543
	15·62	32·77	0·0551	1·6176	0·7546
r = 0·9996	20·19	40·13	0·0701	1·5790	0·7518
	24·17	45·94	0·0828	1·5475	0·7504
Δ = 1·8	29·25	52·57	0·0985	1·5082	0·7477
	34·48	58·45	0·1141	1·4667	0·7413
CYCLOHEXANE	3·11	5·86	0·0117	1·4338	0·4572
	6·84	12·44	0·0253	1·4100	0·4596
w_2 = 330·3	10·26	17·96	0·0375	1·3839	0·4562
	14·25	24·04	0·0573	1·3608	0·4594
r = 0·9993	18·45	29·87	0·0655	1·3341	0·4590
	22·97	35·62	0·0803	1·3064	0·4585
Δ = 0·9	29·02	42·60	0·0993	1·2718	0·4589
	34·31	48·07	0·1153	1·2426	0·4587
CHLOROFORM	3·63	8·30	0·0070	1·6077	0·6244
	8·84	19·59	0·0169	1·5854	0·6242
w_2 = 346·5	15·37	32·77	0·0290	1·5586	0·6243
	26·47	52·92	0·0490	1·5137	0·6231
r = 0·9990	37·85	71·01	0·0686	1·4698	0·6215
	53·26	92·38	0·0939	1·4174	0·6238
Δ = 0·9	72·19	113·74	0·1231	1·3527	0·6200
	89·30	129·77	0·1480	1·2996	0·6178

/continued

TABLE AI-1 continued

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
DICHLOROMETHANE	3·61	26·23	0·0079	1·8822	0·9048
	7·16	50·47	0·0155	1·8584	0·9013
w_2 = 336·5	10·99	75·15	0·0235	1·8355	0·9018
	15·07	99·56	0·0320	1·8081	0·8975
r = 0·9999	19·56	124·69	0·0412	1·7809	0·8950
	24·71	151·10	0·0515	1·7488	0·8902
Δ = 0·7	29·80	175·43	0·0614	1·7203	0·8881
	35·94	202·06	0·0731	1·6855	0·8839

TABLE AI-2: ABSORPTION OF BENZENE BY PDMS V AT VARIOUS LIQUID LOADINGS AT 30°C

	w_1	p_1	ϕ_1	$\ln \overset{V}{\gamma_1}$	χ
6% LOADING	1·31	9·09	0·0139	1·7137	0·7494
	2·54	169·0	0·0267	1·6838	0·7510
w_2 = 103·0	4·38	27·22	0·0451	1·6341	0·7461
	5·49	32·88	0·0559	1·6079	0·7460
r = 0·9994	6·99	39·78	0·0702	1·5715	0·7433
	8·63	46·48	0·0852	1·5323	0·7391
Δ = 1·2	11·28	56·15	0·1086	1·4786	0·7400
	14·16	64·61	0·1326	1·4185	0·7336
10% LOADING	2·23	10·41	0·0160	1·7120	0·7529
	4·10	18·34	0·0291	1·6798	0·7531
w_2 = 152·2	6·20	26·40	0·0435	1·6414	0·7496
	8·40	33·97	0·0578	1·6082	0·7512
r = 0·9994	10·96	41·81	0·0741	1·5667	0·7485
	13·85	49·52	0·0919	1·5202	0·7433
Δ = 1·1	17·18	57·45	0·1115	1·4745	0·7435
	20·84	64·88	0·1321	1·4259	0·7420
30% LOADING	6·22	9·56	0·0146	1·7206	0·7580
	11·92	17·46	0·0275	1·6853	0·7541
w_2 = 468·2	18·94	26·23	0·0430	1·6450	0·7523
	24·96	33·10	0·0560	1·6146	0·7535
r = 0·9993	31·37	39·70	0·0693	1·5815	0·7526
	40·72	48·20	0·0817	1·5344	0·7499
Δ = 0·9	55·35	59·30	0·1162	1·4651	0·7453
	66·52	66·37	0·1364	1·4165	0·7426

TABLE AI-3: ABSORPTION OF BENZENE BY PDMS I AT VARIOUS LIQUID LOADINGS AT 30°C

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
10% LOADING	2·52	10·24	0·0165	1·6648	0·7315
	4·77	18·42	0·0307	1·6286	0·7293
w_2 = 164·8	7·40	27·02	0·0469	1·5880	0·7269
	10·01	34·61	0·0625	1·5493	0·7243
r = 0·9994	12·61	41·41	0·0774	1·5132	0·7228
	15·84	48·94	0·0954	1·4713	0·7219
Δ = 0·6	20·18	57·46	0·1184	1·4148	0·7163
	24·09	64·05	0·1382	1·3682	0·7128
30% LOADING	6·64	9·82	0·0157	1·6709	0·7358
	12·25	17·26	0·0286	1·6350	0·7308
w_2 = 455·9	19·34	25·82	0·0445	1·5969	0·7303
	26·65	33·67	0·0602	1·5578	0·7282
r = 0·9995	33·28	40·06	0·0741	1·5237	0·7262
	42·27	47·79	0·0923	1·4804	0·7244
Δ = 1·4	51·85	54·78	0·1109	1·4326	0·7176
	62·99	61·84	0·1316	1·3822	0·7121

TABLE AI-4: ABSORPTION OF BENZENE BY PDMS OF VARIOUS MOLECULAR WEIGHTS AT 30°C

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
PDMS I	4·58	9·3	0·0148	1·6744	0·7362
	8·69	16·81	0·0278	1·6385	0·7313
w_2 = 333·5	13·09	24·19	0·0413	1·6062	0·7311
	18·37	32·15	0·0569	1·5677	0·7296
r = 0·9995	23·86	39·56	0·0728	1·5299	0·7285
	31·18	48·13	0·0929	1·4799	0·7247
Δ = 1·2	40·40	57·16	0·1173	1·4191	0·7174
	52·55	67·03	0·1474	1·3493	0·7132
PDMS II	3·90	9·21	0·0144	1·6915	0·7402
	8·17	18·29	0·0298	1·6531	0·7390
w_2 = 293·3	12·22	25·96	0·0439	1·6147	0·7343
	16·02	32·60	0·0568	1·5847	0·7351
r = 0·9996	20·56	39·64	0·0717	1·5464	0·7315
	26·43	47·73	0·0904	1·5002	0·7283
Δ = 0·8	32·88	55·50	0·1099	1·4540	0·7268
	40·24	62·94	0·1314	1·4015	0·7214

/continued

TABLE AI-4 continued

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
PDMS III	4·37	9·84	0·0152	1·7049	0·7482
	8·65	18·43	0·0297	1·6648	0·7433
w_2 = 313·2	12·36	25·24	0·0419	1·6337	0·7417
	16·32	31·90	0·0546	1·6029	0·7415
r = 0·9997	21·41	39·53	0·0704	1·5622	0·7380
	27·51	47·57	0·0887	1·5160	0·7342
Δ = 0·8	34·04	55·16	0·1075	1·4711	0·7325
	41·91	62·87	0·1291	1·4179	0·7275
PDMS IV	4·59	9·43	0·0145	1·7120	0·7514
	9·09	17·79	0·0283	1·6764	0·7498
w_2 = 346·5	14·14	26·19	0·0434	1·6365	0·7464
	18·17	32·37	0·0550	1·6093	0·7475
r = 0·9996	23·21	39·31	0·0692	1·5731	0·7451
	30·49	48·05	0·0890	1·5217	0·7397
Δ = 0·9	37·70	55·62	0·1078	1·4760	0·7372
	46·79	63·75	0·1304	1·4215	0·7338

TABLE AI-5: ABSORPTION OF HEXANE BY PDMS OF VARIOUS MOLECULAR WEIGHTS AT 30°C

	w_1	p_1	ϕ_1	$\ln \gamma_1^{V}$	χ
PDMS I	2·99	9·94	0·0148	1·3046	0·3673
	6·19	19·80	0·0301	1·2807	0·3693
w_2 = 291·9	9·77	29·84	0·0467	1·2507	0·3669
	13·64	39·81	0·0641	1·2225	0·3675
r = 0·9993	17·92	49·71	0·0825	1·1906	0·3655
	23·00	60·22	0·1035	1·1548	0·3634
Δ = 1·0	27·92	69·25	0·1229	1·1216	0·3608
	34·29	79·65	0·1468	1·0826	0·3593
PDMS II	3·61	11·39	0·0165	1·3285	0·3763
	6·85	20·76	0·0309	1·3018	0·3741
w_2 = 316·1	10·36	30·15	0·0460	1·2762	0·3742
	14·45	40·11	0·0631	1·2458	0·3724
r = 0·9994	18·80	49·70	0·0805	1·2149	0·3703
	23·78	59·57	0·0997	1·1810	0·3677
Δ = 0·5	29·49	69·68	0·1207	1·1453	0·3660
	35·82	79·57	0·1429	1·1080	0·3641

/continued

TABLE AI-5 continued

	w_1	p_1	ϕ_1	$\ln \gamma_1^V$	χ
PDMS III	3·32	11·25	0·0159	1·3530	0·3892
	6·18	20·12	0·0292	1·3261	0·3855
w_2 = 303·4	9·65	30·05	0·0449	1·2974	0·3838
	13·34	39·77	0·0611	1·2692	0·3833
r = 0·9995	17·50	49·64	0·0786	1·2374	0·3811
	22·12	59·56	0·0973	1·2047	0·3798
Δ = 0·7	27·16	69·19	0·1169	1·1704	0·3776
	33·15	79·33	0·1391	1·1722	0·3756
PDMS IV	3·06	10·78	0·0151	1·3619	0·3936
	6·07	20·48	0·0296	1·3324	0·3895
w_2 = 295·3	9·37	30·31	0·0449	1·3051	0·3889
	12·99	40·10	0·0612	1·2747	0·3864
r = 0·9995	17·28	50·65	0·0799	1·2418	0·3852
	21·57	60·08	0·0977	1·2096	0·3829
Δ = 0·7	26·60	69·98	0·1178	1·1739	0·3804
	32·07	79·58	0·1387	1·1383	0·3791

TABLE AI-6: ABSORPTION OF BENZENE BY PDMS V AT VARIOUS TEMPERATURES

	w_1	p_1	ψ_1	$\ln \gamma_1^S$	χ^*
25°C	15·03	4·52	0·0080	1·7903	0·8122
	93·24	24·08	0·0477	1·6769	0·8000
w_2 = 1964·1	151·17	35·06	0·0751	1·5978	0·7878
	201·58	43·06	0·0977	1·5397	0·7841
r = 0·9907	273·16	52·24	0·1280	1·4624	0·7776
	343·60	63·68	0·1746	1·3491	0·7698
Δ = 2·4	517·21	71·40	0·2175	1·2431	0·7534
	693·66	78·68	0·2715	1·1176	0·7347
	1312·00	89·12	0·4135	0·8202	0·6827
	2452·90	93·66	0·5686	0·5516	0·6479
25°C	16·76	5·06	0·0089	1·7934	0·8178
	52·46	14·68	0·0274	1·7366	0·8088
w_2 = 1963·1	98·47	25·27	0·0503	1·6727	0·8026
	143·76	34·07	0·717	1·6152	0·7983
r = 0·9990	205·58	43·88	0·0995	1·5403	0·7902
	280·17	53·16	0·1309	1·4573	0·7799
Δ = 1·1	371·88	61·82	0·1666	1·3663	0·7684

/continued

TABLE AI-6 continued

	w_1	p_1	ψ_1	$\ln \gamma_1^S$	χ^*
30°C	16·20	6·07	0·0086	1·7849	0·8083
	53·06	18·19	0·0276	1·7240	0·7959
w_2 = 1975·3	94·39	29·19	0·0481	1·6677	0·7909
	143·59	41·86	0·0713	1·6061	0·7865
r = 0·9987	202·53	53·51	0·0977	1·5357	0·7792
	275·46	65·03	0·1284	1·4567	0·7714
Δ = 1·9	368·74	76·21	0·1647	1·3654	0·7610
	512·00	88·23	0·2150	1·2447	0·7472
35°C	16·33	7·44	0·0087	1·7691	0·7924
	55·64	23·52	0·0289	1·7137	0·7886
w_2 = 1975·3	94·39	37·17	0·0481	1·6618	0·7845
	144·20	52·04	0·0717	1·5984	0·7786
r = 0·9992	226·31	71·36	0·1081	1·5020	0·7680
	282·26	81·70	0·1313	1·4420	0·7608
Δ = 0·9	375·34	95·29	0·1673	1·3522	0·7506

TABLE AI-7: ABSORPTION OF CYCLOHEXANE BY PDMS AT 25°C

	w_1	p_1	ψ_1	$\ln \gamma_1^S$	χ^*
	45·08	11·09	0·0266	1·4629	0·5179
w_2 = 1966·2	97·55	21·94	0·0559	1·4027	0·5157
	160·52	32·67	0·0887	1·3372	0·5142
r = 0·9973	245·65	44·17	0·1297	1·2582	0·5134
	394·61	58·45	0·1931	1·1386	0·5110
Δ = 0·3	599·90	70·70	0·2668	1·0045	0·5064
	804·16	78·26	0·3279	0·8993	0·5046
	1044·10	83·82	0·3878	0·7996	0·5017
	1415·60	88·83	0·4620	0·6820	0·4996
	1957·00	92·44	0·5428	0·5644	0·4957
	44·02	10·88	0·0260	1·4675	0·5214
w_2 = 1966·2	94·57	21·43	0·0542	1·4085	0·5186
	156·47	32·06	0·0867	1·3416	0·5147
r = 0·9985	245·91	44·26	0·1298	1·2592	0·5150
	406·52	59·37	0·1987	1·1302	0·5113
Δ = 0·9	584·84	69·98	0·2619	1·0131	0·5063
	862·10	79·88	0·3434	0·8734	0·5046
	1159·80	85·73	0·4130	0·7589	0·5007
	1477·80	89·42	0·4727	0·6656	0·4996
	1720·60	91·25	0·5107	0·6084	0·4998

TABLE AI-8: ABSORPTION OF HEXANE BY PDMS V AT VARIOUS TEMPERATURES

	w_1	p_1	ψ_1	$\ln \gamma_1^S$	χ^*
25°C	17·41	7·64	0·0121	1·4505	0·4754
	56·96	23·07	0·0385	1·3964	0·4719
w_2 = 1958·1	103·44	38·35	0·0678	1·3373	0·4676
	158·47	53·28	0·1002	1·2734	0·4630
r = 0·9980	228·43	68·47	0·1383	1·2001	0·4575
	316·69	83·30	0·1821	1·1199	0·4531
Δ = 0·4	446·54	98·91	0·2389	1·0183	0·4458
30°C	18·36	9·84	0·0127	1·4468	0·4728
	58·37	28·77	0·0393	1·3884	0·4647
w_2 = 1964·2	103·53	47·20	0·0676	1·3384	0·4685
	162·71	66·72	0·1023	1·2683	0·4613
r = 0·9970	231·37	84·91	0·1394	1·1977	0·4567
	322·73	103·50	0·1843	1·1145	0·4508
Δ = 1·7	446·06	121·73	0·2380	1·0192	0·4447
35°C	17·92	11·77	0·0124	1·4453	0·4706
	57·56	34·91	0·0387	1·3905	0·4659
w_2 = 1964·2	105·10	58·36	0·0685	1·3313	0·4623
	160·77	80·90	0·1011	1·2662	0·4562
r = 0·9979	233·60	104·62	0·1405	1·1921	0·4518
	322·15	126·73	0·1839	1·1122	0·4463
Δ = 0·7	452·08	150·26	0·2403	1·0128	0·4404

TABLE AI-9: ABSORPTION OF HEXANE BY DNP(B) - PDMS(C) MIXTURES AT 30°C

	w_A	p_A	ϕ_A	$\ln \gamma_A^V$	$\ln \gamma_A^S$
PDMS I	3·11	10·10	0·0154	1·278	1·352
	6·41	20·00	0·0313	1·252	1·325
w_B = 22·0	10·10	30·06	0·0485	1·222	1·293
	14·00	39·75	0·0659	1·192	1·263
w_C = 268·7	18·43	49·75	0·0850	1·161	1·230
	23·27	59·51	0·1050	1·128	1·196
Δ = 0·5	28·99	69·75	0·1275	1·092	1·158
	35·56	80·04	0·1520	1·053	1·117
PDMS II	2·62	10·18	0·0150	1·313	1·389
	5·40	20·07	0·0304	1·284	1·358
w_B = 13·5	8·42	29·89	0·0466	1·254	1·327
	11·86	40·06	0·0645	1·222	1·294
w_C = 239·9	16·03	51·20	0·0852	1·188	1·257
	19·74	60·04	0·1029	1·157	1·226
Δ = 0·9	24·40	70·01	0·1242	1·122	1·189
	29·76	80·03	0·1474	1·083	1·148
PDMS III	3·21	10·79	0·0155	1·336	1·412
	6·69	21·41	0·0318	1·303	1·378
w_B = 13·6	10·07	30·91	0·0472	1·276	1·350
	13·70	40·21	0·0631	1·247	1·320
w_C = 287·2	18·82	52·01	0·0847	1·209	1·280
	22·88	60·41	0·1011	1·181	1·250
Δ = 0·8	28·17	80·21	0·1271	1·145	1·213
	33·51	79·04	0·1415	1·112	1·178

/continued

TABLE AI-9 continued

	w_A	p_A	ϕ_A	$\ln \gamma_A^V$	$\ln \gamma_A^S$
PDMS IV	3·46	10·53	0·0152	1·337	1·413
	7·19	20·92	0·0310	1·307	1·382
w_B = 15·4	11·16	31·07	0·0473	1·279	1·353
	14·96	39·94	0·0624	1·252	1·325
w_C = 317·9	20·09	50·84	0·0821	1·218	1·290
	25·56	61·15	0·1021	1·183	1·253
Δ = 0·4	30·65	69·76	0·1200	1·153	1·221
	37·45	80·00	0·1428	1·114	1·181
PDMS V	2·60	10·42	0·0150	1·335	1·413
	5·20	20·05	0·0296	1·310	1·387
w_B = 16·0	8·10	29·85	0·0454	1·281	1·356
	11·35	39·96	0·0624	1·252	1·326
w_C = 237·0	14·87	49·85	0·0803	1·221	1·294
	18·65	59·84	0·0996	1·196	1·268
Δ = 0·6	23·31	69·90	0·1203	1·152	1·222

B = DNP

C = PDMS

TABLE AI-10: ABSORPTION OF HEXANE BY SQUALANE (B) - PDMS(C) MIXTURES AT 30°C

	w_A	p_A	ϕ_A	$\ln \gamma_A^V$	$\ln \gamma_A^S$
PDMS I	5·07	10·50	0·0170	1·231	1·305
	10·17	20·18	0·0335	1·203	1·276
w_B = 38·9	15·83	30·07	0·0512	1·177	1·248
	22·07	39·80	0·0697	1·146	1·216
w_C = 388·0	28·99	49·79	0·0899	1·116	1·184
	36·50	59·42	0·1106	1·084	1·151
Δ = 0·6	45·01	69·17	0·1329	1·050	1·116
	54·83	79·03	0·1574	1·014	1·077
PDMS II	4·88	10·26	0·0161	1·254	1·329
	9·93	20·00	0·0321	1·227	1·307
w_B = 37·9	15·59	30·03	0·0495	1·199	1·272
	21·64	39·76	0·0675	1·169	1·241
w_C = 395·0	28·30	49·50	0·0864	1·140	1·210
	35·89	59·45	0·1071	1·107	1·176
Δ = 0·3	44·11	69·06	0·1285	1·074	1·141
	54·09	79·25	0·1532	1·035	1·101
PDMS III	3·45	10·42	0·0163	1·256	1·333
	7·00	20·25	0·0325	1·228	1·304
w_B = 30·9	10·98	30·36	0·0500	1·201	1·275
	15·29	40·36	0·0683	1·172	1·245
w_C = 271·5	20·04	50·28	0·0876	1·142	1·213
	25·07	59·72	0·1073	1·110	1·180
Δ = 0·5	30·56	68·96	0·1278	1·079	1·147
	37·75	79·72	0·1532	1·041	1·107

/continued

TABLE AI-10 continued

	w_A	p_A	ϕ_A	$\ln \gamma_A^V$	$\ln \gamma_A^S$
PDMS IV	4·36	10·19	0·0158	1·261	1·339
	8·96	20·03	0·0319	1·233	1·310
w_B = 39·0	14·42	30·71	0·0504	1·202	1·277
	19·79	40·27	0·0678	1·175	1·248
w_C = 355·5	25·88	50·09	0·0871	1·144	1·216
	32·39	59·57	0·1066	1·114	1·184
Δ = 0·8	40·05	69·52	0·1286	1·080	1·149
	48·84	79·60	0·1525	1·044	1·111
PDMS V	3·06	10·17	0·0155	1·280	1·362
	6·33	20·14	0·0316	1·250	1·330
w_B = 25·1	9·96	30·12	0·0488	1·217	1·296
	13·89	40·19	0·0668	1·191	1·268
w_C = 257·9	17·99	49·67	0·0848	1·162	1·238
	22·65	59·33	0·1045	1·130	1·205
Δ = 2·0	28·21	69·61	0·1269	1·094	1·167
	33·98	79·13	0·1490	1·061	1·132

B = Squalane

C = PDMS

TABLE AI-11: ABSORPTION OF CHLOROFORM BY DNP AND SQ AT VARIOUS LIQUID LOADINGS AT 30°C

	w_1	p_1	x_1	$\ln \gamma_1$	χ
30% DNP	8·04	3·93	0·0598	-1·2822	-0·4687
	16·02	7·78	0·1124	-1·2313	-0·4649
w_2 = 443·6	23·90	11·54	0·1589	-1·1835	-0·4603
	33·34	15·99	0·2086	-1·1301	-0·4548
r = 0·9999	42·63	20·30	0·2520	-1·0805	-0·4486
	53·71	25·40	0·2980	-1·0245	-0·4399
Δ = 1·0	66·11	30·94	0·3432	-0·9688	-0·4326
	84·15	38·80	0·3995	-0·8947	-0·4208
20% DNP	5·69	3·95	0·0602	-1·2841	-0·4711
	11·23	7·75	0·1122	-1·2333	-0·4669
w_2 = 311·6	16·77	11·55	0·1588	-1·1822	-0·4588
	23·45	16·06	0·2088	-1·1265	-0·4510
r = 0·9999	30·29	20·63	0·2542	-1·0733	-0·4430
	37·82	25·56	0·2985	-1·0200	-0·4353
Δ = 0·7	46·77	31·35	0·3448	-0·9604	-0·4246
	59·34	39·21	0·4004	-0·8864	-0·4117
30% SQUALANE	4·07	4·74	0·0292	-0·3786	0·6312
	12·17	13·74	0·0825	-0·3542	0·6272
w_2 = 479·3	16·42	18·20	0·1082	-0·3438	0·6235
	25·79	27·52	0·1601	-0·3228	0·6155
r = 0·9999	38·52	39·25	0·2216	-0·2937	0·6095
	55·15	53·07	0·2895	-0·2606	0·6026
Δ = 1·26	76·05	68·19	0·3598	-0·2280	0·5921
	99·28	82·75	0·4232	-0·1977	0·5823

/continued

TABLE AI-11 continued

	w_1	p_1	x_1	$\ln \gamma_1$	χ
20% SQUALANE	2·75	5·07	0·0311	-0·3740	0·6349
	6·17	11·14	0·0671	-0·3571	0·6327
w_2 = 303·6	10·21	17·95	0·1064	-0·3412	0·6272
	17·82	29·88	0·1721	-0·3129	0·6189
r = 0·9999	25·98	41·55	0·2326	-0·2854	0·6117
	34·35	52·61	0·2861	-0·2573	0·6086
Δ = 1·5	43·28	63·17	0·3355	-0·2343	0·6017
	56·99	77·60	0·3994	-0·2036	0·5928

TABLE AI-12: ABSORPTION OF DICHLOROMETHANE BY DNP AND SQ AT VARIOUS LIQUID LOADINGS AT 30°C

	w_1	p_1	x_1	$\ln \gamma_1$	χ
30% DNP	5·74	10·69	0·0597	-1·0417	-0·0365
	10·75	19·85	0·1062	-0·9994	-0·0301
w_2 = 445·9	16·30	29·83	0·1526	-0·9555	-0·0233
	22·22	40·31	0·1972	-0·9109	-0·0154
r = 0·9990	30·31	54·32	0·2509	-0·8543	-0·0042
	38·67	68·29	0·2994	-0·8028	0·0050
Δ = 0·8	49·49	85·66	0·3536	-0·7431	0·0158
	60·41	102·51	0·4004	-0·6887	0·0270
20% DNP	4·97	13·24	0·0731	-1·0312	-0·0363
	7·61	20·14	0·1079	-1·0011	-0·0334
w_2 = 310·1	11·44	30·03	0·1539	-0·9568	-0·0258
	15·51	40·30	0·1977	-0·9138	-0·0189
r = 0·9991	21·25	54·55	0·2525	-0·8562	-0·0077
	27·31	68·90	0·3027	-0·8047	-0·0054
Δ = 0·8	34·90	86·54	0·3568	-0·7421	0·0135
	44·64	107·85	0·4150	-0·6741	0·0271
30% SQUALANE	5·33	25·10	0·0523	-0·0573	1·1340
	10·95	49·50	0·1019	-0·0456	1·1207
w_2 = 480·6	17·08	74·02	0·1503	-0·0331	1·1082
	23·90	99·23	0·1984	-0·0191	1·0967
r = 0·9999	31·75	125·33	0·2475	-0·0077	1·0815
	42·17	156·50	0·3040	0·0073	1·0652
Δ = 2·1	53·33	185·99	0·3558	0·0211	1·0496
	67·21	217·62	0·4104	0·0340	1·0306

/continued

TABLE AI-12 continued

	w_1	p_1	x_1	$\ln \gamma_1$	χ
20% SQUALANE	3·41	25·37	0·0528	-0·0547	1·1364
	7·01	49·95	0·1027	-0·0442	1·1217
w_2 = 304·8	10·85	74·48	0·1505	-0·0286	1·1127
	15·13	99·43	0·1982	-0·0156	1·1006
r = 0·9999	20·09	125·72	0·2471	-0·0028	1·0870
	25·54	151·94	0·2944	0·0102	1·0741
Δ = 1·7	33·08	183·79	0·3508	0·0237	1·0556
	43·34	220·94	0·4145	0·0392	1·0343

TABLE AI-13: ABSORPTION OF ETHYL ACETATE BY SQUALANE AT VARIOUS LIQUID LOADINGS AT 30°C

	w_1	p_1	x_1	$\ln \gamma_1$	χ
BULK	15·87	7·62	0·0357	0·5957	1·4505
	36·39	16·51	0·0783	0·5828	1·4332
$w_2 = 2056{\cdot}9$	54·41	23·55	0·1126	0·5730	1·4201
	78·80	31·97	0·1553	0·5566	1·3996
$r = 0{\cdot}9990$	106·64	40·40	0·1992	0·5405	1·3796
	137·23	48·25	0·2425	0·5206	1·3557
$\Delta = 0{\cdot}7$	171·70	55·67	0·2860	0·4978	1·3288
40% LOADING	74·87	9·19	0·0432	0·5910	1·4450
	167·33	19·23	0·0917	0·5761	1·4250
$w_2 = 7950{\cdot}0$	251·66	27·36	0·1319	0·5649	1·4100
	353·55	35·99	0·1760	0·5501	1·3913
$r = 0{\cdot}9999$	482·57	45·30	0·2256	0·5302	1·3671
	610·60	53·10	0·2693	0·5110	1·3442
$\Delta = 0{\cdot}7$	732·30	59·45	0·3065	0·4938	1·3241
	947·85	68·59	0·3639	0·4642	1·2900
30% LOADING	53·04	8·56	0·0405	0·5848	1·4389
	106·72	16·34	0·0783	0·5715	1·4215
$w_2 = 6025{\cdot}8$	166·71	24·18	0·1172	0·5596	1·4056
	234·76	32·06	0·1575	0·5452	1·3872
$r = 0{\cdot}9999$	309·43	39·64	0·1977	0·5293	1·3674
	398·79	47·49	0·2410	0·5109	1·3449
$\Delta = 0{\cdot}8$	471·25	53·05	0·2729	0·4969	1·3280

/continued

TABLE AI-13 continued

	w_1	p_1	x_1	$\ln \gamma_1$	χ
20% LOADING	27·33	6·78	0·0324	0·5771	1·4319
	59·30	14·08	0·0676	0·5695	1·4205
w_2 = 3921·8	94·67	21·37	0·1038	0·5577	1·4048
	132·52	28·40	0·1395	0·5456	1·3890
r = 0·9999	188·76	37·65	0·1876	0·5303	1·3691
	243·07	45·25	0·2293	0·5130	1·3477
Δ = 1·1	322·53	54·70	0·2830	0·4910	1·3210
	404·98	62·68	0·3314	0·4685	1·2943
10% LOADING	19·96	9·35	0·0465	0·5356	1·3881
	37·33	16·73	0·0836	0·5301	1·3782
w_2 = 1963·7	57·22	24·42	0·1227	0·5238	1·3675
	82·83	33·06	0·1684	0·5093	1·3478
r = 0·9999	106·14	40·22	0·2060	0·5029	1·3378
	134·68	47·84	0·2476	0·4912	1·3224
Δ = 1·8	173·20	56·49	0·2974	0·4733	1·3002
	219·80	64·75	0·3495	0·4476	1·2694

TABLE AI-14: ABSORPTION OF ETHYL ACETATE BY DNP AT VARIOUS LIQUID LOADINGS AT 30°C

	w_1	p_1	x_1	ln γ_1	χ
BULK	24·40	5·35	0·0542	-0·1754	0·5104
	54·05	11·37	0·1127	-0·1539	0·5107
w_2 = 2022·8	93·35	18·53	0·1798	-0·1340	0·5059
	121·23	23·12	0·2217	-0·1222	0·5021
r = 0·9998	160·53	28·95	0·2738	-0·1094	0·4952
	207·60	35·14	0·3278	-0·0963	0·4877
Δ = 1·6	264·22	41·76	0·3829	-0·0793	0·4835
40% LOADING	100·89	5·62	0·0569	-0·1757	0·5091
	233·39	12·35	0·1226	-0·1556	0·5050
w_2 = 7938·5	320·26	16·45	0·1608	-0·1412	0·5050
	454·94	22·27	0·2140	-0·1245	0·5027
r = 0·9996	631·67	29·11	0·2743	-0·1058	0·4992
	771·93	33·97	0·3160	-0·0934	0·4964
Δ = 0·7	1096·30	43·62	0·3962	-0·0706	0·4898
30% LOADING	89·47	6·50	0·0661	-0·1789	0·5024
	186·52	12·87	0·1285	-0·1620	0·4959
w_2 = 6008·8	316·01	20·60	0·1999	-0·1342	0·4976
	407·50	25·50	0·2437	-0·1194	0·4963
r = 0·9994	513·48	30·70	0·2888	-0·1041	0·4952
	590·40	34·17	0·3183	-0·0946	0·4938
Δ = 1·3	714·93	39·33	0·3611	-0·0810	0·4920
	935·38	47·23	0·4252	-0·6202	0·4881

/continued

TABLE AI-14 continued

	w_1	p_1	x_1	$\ln \gamma_1$	χ
20% LOADING	37·59	4·08	0·0428	-0·2110	0·4782
	91·14	9·52	0·0979	-0·1908	0·4776
w_2 = 3990·3	145·21	14·63	0·1474	-0·1711	0·4786
	202·13	19·60	0·1940	-0·1537	0·4783
r = 0·9993	262·19	24·43	0·2379	-0·1381	0·4772
	329·87	29·50	0·2820	-0·1201	0·4790
Δ = 0·5	403·29	34·47	0·3244	-0·1051	0·4783
	483·53	39·46	0·3654	-0·0893	0·4974
10% LOADING	34·55	6·97	0·0761	-0·2499	0·4248
	60·99	11·91	0·1269	-0·2265	0·4277
w_2 = 1994	89·59	16·95	0·1759	-0·2009	0·4339
	124·09	22·71	0·2282	-0·1693	0·4456
r = 0·9973	170·25	29·64	0·2886	-0·1385	0·4542
	213·15	35·35	0·3368	-0·1175	0·4572
Δ = 3·2	249·16	39·69	0·3725	-0·1029	0·4586
	294·81	44·67	0·4126	-0·0875	0·4595

TABLE AI-15: ADSORPTION OF SOLUTES BY BARE CELITE AT 30°C

	w_1	p_1	w_1/W	$p/p°$
CHLOROFORM	0·29	4·85	0·167	0·020
	0·59	13·18	0·342	0·055
	0·86	23·37	0·491	0·097
W = 1·7411 g	1·09	35·14	0·626	0·146
	1·29	47·31	0·741	0·197
	1·59	70·27	0·913	0·292
	1·76	84·05	1·011	0·349
	1·90	96·53	1·091	0·401
	2·01	105·80	1·154	0·439
DICHLOROMETHANE	0·33	25·27	0·197	0·049
	0·51	50·23	0·305	0·097
	0·66	75·71	0·395	0·146
W = 1·6717 g	0·80	100·31	0·476	0·193
	0·93	125·27	0·556	0·241
	1·05	150·31	0·628	0·289
	1·15	174·18	0·691	0·335
	1·25	199·65	0·748	0·384
	1·36	223·48	0·811	0·429
	1·49	256·63	0·891	0·494

/continued

TABLE AI-15 continued

	w_1	p_1	w_1/W	$p/p°$
ETHYL ACETATE	1·51	6·21	0·079	0·052
	2·01	12·10	0·105	0·102
	2·48	18·28	0·129	0·153
W = 19·1868 g	2·95	24·36	0·154	0·204
	3·40	30·18	0·177	0·253
	3·87	36·31	0·202	0·305
	4·36	42·66	0·227	0·358
	4·81	48·80	0·250	0·410
	5·38	56·20	0·280	0·472
	6·03	64·22	0·314	0·539

W = weight of Celite used in grams

TABLE AI-16: ABSORPTION OF CHLOROFORM BY SQUALANE(B)- DNP(C) MIXTURES AT 30°C

	w_1	p_1	x_1	$\ln \gamma_1$
$n_B:n_C$ = 3:1	7·84	6·54	0·0578	-0·7389
	15·62	12·85	0·1088	-0·6975
w_B = 336·8	24·22	19·58	0·1592	-0·6575
	33·94	26·96	0·2097	-0·6135
w_C = 115·1	44·88	34·95	0·2597	-0·5685
	54·83	41·86	0·3000	-0·5327
Δ = 0·9	69·59	51·69	0·3523	-0·4830
	82·93	59·90	0·3933	-0·4462
$n_B:n_C$ = 1:1	8·89	4·5	0·0530	-1·0258
	16·78	8·40	0·0955	-0·9913
w_B = 276·3	29·99	14·89	0·1587	-0·9278
	41·72	20·50	0·2079	-0·8783
w_C = 284·0	50·86	24·85	0·2424	-0·8395
	63·33	30·59	0·2848	-0·7935
Δ = 1·5	80·85	38·38	0·3371	-0·7356
	99·80	46·57	0·3856	-0·6773
$n_B:n_C$ = 1:3	8·09	4·91	0·0691	-1·2053
	15·57	9·36	0·1251	-1·1531
w_B = 100·1	24·81	14·83	0·1855	-1·0878
	34·53	20·48	0·2407	-1·0257
w_C = 282·9	46·14	27·08	0·2975	-0·9590
	59·14	34·32	0·3519	-0·8901
Δ = 1·3	71·52	40·96	0·3963	-0·8326
	87·17	49·10	0·4445	-0·7666

$n_B:n_C$ = approximate mole ratio of absorbent mixture.

TABLE AI-17: ABSORPTION OF DICHLOROMETHANE BY SQUALANE(B) - DNP(C) MIXTURES AT 30°C

	w_1	p_1	x_1	$\ln \gamma_1$
$n_B:n_C$ = 3:1	5·25	18·08	0·0551	-0·4373
	9·75	32·76	0·0977	-0·4157
w_B = 336·8	19·16	62·01	0·1755	-0·3648
	25·34	80·00	0·2197	-0·3360
w_C = 110·1	33·95	103·57	0·2739	-0·2988
	41·76	123·37	0·3170	-0·2707
Δ = 1·2	53·08	149·97	0·3710	-0·2341
	63·90	173·29	0·4152	-0·2033
$n_B:n_C$ = 1:1	6·23	12·78	0·0530	-0·7453
	12·31	24·87	0·0996	-0·7103
w_B = 266·0	20·74	41·15	0·1572	-0·6635
	30·55	59·41	0·2155	-0·6127
w_C = 284·8	45·25	85·34	0·2892	-0·5459
	53·37	98·75	0·3243	-0·5150
Δ = 1·1	67·54	121·14	0·3778	-0·4645
	87·21	149·81	0·4395	-0·4047
$n_B:n_C$ = 1:3	4·76	11·40	0·0588	-0·9629
	10·30	24·36	0·1192	-0·9105
w_B = 91·4	17·21	40·09	0·1844	-0·8494
	25·59	58·59	0·2517	-0·7818
w_C = 284·5	34·98	78·29	0·3150	-0·7171
	44·84	98·01	0·3708	-0·6565
Δ = 1·0	58·28	123·35	0·4338	-0·5846
	74·56	151·46	0·4950	-0·5126

$n_B:n_C$ = approximate mole ratio of absorbent mixture

TABLE AI-18: ABSORPTION OF ETHYL ACETATE BY SQUALANE(B) - DNP(C) MIXTURES AT 30°C

	w_1	p_1	x_1	$\ln \gamma_1$
$n_B:n_C$ = 3:1	103·40	7·10	0·0466	0·2591
	220·43	14·42	0·0943	0·2612
w_B = 7719·4	355·60	22·05	0·1438	0·2630
	490·48	28·78	0·1881	0·2601
w_C = 2415·0	633·24	35·16	0·2303	0·2575
	777·66	40·98	0·2687	0·2557
Δ = 0·9	1014·20	49·07	0·3239	0·2479
	1209·60	54·84	0·3636	0·2428
$n_B:n_C$= 1:1	140·50	9·52	0·0761	0·0612
	306·83	19·26	0·1524	0·0697
w_B = 4073·0	507·32	29·31	0·2292	0·0807
	726·99	38·50	0·2988	0·0873
w_C = 4073·3	1005·90	48·03	0·3709	0·0912
	1331·60	56·85	0·4384	0·0917
Δ = 0·8	1523·70	61·24	0·4718	0·0921
	1765·70	66·03	0·5086	0·0917
$n_B:n_C$ = 1:3	143·00	6·74	0·0607	-0·0583
	306·09	13·70	0·1216	-0·0438
w_B = 2654·6	498·58	21·06	0·1839	-0·0289
	696·92	27·80	0·2396	-0·0163
w_C = 7881·1	953·22	35·36	0·3012	-0·0053
	1146·00	40·46	0·3413	0·0038
Δ = 1·2	1518·90	48·71	0·4071	0·0120
	1990·20	57·50	0·4736	0·0256

$n_B:n_C$ = approximate mole ratio of absorbent mixture.

Appendix 11

The Computer Programs

Two computing systems were used for the programs written for work in this Thesis. The first was a Commodore 'PET' 32K microcomputer and programs were written in 'CBM BASIC Version 4.0'. The second system used was a Honeywell 'Multics' mainframe computer at the Avon Universities' Computer Centre. The BASIC language was also employed for programs on this system.

Five programs were written and these are listed and discussed in the following pages:

AII-1 'FLO-HUG' - Analysis of a binary absorption isotherm in terms of Flory-Huggins theory.

AII-2 'FLOHUG-TERNARY' - Analysis of a series of ternary isotherms in terms of Flory-Huggins theory.

AII-3 'PARMISC' - Calculates phase limits of a partially miscible system using the 'tangent through the origin' method.

AII-4 'FLORY-EOS' - Prediction of interaction parameters from Flory's equation of state theory.

A II-5 'UNIFAC' - Application of UNIFAC method to polymer solutions.

AII-1 PROGRAM 'FLO-HUG'

The program 'FLO-HUG' was written for the 'PET' microcomputer and analysed absorption isotherms in terms of classical binary Flory-Huggins theory based on the treatment in Section 3.

Lines 140-160 of the program allowed the results to be calculated in terms of volume or segment fraction and this was followed by the reading in of the absorbent data required for the calculations (Line 300) and the experimental observations of absorbate weights and pressures (Line 410). The weights of absorbate were corrected for buoyancy effects when the MS microbalance was used before the calculation of concentration fractions (Lines 480-510) and activity coefficients (Lines 520-560).

Interaction parameters were calculated using equation (3.5) (Lines 850-920) and a linear least squares fit procedure of interaction parameter and volume or segment fraction was used to calculate best fit values of χ° and χ'. The best fit values were then used to calculate the values of χ at each experimental concentration in order to calculate best fit activity coefficients (Lines 1430-1460) and the RMSD (Lines 1470-1520).

The best fit values were used to predict the solution properties at 0·1 volume fractions across the concentration range (Lines 1630-2050). Lines 180 and 2420 of the program were control statements to allow output to a printer. The program reproduced in the following pages as an example is that for the isotherm of n-Hexane in PDMS on the MS balance at 30°C and is followed by a sample output.

When analysing results for polymer-solvent systems on the QB balance the same program could be used except that the buoyancy corrections (Line 420) were not required.

The same program was also used to treat the results of the ternary mixtures of hexane, PDMS and DNP or SQ in Chapter 6 as a pseudo-binary system. This necessitated redefinition of the size ratio (Lines 720-750) according to equation (3.11). Changes to the expressions defining the concentration fractions (Lines 480-510) were also necessary.

A modified version of the program was also used when analysing the isotherms for DNP or SQ-solvent systems in which the analysis was based on mole fraction activity coefficients. Thus the selection of volume or segment fractions was unnecessary and the expressions for activity coefficients and interaction parameters needed to be redefined. The points noted above about needing to account for buoyancy effects when using the MS microbalance and the modifications necessary for ternary mixtures were also pertinent with these systems.

```
100 REM  ***** PROGRAM FLO-HUG.    PETBASIC  C. G.J.PRICE   02/12/81. *****
110 REM THIS PROGRAM CALCULATES ACTIVITY COEFFICIENTS AND INTERACTION
120 REM PARAMETERS IN TERMS OF VOLUME OR SEGMENT FRACTION OF SOLUTE IN SOLN.
130 REM IF MORE THAN 20 DATA POINTS ARE USED ARRAYS MUST BE REDIMENSIONED
140 INPUT"DO YOU WANT VOLUME OR SEGMENT FRACTIONS?";T$
141 IF T$="VOLUME" GOTO 150
142 IF T$ <> "SEGMENT" GOTO 140
150 IF T$="VOLUME" THEN Q9=1
160 IF T$="SEGMENT" THEN Q9=2
179 GOTO 185
180 OPEN1,4:CMD1
185 PRINT "▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒"
190 PRINT "CALCULATION OF ACTIVITY COEFFICIENTS AND FLORY HUGGINS PARAMETERS"
195 PRINT "▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒"
196 PRINT:PRINT
200 READ A$:PRINT A$
220 PRINT:PRINT:PRINT
230 DIM WT(20),W(20),PHI(20),P(20),PG(20),X(20),F(20),LGF(20),LNG(20),G(20)
240 DIM Q(20),KHI(20),Z(20),CHI(20),LCG(20),DEV(20)
250 REM
260 REM
270 REM DATA INPUT AND CALCULATION OF CONCENTRATIONS AND ACTIVITY COEFFICIENTS
280 REM
290 REM
300 READ N,T,M1,D1,P0,B,V1,W2,D2,V2,M2,VV,VS
310 REM N=NO.OF DATA POINTS,T=ABSOLUTE TEMP.,D1=DENSITY OF VAPOUR,M1=MOL.WT
320 REM P0=SVP.OF VAPOUR,B=2ND.VIRIAL COEFF.OF VAPOUR,V1=MOLAR VOLUME OF VAPOUR
330 REM W2=WEIGHT OF SAMPLE,D2=DENSITY OF SAMPLE,V2=MOLAR VOLUME OF SAMPLE
340 REM M2=MOL.WT OF SAMPLE,VV=SPECIFIC VOL.OF VAPOUR,VS=SPECIFIC VOL.OF SAMPLE
350 IF Q9=1 GOTO 390:IF Q9=2 GOTO 370
370 PRINT " WEIGHT           PRESSURE         MOLE FRAC        SEG FRAC"
380 GOTO 400
390 PRINT " WEIGHT           PRESSURE         MOLE FRAC.       VOL FRAC"
395 PRINT
400 FOR I=1TO N
410 READ W(I),P(I)
420 LET WT(I)=W(I)+(7.4463E-2*P(I))+(6.9076E-6*P(I)*W(I))-(1.523E-4*W(I))
430 REM
440 REM  THIS IS A BOUYANCY CORRECTION TO THE OBSERVED WEIGHT
450 REM
460 IF Q9=1 GOTO 500:IF Q9=2 GOTO 480
480 LET PHI(I)=(WT(I)*VV)/((WT(I)*VV)+(W2*VS))
490 GOTO 510
500 LET PHI(I)=(WT(I)/D1)/((WT(I)/D1)+(W2/D2))
510 LET X(I)=(WT(I)/M1)/((WT(I)/M1)+(W2/(V2*D2*1E3)))
520 LET F(I)=P(I)/(P0*PHI(I))
530 LET LGF(I)=LOG(F(I))
540 LET C1=(V1-B)/(62.36*T)
550 LET C2=(B*B)/(((62.36*T)↑2)*2)
560 LET LNG(I)=LGF(I)+(C1*(P0-P(I)))+(C2*((P0↑2)-(P(I)↑2)))
570 LET G(I)=EXP(LNG(I))
580 REM "G(I)= ACTIVITY COEFFICIENT"
590 PRINT LEFT$(STR$(WT(I)),7),LEFT$(STR$(P(I)),7),LEFT$(STR$(X(I)),7),
600 PRINT LEFT$(STR$(PHI(I)),7)
610 NEXT I
620 PRINT:PRINT:PRINT
630 PRINT "UNCORR'D          LOG(E) OF        CORR'D           LOG(E) OF"
640 PRINT "ACT.COEFF.        ACT.COEFF.       ACT.COEFF.       ACT.COEFF."
650 PRINT
```

```
660 FOR I=1 TO N
670 PRINT LEFT$(STR$(F(1)),7),LEFT$(STR$(LGF(I)),7),LEFT$(STR$(G(1)),7),
680 PRINT LEFT$(STR$(LNG(I)),7)
690 NEXT I
700 IF Q9=1 GOTO 740:IF Q9=2 GOTO 720
720 LET R=(M2*VS)/(M1*VV)
730 GOTO 750
740 LET R=V2/V1
750 LET R$=LEFT$(STR$(R),6)
760 PRINT:PRINT
770 PRINT "SIZE RATIO OF COMPONENTS,R=";R$
780 REM  R=SIZE RATIO OF SOLVENT AND SOLUTE
790 REM
800 REM
810 REM LEAST SQUARES FIT OF INTERACTION PARAMETER WITH CONCENTRATION
820 REM
830 REM
840 FOR I=1 TO N
850 IF Q9=1 GOTO 890:IF Q9=2 GOTO 870
870 LET PHI(I)=(W2*VS)/((W2*VS)+(WT(I)*VV))
880 GOTO 900
890 LET PHI(I)=(W2/D2)/(W2/D2+WT(I)/D1)
900 REM  NOTICE THAT HERE VOLUME FRACTION IS THAT OF THE POLYMER
910 LET Q(I)=(1-1/R)*PHI(I)
920 LET KHI(I)=(LNG(I)-Q(I))/(PHI(I)↑2)
930 REM KHI(I)=EXPERIMENTAL VALUE OF INTERACTION PARAMETER
940 LET W=W+PHI(I)
950 LET U=U+(PHI(I)↑2)
960 LET Y=Y+(PHI(I)*KHI(I))
970 LET Z=Z+KHI(I)
980 LET Z2=Z2+(KHI(I)*KHI(I))
990 NEXT I
1000 LET A=(N*U)-(W*W)
1010 LET G1=((N*Y)-(W*Z))/A
1020 LET I1=((U*Z)-(W*Y))/A
1030 LET C8=SQR(U*Z2)
1040 LET C9=Y/C8
1050 PRINT:PRINT
1060 PRINT "EQUATION EXPRESSING CONCENTRATION DEPENDENCE OF KHI IS :-"
1070 PRINT:PRINT
1080 LET I$=LEFT$(STR$(I1),6)
1090 LET G$=LEFT$(STR$(G1),6)
1100 PRINT "            KHI=  KHI0 + KHI1 X PHI"
1110 PRINT
1120 PRINT"            KHI=";I$;"+";G$;" X PHI"
1130 PRINT:PRINT:PRINT
1140 LET K9=I1+G1
1150 FOR I=1 TO N
1160 LET Z(I)=KHI(I)-((G1*PHI(I))+I1)
1170 LET Z1=Z1+(Z(I)*Z(I))
1180 NEXT I
1190 LET Z4=SQR(((Z1/N)*U)/A)
1200 LET Z4$=LEFT$(STR$(Z4),4)
1205 LET Z6$=RIGHT$(STR$(Z4),5)
1210 LET Z5=SQR(Z1/A)
1220 LET Z5$=LEFT$(STR$(Z5),4)
1225 LET Z7$=RIGHT$(STR$(Z5),5)
1230 PRINT "STANDARD DEVIATION OF KHI0=";Z4$;Z6$
1240 PRINT
1250 PRINT "STANDARD DEVIATION OF KHI1=";Z5$;Z7$
1260 PRINT:PRINT
1270 LET C9$=LEFT$(STR$(C9),7)
1280 PRINT "CORRELATION COEFFICIENT OF FIT =";C9$
1290 LET C9$=LEFT$(STR$(C9),7)
1300 PRINT:PRINT
```

```
1310 REM
1320 REM
1330 REM COMPARISON OF EXPERIMENTAL DATA WITH THAT FROM COMPUTED FIT
1340 REM
1350 REM
1360 IF Q9=1 GOTO 1400:IF Q9=2 GOTO 1380
1380 PRINT "SEGMENT          EXPT'L             CALC'D           LOG(E) OF";
1385 PRINT "        DIFFERENCE"
1390 GOTO 1410
1400 PRINT "VOLUME           EXPT'L             CALC'D           LOG(E) OF";
1405 PRINT "        DIFFERENCE"
1410 PRINT "FRAC.OF          INTERACTION        INTERACTION      ACTIVITY";
1415 PRINT "         FROM"
1420 PRINT "POLYMER          PARAMETER          PARAMETER        COEFF.":
1425 PRINT "            EXPT'L"
1427 PRINT
1430 FOR I=1 TO N
1440 LET CHI(I)=I1+G1*PHI(I)
1450 REM CHI(I)= CALCULATED VALUE OF INTERACTION PARAMETER
1460 LET LCG(I)=Q(I)+(CHI(I)*PHI(I)*PHI(I))
1470 LET DEV(I)=LNG(I)-LCG(I)
1480 PRINT LEFT$(STR$(PHI(I)),7),LEFT$(STR$(KHI(I)),7),LEFT$(STR$(CHI(I)),7),
1490 PRINT LEFT$(STR$(LNG(I)),7),LEFT$(STR$(DEV(I)),6);RIGHT$(STR$(DEV(I)),5)
1500 LET DEV=DEV+(ABS(DEV(I))↑2)
1510 NEXT I
1520 LET DV=SQR(DEV/N)
1530 PRINT:PRINT
1540 LET D1$=LEFT$(STR$(DV),5)
1550 LET D2$=RIGHT$(STR$(DV),5)
1560 PRINT "ROOT MEAN SQUARE DEVIATION=";D1$;D2$
1570 PRINT:PRINT
1580 REM
1590 REM
1600 REM CALCULATION OF COMPUTED VALUES ACROSS CONCENTRATION RANGE
1610 REM
1620 REM
1630 FOR J=0 TO 1 STEP 0.1
1640 LET PHI(J)=1-J
1650 LET Q(J)=(1-1/R)*PHI(J)
1660 LET CHI(J)=I1+(G1*PHI(J))
1670 LET LNG(J)=Q(J)+(CHI(J)*PHI(J)*PHI(J))
1680 LET G(J)=EXP(LNG(J))
1690 REM
1700 REM
1710 REM CALCULATION OF INFINITE DILUTION DATA
1720 REM
1730 REM
1740 IF J=0 GOTO 1760
1750 IF J>0 GOTO 2150
1760 LET L$=LEFT$(STR$(LNG(J)),7)
1770 PRINT "LOG(E) OF ACTIVITY COEFF. AT INFINITE DILUTION=";L$
1780 LET F2=LNG(J)-(C1*P0)-(C2*P0*P0)
1790 LET F1=EXP(F2):F1$=LEFT$(STR$(F1),7)
1800 PRINT
1810 LET F1$=LEFT$(STR$(F1),7)
1820 PRINT "UNCORRECTED ACTIVITY COEFFICIENT AT INFINITE DILUTION=";F1$
1830 PRINT
1840 LET F3=EXP(LNG(J)):F3$=LEFT$(STR$(F3),7)
```

```
1860 PRINT
1870 IF Q9=1 GOTO 1910:IF Q9=2 GOTO 1890
1890 PRINT "CORRECTED SEGMENT FRACTION ACTIVITY COEFFICIENT=";F3$
1900 GOTO 2020
1910 PRINT "CORRECTED VOLUME FRACTION ACTIVITY COEFFICIENT=";F3$
1920 LET F4=F3*D2/D1:F4$=LEFT$(STR$(F4),7)
1940 PRINT
1950 PRINT "CORRECTED WEIGHT FRACTION ACTIVITY COEFFICIENT=";F4$
1960 PRINT
1970 LET F5=F3*(1/R)
1980 LET F5$=LEFT$(STR$(F5),5):F6$=RIGHT$(STR$(F5),4)
2000 PRINT "CORRECTED MOLE FRACTION ACTIVITY COEFFICIENT=";F5$;F6$
2010 PRINT
2020 LET K9$=LEFT$(STR$(K9),7)
2030 PRINT "INTERACTION PARAMETER AT INFINITE DILUTION =";K9$
2040 PRINT
2050 LET K=(62.36*T)/(V1*P0*F1):K$=LEFT$(STR$(K),6)
2070 PRINT "PARTITION COEFFICIENT =";K$
2080 PRINT:PRINT:PRINT
2085 PRINT "PREDICTED VALUES FROM BEST FIT PARAMETERS"
2086 PRINT:PRINT
2090 IF Q9=1 GOTO 2130
2100 IF Q9=2 GOTO 2110
2110 PRINT "SEG.FRAC       SEG.FRAC      INTERACTION       ACTIVITY";
2115 PRINT "       LOG(E) OF
2120 GOTO 2140
2130 PRINT "VOL.FRAC       VOL.FRAC      INTERACTION       ACTIVITY";
2135 PRINT "       LOG(E) OF"
2140 PRINT "OF VAPOUR      OF POLYMER    PARAMETER         COEFF.  ";
2145 PRINT "       ACT.COEFF."
2147 PRINT
2150 PRINT "   ";J,LEFT$(STR$(PHI(J)),4),LEFT$(STR$(CHI(J)),7),
2160 PRINT LEFT$(STR$(G(J)),7),LEFT$(STR$(LNG(J)),7)
2170 NEXT J
2180 PRINT:PRINT
2190 PRINT  "DATA USED:-"
2200 PRINT "      NO. OF DATA POINTS=";N
2210 PRINT "      ABSOLUTE TEMPERATURE=";T;"KELVIN"
2220 PRINT "      SVP OF VAPOUR =";P0;"TORR"
2230 PRINT "      DENSITY OF VAPOUR =";D1;"G/CC"
2240 PRINT "      2ND VIRIAL COEFF. OF VAPOUR =";B;"L/MOL"
2250 PRINT "      MOLAR VOLUME OF VAPOUR =";V1;"L/MOL"
2260 PRINT "      DENSITY OF SAMPLE=";D2;"G/CC"
2270 PRINT "      MOLAR VOLUME OF SAMPLE =";V2;"L/MOL"
2280 PRINT "      SPECIFIC VOLUME OF VAPOUR=";VV;"CC/G"
2290 PRINT "      SPECIFIC VOLUME OF SAMPLE=";VS;"CC/G"
2300 PRINT "      MOLECULAR WEIGHT OF VAPOUR=";M1;"G/MOL"
2310 PRINT "      MOLECULAR WEIGHT OF SAMPLE=";M2;"G/MOL"
2320 PRINT:PRINT
2330 PRINT "WEIGHT OF SAMPLE USED =";W2;"MG"
2340 PRINT:PRINT
2350 PRINT "CALCULATED BY PROGRAM 'FLO-HUG'     PETBASIC    GJP. 10/10/81"
2354 REM
2355 REM DATA IS ENTERED IN THE SUCCEEDING LINES
2356 REM
2360 DATA "FOR HEXANE IN PDMS.   ■RUN MB7■     22/06/82"
2370 DATA 7,302.99,86.1766,0.6505,185.855,-1.84499,0.13248,1964.2,0.9655,92.0
2380 DATA 89000,1.1565,0.8410
2390 DATA 17.63,9.84,56.23,28.77,100.00,47.20,157.7,66.72
2400 DATA 224.95,84.91,314.85,103.505,436.7,121.733
2420 PRINT#1:CLOSE1
2430 END
```

```
CALCULATION OF ACTIVITY COEFFICIENTS AND FLORY HUGGINS PARAMETERS


FOR HEXANE IN PDMS.    RUN M87       22/06/82


 WEIGHT              PRESSURE           MOLE FRAC.         VOL FRAC

 18.361              9.84              .90597             .01368
 58.374              28.77              .96838             .04224
 103.53              47.2              .98192             .07255
 162.71              66.72              .98842             .10949
 231.37              84.91              .99183             .14881
 322.73              103.50              .99413             .19605
 446.06              121.73              .99574             .25209


UNCORR'D            LOG(E) OF           CORR'D              LOG(E) OF
ACT.COEFF.          ACT.COEFF.          ACT.COEFF.          ACT.COEFF.

 3.8688              1.3529             3.9414              1.3715
 3.6640              1.2985             3.7254              1.3151
 3.5001              1.2528             3.5518              1.2674
 3.2786              1.1874             3.3202              1.2000
 3.0699              1.1216             3.1029              1.1323
 2.8405              1.0439             2.8654              1.0527
 2.5981              .95481             2.6159              .96161

 SIZE RATIO OF COMPONENTS,R= 694.4

 EQUATION EXPRESSING CONCENTRATION DEPENDENCE OF KHI IS :-

            KHI=  KHI0 + KHI1 X PHI

            KHI= .3453+ .0519 X PHI


 STANDARD DEVIATION OF KHI0= 8.43E-03

 STANDARD DEVIATION OF KHI1= 9.59E-03

 CORRELATION COEFFICIENT OF FIT = .99686

 VOLUME              EXPT'L              CALC'D             LOG(E) OF          DIFFERENCE
 FRAC.OF             INTERACTION         INTERACTION        ACTIVITY           FROM
 POLYMER             PARAMETER           PARAMETER          COEFF.             EXPT'L

  .98631              .39745              .39661             1.3715              8.1734E-04
  .95775              .39116              .39513             1.3151             -3.6427E-03
  .92744              .39686              .39355             1.2674              2.8444E-03
  .89050              .39194              .39163             1.2000              2.4408E-04
  .85118              .38978              .38959             1.1323              1.3697E-04
  .80394              .38671              .38714             1.0527             -2.7925E-04
  .74790              .38399              .38423             .96161             -1.3499E-04
```

```
ROOT MEAN SQUARE DEVIATION= 1.789E-03


LOG(E) OF ACTIVITY COEFF. AT INFINITE DILUTION= 1.3958

UNCORRECTED ACTIVITY COEFFICIENT AT INFINITE DILUTION= 3.9601


CORRECTED VOLUME FRACTION ACTIVITY COEFFICIENT= 4.0385

CORRECTED WEIGHT FRACTION ACTIVITY COEFFICIENT= 5.9942

CORRECTED MOLE FRACTION ACTIVITY COEFFICIENT= 5.81E-03

INTERACTION PARAMETER AT INFINITE DILUTION = .39732

PARTITION COEFFICIENT = 193.7


PREDICTED VALUES FROM BEST FIT PARAMETERS

VOL.FRAC         VOL.FRAC        INTERACTION        ACTIVITY         LOG(E) OF
OF VAPOUR        OF POLYMER      PARAMETER          COEFF.           ACT.COEFF.

    0              1             .39732           4.0385            1.3958
    .1              .9             .39213           3.3747            1.2163
    .2              .8             .38693           2.8476            1.0464
    .3              .7             .38174           2.4255            .88604
    .4              .6             .37654           2.0848            .73469
    .5              .5             .37135           1.8078            .59211
    .6              .4             .36615           1.5809            .45800
    .7              .3             .36096           1.3938            .33205
    .8              .2             .35576           1.2385            .21394
    .9              .09             .35057           1.1088            .10336

DATA USED:-
      NO. OF DATA POINTS= 7
      ABSOLUTE TEMPERATURE= 302.99 KELVIN
      SVP OF VAPOUR = 185.855 TORR
      DENSITY OF VAPOUR = .6505 G/CC
      2ND VIRIAL COEFF. OF VAPOUR =-1.84499 L/MOL
      MOLAR VOLUME OF VAPOUR = .13248 L/MOL
      DENSITY OF SAMPLE= .9655 G/CC
      MOLAR VOLUME OF SAMPLE = 92 L/MOL
      SPECIFIC VOLUME OF VAPOUR= 1.1565 CC/G
      SPECIFIC VOLUME OF SAMPLE= .841 CC/G
      MOLECULAR WEIGHT OF VAPOUR= 86.1766 G/MOL
      MOLECULAR WEIGHT OF SAMPLE= 89000 G/MOL


WEIGHT OF SAMPLE USED = 1964.2 MG


CALCULATED BY PROGRAM 'FLO-HUG'    PETBASIC    GJP. 10/10/81
```

AII-2 PROGRAM 'FLOHUG-TERNARY'

This program was written to apply the least squares fit method described in Section 3.4 to the isotherms for mixed absorbent systems, that for the system SQ-DNP-dichloromethane being reproduced in the following pages. It was written for use on the 'Multics' computer.

The pure component data, densities, molar volumes and molecular weights were read in (Lines 230-240) followed by the number of isotherms and experimental points, weights of absorbents, measured absorbate weights and pressures and these used to calculate concentration fractions and interaction parameters (Lines 330-490). The differentials for the least squares fit were calculated (Lines 580-620) and the initial estimates of the interaction parameters obtained (Lines 650-950). The fit was performed by setting up the simultaneous equations (Lines 1060-1420), solving them in a subroutine (Lines 2330-2700) and correcting the initial estimates (Lines 1440-1480). The program was run in 'extended precision' basic which carried calculations to a higher precision than normal in order to prevent potential errors in the solution of the equations.

If the corrected values were not accurate to three decimal places then the calculation was worked through again with the new values as initial estimates. When this accuracy was achieved values of activity coefficients were calculated using these best fit interaction parameters (1980-2100) and these were compared to the experimental values to calculate a RMSD for the fit.

The results from the appropriate isotherms were fed into the programs in Lines 2720-2800.

```
00100 rem ******************************************************************
00110 rem *******************    "FLOHUG.BASIC"    *************************
00120 rem ******************************************************************
00130  rem    COPYRIGHT  G.J.PRICE.    Sept.1982.
00140 rem
00150 rem Program to fit experimental data to ternary form of Flory-Huggins equation
00160 rem This program is to be run in "extended precision" basic to avoid errors on solving similtaneous equations
00170 file #1: "Re_flo"
00180 scratch #1
00190 dim d(10,100)
00200 margin #1: 130
00210 rem No dimensioning necessary for other arrays since less than 10 elements in each
00220 read a$,b$,c$
00230 read m1,p0,v1,v2,v3,d1,d2,d3,b,t9
00240 read m2,m3
00250   c1=p0*(v1-b)/(62.36*t9)
00260   c2=(p0*p0)*(b*b)/(((62.36*t9)^2)*2)
00270 print #1: "Experimental data fit to the Flory-Huggins ternary equation ";
00280 print #1:  "for solutions of ";a$;" (A) in ";b$;" (B) and ";c$;" (C)"
00290 print #1: \print #1:
00300 print #1: "Weight (g)","Weight (g)","Weight (mg)","Pressure (t)","Mole Fraction","Activity","Volume Fraction"
00310 print #1: b$,c$,a$,a$,a$,a$,a$
00320 print #1: \print #1:
00330 read m,n
00340 for j=1 to m
00350 read b(j),c(j)                          'weights of each liquid phase
00360 g(j)=(b(j)/d2)/(b(j)/d2+c(j)/d3)
00370 e(j)=(b(j)/m2)/(b(j)/m2+c(j)/m3)
00380 r(j)=(e(j)*v2+(1-e(j))*v3)/v1
00390 next j
00400 for j=1 to m
00410 for i=1 to n
00420 read w(j,i)
00430   v(j,i)=((w(j,i)*1e-3)/d1)/((w(j,i)*1e-3)/d1+b(j)/d2+c(j)/d3)
00440 x(j,i)=((w(j,i)*1e-3)/m1)/((w(j,i)*1e-3)/m1+b(j)/m2+c(j)/m3)
00450 h(j,i)=(b(j)/d2)/(b(j)/d2+c(j)/d3+(w(j,i)*1e-3)/d1)
00460 i(j,i)=1-v(j,i)-h(j,i)
00470 read p(j,i)
00480   a(j,i)=p(j,i)/p0
00490 z(j,i)=log(a(j,i)/x(j,i))+c1*(1-a(j,i))+c2*(1-a(j,i)^2)
00500 print #1:  b(j),c(j),w(j,i),p(j,i),x(j,i),a(j,i),v(j,i)
00510 next i
00520 print #1:
00530 next j
```

```
00540 for j=1 to m
00550   j1=10*j
00560 for i=1 to n
00570   i1=j1+i
00580   d(1,i1)=(1-v(j,i))*h(j,i)*v1
00590   d(2,i1)=(1-v(j,i))*i(j,i)*v1
00600   d(3,i1)=-h(j,i)*i(j,i)*v1
00610   d(4,i1)=(v(j,i)/(v(j,i)+h(j,i)))*d(1,i1)
00620   d(5,i1)=(v(j,i)/(v(j,i)+i(j,i)))*d(2,i1)
00630 next i
00640 next j
00650 for j= 1 to m
00660 for i= 1 to n
00670 if j<>1 goto 710
00680 if i<>n/2 goto 710
00690 k(1)=(z(j,i)-log(v(j,i)/x(j,i))-(1-1/r(j))*(1-v(j,i)))/((1-v(j,i))^2)/v1
00700 rem k(1)=approx. value of Khi AB0 from 1'st isotherm
00710 if j<>m goto 770
00720 if i<>n/2 goto 770
00730   k2=log(a(j,i)/x(j,i))+(c1*(1-a(j,i)))+(c2*(1-(a(j,i)^2)))
00740 k(2)=(z(j,i)-log(v(j,i)/x(j,i))-(1-1/r(j))*(1-v(j,i)))/((1-v(j,i))^2)/v1
00750 rem k(2)=approx. value of Khi AC0 from m'th isotherm
00760 if m=2*(int(m/2)) goto 790
00770 if j<>(m+1)/2 goto 840
00780 goto 800
00790 if j<>m/2 goto 840
00800 if i<>n/2 goto 840
00810   k3=log(a(j,i)/x(j,i))+(c1*(1-a(j,i)))+(c2*(1-(a(j,i)^2)))
00820 k1=(z(j,i)-log(v(j,i)/x(j,i))-(1-1/r(j))*(1-v(j,i)))/((1-v(j,i))^2)/v1
00830 rem k1=approx. value of khi from middle point on middle isotherm
00840 next i
00850 next j
00860 if m=2*int(m/2) goto 890
00870   j=(m+1)/2
00880 goto 900
00890 j=m/2
00900   i=n/2
00910 rem k(3)=approx. value of Khi BC from k1,k(1) and k(2)
00920   k(3)=(h(j,i)*k(1)+i(j,i)*k(2)-(h(j,i)+i(j,i))*k1)*(h(j,i)+i(j,i))/(h(j,i)*i(j,i))
00930   k(4)=0
00940   k(5)=0
00950 rem sets initial values of Khi AB1 and Khi AC1 at zero
00960 print #1: \print #1:
00970 print #1:      "Starting values of interaction parameters are:-"
```

```
00980 print #1:
00990 print #1:       "Khi AB0=";k(1);"Khi AC0=";k(2);"Khi BC=";k(3);"Khi AB1=";k(4);"Khi AC1=";k(5)
01000 print #1:
01010 print #1: \print #1: \print #1: \print #1:
01020 print #1:  "Values of interaction parameters for successive iterations"
01030 print #1: \print #1:
01040 print #1:  "Iteration"," Khi AB0"," Khi AC0"," Khi BC"," Khi AB1"," Khi AC1"
01050 print #1:
01060 for j= 1 to m
01070 for i=1 to n
01080   o(j,i)=(h(j,i)*(k(1)+(v(j,i)/(v(j,i)+h(j,i))*k(4)))+i(j,i)*(k(2)+(v(j,i)/(v(j,i)+i(j,i))*k(5))))
01090   o(j,i)=(o(j,i)-h(j,i)*i(j,i)*k(3)/(h(j,i)+i(j,i)))/(h(j,i)+i(j,i))
01100 rem o is the calculated overall interaction parameter
01110   j(j,i)=log(v(j,i)/a(j,i))+(1-v(j,i))*(1-1/r(j))+(1-v(j,i))*(1-v(j,i))*o(j,i)*v1-c1*(1-a(j,i))-(c2*(1-(a(j,i)^2)))
01120 rem j= delta F
01130   n(j,i)=(1/v(j,i))+((1/r(j))-1)+(2*(v(j,i)-1)*o(j,i)*v1)+((1-v(j,i))*v1)*((h(j,i)/(h(j,i)+i(j,i))^2)*k(4)+((i(j,i)/(i(j,i)+h(
j,i)))^2)*k(5))
01140 rem n= dF/dpni
01150   t(j,i)=c1+(2*c2*a(j,i))-(1/a(j,i))
01160 rem t= dF/da
01170   s(j,i)=1/0.0018/a(j,i)
01180   z(j,i)=(w(j,i)+((c(j)*1e3)/d3+(b(j)*1e3)/d2)*d1)/(0.03+(0.03+0.002*((c(j)*1e3)/d3+(b(j)*1e3)/d2)*d1)*v(j,i))
01190 rem s= Root-weight of activity
01200 rem z= Root-weight of volume fraction
01210   l(j,i)=((n(j,i)/z(j,i))^2)+((t(j,i)/s(j,i))^2)
01220 next i
01230 next j
01240 rem Reset summations for next iteration
01250 for e=1 to 5
01260 y(e)=0
01270 for g=1 to 5
01280 u(e,g)=0
01290 next g
01300 next e
01310 for j= 1 to m
01320   j1=10*j
01330 for i=1 to n
01340   i1=j1+i
01350 for e=1 to 5
01360   y(e)=y(e)+((j(j,i)*d(e,i1)/l(j,i)))
01370 for g=1 to 5
01380   u(e,g)=u(e,g)+(d(g,i1)*d(e,i1)/l(j,i))
01390 next g
01400 next e
```

```
01410 next i
01420 next j
01430 gosub 2330
01440 for v=1 to 5
01450   k(v)=k(v)-q(v)
01460 goto 1480
01470 rem q=adjustment to parameter to improve fit
01480 next v
01490   z9=z9+1                 'z9 counts no. of loops needed
01500 print #1:  z9,k(1),k(2),k(3),k(4),k(5)
01510 if z9=20 goto 1590
01520 for e1=1 to 5
01530 if abs(q(e1))> 1e-3 goto 1580
01540 rem This sets 3 d.p. accuracy on Khi values
01550 next e1
01560 k1=k(1)*v1 \ k2=k(2)*v1 \ k3=k(3)*v1 \k4=k(4)*v1 \ k5=k(5)*v1
01570 goto 1610
01580 goto 1060
01590 print    "Three figure accuracy not obtained in twenty iterations"
01600 goto 5000
01610 print #1: \print #1: \print #1:
01620 print #1:    "Corrected values of interaction parameters (accurate to three d.p.) are:-"
01630 print #1:
01640 print #1:  " ","Khi AB0 =";k(1)," ","Khi AB0 x V0 =";k1
01650 print #1:  " ","Khi AC0 =";k(2)," ","Khi AC0 x V0 =";k2
1655 print k3
01660 print #1:  " ","Khi BC  =";k(3)," ","Khi BC x V0  =";k3
01670 print #1:  " ","Khi AB1 =";k(4)," ","Khi AB1 x V0 =";k4
01680 print #1:  " ","Khi AC1 =";k(5)," ","Khi AC1 x V0 =";k5
01690 print #1:
01700 for j= 1 to m
01710  j1=10*j
01720 for i= 1 to m
01730   i1=j1+1
01740 for e=1 to 5
01750 f(j,i)=f(j,i)-d(e,j1)*q(e)
01760 next e
01770 rem f=Lagrange undetermined multiplier (lambda)
01780 f(j,i)=(j(j,i)-f(j,i))/l(j,i)
01790 s9=s9+f(j,i)*j(j,i)
01800 rem s9= sun of squares of deviations
01810 next i
01820 next j
01830 print #1: \print #1: \print #1:
```

```
01840 print #1: "Mole Fraction","Vol. Fraction","Experimental","Calculated","Difference",
01850 print #1: "Experimental","Calculated","Difference"
01860 print #1:a$,a$,"ln(Gamma)","ln(Gamma)"," ","  Khi  ","  Khi"
01870 print #1:
01880 for j=1 to m
01890 for i=1 to n
01900 n(j,i)=z(j,i)=s(j,i)=t(j,i)=l(j,i)=j(j,i)=n(j,i)=0
01910  f(j,i)=0
01920 rem resets arrays for further calculations
01930 next i
01940 next j
01950 for j=1 to m
01960 for i=1 to n
01970  s(j,i)=(h(j,i)*(k1+(v(j,i)/(v(j,i)+h(j,i))*k4))+i(j,i)*(k2+(v(j,i)/(v(j,i)+i(j,i))*k5)))
01980  s(j,i)=(s(j,i)-h(j,i)*i(j,i)*k3/(h(j,i)+i(j,i)))/(h(j,i)+i(j,i))
01990 rem s=calculated interaction parameter
02000 z(j,i)=log(a(j,i)/x(j,i))+c1*(1-a(j,i))+c2*(1-a(j,i)^2)
02010 rem z=experimental ln(activity coefficient)
02020  t(j,i)=log(v(j,i)/x(j,i))+(1-(1/r(j)))*(1-v(j,i))+((1-v(j,i))^2)*s(j,i)
02030 rem t="calculated" ln(activity coefficient)
02040 rem j=experimental interaction parameter
02050 j(j,i)=(z(j,i)-log(v(j,i)/x(j,i))-(1-1/r(j))*(1-v(j,i)))/((1-v(j,i))^2)
02060  f(j,i)=j(j,i)-s(j,i)
02070  n(j,i)=z(j,i)-t(j,i)
02080  d7=d7+f(j,i)*f(j,i)
02090  d9=d9+n(j,i)^2
02100 print #1: x(j,i),v(j,i),z(j,i),t(j,i),n(j,i),j(j,i),s(j,i),f(j,i)
02110 next i
02120 print #1:
02130 next j
02140  d8=sqr(c9/(m*n))
02150  d6=sqr(c7/(m*n))
02160 print #1: \print #1: \print #1:
02170 print #1: "Root mean square deviation of ln(activity coefficient) =";d8
02180 print #1:
02190 print #1: "Root mean square deviation of interaction parameter =";d6
02200 print #1: \ print #1: \print #1:
02210 print #1: "   DATA USED :"
02220 print #1: "                              ",a$,b$,c$
02230 print #1: "     Molar Volume (l/mol)",v1,v2,v3
02240 print #1: "     Molecular Weight    ",m1,m2,m3
02250 print #1: "     Density (g/ml)      ",d1, 12,d3
02260 print #1: "     S.V.P. (torr)       ",p0
02270 print #1: "     2nd Virial Coeff.   ",b
```

```
02280 print #1:
02290 print #1: "Temperature of Isotherms =";t9;" K"
02300 print #1: \print #1: \print #1:
02310 print #1: "Calculated using program 'FLOHUG.BASIC'.   C. G.J.Price   1982."
02320 goto 5000
02330 rem This subroutine solves similtaneous equations by Gaussian elimination
02340 z=5
02350 n1=z+1
02360 rem z = number of equations to be solved i.e. 5
02370 n9=z-1
02380 for k=1 to z
02390 u(k,n1)=y(k)
02400 next k
02410 for k= 1 to n9
02420 k1=k+1
02430 for i=k1 to z
02440 if u(k,k)<> 0 goto 2540
02450 for c=k1 to z
02460 if u(c,k)=0 goto 2530
02470 for j=1 to n1
02480 u(n1,j)=u(k,j)
02490 u(k,j)=u(c,j)
02500 u(c,j)=u(n1,j)
02510 next j
02520 goto2540
02530 next c
02540 f=u(i,k)/u(k,k)
02550 for j=k to n1
02560 u(i,j)=u(i,j)-f*u(k,j)
02570 next j
02580 next i
02590 next k
02600 for j=1 to z
02610 i=z+1-j
02620 z8=i+1
02630 s=0
02640 if i=z goto 2680
02650 for k=z8 to z
02660 s=s+u(i,k)*q(k)
02670 next k
02680 q(i)=(u(i,n1)-s)/u(i,i)
02690 next j
02700 return
2710 rem DATA TO BE ENTERED IN THE SUCCEDING LINES
```

```
2711 rem
2712 rem ENSURE THAT DATA HAS SQUALANE =B AND DNP = C AS APPROPRIATE !
2720 data "CHLOROFORM","SQUALANE","DNP"
2725 data 119.378,240.8,0.08118,0.52742,0.43742,1.4705,0.8017,0.963
2730 data -1.16,302.99,422.82,418.62
2740 data 5,8
2745 data 0.4793,0,0.3368,0.1151,0.2763,0.2840,0.1001,0.2827,0,0.4436
2750 data 4.07,4.74,12.17,13.375,16.415,18.20,25.79,27.52,38.52,39.25,55.15,53.065,76.05,68.19,99.28,82.75
2760 data 7.84,6.54,15.62,12.85,24.22,19.575,33.94,26.955,44.88,34.945,54.83,41.855,69.59,51.69,82.93,59.9
2770 data 8.89,4.5,16.78,8.4,29.97,14.885,41.72,20.495,50.86,24.85,63.325,30.59,80.85,38.38,99.80
2771 data 46.57
2780 data 8.09,4.91,15.57,9.36,24.805,14.825,34.525,20.475,46.14,27.075,59.14,34.32,71.52,40.96,87.165,49.1
2790 data 8.04,3.93,16.02,7.78,23.9,11.54,33.344,15.985,42.625,20.3,53.705,25.395,66.11,30.935,84.15,38.795
5000 end
```

The output from this program is reproduced on pages 299-301

```
ACTIVITY COEFFICIENTS AND INTERACTION PARAMETERS for a solution of PDMS in BENZENE at  298.15  K

Calculated by the UNIFAC group contribution method


Vol.Frac     Wt.Frac       Config'n      Residual      Free Vol.     Overall       Overall       Vol.Frac     Log (e) of
Solvent      Solvent       ln(act)       ln(act)       ln(act)       ln(act)       Activity      Khi          Gamma (vol)


 0.000001     9.00918 E-7  -12.891        0.635734      0.05428      -12.201        5.02558 E-6   0.615517     1.61454
 0.02         1.80541 E-2  -3.00461       0.607387      5.19649 E-2  -2.34526       9.58221 E-2   0.611949     1.56676
 0.04         3.61801 E-2  -2.32864       0.579845      4.97075 E-2  -1.69908       0.182851      0.608427     1.51979
 0.06         5.43783 E-2  -1.94039       0.553096      4.75072 E-2  -1.33979       0.2619        0.604951     1.47362
 0.08         7.26493 E-2  -1.66999       0.527126      4.53637 E-2  -1.0975        0.333705      0.60152      1.42823
 0.1          9.09933 E-2  -1.46417       0.501922      4.32764 E-2  -0.918974      0.398928      0.598133     1.38361
 0.2          0.183826     -0.858463      0.386961      3.36642 E-2  -0.437838      0.64543       0.581843     1.1716
 0.3          0.278555     -0.541791      0.289378      2.53806 E-2  -0.227032      0.796895      0.566576     0.97694
 0.4          0.375239     -0.344286      0.207866      0.018366     -0.118054      0.888648      0.552281     0.798237
 0.5          0.473938     -0.212737      0.14127       1.25645 E-2  -5.89028 E-2   0.942798      0.538926     0.634244
 0.6          0.574717     -0.12346       8.85653 E-2   7.92317 E-3  -2.69714 E-2   0.973389      0.526524     0.483854
 0.7          0.677642     -6.38369 E-2   4.88445 E-2   4.39214 E-3  -1.06002 E-2   0.989456      0.515189     0.346075
 0.8          0.782782     -2.63516 E-2   2.13035 E-2   1.92409 E-3  -3.12408 E-3   0.996881      0.505358     0.22002
 0.9          0.890209     -6.16894 E-3   5.23102 E-3   4.74221 E-4  -4.63697 E-4   0.999536      0.499424     0.104897

Vol.Frac     Seg.Frac       Khi(seg)     Ln(gamma)(seg)

 0.000001     9.5082 E-7    0.6659        1.66497
 0.02         1.90351 E-2   0.66108       1.61621
 0.04         3.81077 E-2   0.656321      1.56825
 0.06         0.057218      0.651622      1.52109
 0.08         0.076366      0.646983      1.47472
 0.1          9.55519 E-2   0.642402      1.42911
 0.2          0.192053      0.620345      1.21215
 0.3          0.289517      0.599627      1.01251
 0.4          0.38796       0.580166      0.828799
 0.5          0.487395      0.561902      0.659778
 0.6          0.587838      0.544818      0.504333
 0.7          0.689304      0.52899       0.361473
 0.8          0.791809      0.514792      0.230311
 0.9          0.895369      0.504363      0.110056
```

Vol.Frac.	Khi(adj)	Ln(G'ma)(adj)	Seg.Frac.	Khi(adj)	Ln(G'ma)(adj)
0.000001	0.7588	1.75782	9.5082 E-7	0.8142	1.81327
0.02	0.752367	1.70162	1.90351 E-2	0.806557	1.7562
0.04	0.745979	1.64656	3.81077 E-2	0.798969	1.70024
0.06	0.739637	1.59263	0.057218	0.791437	1.64537
0.08	0.733341	1.5398	0.076366	0.783958	1.59157
0.1	0.727088	1.48806	9.55519 E-2	0.776532	1.53883
0.2	0.69647	1.24496	0.192053	0.740164	1.29036
0.3	0.666875	1.02609	0.289517	0.704992	1.06569
0.4	0.638251	0.829186	0.38796	0.670931	0.862799
0.5	0.610568	0.652155	0.487395	0.637921	0.679753
0.6	0.583838	0.493024	0.587838	0.605942	0.514716
0.7	0.558174	0.349943	0.689304	0.575067	0.365921
0.8	0.534015	0.221166	0.791809	0.545666	0.231649
0.9	0.513752	0.10504	0.895369	0.51988	0.110226

Adjusted values calculated using inf.diln. Khi of 0.7588 (Vol.Frac). and 0.8142 (Seg. Frac).

AII-3 PROGRAM 'PARMISC'

This program was used to calculate the miscibility limit of the polymer rich phase in a partially miscible system using the 'Tangent through the Origin' treatment described in Section 6.2. It was run on the 'PET' microcomputer.

The mathematical basis of the program was simple. A tangent to the free energy curve was constucted subject to the condition that it passed through the origin. If the curve was described by a function G(x), the slope of the tangent at a point x_i, where the function has the value $G(x_i)$, was given by the derivative $G'(x_i)$. Thus the equation of the tangent was

$$G(x_i) = G'(x_i)\, x_i + I$$

where I was the intercept on the G(x) axis and, in this case, needed to be zero.

Lines 140-200 input the required data - molar volumes of the two components and the interaction parameter. For a range of mole fractions from 0·01 to 0·99 the values of G(x) and G'(x) were calculated using equations (6.2) and (6.3) and the intercept found as above. The sign of the intercept was compared to that at the previous concentration and the calculation repeated until the sign changed from negative to positive (or vice versa). The concentrations where this occurred were then used to provide the limits between which the concentration was further narrowed down until a value accurate to four decimal places was found where the tangent passed through the origin. This could take some time and so the program carried a 'Running' sign to prevent mistakes! (Lines 240-250.)

The value was then converted to mole and weight fractions and percentage compositions and printed out.

The program is reproduced in the following pages followed by the results for the PDMS-DNP system.

```
100 REM CALCULATION OF MISCIBILITY LIMIT OF A BINARY MIXTURE
110 REM ASSUMING THAT ONE COMPONENT IS INSOLUBLE IN THE OTHER
120 REM C. G.J.PRICE.   1983.
130 PRINT "▣"
140 PRINT "▶▶▶▶▶RCALCULATION OF MISCIBILITY LIMIT■"
150 PRINT:PRINT:PRINT
160 INPUT "WHAT IS THE MOLAR VOLUME OF  THE SMALLER COMPONENT (1)";V1:PRINT
170 INPUT "AND ITS MOLECULAR WEIGHT";M1:PRINT
180 INPUT "WHAT IS THE MOLAR VOLUME OF  THE LARGER COMPONENT (2)";V2:PRINT
190 INPUT "AND ITS MOLECULAR WEIGHT";M2:PRINT
200 INPUT  "WHAT IS THE INTERACTION PARAMETER ";K
210 R=V2/V1
220 DIM X(100),X2(100),V(100),V2(100),VM(100),G(100),DG(100),D(100)
230 FOR I=1 TO 99
240 PRINT "▣":PRINT"▶▶▶▶▶▶QQQQQQQQQ▶▶▶▶PROGRAM RUNNING":PRINT
250 PRINT "▶▶▶▶▶▶▶▶▶▶▶▶▶▶▶▶";I
260 V(I)=I/100:V2(I)=1-V(I)
270 X(I)=(R*V(I))/(1+(R*V(I))-V(I)):X2(I)=1-X(I)
280 VM(I)=X(I)*V1+X2(I)*V2
290 G(I)=X(I)*LOG(V(I))+X2(I)*LOG(V2(I))+V(I)*V2(I)*K*VM(I)
300 DG(I)=LOG(X(I)*V1/(X2(I)*V2))-(V1-V2)/VM(I)
310 DG(I)=DG(I)+V1*V2*K/VM(I)*((1-2*X(I))-(X(I)-X(I)↑2)*(V1-V2)/VM(I))
320 REM DG=DIFFERENTIAL OF FREE ENERGY
330 D(I)=G(I)+DG(I)*X2(I)
340 REM D=INTERCEPT OF TANGENT
350 IF I=1 GOTO 390
360 IF SGN(D(I))=SGN(D(I-1)) GOTO 390
370 V8=V(I-1):V9=V(I)
380 GOTO 400
390 NEXT I
400 FOR I=0 TO 10
410 V(I)=V8+(V9-V8)/10*I:V2(I)=1-V(I)
420 X(I)=(R*V(I))/(1+(R*V(I))-V(I)):X22(I)=1-X(I)
430 VM(I)=X(I)*V1+X2(I)*V2
440 G(I)=X(I)*LOG(V(I))+X2(I)*LOG(V2(I))+V(I)*V2(I)*K*VM(I)
450 REM G=TOTAL FREE ENERGY OF MIXING
460 DG(I)=LOG(X(I)*V1/(X2(I)*V2))-(V1-V2)/VM(I)
470 DG(I)=DG(I)+V1*V2*K/VM(I)*((1-2*X(I))-(X(I)-X(I)↑2)*(V1-V2)/VM(I))
480 D(I)=G(I)+DG(I)*X2(I)
490 IF I=0 GOTO 550
500 IF SGN(D(I))=SGN(D(I-1)) GOTO 550
510 V8=V(I-1):V9=V(I)
520 V7=V2(I):X9=X(I)
530 IF Z=3 GOTO 570:REM Z SETS ACCURACY OF LIMIT
540 GOTO 560
550 NEXT I
560 Z=Z+1:GOTO 400
570 READ  S$
```

```
590 OPEN1,4:CMD1
600 PRINT"⊐"
610 PRINT S$
620 PRINT "────────────────────────────────────────"
630 PRINT:PRINT
640 PRINT "MISCIBILITY LIMIT LIES AT A VOLUME FRACTION OF ";V8;
650 PRINT"FOR COMPONENT 1 AND ";V7;" FOR COMPONENT 2"
660 PRINT:PRINT "MOLE FRACTION OF COMPONENT 1 IS ";X9
670 D1=M1*1E-3/V1:D2=M2*1E-3/V2
680 W9=V8/D1/(V8/D1+(1-V8)/D2)
690 PRINT:PRINT "WEIGHT FRACTION OF COMPONENT 2 IS ";1-W9
700 PRINT:PRINT:PRINT "MOLAR VOLUME OF COMPONENT 1 IS";V1
710 PRINT:PRINT "MOLAR VOLUME OF COMPONENT 2 IS";V2
720 PRINT:PRINT  "THE INTERACTION PARAMETER IS ":K
730 PRINT#1:CLOSE1
740 DATA " DNP (1) IN PDMS V (2) AT 302.99 K"
```

```
 DNP (1) IN PDMS V (2) AT 302.99 K
────────────────────────────────────────


MISCIBILITY LIMIT LIES AT A VOLUME FRACTION OF  .091502 FOR COMPONENT 1 AND  .90
8497  FOR COMPONENT 2

MOLE FRACTION OF COMPONENT 1 IS  .955273115

WEIGHT FRACTION OF COMPONENT 2 IS  .908282823


MOLAR VOLUME OF COMPONENT 1 IS .4347

MOLAR VOLUME OF COMPONENT 2 IS 92.18

THE INTERACTION PARAMETER IS  4.145
```

AII.4 PROGRAM 'FLORY-EOS'

This program was written for the 'PET' microcomputer. It calculated the value of the interaction parameter predicted from Flory's 'equation of state' theory as described in Sections 1.10.(iii) and 7.2.

The data needed was read in Lines 170-210 and consisted of the densities, reduced volumes and characteristic pressures of the components, molecular weight of the solvent and name of the system. In addition the temperature of the solution had to be specified together with three 'adjustable' parameters X_{12}, Q_{12} and s_1/s_2. Other characteristic data was calculated from these using the expressions in Section 1.1.

The program calculated the interaction parameters using equation (1.45) over a series of segment fraction concentrations and the results printed (Line 490). The required data was contained in Lines 580-610.

The program is reproduced in the following pages and was for the application of the theory to PDMS solutions in benzene at 30°C.

```
100 REM ********* FLORY-EOS *********
110 REM
120 REM CLCULATION OF INTERACTION PARAMETER BY FLORY'S EQUATION OF STATE THEORY
130 REM
140 REM C. G.J.PRICE.   1984.
150 REM
160 OPEN1,4:CMD1
170 READ T9,X1,Q,S
180 REM TEMP,X12,S1/S2
190 READ D1,V1,P1,M1
200 READ D2,V2,P2
210 READ A$
220 REM DENSITY,REDUCED VOLUME,CHARCTERISTIC PRESSURE (D,V-,P*)
230 PRINT "FLORY THEORY APPLIED TO ";A$:PRINT:PRINT
240 PRINT "SEG.FRAC","  KHI  ":PRINT
250 LET T1=V1↑(4/3)/(V1↑(1/3)-1)*T9
260 LET T2=V2↑(4/3)/(V2↑(1/3)-1)*T9
270 REM CHARACTERISTIC TEMPERATURES T*
280 LET U1=1/(V1*D1)
290 LET U2=1/(V2*D2)
300 REM U=V*
310 I=0.001
320 LET S1=I
330 LET N=N+1
340 LET S2=1-I
350 REM SEGMENT FRACTIONS
360 LET SB=S2/(S*S1+S2)
370 REM SURFACE FRACTION OF COMPONENT 2
380 TA=(S1*P1/T1+S2*P2/T2)/(S1*P1+S2*P2-S1*SB*X1)
390 TM=T9*TA
400 TL=S1*T9/T1+S2*T9/T2
410 LET VO=S1*V1+S2*V2
420 LET T0=(VO↑(1/3)-1)/(VO↑(4/3))
430 VE=3*(VO↑(7/3))*(TM-TL)/(4-3*(VO↑(1/3)))
440 VM=VO+VE
450 X=X1-VM*T9*Q
460 LET PM=S1*P1+S2*P2-S1*SB*X1
470 LET K1=(LOG((V1↑(1/3)-1)/(VM↑(1/3)-1)))*3*(T9/T1)+((1/V1)-(1/VM))
480 LET KHI=(K1*P1*U1*M1+(U1*M1*X*(SB↑2)/VM))/(8.314*T9*S2*S2)
490 PRINT S1,KHI
500 IF I=0.999 GOTO 560
510 IF I<0.05 THEN I=0.05: GOTO 320
520 IF I<0.3 THEN I=I+0.05:GOTO 320
530 IF I>0.90 THEN I=0.999
540 IF I=0.999 GOTO 320
550 I=I+0.1:GOTO 320
560 REM
570 PRINT:PRINT:PRINT "X12= ";X1;" AND Q12= ";Q;"  S1/S2= ";S
580 DATA 303.15,22.00,-.0305,1.05
590 DATA 0.8684,1.2916,623,78.113
600 DATA 0.9654,1.2317,339
610 DATA "BENZENE IN PDMS  "
620 PRINT:PRINT:PRINT
630 PRINT#1:CLOSE1
640 END
```

```
FLORY THEORY APPLIED TO BENZENE IN PDMS

SEG.FRAC            KHI

 1E-03            .797860613
 .05            .785632445
 .1            .774291152
 .15            .763924745
 .2            .754392805
 .25            .74558107
 .3            .737395803
 .4            .722606848
 .5            .709544583
 .6            .697865826
 .7            .687320276
 .8            .677721722
 .9            .668928918
 .999            .664320074

X12=  22  AND Q12= -.0305   S1/S2=  1.05
```

AII.5 PROGRAM 'UNIFAC'

This program, written for the 'Multics' computer, applies the UNIFAC group contribution method to polymer-solvent systems as described in Sections 1.1 and 7.3.

The number of functional groups in solution and the solution temperature were read (Line 370) and the UNIFAC parameters (R and Q) for each group and the numbers of each group etc., also read (Lines 420-570) along with the group interaction parameters. The pure component data needed was also read in (Line 620).

The first calculation was made for a volume fraction of 1 x 10^{-6} to simulate an infinite dilution value. It was found that lower values did not significantly change the results. A value of zero cannot be used due to the logarithm terms in the equations. Calculations were then performed over the whole range of concentrations. At each volume fraction, values of segment and surface fractions were calculated (Lines 940-980). The three contributions to the solution activity were then calculated (Lines 1110-2490) using the expressions in Section 1.1.

The total activity and activity coefficients were found (Lines 2520-2580) and these used to calculate volume and segment fraction based interaction parameters (Lines 2500-2710).

The adjustments to the method described in Chapter 7 were incorporated by reading in the experimental value of the infinite dilution interaction parameter (Line 3000), calculating the required adjustments (Lines 3020-3030) and applying these to the data (Lines 3060-3110). Finally, the required data was entered (Lines 3160-3280).

The program and output reproduced in the following pages is for the benzene-PDMS system at 25°C.

```
00100 rem *****************************************************************
00110 rem **** Basic program to apply UNIFAC method to polymer solutions.**
00120 rem *****************************************************************
00130 rem *****************************************************************
00140 rem *******************   UNIFAC.BASIC   ****************************
00150 rem *****************************************************************
00160 rem *****************************************************************
00170 rem ****************   c. G.J.PRICE   Feb. 1983 *********************
00180 rem *****************************************************************
00190 rem
00200 rem The program applies the UNIFAC group contribution method to
00210 rem solutions of a polymer (2) in a solvent (1) and includes a
00220 rem correction for free volume of mixing effects.
00230 rem
00240 rem FOR A BINARY MIXTURE OF ONE POLYMER AND ONE SOLVENT
00250 rem
00260 rem
00270 file #1: "Results_UNIFAC"
00280 scratch #1
00290 rem
00300 rem ********* DATA INPUT **************
00310 rem
00320 rem
00330 dim n$(50),r(50),q(50),z(50),m(50),y(50),c$(50),o(50)
00340 dim s(50),i(50),l(50),x(50),d(50),j(50),n(50)
00350 dim p(50),u(50),a(50,50),w(50),b(50,50),c(50,50),k(50,50)
00360 dim f(50),t(50),v(50),e(50),g(50),h(50)
00370 read b,t9
00380 rem  b= total no.of functional groups in the solution
00390 rem  t9= Absolute temperature of the solution
00400 rem
00410 for j= 1 to b
00420 read n$(j),r(j),q(j),z(j),m(j),y(j)
00430 rem  n$= name of functional group j
00440 rem  r=volume parameter,q=surface parameter of group j
00450 rem z=No. of j groups in the molecule where it appears
00460 rem m= "molecular"mass of group j
00470 rem y is +ve if j is in the solvent, -ve if in the polymer
00480 next j
00490 for j= 1 to b
00500 for i= 1 to b
00510 read a(j,i)
00520 rem a(j,i) is the interaction parameter for group i with group j
00530   a(j,i)=exp(-(a(j,i)/t9))
```

```
00540 next i
00550 next j
00560 read c1
00570 rem c1= Number of components
00580 for i= 1 to c1
00590 read c$(i)
00600 rem c$=names of polymer and solvent(s)
00610 next i
00620 read d1,d2,m1,m2,m3,u1,u2
00630 rem ***solvent is component 1, polymer is component 2
00640 rem d= density of component
00650 rem m1=Molecular weight of solvent
00660 rem m2="Molecular" weight of a polymer segment
00670 rem m3 is the approx. molecular weight of the polymer.
00680 rem u is the specific hard core volume
00690 rem
00700 rem
00710 rem
00720   z=10
00730 rem z= coordination number of a polymer segment
00740 margin #1: 135
00750 print #1:   "ACTIVITY COEFFICIENTS AND INTERACTION PARAMETERS for ";
00760 print #1:   "a solution of ";c$(2);" in ";c$(1);" at ";t9;" K"
00770 print #1:
00780 print #1:   "Calculated by the UNIFAC group contribution method"
00790 print #1:
00800 print #1:
00810 print #1:
00820 print #1:   "Vol.Frac","Wt.Frac","Config'n","Residual","Free Vol.","Overall",
00830 print #1:   "Overall","Vol.Frac","Log (e) of"
00840 print #1:   "Solvent ","Solvent ","ln(act)  ","ln(act)  ","ln(act)  ","ln(act) ",
00850 print #1:   "Activity","Khi       ","Gamma (vol)   "
00860 print #1:
00870   p1=1e-6
00880 goto 900
00890   p1=0.02
00900 rem p1 is the volume fraction of solvent in the solution
00910   p2=1-p1
00920   n=n+1
00930   w1=(p1*d1)/((p1*d1)+(p2*d2))
00940   w2=(p2*d2)/((p1*d1)+(p2*d2))
00950   s1=(w1*u1)/((w1*u1)+(w2*u2))
00960   s2=(w2*u2)/((w2*u2)+(w1*u1))
00970 rem s=hard core segment fractions
```

```
00980 rem   w= weight fraction of component
00970 rem
01000 rem Must set all values to zero for next calculation
01010 rem
01020   s3=s4=s5=s6=s7=0
01030   l1=l2=l3=l4=l5=l6=l7=l8=0
01040   x1=x2=x3=x4=0
01050   e1=e2=e3=0
01060   r1=r2=q1=q2=0
01070   o1=o2=o3=o4=o5=0
01080 rem
01090 rem ************* CALCULATION OF COMBINATORIAL ACTIVITY   **********
01100 rem
01110 for j=1 to b
01120 if y(j)=1 goto 1140
01130 if y(j)=-1 goto 1180
01140   r1=r1+(z(j)*r(j)/m1)
01150   q1=q1+(z(j)*q(j)/m1)
01160 rem r=volume parameter,q=surface parameter of components
01170 goto 1200
01180   r2=r2+(z(j)*r(j)/m2)
01190   q2=q2+(z(j)*q(j)/m2)
01200 next j
01210   v1=(r1*w1)/((r1*w1)+(r2*w2))
01220   t1=(q1*w1)/((q1*w1)+(q2*w2))
01230   v2=(r2*w2)/((r2*w2)+(r1*w1))
01240   t2=(q2*w2)/((q2*w2)+(q1*w1))
01250   l1=log(v1)+v2+((z/2*m1*q1)*(log(t1/v1)-1+(v1/t1)))
01260 rem
01270 rem
01280 rem **********CALCULATION OF RESIDUAL ACTIVITY   *************
01290 rem
01300 rem
01310 rem ***CALCULATION OF GROUP ACTIVITIFS IN THE SOLUTION
01320 rem
01330 for j=1 to b
01340 if y(j)=1 goto 1360
01350 if y(j)=-1 goto 1400
01360   u(j)=w1*m(j)*z(j)/m1
01370 rem u= weight fraction of group j
01380 rem
01390 goto 1410
01400   u(j)=w2*m(j)*z(j)/m2
01410 next j
```

```
01420 for j= 1 to b
01430   p(j)=(u(j)*q(j)/m(j))
01440 rem o=surface pararmeter of group j in the solution
01450   s3=s3+p(j)
01460 next j
01470 for j= 1 to b
01480   o(j)=p(j)/s3
01490 next j
01500   s5=s6=s7=0
01510 for j= 1 to b
01520   s5=0
01530 if y(j)=1 goto 1550
01540 if y(j)=-1 goto 1610
01550 for i= 1 to b
01560   k(i,j)=o(i)*a(i,j)
01570   s5=s5+k(i,j)
01580   k(i,j)=0
01590 next i
01600   l(j)=s5
01610 next j
01620 for i= 1 to b
01630   s6=s7=0
01640 for j= 1 to b
01650   b(i,j)=o(j)*a(j,i)
01660   s6=s6+b(i,j)
01670   b(i,j)=0
01680 next j
01690 for j=1 to b
01700   c(j,i)=a(j,i)*o(i)/s6
01710 next j
01720 next i
01730 for i=1 to b
01740   s7=0
01750 if y(i)=-1 goto 1810
01760 for j=1 to b
01770   s7=s7+c(i,j)
01780   c(i,j)=0
01790 next j
01800   n(i)=s7
01810 next i
01820 rem
01830 rem ***CALCULATION OF GROUP ACTIVITIES IN THE PURE SOLVENT
01840 for j=1 to b
01850   u(j)=0
```

```
01860 next j
01870   o1=0
01880 for j=1 to b
01890 if y(j)=-1 goto 1930
01900   d(j)=m(j)*z(j)/m1
01910   j(j)=d(j)*q(j)/m(j)
01920   o1=o1+j(j)
01930   d(j)=0
01940 next j
01950 for j=1 to b
01960   x(j)=j(j)/o1
01970 next j
01980 for j=1 to b
01990   o2=0
02000 for i=1 to b
02010 if y(i)=-1 goto 2040
02020   k(i,j)=x(i)*a(i,j)
02030   o2=o2+k(i,j)
02040 next i
02050   i(j)=o2
02060 next j
02070 for i= 1 to b
02080 if y(i)=-1 goto 2180
02090   o3=o4=0
02100 for j=1 to b
02110 if y(j)=-1 goto 2140
02120   b(i,j)=x(j)*a(j,i)
02130   o3=o3+b(i,j)
02140 next j
02150 for j=1 to b
02160   c(j,i)=a(j,i)*x(i)/o3
02170 next j
02180 next i
02190 for i=1 to b
02200   o4=0
02210 if y(i)=-1 goto 2260
02220 for j=1 to b
02230   o4=o4+c(i,j)
02240 next j
02250   s(i)=o4
02260 next i
02270 for i=1 to b
02280 if y(i)=-1 goto 2310
02290   u(i)=q(i)*z(i)*((1-log(l(i))-n(i))-(1-log(i(i))-s(i)))
```

```
02300   l2=l2+u(i)
02310 next i
02320 rem l2=log(e) of residual activity coefficient
02330 rem
02340 rem
02350 rem *******CALCULATION OF FREE VOLUME EFFECTS *************
02360 rem
02370 rem
02380   e1=(1/d1)/(15.17*1.28*r1)
02390 rem e1= reduced volume of solvent
02400   e3=((w1/d1)+(w2/d2))/(((w1*r1)+(w2*r2))*15.17*1.28)
02410 rem e3= reduced volume of solution
02420   c=1.1
02430 rem c= the estimated number of external degrees of freedom
02440   x1=(e1^(1/3))-1
02450   x2=(e3^(1/3))-1
02460   x3=(e1/e3)-1
02470   x4=(1-(1/(e1^(1/3))))
02480   l3=(3*c*log(x1/x2))-(c*(x3/x4))
02490 rem l3=Activity coefficient due to equation of state effects
02500   l4=l1+l2+l3
02510 rem *******l5=TOTAL ACTIVITY COEFFICIENT*******
02520   l5=exp(l4)
02530   l6=l4-log(p1)
02540 l9=l4-log(s1)
02550   f(n)=l6
02560 w(n)=l9
02570 rem l6= activity coefficient of solvent
02580 rem f= vol. frac. ln(gamma) ;u= seg.frac. ln(gamma)
02590 rem
02600 rem
02610 rem ************ CALCULATION OF INTERACTION PARAMETERS. ************
02620 rem
02630 rem
02640   r9=(m3*d1)/(m1*d2)
02650 rem r9=size ratio by volumes
02660   k1=(l4-log(p1)-((1-(1/r9))*p2))/(p2*p2)
02670 rem k1=volume fraction interaction parameter
02680   r8=(m3*u2)/(m1*u1)
02690 rem r8=size ratio by segments
02700   k2=(l4-log(s1)-((1-(1/r8))*s2))/(s2*s2)
02710 rem k2=segment fraction interaction parameter
02720   v(n)=p1
02730 e(n)=s1
```

```
02740   h(n)=k2
02750 g(n)=k1
02760 rem v=vol.frac. ; s=seg.frac. ;
02770 rem t=seg.frac khi ; d= vol.frac.khi
02780 print #1:   p1,w1,l1,l2,l3,l4,l5,k1,l6
02790 rem
02800 rem
02810 if p1<1e-3 goto 890
02820 if p1>0.8 goto 2880
02830 if p1>0.09 goto 2860
02840   p1=p1+0.02
02850 goto 910
02860   p1=p1+0.10
02870 goto 910
02880 rem
02890 for i=1 to n
02900   j(i)=m(i)=y(i)=q(i)=i(i)=0
02910 next i
02920 print #1:
02930 print #1:
02940 print #1:   "Vol.Frac","Seg.Frac","  Khi(seg)  ","Ln(gamma)(seg)"
02950 print #1:
02960 for i=1 to n
02970 print #1:  v(i),e(i),h(i),w(i)
02980 next i
02990 print #1:\print #1:
03000 read q9,q7
03010 rem q9 =infinite dilution vol. frac khi
03020 q8=q9-g(1)
03030 q6=q7-h(1)
03040 print #1: "Vol.Frac.","Khi(adj)","Ln(G'ma)(adj)","Seg.Frac.","Khi(adj)","Ln(G'ma)(adj)"
03050 print #1:
03060 for i=1 to n
03070 j(i)=g(i)+q8*(1-v(i))
03080 m(i)=h(i)+q6*(1-e(i))
03090 y(i)=j(i)*(1-v(i))^2+(1-1/r9)*(1-v(i))
03100 i(i)=m(i)*(1-e(i))^2+(1-1/r8)*(1-e(i))
03110 print #1: v(i),j(i),y(i),e(i),m(i),i(i)
03120 next i
03130 print #1: \print #1:
03140 print #1: "Adjusted values calculated using inf.diln. Khi of ";q9;" (Vol.Frac). and ";q7; "(Seg. Frac)."
03150 rem DATA IS ENTERED IN THE SUCCEEDING LINES.
03160 data 3,298.15
03170 data "ACH",0.5313,0.400,6,13.02,1
```

```
03180 data "SiO",1.1044,0.466,1,43.185,-1
03190 data "CH3",0.9011,0.848,2,15.03,-1
03200 data 0,254.3,-11.12
03210 data 293.8,0,109.3
03220 data 61.13,327.0,0
03230 data 2
03240 data "BENZENE"
03250 data "PDMS"
03260 data 0.8738,0.9699,78.1134,73.245
03270 data 89000,0.886,0.8395
03280 data 0.7588,0.8142
05000 end
```

The output from this program is reproduced on pages 282-283.

Experimental data fit to the Flory-Huggins ternary equation for solutions of CHLOROFORM (A) in SQUALANE (B) and DNP (C)

Weight (g) SQUALANE	Weight (g) DNP	Weight (mg) CHLOROFORM	Pressure (t) CHLOROFORM	Mole Fraction CHLOROFORM	Activity CHLOROFORM	Volume Fraction CHLOROFORM
0.4793	0	4.07	4.74	2.91977 E-2	1.96844 E-2	4.60816 E-3
0.4793	0	12.17	13.375	8.25116 E-2	0.055544	0.013654
0.4793	0	16.415	18.2	0.108179	7.55814 E-2	1.83293 E-2
0.4793	0	25.79	27.52	0.160073	0.114286	2.84993 E-2
0.4793	0	38.52	39.25	0.221577	0.162998	4.19761 E-2
0.4793	0	55.15	53.065	0.28954	0.22037	5.90285 E-2
0.4793	0	76.05	68.19	0.359788	0.283181	7.96172 E-2
0.4793	0	99.28	82.75	0.42318	0.343646	0.101469
0.3368	0.1151	7.84	6.54	5.77513 E-2	2.71595 E-2	9.7833 E-3
0.3368	0.1151	15.62	12.85	0.108824	5.33638 E-2	1.93043 E-2
0.3368	0.1151	24.22	19.575	0.159201	8.12915 E-2	0.029618
0.3368	0.1151	33.94	26.955	0.209695	0.111939	4.10168 E-2
0.3368	0.1151	44.88	34.945	0.259731	0.14512	5.35302 E-2
0.3368	0.1151	54.83	41.855	0.300037	0.173816	6.46309 E-2
0.3368	0.1151	69.59	51.69	0.352347	0.214659	8.06265 E-2
0.3368	0.1151	82.93	59.9	0.393323	0.248754	9.46198 E-2
0.2763	0.284	8.89	4.5	5.29519 E-2	1.86877 E-2	9.36426 E-3
0.2763	0.284	16.78	8.4	9.54612 E-2	3.48837 E-2	1.75295 E-2
0.2763	0.284	29.99	14.885	0.158687	6.18148 E-2	0.030903
0.2763	0.284	41.72	20.495	0.207854	8.51121 E-2	4.24767 E-2
0.2763	0.284	50.86	24.85	0.242354	0.103198	5.13051 E-2
0.2763	0.284	63.325	30.59	0.284833	0.127035	6.30859 E-2
0.2763	0.284	80.85	38.38	0.337088	0.159385	7.91627 E-2
0.2763	0.284	99.8	46.57	0.385629	0.193397	9.59371 E-2
0.1001	0.2829	8.09	4.91	6.91295 E-2	2.03904 E-2	1.29713 E-2
0.1001	0.2829	15.57	9.36	0.125054	3.88704 E-2	2.46687 E-2
0.1001	0.2829	24.805	14.825	0.185469	6.15656 E-2	3.87337 E-2
0.1001	0.2829	34.525	20.475	0.240657	8.50291 E-2	5.31056 E-2
0.1001	0.2829	46.14	27.075	0.29753	0.112438	6.97259 E-2
0.1001	0.2829	59.14	34.32	0.351863	0.142525	8.76493 E-2
0.1001	0.2829	71.52	40.96	0.396328	0.1701	0.104088
0.1001	0.2829	87.165	49.1	0.444489	0.203904	0.124033
0	0.4436	8.04	3.93	5.97585 E-2	1.63206 E-2	1.17301 E-2
0	0.4436	16.02	7.78	0.112404	0.032309	2.31037 E-2
0	0.4436	23.9	11.54	0.158908	4.79236 E-2	3.40807 E-2
0	0.4436	33.344	15.985	0.208601	6.63829 E-2	4.69158 E-2
0	0.4436	42.625	20.3	0.25203	8.43023 E-2	5.92012 E-2
0	0.4436	53.705	25.395	0.298019	0.105461	7.34596 E-2
0	0.4436	66.11	30.935	0.34323	0.128468	8.89189 E-2
0	0.4436	84.15	38.795	0.399475	0.161109	0.110502

```
Starting values of interaction parameters are:-

Khi AB0= 7.58264 Khi AC0=-5.61747 Khi BC= 10.6976 Khi AB1= 0 Khi AC1= 0



Values of interaction parameters for successive iterations

Iteration        Khi AB0        Khi AC0        Khi BC        Khi AB1        Khi AC1

 1               7.55453        -6.21006       10.939        -2.21579       10.7371
 2               7.55673        -6.21606       10.9424       -2.27999       10.8586
 3               7.55676        -6.21615       10.9424       -2.28101       10.8604
 4               7.55676        -6.21615       10.9424       -2.28102       10.8604

Corrected values of interaction parameters (accurate to three d.p.) are:-

                 Khi AB0 = 7.55676                             Khi AB0 x V0 = 0.613458
                 Khi AC0 =-6.21615                             Khi AC0 x V0 =-0.504627
                 Khi BC  = 10.9424                             Khi BC x V0  = 0.888302
                 Khi AB1 =-2.28102                             Khi AB1 x V0 =-0.185173
                 Khi AC1 = 10.8604                             Khi AC1 x V0 = 0.881647


Mole Fraction  Vol. Fraction  Experimental  Calculated    Difference    Experimental  Calculated    Difference
CHLOROFORM     CHLOROFORM     ln(Gamma)     ln(Gamma)                     Khi           Khi

 2.91977 E-2    4.60816 E-3   -0.378649     -0.397108      1.84589 E-2   0.631234      0.612604      1.86302 E-2
 8.25116 E-2    0.013654      -0.380714     -0.370019     -1.06952 E-2   0.599936      0.610929     -1.09934 E-2
 0.108179       1.83293 E-2   -0.343845     -0.356807      1.29628 E-2   0.623515      0.610064      1.34513 E-2
 0.160073       2.84993 E-2   -0.322807     -0.329771      6.96389 E-3   0.615559      0.60818       7.37844 E-3
 0.221577       4.19761 E-2   -0.293686     -0.297203      3.51677 E-3   0.609516      0.605685      3.83166 E-3
 0.28954        5.90285 E-2   -0.260552     -0.260642      9.07071 E-5   0.60263       0.602527      1.02401 E-4
 0.359788       7.96172 E-2   -0.227989     -0.222392     -5.59697 E-3   0.592107      0.598715     -6.6072 E-3
 0.42318        0.101469      -0.197707     -0.187704     -1.00036 E-2   0.582278      0.594668     -1.23905 E-2

 5.77513 E-2    9.7833 E-3    -0.738923     -0.729739     -9.18427 E-3   0.209807      0.219174     -9.36667 E-3
 0.108824       1.93043 E-2   -0.697517     -0.690147     -7.37001 E-3   0.217362      0.225025     -7.66304 E-3
 0.159201       0.029618      -0.657487     -0.650223     -7.26397 E-3   0.22314       0.230854     -7.71418 E-3
 0.209695       4.10168 E-2   -0.613539     -0.609334     -4.20541 E-3   0.232167      0.23674      -4.57287 E-3
 0.259731       5.35302 E-2   -0.568451     -0.567958     -4.93057 E-4   0.242049      0.242599     -5.50434 E-4
 0.300037       6.46309 E-2   -0.53273      -0.534019      1.2891 E-3    0.248797      0.247323      1.47338 E-3
 0.352347       8.06265 E-2   -0.483035     -0.489188      6.15277 E-3   0.260714      0.253434      7.27923 E-3
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0.393323       9.46198 E-2   -0.446181      -0.453487       7.30609 E-3   0.267095       0.258182       8.91295 E-3

5.29519 E-2    9.36426 E-3   -1.02589       -1.02307       -2.81431 E-3  -0.119268      -0.116401      -2.86778 E-3
9.54612 E-2    1.75295 E-2   -0.991324      -0.985028      -6.2959 E-3   -0.117423      -0.1109        -6.5226 E-3
0.158687       0.030903      -0.927843      -0.926256      -1.58624 E-3  -0.103815      -0.102126      -1.68903 E-3
0.207854       4.24767 E-2   -0.878284      -0.878644       3.60139 E-4  -9.43655 E-2   -9.47583 E-2    3.92777 E-4
0.242354       5.13051 E-2   -0.839459      -0.844186       4.7261 E-3   -8.40224 E-2   -8.92735 E-2    5.25108 E-3
0.284833       6.30859 E-2   -0.793525      -0.800522       6.99731 E-3  -7.41587 E-2   -0.08213        7.97133 E-3
0.337088       7.91627 E-2   -0.735616      -0.744868       9.25182 E-3  -6.17814 E-2   -7.26923 E-2    1.09109 E-2
0.385629       9.59371 E-2   -0.677265      -0.69118        1.39147 E-2  -4.61841 E-2   -6.32086 E-2    1.70245 E-2

6.91295 E-2    1.29713 E-2   -1.20531       -1.19917       -6.14493 E-3  -0.354336      -0.348028      -6.30752 E-3
0.125054       2.46687 E-2   -1.1532        -1.14302       -1.01793 E-2  -0.350566      -0.339865      -1.07008 E-2
0.185469       3.87337 E-2   -1.08783       -1.07925       -8.58398 E-3  -0.339338      -0.330048      -9.28972 E-3
0.240657       5.31056 E-2   -1.0258        -1.01796       -7.83792 E-3  -0.328767      -0.320025      -8.74177 E-3
0.29753        6.97259 E-2   -0.958969      -0.951512      -7.4569 E-3   -0.317075      -0.308458      -8.61663 E-3
0.351863       8.76493 E-2   -0.890055      -0.884696      -5.35867 E-3  -0.302464      -0.296026      -6.43776 E-3
0.396328       0.104088      -0.832623      -0.827438      -5.18592 E-3  -0.291134      -0.284673      -6.46096 E-3
0.444489       0.124033      -0.76658       -0.762667      -3.91228 E-3  -0.276072      -0.270973      -5.09866 E-3

5.97585 E-2    1.17301 E-2   -1.28221       -1.30605        2.38385 E-2  -0.469878      -0.494285       2.44077 E-2
0.112404       2.31037 E-2   -1.23134       -1.24865        1.73144 E-2  -0.466115      -0.484258       0.018143
0.158908       3.40807 E-2   -1.18355       -1.19572        1.21728 E-2  -0.461533      -0.47458        0.013047
0.208601       4.69158 E-2   -1.13011       -1.13668        6.57456 E-3  -0.456026      -0.463264       7.23773 E-3
0.25203        5.92012 E-2   -1.08055       -1.08286        2.31142 E-3  -0.449821      -0.452432       2.61146 E-3
0.298019       7.34596 E-2   -1.02456       -1.02345       -1.11152 E-3  -0.441156      -0.439862      -1.29478 E-3
0.34323        8.89189 E-2   -0.968829      -0.962482      -6.34735 E-3  -0.433879      -0.426232      -7.64679 E-3
0.399475       0.110502      -0.894695      -0.882884      -1.18103 E-2  -0.42213       -0.407204      -1.49269 E-2


Root mean square deviation of ln(activity coefficient) = 8.89835 E-3

Root mean square deviation of interaction parameter = 9.70629 E-3


  DATA USED :
                            CHLOROFORM    SQUALANE     DNP
   Molar Volume (l/mol)      0.08118       0.52742      0.43742
   Molecular Weight          119.378       422.82       418.62
   Density (g/ml)            1.4705        0.8017       0.963
   S.V.P. (torr)             240.8
   2nd Virial Coeff.        -1.16

Temperature of Isotherms = 302.99  K


Calculated using program 'FLOHUG.BASIC'.   C. G.J.Price   1982.
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