An N.M.R. Spectroscopic Investigation of Molecular Interactions in Solution

A thesis

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by

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Summary

Whilst molecular complex formation in aromatic solvents has been studied by nuclear magnetic resonance for many years, and much useful information has been obtained, a number of problems associated with these studies remain unresolved. The most important of these may be summarized as: a) which of the three concentration scales in current use (namely mole fraction, molarity and molality) give equilibrium quotient and excess shielding values which are independant of the data evaluation procedure used, b) which data evaluation techniques give thermodynamically valid results which are independant of the nature of the inert solvent used and the particular composition of the systems measured, c) are any of the solvents and references used inert and hence non-complexing with aromatics, and d) what is the effect of substituents, on the aromatic solvents, on the type of complexes formed. The work reported in this thesis is directed towards resolving these problems. The following conclusions are obtained: a) if a correction is made for the difference in the molar volumes of the aromatic and inert solvents and if the double reciprocal plot devised by Benesi and Hildebrand is used then thermodynamically valid results are obtained using the mole fraction concentration scale, b) thermodynamically valid results are only obtained on the molarity scale if the limiting slope of the BH plot is used, c) cyclohexane is believed to be a genuinely inert solvent and a suitable reference material, but both carbon tetrachloride and tetramethylsilane interact with aromatic molecules, and d) chlorine substituents on an aromatic ring appear to alter the characteristics of the aromatic molecule sufficiently to enable an n-type complex to be formed in addition to the expected π-complex. Finally, during these investigations the variation of the combined anisotropy and dispersive medium screenings ($\sigma_a + \Delta\sigma_w$) of mixtures with composition are shown to be related to the thermodynamics of perfect and imperfect mixtures.

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NOTE ON THE UNITS USED IN THIS THESIS

The units used in reporting work in the scientific literature are being standardized to conform to the recently proposed S.I. (Système International d' Unités) convention. As this system is now acceptable to the Chemical Society (London), S.I. units have been used throughout this thesis. However, in a few instances, equations related to the 'ring current' screenings are quoted directly from the literature.

CONTENTS

CHAPTER 6

CHAPTER 7

Page

CHAPTER 8

CHAPTER 9

CHAPTER 10

Page

Interactions Between the Haloforms and some Chlorobenzenes, and the Self-Association Complexes of these Chlorobenzenes

ILLUSTRATIONS

CHAPTER 1

Theoretical Considerations of Nuclear Magnetic Resonance Spectroscopy

1.1 Introduction

In 1924 Pauli[1] suggested that some atomic nuclei, in addition to acting as point electrostatic charges, possess angular momenta and hence magnetic moments which in an applied magnetic field experience a torque and thus adopt specific orientations corresponding to different energy states. The phenomenon of nuclear magnetic resonance (n.m.r.) is observed when transitions between these energy states are induced by a second magnetic field rotating in a plane perpendicular to the first. The angular momentum operator for the nucleus is quantized and thus, as shown by Stern and Gerlach[2-3], only discrete values of the nuclear magnetic moment are possible. Corresponding to these the nucleus has 2I+1 separate energy levels, where I the nuclear spin quantum number, is a characteristic of each nuclear species. Rabi et. al.[4] were able to obtain the maximum value of the proton magnetic moment, by passing a beam of hydrogen molecules through a steady magnetic field B_0, using the fact that the highest and lowest nuclear energy levels, corresponding to the two beams, were separated by an energy difference of $2\mu B_0$, μ being the maximum value of the magnetic moment. In general a nucleus of spin I has successive sub-levels separated by $\mu B_0/I$ and the frequency of the rotating magnetic field necessary to cause transitions between these levels is $\frac{\mu B_0}{Ih}$. The first detection of n.m.r.[5] was by passing a hydrogen beam successively through two oppositely inclined magnetic fields of similar gradients, the first to separate the beam and the second to refocus it onto a detector. It was found that the application of an oscillating magnetic field between the two original fields reduced the efficiency of the refocussing resulting in a sudden drop in the density of molecules reaching the detector. This occurred when the frequency of the oscillating field was equal to that required to induce transitions between the nuclear energy levels, i.e. when the oscillating frequency

corresponded to $\frac{\mu B_o}{Ih}$. The first n.m.r. signals from bulk matter were independantly observed in 1945 by Purcell, Torrey and Pound[6] in paraffin wax and by Bloch, Hansen and Packard[7] in water. The n.m.r. method is now well established and is invaluable in the study of certain nuclear properties and in the determination of molecular structure[8-12].

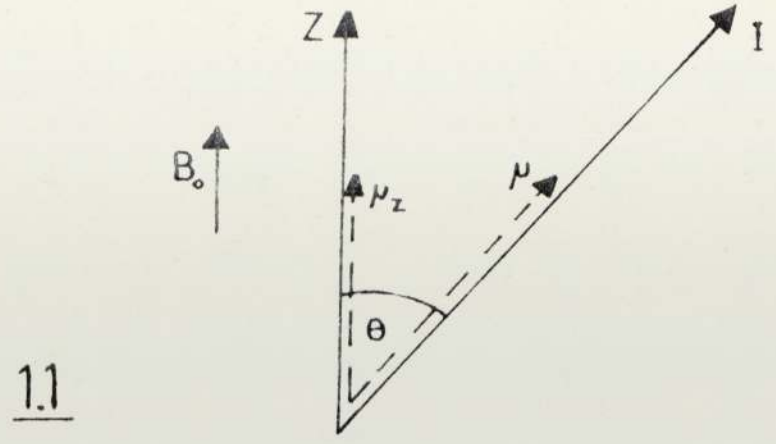
In considering the theory of n.m.r. it is convenient to first examine the properties of discrete nuclei in a magnetic field, thus leading to the basic equation for resonance. A classical treatment of resonance then yields the requirement for an additional rotating field B_1, its direction of rotation being obtained from quantum mechanical considerations. Assemblies of similar nuclei are then considered in dealing with the nuclear energy level distribution, saturation and relaxation effects. Finally, nuclei in various molecular environments are considered in dealing with the chemical shift and chemical exchange phenomena.

1.2 Nuclei in a Magnetic Field

The magnetic moment and angular momentum of those nuclei possessing magnetic moments behave as parallel vectors (figure 1.1) related by

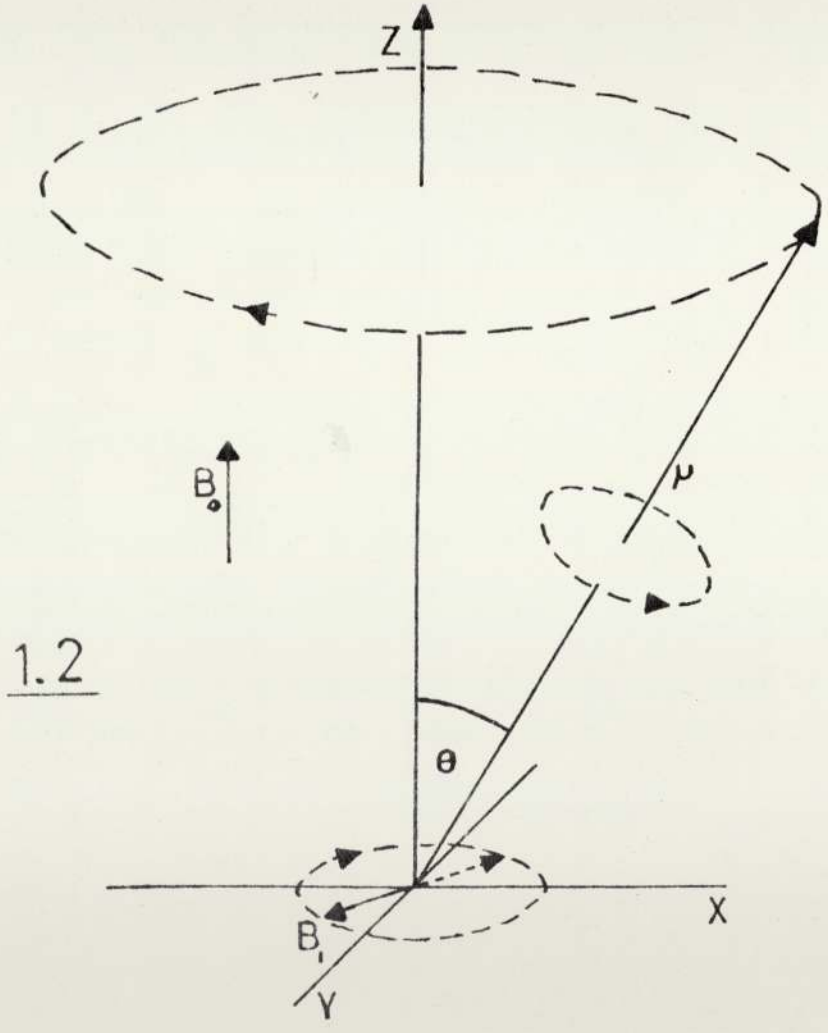
$$\bar{\mu} = \gamma \bar{I}\hbar \qquad 1,1$$

where γ is an empirical constant, known as the magnetogyric ratio, characteristic of each nuclear species. The maximum measurable component of the angular momentum of a nucleus is an integral or half-integral multiple of $\hbar$, therefore the component in any particular direction has values between I and -I . This quantization places the same restriction on μ which thus has discrete components, corresponding to different orientations to the applied field direction, these being defined by a set of observable values $^{m\mu}/I$, where m (the magnetic quantum number) varies from I to -I. These nuclear states are normally degenerate but on applying an external field become separated into the predicted 2I+1 levels. A nucleus,in a uniform magnetic field B_o in the negative z-



1.1

The relationship between the magnetic moment and the spin angular momentum, I.



1.2

Vectorial representation of the classical Larmor precession.

direction, has an energy E_z, relative to that in zero field, given by

$$E_z = -\mu_z B_o \qquad 1,2$$

where the values of μ_z are governed by the allowed values of I as defined above. The permitted nuclear energy levels will thus be $-m\mu B_o/I$ or

$$-\mu B_o, -\left(\frac{I-1}{I}\right)\mu B_o, \ldots\ldots\ldots \left(\frac{I-1}{I}\right)\mu B_o, \mu B_o .$$

Consequently these nuclear levels have an energy separation of $\mu B_o/I$. The selection governing nuclear transitions is $\Delta m = \pm 1$[13], thus transitions between successive levels form the basis of n.m.r. experiments, and for these to occur, the Bohr frequency condition must be observed giving the basic n.m.r. equation

$$\nu = \mu B_o/Ih = \gamma B_o/2\pi \qquad 1,3$$

1.3 Resonance Criteria

a) Classical Treatment of Nuclear Magnetic Resonance

Simple magnetic theory[14] shows that

$$\bar{L} = \bar{\mu} \times \bar{B}_o \qquad 1,4$$

where $\bar{\mu}$ is the magnetic moment, $\bar{B}_o$ the applied field and $\bar{L}$ is the rate of change of angular momentum with time (torque). Since

$$\gamma = \bar{\mu}/\bar{p} \qquad 1,5$$

$\bar{L}$ may be written as

$$\bar{L} = d\bar{p}/dt = \gamma \bar{p} \times \bar{B}_o \qquad 1,6$$

If the vector $\bar{p}$ (the angular momentum) is rotated with an angular velocity ω_o, the rate of change of $\bar{p}$ is

$$d\bar{p}/dt = \omega_o \times \bar{p} \qquad 1,7$$

Thus the effect of the magnetic field B_o is equivalent to rotation with an angular velocity

$$\omega_o = \gamma \bar{B}_o \qquad 1,8$$

The magnetic dipole will therefore precess about the direction of $\bar{B}_o$ with this angular velocity usually referred to as the Larmor angular frequency:

$$\nu_o = \gamma \bar{B}_o/2\pi \qquad 1,9$$

In order to appreciate the significance of this a new co-ordinate system is set up such that the static magnetic field is stationary within it i.e. it is effectively reduced to zero. This is achieved by rotating this co-ordinate frame about the $\bar{B}_o$ direction with the Larmor angular frequency. If another smaller constant magnetic field $\bar{B}_1$ is introduced perpendicular to $\bar{B}_o$ (figure 1.2) but rotating about that direction such that its angular frequency is different from that of the Larmor precession, $\bar{B}_1$ will also be rotating in the rotating co-ordinate frame. Thus it exerts a varying torque $\bar{\mu} \times \bar{B}_1$ on the nucleus, tending to tip the nuclear moment towards the plane perpendicular to $\bar{B}_o$. Whilst $\bar{B}_1$ is moving in the rotating frame the direction of the torque will vary rapidly, and only a slight wobbling perturbation of the steady precessional motion will be observed. When the field $\bar{B}_1$ rotates at the Larmor frequency it will behave (in the rotating frame) as a constant field and the torque, being always in the same direction, will cause large oscillations in the angle between $\bar{\mu}$ and $\bar{B}_o$. Hence, if the rate of rotation of $\bar{B}_1$ is varied through the Larmor frequency, the oscillations will increase and be greatest at that frequency, and will show as a resonance phenomenon. Normally, a linearly oscillating field is applied which can be regarded as a superposition of two contra-rotating fields; only that component having the correct sense synchronizing with the precessing magnetic moment.

b) Quantum Mechanical Consideration of the Rotating Field, B_1

When a nucleus of magnetic moment $\bar{\mu}$ is placed in a magnetic field the Hamiltonian operator for the system is given by

$$\mathcal{H} = -\bar{\mu} \cdot \bar{B}_o \qquad 1,10$$

Thus, from equation 1,1

$$\mathcal{H} = -\gamma \overline{I\hbar} \cdot \overline{B}_o \qquad 1,11$$

There are m expected values of I and hence of $\mathcal{H}$, thus the energy levels are

$$E = -\gamma \hbar m \overline{B}_o \qquad 1,12$$

In order to induce transitions between these energy states a perturbation must be introduced. This may suitably be done by the application of an oscillating magnetic field whose direction may be decided from the properties of spin operators and eigenfunctions appropriate to a nucleus of spin I. A set of spin angular momentum operators I_x, I_y, I_z and I_z^2 can be defined for such a nucleus. Restricting the argument to nuclei of spin $I = \frac{1}{2}$ for simplicity, then for an isolated nucleus there will be two independent states whose degeneracy may be removed by the application of a magnetic field. The eigenfunctions for these states are denoted by $\alpha (I=+\frac{1}{2})$ and $\beta (I=-\frac{1}{2})$. and using these two functions as a basis all three components of I may be represented by 2 x 2 matrices. These are the well-known Pauli matrices[15]

$$I_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \; ; \; I_y = \tfrac{1}{2}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \; ; \; I_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \qquad 1,13 - 1,15$$

The convention used for any operator P is that $(\alpha|P|\alpha)$, $(\alpha|P|\beta)$, $(\beta|P|\alpha)$ and $(\beta|P|\beta)$ are respectively the top left, top right, bottom left and bottom right elements in the matrix. The probability of a transition occurring between the two spin states is therefore governed by the elements $(\alpha|P|\beta)$ and $(\beta|P|\alpha)$. If the oscillating magnetic field is applied along the z-axis the relevant elements are

$$(\alpha|I_z|\beta) = 0 \quad ; \quad (\beta|I_z|\alpha) = 0 \qquad 1,16 - 1,17$$

i.e. this arrangement of steady and oscillating fields cannot result in a transition. However, if the oscillating field is applied along the x- or y-axes then

$$\left.\begin{aligned} (\alpha|I_x|\beta) &= \tfrac{1}{2} \quad ; \quad (\beta|I_x|\alpha) = \tfrac{1}{2} \\ (\alpha|I_y|\beta) &= \tfrac{1}{2}i \quad ; \quad (\beta|I_y|\alpha) = -\tfrac{1}{2}i \end{aligned}\right\} \qquad 1,18 - 1,21$$

i.e. either of these arrangements results in a finite probability of a transition occurring.

The energy change when such a transition takes place is

$$\Delta E = \gamma \hbar B_o \qquad 1,22$$

and the frequency of the oscillating field is given by

$$\nu = \Delta E/h = \gamma B_o/2\pi \qquad 1,23$$

1.4 Nuclear Energy Level Distribution

It is necessary to consider an assembly of similar nuclei when discussing the nuclear energy level distribution. At resonance the probabilities of transitions occurring by absorption or emission of energy are identical, the effect of spontaneous emission being negligible[16]. Nuclear resonance signals are only observed if there is a nett change in the system, and this is governed by the distribution of nuclei between the various energy levels. If two energy levels 1 and 2 are considered, containing n_1 and n_2 nuclei, the nett change in the system is $P(n_1-n_2)$ where P is the probability of a transition occurring. In the absence of a radio frequency field B_1, the number of nuclei (n_i) in a particular nuclear level with energy E_i at thermal equilibrium at temperature T_i is given by the Boltzmann distribution as

$$n_i/n = \exp(-E_i/kT_i) \Big/ \sum_i \exp(-E_i/kT_i) \qquad 1,24$$

where n is the total number of nuclei. The probability (p^m) that any nucleus will occupy a particular level of magnetic quantum number m, is given by

$$p^m = (1/2I+1)\left[\exp({}^m\mu B_o/IkT_i)\right] \cong (1/2I+1)\left[1+ {}^m\mu B_o/IkT_i\right] \qquad 1,25$$

Hence the distribution of nuclei favours the lower energy state and, for a nucleus of spin $I = \frac{1}{2}$, the probabilities that the nucleus is in the upper or lower energy states are

$$P_{upper} = \tfrac{1}{2}(1-\mu B_o/kT_i) \quad ; \quad P_{lower} = \tfrac{1}{2}(1+\mu B_o/kT_i) \qquad 1,26 - 1,27$$

Thus the higher the applied field the greater the sensitivity of the n.m.r. experiment due to the increase in the excess population of nuclei in the lower energy state. Normally therefore, a nett absorption

of energy is obtained and n.m.r. signals are observed. However, these can weaken and eventually disappear with increasing intensity of the radio frequency field B_1 as n_{excess}, the number of excess nuclei in the lower energy state (i.e. $n_{lower} - n_{upper}$), tends to zero due to the slow return from an excited state to the ground state after an absorption of energy. This phenomenon, which has no equivalent in optical spectroscopy[17-18] is known as saturation.

1.5 Saturation

Saturation is primarily seen as a reduction in the intensity of an absorption due to a decrease in n_{excess} resulting in a reduced nett absorption of energy occurring; the reduction increasing with the amplitude of the oscillating field B_1. Saturation also affects the spectrum by broadening the resonance lines and also by affecting some lines more than others. For an assembly of nuclei of spin $I=\frac{1}{2}$, in the absence of the radio frequency field, the rate of change of the excess nuclei, n, per m^3 in the ground state is given by

$$dn/dt = {}^{n_o} - {}^{n}/T_1 \qquad 1,28$$

where n_o is the value of n at thermal equilibrium and T_1 is a relaxation time. On applying the radio frequency field the energy absorbed is 2nP where P is the probability per unit time for a transition to occur under the influence of radiation. Hence

$$dn/dt = ({}^{n_o} - {}^{n}/T_1) - 2nP \qquad 1,29$$

The steady state value of the excess number, n_s, is given by

$${}^{n_s}/n = (1 + 2T_1P)^{-1} \qquad 1,30$$

A value for P can be obtained from standard radiation theory[18], if it is assumed that the probability of a transition in unit time between two states having magnetic quantum numbers m and m' may be defined by

$$P_{m \rightarrow m'} = \gamma^2 B_1^2 \left| (m' | I_x | m) \right|^2 \delta(\nu_{mm'} - \nu) \qquad 1,31$$

where B_1 is the amplitude of the radio frequency field rotating in the correct sense in a plane at right angles to the main field B_o, and $(m'|I_x|m)$ is the appropriate matrix element of the nuclear spin operator I_x. Since $\delta(\nu_{mm'} - \nu)$ is the Dirac delta function which is zero except when $\nu_{mm'} = \nu$ it may be seen that an infinitely sharp absorption or emission line is predicted. As this is unreal, it is replaced by a shape function $g(\nu)$ normalized by

$$\int_0^\infty g(\nu)\, d\nu = 1 \qquad 1,32$$

Using the selection rule[19] $\Delta m = -1$ it follows that

$$(m'|I_x|m)^2 = \tfrac{1}{4}(I + m)(I - m + 1) \qquad 1,33$$

hence

$$P_{m \to m-1} = \tfrac{1}{4}\gamma^2 B_1^2 (I + m)(I - m + 1)\, g(\nu) \qquad 1,34$$

which for $I = \tfrac{1}{2}$ reduces to

$$P = \tfrac{1}{4}\gamma^2 B_1^2 g(\nu) \qquad 1,35$$

Therefore

$$n_{s/n} = \left[1 + \tfrac{1}{2}\gamma^2 B_1^2 g(\nu) T_1\right]^{-1} \qquad 1,36$$

The right hand side of equation 1,36 is usually denoted by Z and is called the saturation factor. On applying a large amplitude radio frequency field the excess number of nuclei in the lower energy level, n_s, will become very small and the spin system is said to be saturated. This is greatest at the radio frequency which gives a maximum value for the shape function $g(\nu)$, and a further relaxation time, T_2, may be defined such that

$$T_2 = \tfrac{1}{2} g(\nu)_{max} \qquad 1,37$$

and thus

$$Z_o = \left[1 + \gamma^2 B_1^2 T_1 T_2\right]^{-1} \qquad 1,38$$

where Z_o is the saturation factor for a maximum value of $g(\nu)$.

1,6 Relaxation Processes

The spin-lattice relaxation results in the restoration of the original distribution of energy levels in a system by removing energy from an excited spin state, so allowing a nucleus to return to a lower energy state; the spin-spin relaxation results in phase loss.

a) Spin-lattice Relaxation

In a bulk sample molecules are undergoing random translational and rotational motion, thus any nuclear magnetic moment which may be present will experience a rapidly fluctuating magnetic field produced by neighbouring magnetic moments. If the motion contains a frequency which is synchronous with the precessional frequency of a neighbouring nucleus then this nucleus will experience a radiofrequency field capable of inducing a transition; preferentially a stimulated emission of energy from the spin system rather than an absorption, thus transferring energy to the surrounding lattice. A spin-lattice relaxation time is associated with this process and may be defined, in terms of the probability of a spin-lattice transition occurring, as follows. When an assembly of nuclear spins of $I = \frac{1}{2}$ is placed in a steady magnetic field the initial population of the two spin states is equal and a finite time is required for the spin populations to reach their new equilibrium value. If n_2 and n_1 are the number of nuclei per unit volume in the upper and lower states respectively, then it is possible to evaluate the rate of change of the excess number of nuclei per unit volume, n, as a function of time. If the upward and downward transition probabilities are P_1 and P_2 respectively (for the interaction of a nucleus with other molecular degrees of freedom) where simple thermodynamics requires that

$$P_2 \text{ (upper} \rightarrow \text{ lower)} > P_1 \text{ (lower} \rightarrow \text{ upper)},$$

then at equilibrium (in the presence of a magnetic field) the total number of upward and downward transitions per unit time must be equal i.e.

$$n_1 P_1 = n_2 P_2 \qquad 1,39$$

As the Boltzmann distribution of nuclei between two energy levels is given by

$$n_2/n_1 = \exp\left(-2\mu B_o/kT\right) \approx 1 - 2\mu B_o/kT \qquad 1,40$$

it follows that

$$P_1/P_2 = n_2/n_1 = \exp\left(-2\mu B_o/kT\right) \qquad 1,41$$

Provided that the interaction is small compared with the total energy of the system, i,e. the temperature is stationary, then P_1/P_2 is independant of n_1 and n_2; therefore if P is the mean of P_1 and P_2 then

$$P_1 = P\exp\left(-\mu B_o/kT\right) \quad ; \quad P_2 = P\exp\left(+\mu B_o/kT\right) \qquad 1,42 - 1,43$$

Thus the rate of change of the populations is

$$dn_1/dt = -dn_2/dt = n_2P_2 - n_1P_1 \qquad 1,44$$

Since an upward transition decreases and a downward transition increases the excess number of nuclei by 2 then

$$dn/dt = 2\,(n_2P_2 - n_1P_1) \qquad 1,45$$

expansion of the exponential in P_1 and P_2 by assuming that $\mu B_o/kT \ll 1$ then gives

$$dn/dt = -2P\left[n - (n_1 + n_2)\mu B_o/kT\right] \qquad 1,46$$

If an equilibrium value of the excess number of nuclei in the lower energy state, n_{eq}, is defined as

$$n_{eq} = (n_1 + n_2)\mu B_o/kT \qquad 1,47$$

it follows that equation 1,46 becomes

$$dn/dt = -2P\left[n - n_{eq}\right] \qquad 1,48$$

and integration of 1,48 leads to

$$n - n_{eq} = (n_o - n_{eq})\exp\,(-2\,Pt) \qquad 1,49$$

where n_o is the initial value of n. The spin-lattice relaxation time T_1, the characteristic half-life time for the relaxation of a nucleus from an excited state to the ground state, may be defined by

$$T_1 = 1/2P \qquad 1,50$$

thus giving

$$n - n_{eq} = (n_o - n_{eq})\exp\left(-t/T_1\right) \qquad 1,51$$

showing that the rate at which the excess population reaches its equilibrium value is governed exponentially by T_1.

b) Spin-Spin Relaxation

In addition to interacting with the lattice, magnetic nuclei can also interact among themselves. Each nuclear magnet is acted upon by the steady magnetic field, B_o, and also by the small local magnetic field, B_{loc}, produced by the precessional motion of neighbouring nuclear magnets. These local fields have both oscillating (B_{osc}) and static components (B_{stat}), thus nucleus j producing a magnetic field oscillating at its Larmor frequency may induce a transition in nucleus k. The energy for the process comes from j and a simultaneous re-orientation of 'flip-flop' of both nuclei results. Only identical nuclei are capable of undergoing spin-exchange and no restoration of the distribution of spin states following an absorption of energy is achieved because the total spin energy remains constant throughout the process. Due to the small variations in B_{loc} nuclear dipoles which are precessing in phase at one instant of time get out of phase in a time T_2, the spin-spin relaxation time. The foregoing description of the n.m.r. phenomenon relating to bulk systems is dependent on a consideration of individual nuclei, but it is also possible to approach the phenomenon directly from a macroscopic viewpoint and so obtain a further insight into the n.m.r. parameters.

1.7 N.M.R. in Macro Samples

Bloch[20-22] has described the bulk magnetization of a sample using a series of phenomenological equations. An assembly of nuclei in an applied field have their various spin states occupied to different extents, thus giving the sample a magnetic susceptibility. If $\bar{M}$ is the magnetic moment per unit volume of a substance placed in a magnetic field $\bar{B}_o$, then this is related to the static susceptibility χ_o by

$$\bar{M} = \bar{B}_o \chi_o \qquad 1,52$$

When an oscillating magnetic field $\bar{B}_1$ is applied in a manner suitable to cause resonance, the total magnetisation of the sample, $\bar{M}$, becomes time dependent and by analogy to the equation of motion of a single precessing nucleus (equation 1,6)

$$d\bar{M}/dt = \gamma(\bar{M} \times \bar{B}) \qquad 1,53$$

where $\bar{B}$ is the vector sum of $\bar{B}_o$ and $\bar{B}_1$ which may be resolved into its constituent parts along the co-ordinate axes:

$$B_z = B_o \;;\; B_x = B_1 \cos\omega_1 t \;;\; B_y = -B_1 \sin\omega_1 t \qquad 1,54 - 1,56$$

where ω_1 is the angular velocity of $\bar{B}_1$.

Consider the effect on a set of equivalent nuclei, of spin $I = \frac{1}{2}$, in a steady magnetic field $\bar{B}_o$ in the z-direction. $\bar{M}$ has only a z component, the individual nuclei precessing about the z-direction with random phases, with the x and y components averaging to zero in forming $\bar{M}$. Similarly, if the assembly of nuclei is exposed to a rotating field $\bar{B}_1$, at fields far removed from resonance the individual nuclei are still out of phase and $\bar{M}$ still only has a z-component. Thus the magnetization vector $\bar{M}_{B_o}$ will still be coincident with the z-axis. As the applied field $\bar{B}_1$ approaches the value required for resonance the nuclei will start to precess in phase giving non-zero values of M_x and M_y. Hence the magnetization vector will move away from the z-axis, and will precess about the new direction with the Larmor frequency as shown in figure 1.3. In the steady state condition the components of the bulk magnetization $\bar{M}_B$, due to the static field $\bar{B}_o$, then become

$$(dM_x/dt)_{B_o} = \gamma B_o M_y \;;\; (dM_y/dt)_{B_o} = -\gamma B_o M_x \;;\; (dM_z/dt)_{B_o} = 0 \qquad 1,57 - 1,59$$

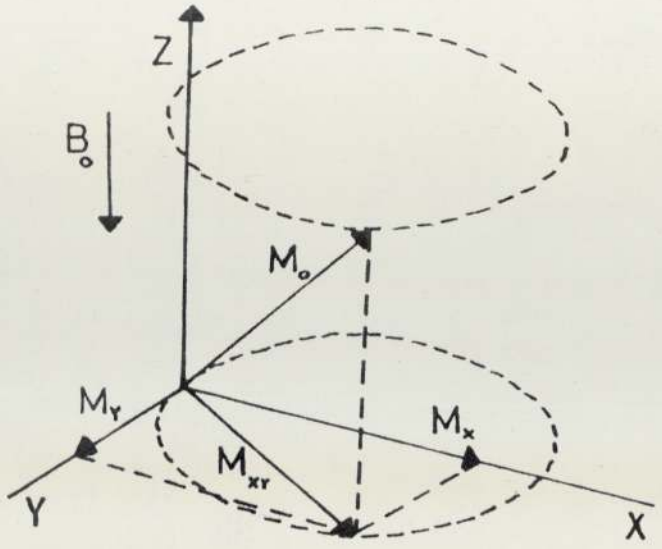
and the components due to the applied field $\bar{B}_1$ become

$$(dM_x/dt)_{B_1} = \gamma M_z B_1 \sin\omega_1 t \;;\; (dM_y/dt)_{B_1} = \gamma M_z B_1 \cos\omega_1 t \qquad 1,60 - 1,61$$

$$(dM_z/dt)_{B_1} = \gamma(-M_x B_1 \sin\omega_1 t - M_y B_1 \cos\omega_1 t) \qquad 1,62$$

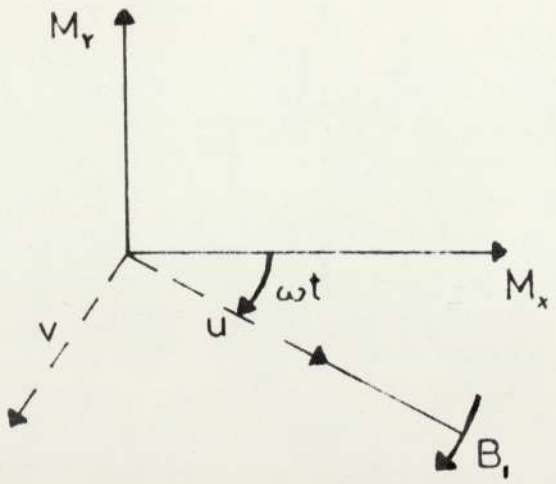
Thus combining equations 1,57 - 1,59 with equations 1,60 - 1,62 gives the overall equations of motion for the components of the total magnetization vector at resonance, M_T, as

1.3



The magnetization vector precessing about the z-axis with non zero values of M_x and M_y.

1.4



Transverse components of the magnetic moment referred to fixed axes (full lines) and axes rotating with the r.f. field (dotted lines).

$$dM_x/dt = \gamma(M_y B_0 + M_z B_1 \sin\omega_1 t) \qquad 1,63$$

$$dM_y/dt = \gamma(M_z B_1 \cos\omega_1 t - M_x B_0) \qquad 1,64$$

$$dM_z/dt = \gamma(-M_x B_1 \sin\omega_1 t - M_y B_1 \cos\omega_1 t) \qquad 1,65$$

The effect of the relaxation processes must also be taken into account. Before resonance the spin system and lattice are at thermal equilibrium and M_z is equal to the static magnetization, M_0. After resonance has occurred the spin system and lattice are no longer at thermal equilibrium and M_z does not remain constant, but approaches M_0 at a rate governed by the spin-lattice relaxation time T_1 which in the macroscopic system is termed the longitudinal relaxation time. This rate is

$$dM_z/dt = M_0 - M_z/T_1 \qquad 1,66$$

The individual nuclei will also be in phase after resonance and M_x and M_y will still have finite values. Due to the effects of spin-spin relaxation and the resulting on-set of phase incoherence these components will decay to zero in a time T_2. This has been described as the transversal relaxation time because it governs the time dependence of the transverse magnetization components M_x and M_y. The rate of decay is given by

$$dM_x/dt = -M_x/T_2 \; ; \; dM_y/dt = -M_y/T_2 \qquad 1,67 - 1,68$$

Combination of equations 1,66 - 1,68 with equations 1,63 - 1,65 leads to the Bloch equations for describing the actual behaviour of a macroscopic sample during an n.m.r. experiment:

$$dM_x/dt = \gamma(M_y B_z + M_z B_1 \sin\omega_1 t) - M_x/T_2 \qquad 1,69$$

$$dM_y/dt = \gamma(M_z B_1 \cos\omega_1 t - M_x B_z) - M_y/T_2 \qquad 1,70$$

$$dM_z/dt = \gamma(-M_x B_1 \sin\omega_1 t - M_y B_1 \cos\omega_1 t) + (M_0 - M_z/T_1) \qquad 1,71$$

The Bloch equations take a simpler form if they are referred to a set of axes rotating with the applied radiofrequency field B_1. In this rotating frame both B_0 and B_1 are fixed and the frame rotates with a

frequency ω, passage through resonance is achieved by varying ω, exact resonance occurring when $\omega = \omega_0$. The components of M along and perpendicular to the direction of B_1 are identified as u (in-phase component of M) and v (out-of-phase component of M) (figure 1.4). The relationships between the components are

$$M_x = u\cos\omega t - v\sin\omega t;\quad M_y = -u\sin\omega t - v\cos\omega t \qquad 1,72 - 1,73$$

Substitution of 1,72 and 1,73 into the Bloch equations, noting that $\gamma B_0 = \omega_0$, gives

$$du/dt + u/T_2 + (\omega_0 - \omega)v = 0 \qquad 1,74$$

$$dv/dt + v/T_2 - (\omega_0 - \omega)u + \gamma B_1 M_z = 0 \qquad 1,75$$

$$dM_z/dt + (M_z - M_0/T_1) - \gamma B_1 v = 0 \qquad 1,76$$

The solution of these equations is obtained by assuming that the resonance signal is oberved under steady state or slow passage conditions, when the absorption of r.f. energy is just balanced by the transfer of energy from the nuclei to the lattice so that $dM_z/dt = 0$, hence

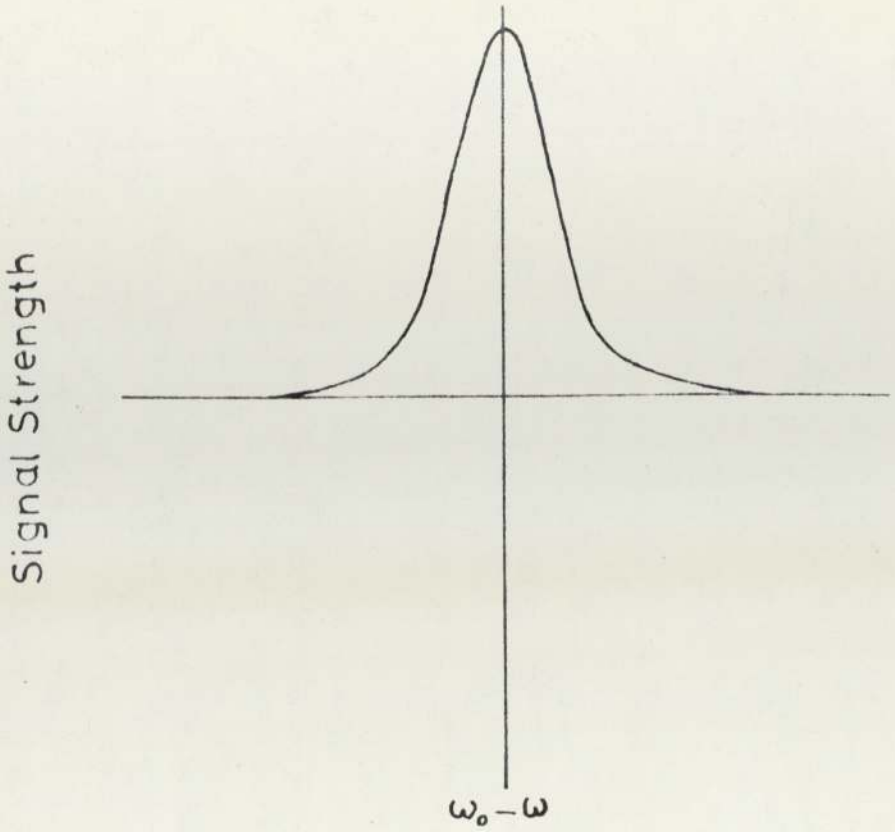
$$u = M_0\gamma B_1 T_2^2(\omega_0 - \omega)/D;\quad v = -M_0\gamma B_1 T_2/D \qquad 1,77 - 1,78$$

$$M_z = M_0\left(1 + T_2^2(\omega_0 - \omega)^2\right)/D \qquad 1,79$$

where $$D = 1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 B_1^2 T_1 T_2 \qquad 1,80$$

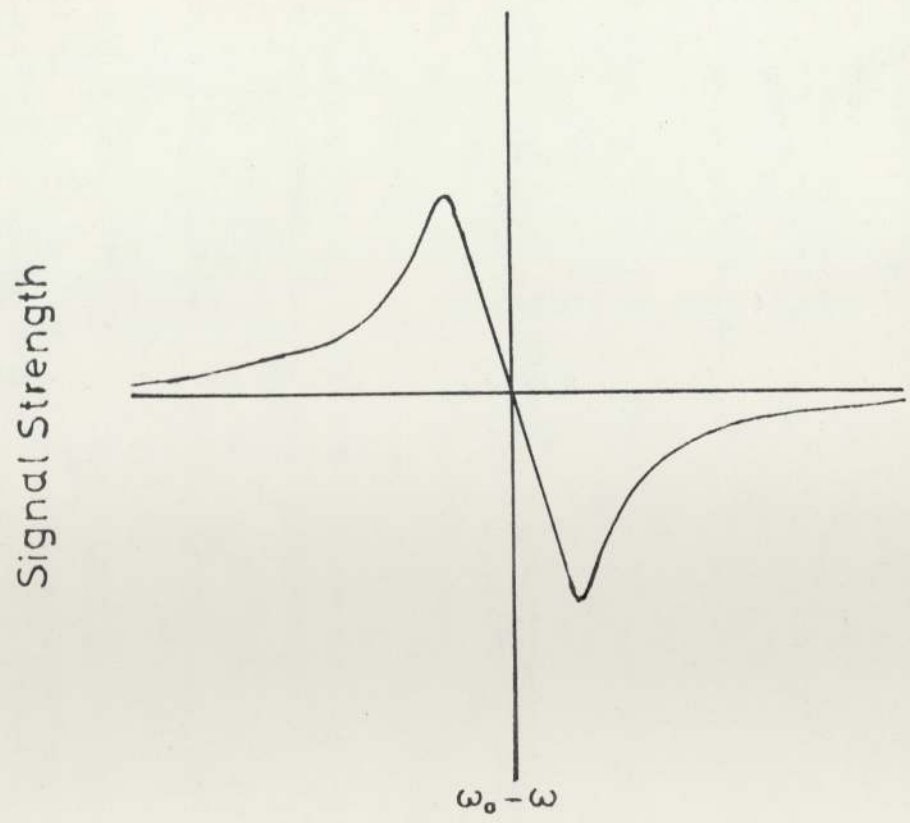
From equation 1,78 it may be seen that when B_1 is about 10^{-7} tesla and T_1 and T_2 no greater than a few seconds, the absorption or 'v-mode' signal should be proportional to $\gamma B_1 T_2/(1 + T_2^2(\omega_0 - \omega)^2)$. This describes a Lorentzian line shape[20, 23] as shown in figure 1.5. At the centre when the resonance condition is exactly fulfilled $\omega_0 - \omega = 0$ and the signal height is proportional to $\gamma B_1 T_2$. In certain cases it is preferable to use the dispersion or 'u-mode' signal, and this is shown in figure 1.6. The terms u- and v-mode are sometimes replaced by the Bloch susceptibilities χ' and χ'' and these are also shown in the above figures. The area under an absorption curve can be obtained

1.5



Absorption line shape (v-mode or χ'') for n.m.r. resonance.

1.6



Dispersion line shape (u-mode or χ') for n.m.r. resonance.

by the integration of the v term over all values of $\omega_o - \omega$. The result is directly proportional to χ_o which from equation 1,52 is a direct function of the number of nuclei per unit volume. Hence the area under each resonance is a direct indication of the number of nuclei of a particular type undergoing resonance.

1.8 Factors Affecting Line Shape

It has been shown that a nuclear magnetic absorption line can be approximately represented by a Lorenztian curve[20, 23]. A quantum mechanical approach to n.m.r. predicts an infintely sharp absorption line; however, for identical nuclei, absorption occurs over a small but finite frequency range due to several line broadening effects. The width of a line is defined as its width at half height expressed in terms of the applied field or frequency. Half-height line widths vary from 10^{-9} tesla in some liquids to 10^{-4} tesla in solids. The various factors affecting this width will now be discussed.

a) Spin-lattice Relaxation

The lifetime of a nucleus in a given spin-state is limited by the spin-lattice relaxation mechanism and thus there is an uncertainty in the lifetime of that spin-state which is of the order of 2 T_1. Since the Uncertainty Principle requires that

$$\Delta E . \Delta t \approx \hbar \qquad 1,81$$

and since

$$\Delta E = h \Delta \nu \qquad 1,82$$

it follows that

$$\Delta \nu = \hbar / 2 T_1 h \quad , \text{ i.e. } \Delta \nu = 1 / 4\pi T_1 \qquad 1,83 - 1,84$$

Equation 1,84 gives the uncertainty or spread in frequency of a given absorption line due to the limitation placed on a nucleus remaining in a particular spin-state by the spin-lattice relaxation mechanism. For liquids having very short T_1 values this type of broadening is often roughly equal to that originating from magnetic dipolar broadening.

b) Spin-spin Relaxation

In a similar manner the spin-spin relaxation process introduces an uncertainty into the life-time of the nuclear spin-state and so causes uncertainty in the frequency at which resonance will occur, leading to broadened absorption lines.

c) Magnetic Dipolar Broadening

The magnetic environment of a nucleus may be modified by fields produced by the magnetic moments of fixed neighbouring nuclei. These have both static and rotating components both of which produce line broadening; the rotating component resulting in the spin-spin relaxation broadening (see b) above). The static field, which results in the magnetic dipolar broadening, is given by

$$B_{stat} = \mu/r^3 (1 - 3\cos^2\theta) \qquad 1,85$$

at a nucleus distance r away from the nucleus under consideration, and lying on a line inclined at an angle θ to the magnetic dipolar axis. In the solid state adjacent nuclei maintain approximately the same orientation with respect to each other and over the whole sample, if amorphous, all values of θ between 0 and 2π rad are allowed. Thus the resultant local field can have any values between $\pm 2\mu/r^3$. The effective field at a nucleus is therefore $B_o \pm 2\mu/r^3$ and resonance will occur over a range of frequencies and the line will be broadened. If B_{loc} is taken as the spread of the local field then the resonance equation gives the range of frquencies of Larmor precession as

$$\Delta\nu = \mu B_{loc}/Ih \qquad 1,86$$

In a solid many nuclei will be precessing at identical frequencies, hence this form of broadening is very efficient and line widths are large. In liquids and gases, where the molecules are allowed rapid random motion, the magnetic field at any one nucleus due to its neighbours effectively averages to zero. The molecular motions necessary to produce this averaging being of shorter time than that

required for the observation of a nuclear resonance signal, the effect of magnetic dipolar broadening on line widths in liquid and gaseous samples is negligible.

d) Electric Quadruple Effects

Nuclei having values of $I > \frac{1}{2}$ may possess non spherically symmetrical nuclear charge distributions resulting in their having a quadrupole moment, Q. Such a nucleus, in an excited spin-state, may, by interaction of its quadrupole moment with the unsymmetrical local electric fields, transfer its spin energy to the lattice; this spin-lattice relaxation may have a lifetime of as little as 10^{-4}s associated with it, resulting in very broad lines. The main effect in liquids and gases is to place an uncertainty on the energy levels and thus increase the line width.

e) Transient Effects

The steady state solution of the Bloch equations (section 1.7) assumes that equilibrium has been attained between the r.f. field and the nuclear magnetization. In practice the time taken to reach equilibrium is appreciable and thus a restriction is placed upon the rate at which resonance is traversed. The static nuclear magnetization at thermal equilibrium is M_o which is reduced to $Z_o M_o$ in the steady state, where Z_o is the saturation factor. Thus if the resonance line is entered too rapidly the signal will be strong at first and then become weaker as the magnetization is reduced from M_o to $Z_o M_o$, leading to distortion of the line shape.

Saturation will also affect the line shape of a resonance signal (section 1.5). It has been shown that the approach to equilibrium of a spin system is governed by the characteristic time T_1 (section 1.6a)). However, when the irradiating frequency is appreciable this must be modified to $T_1 Z_o$ meaning that equilibrium is attained more rapidly and is accompanied by broadening of the line.

1.9 The Chemical Shift

Any isotopic nucleus has a number of resonant frequencies depending upon its chemical environment and differences between any two of these result in a chemical shift; this phenomenon being a general one for all nuclei. It was first observed for metals and metal salts by Knight[24], and later by Proctor and Yu[25] for ^{14}N compounds and by Dickinson[26] for ^{19}F. Whenever two or more nuclei of the same isotopic species have a different environment, a separate resonance is observed for each group, with an intensity proportional to the number of nuclei in that group. This chemical shift is directly proportional to the applied field strength and arises from small intramolecular and intermolecular contributions to the actual field experienced by a particular nucleus. These contributions have their origin in the various circulations of electrons in the molecule, together with effects associated either with individual atoms or with the medium as a whole. These effects may be represented by the expression

$$B = B_o(1 - \sigma) \qquad 1,87$$

where B_o is the applied field, B the actual field experienced by a nucleus and σ the shielding constant for the nucleus in its particular environment. If two nuclei of the same isotopic species, in environments i and j, have shielding constants σ_i and σ_j at the same value of B_o, then the chemical shift of nucleus i relative to nucleus j is given by

$$\delta_{ij} = (B_i - B_j)/B_o = \sigma_j - \sigma_i \qquad 1,88$$

Since it is not possible to measure the resonance position of a given nucleus stripped of all its electrons, (which it would be necessary to do if one required an absolute reference position) absolute chemical shifts cannot be determined. Thus all chemical shifts are measured relative to a reference compound, which for protons is usually tetramethylsilane, and are then conveniently defined as the dimensionless quantity δ:

$$\delta = (B - B_r / B_o) \times 10^6 \text{ ppm} \qquad 1,89$$

where B is the resonance field of the nuclei under observation and B_r is that for the reference compound. Since it is experimentally easier to determine the difference in frequency of the two signals at resonance, rather than the magnetic field strengths required, δ is generally redefined in terms of frequency as

$$\delta = (\nu - \nu_r / \text{oscillator frequency}) \times 10^6 \text{ ppm} \qquad 1,90$$

where ν and ν_r are the frequencies corresponding to B and B_r in equation 1,89. Because the majority of the work reported in this thesis depends upon the measurement of chemical shifts a detailed and critical discussion of the various screening terms which contribute to the chemical shift is given in chaper 5. Both internal referencing (reference and unknown in same tube) and external referencing (reference in a separate capillary placed in the main tube) are possible and these methods are discussed in chapter 4.

1.10 Spin-spin Coupling

Examination of spectra under high resolution often reveals that the chemically shifted bands are themselves composed of several peaks. This added multiplicity was first noticed by Proctor and Yu[27] for the ^{121}Sb resonance in $NaSbF_6$ which was composed of seven equally spaced lines. To discuss spin-spin coupling fully it is necessary to consider all possible magnetic interactions.[28] There are a number of these which result in the observed multiplicity, but not all of these are equally important. The interactions may be grouped as follows. Firstly there are various electron interactions namely electron orbital-orbital, orbital-spin, spin-spin and spin-external field. Secondly there is the nucleus-electron-electron-nucleus interaction and finally there is an intermolecular dipole-dipole interaction which gives rise to the broad lines observed in solids (section 1.8c)),

and averages to zero when all possible molecular orientations are equally probable. It therefore follows that all these factors affect the number of lines, line separations and coupling constants when spin-spin coupling occurs between non-equivalent nuclei. The detailed theory can clearly become extremely complex and it is convenient to make the point here that two types of spin-spin coupled spectra exist, namely first and second order. The former is the simplest and results in couplings which have regular line spacings and intensities, and only this type will be considered here.

Defining an absorption band as the signal arising from one set of identical nuclei, the number of peaks, as constituent lines of such a band arising from coupling, may be predicted. The number of lines in the spectrum for nucleus A in a molecule AX_n, where A and X are non-equivalent, is given by $2nI_x + 1$ where I_x is the spin quantum number of X, and the relative intensities are given by the n th binomial coefficients, i.e.

$$1, n, \frac{n(n-1)}{2!}, \quad \frac{n(n-1\ \ n-2)}{3!}, \quad \ldots\ldots \quad \frac{n(n-1)\ \ldots\ (n-r+1)}{r!} .$$

where n is the number of magnetically equivalent nuclei, and similarly for X. The multiple lines are equally spaced and the magnitude of the splitting, known as the 'coupling or spin-spin interaction constant', is denoted by J_{AX} and quoted in Hz (and is independant of field strength[29]). Considering a nucleus of spin $I = \frac{1}{2}$, the possible spin states are those with m equal to $\pm \frac{1}{2}$. Labelling the state $m = +\frac{1}{2}$ as α and the state $m = -\frac{1}{2}$ as β, a group containing three nuclei (e.g. $CH_3\cdot$) has the following proton spin configurations :

	$\alpha\alpha\beta$	$\alpha\beta\beta$	
$\alpha\alpha\alpha$	$\alpha\beta\alpha$	$\beta\alpha\beta$	$\beta\beta\beta$
	$\beta\alpha\alpha$	$\beta\beta\alpha$	
Total spin $+\frac{3}{2}$	$\frac{1}{+2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

Because of the various effects discussed previously an adjacent nucleus sees four energy states of the group considered above and hence four values of the local field corresponding to the four values of the local field corresponding to the four values of total spin. The two states of total spin $\pm\frac{1}{2}$ are each three times as numerous as those with total spin $\pm\frac{3}{2}$, hence a quartet is observed with relative line intensities 1:3:3:1. Spin-spin coupling is a mutual effect, such that any nucleus which causes splitting of another resonance must itself show splitting of a similar magnitude, the number of lines into which it is itself split being governed by the number of nuclei in the group to which it is coupled. Spectra may be classified using the symbols A, B, C ... X, Y, Z to characterize individual nuclei within a nuclear spin system. The letters A, B, C represent magnetically non-equivalent nuclei of the same species having small relative chemical shifts of the same order of magnitude as the coupling constant between them. X, Y and Z are used to represent a similar set of nuclei, not necessarily of the same species as the first set, but having a large chemical shift from the first set. The symbols A and A' are used to denote nuclei which are chemically but not magnetically equivalent (i.e. they have the same chemical shift but do not couple equally to all other resonant nuclei in the molecule).

1.11 Chemical Exchange Phenomena

Since the spin-lattice relaxation time T_1 must be longer than 0.1s to obtain a high resolution n.m.r. spectrum, this very long time scale inherent in the method allows many phenomena occurring in shorter times to affect the resonance signal. Defining τ_A and τ_B as the first order lifetimes of a magnetic nucleus X in two molecular environments A and B the probability of X in A moving to B is $1/\tau_A$ and vice versa; and $\omega_A - \omega_B$ is the chemical shift difference of X in the two environments, measured in rad s^{-1}. When no exchange is taking

place $\tau_A = \tau_B = \infty$, and two distinct signals will be observed with a chemical shift of $\omega_A - \omega_B$. Provided that the chemical shift difference between the sites is sufficiently large, two distinct signals will also be seen when the rate of exchange is reasonably slow ($\tau_A \gg (\omega_A - \omega_B)^{-1} \ll \tau_B$) and the separation will still be $\approx \omega_A - \omega_B$, but both lines will be broadened due to the exchange. As the rate of exchange increases these lines eventually coalesce and a new single resonance position is obtained at some intermediate frequency, ω:

$$\omega = p_A \omega_A + p_B \omega_B \qquad 1,91$$

where

$$p_A = \tau_A / \tau_A + \tau_B \; ; \; p_B = \tau_B / \tau_A + \tau_B \qquad 1,92 - 1,93$$

i.e. p_A and p_B are the fractions of the population of X in environments A and B respectively. Thus the position of the line depends upon the population of the two sites.

1.12 Investigations to be Carried Out in This Thesis

Many phenomena in solution can be studied by making use of the chemical exchange effect; one that has received considerable attention recently is dipole-induced dipole interactions[30-32]. Investigations of this type form the basis of that part of the work described in this thesis which is directed towards studying molecular interactions in solution. As a result of n.m.r. studies, two parameters appertaining to the interaction are obtained, namely the equilibrium quotient (K) and the excess shielding (Δ_c) for the solute in the complex compared with free solute. Therefore, if dipole-induced dipole complexes formed between polar solutes (and nonpolar solutes with strongly polar bonds) and aromatic solvents are considered these can be investigated by studying the dependance of the observed solute time-average chemical shift on sample composition. There are a number of

methods of obtaining K and Δ_c from the experimental measurements and these have not previously been examined critically in any detail. In order to carry out such an examination several problems must be resolved, the most important of which are a) which is the most thermodynamically valid concentration range and scale to use, b) which solvents are inert (the above investigations being generally carried out in an inert solvent) and hence which is the best solvent and reference to use, c) what is the effect of the various medium screenings on the results obtained and which of these will have to be considered in any new experimental procedure and d) what is the effect of aromatic substituents on the type of interaction obtained, it being known that a methyl group does not alter the type of complex formed[31,33].

CHAPTER 2

Experimental Methods for the Observation of High Resolution Nuclear Magnetic Resonance

2.1 Introduction

In order to observe a n.m.r. signal from any nucleus the fundamental equation

$$\nu_0 = \frac{\gamma B_0 (1-\sigma)}{2\pi} \qquad 2,1$$

must be obeyed. It is evident that it is possible to bring any particular nucleus into resonance either by varying the applied field B_0 or the radiofrequency field ν_0, the other remaining constant. The stationary magnetic field required to observe nuclear magnetic resonance may be derived from either a permanent or an electromagnet operating at field strengths of 1 - 2.5 tesla; superconducting magnets are also available with fields up to 5 tesla. The rotating field is generally derived by passing a signal, from a r.f. oscillator, through a coil around the sample situated in a stationary field. Because of the shielding of nuclei, equation 2,1 requires that either the field or the frequency must be swept over a small range in order to detect the spectrum for a given nucleus. Two principle means of detecting the n.m.r. signal are available using either a single coil, due to Bloch, Hansen and Packard[7], or two crossed coils, due to Purcell, Torrey and Pound[6].

2.2 Requirements of a N.M.R. Spectrometer

The basic requirements of a n.m.r. spectrometer capable of producing permanent high resolution spectra are

a) a magnet with a very homogeneous and stable field (in the range 1 - 2.5 tesla),

b) a probe (or sample holder containing the radiofrequency coil or coils,

c) a sweep unit to linearly vary the main magnetic field over a small range (alternatively it may be kept fixed),

d) a r.f. source (oscillator) of high stability (1 part in 10^9) operating at a fixed frequency in the range 4 - 100 MHz (or varying over a small range of a few kHz),

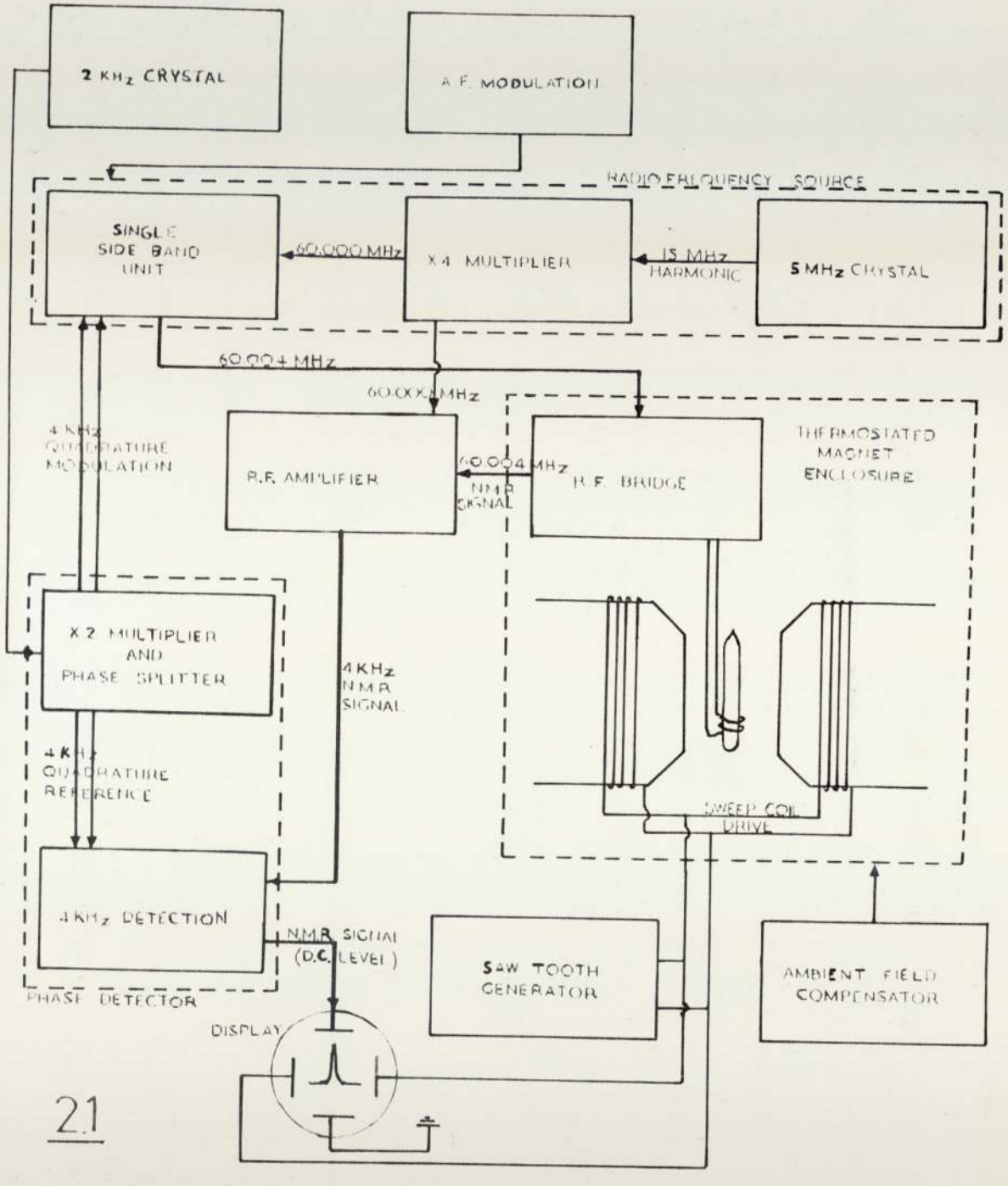
e) a r.f. receiver and amplifier,

f) an oscilloscope and/or pen recorder for permanent presentation of the spectrum.

The requirements for these individual components will now be discussed in detail by considering the Perkin-Elmer R10 Spectrometer, the commercial spectrometer used in the present work; the basic arrangement of which is shown in figure 2.1.

2.3 The Magnet Assembly

The Perkin-Elmer R10 Spectrometer employs a 1.4092 tesla permanent magnet, with pole faces of 250 mm diameter and a separation of 25 mm which necessitates a radiofrequency detection system operating at approximately 60MHz. At low frequencies such as this the permanent magnet, at the time of the design of the instrument, had the advantages of easier operation and greater retention of resolution when compared with an electro-magnet; but it suffers from the disadvantages of only operating at one field strength and thus needing a separate r.f. oscillator tuned to the appropriate frequency for each nuclear type studied. In order to provide the continuously varying field B_o in the field sweep mode of operation, sweep coils are wound on the pole pieces and a direct current saw-tooth wave form applied to these. This voltage, which may be derived either from the time base for the oscilloscope or alternatively from a high grade computer potentiometer synchronized with the rotation of the recorder drum, goes via a cathode follower to the sweep coils. The spectrometer employs a twin-T bridge signal detection system housed in a mu metal box placed directly on the probe unit, which is held between the magnet pole pieces by an aluminium bar. The sample coil is wound on a hollow glass former in



Schematic diagram of the Perkin-Elmer R10 N.M.R. Spectrometer.

which the sample is spun by means of an air turbine.

2.4 Optimisation of Magnet Performance

The previously mentioned magnet dimensions are necessary in order to obtain an ultimate field homogeneity of about 3 parts in 10^9 over a volume of $10^{-8} m^3$ and also to accommodate the r.f. probe. The ratio of pole face diameter to separation must be of the order of 10 : 1 to ensure that the central portion of the field has a 'flat' contour and does not suffer from 'edge' effects (i.e. bending of the lines of magnetic flux near the edge of the pole pieces). The pole faces must be parallel, free from machining marks and almost optically flat[34]; and the pole cap material must be metallurgically uniform. Homogeneity is improved from an intrinsic value of 1 part in 10^6 by eliminating field gradients in the region of the sample by adjusting the d.c. voltages in nine sets of Golay field coils arranged in pairs on the pole faces; shimming currents being quickly generated which produce opposing field gradients in specified directions. A further, apparent, improvement in homogeneity of the magnetic field is achieved by spinning the sample about an axis perpendicular to the applied field direction. This arises because if the field variation over the sample is $\pm \Delta B_o$ and a nucleus within the sample experiences the whole of the variation in time t then the faster the sample spins the more closely does each magnetic nucleus behave as if it 'sees' the average field, B_o; this effect becomes significant when $t \ll 2\pi/\gamma \Delta B_o$. The magnetic field is further stabilized by enclosing it is an aluminium box, lined with expanded polystyrene, containing temperature sensing devices and heating elements. These enable the magnet temperature to be thermostatted to $306.56K \pm 0.001K$, thus reducing the problem of field drift to a minimum. There remains a persistent field drift due to magnet ageing but since this is very small and varies linearly with time it is not corrected for in the R10 spectrometer.

However, the larger variations in the external magnetic field are corrected for by means of a field compensator in which coils placed on or near the magnetic pole pieces sense any variation in the magnetic field and apply a correcting current through further coils wound on the pole pieces.

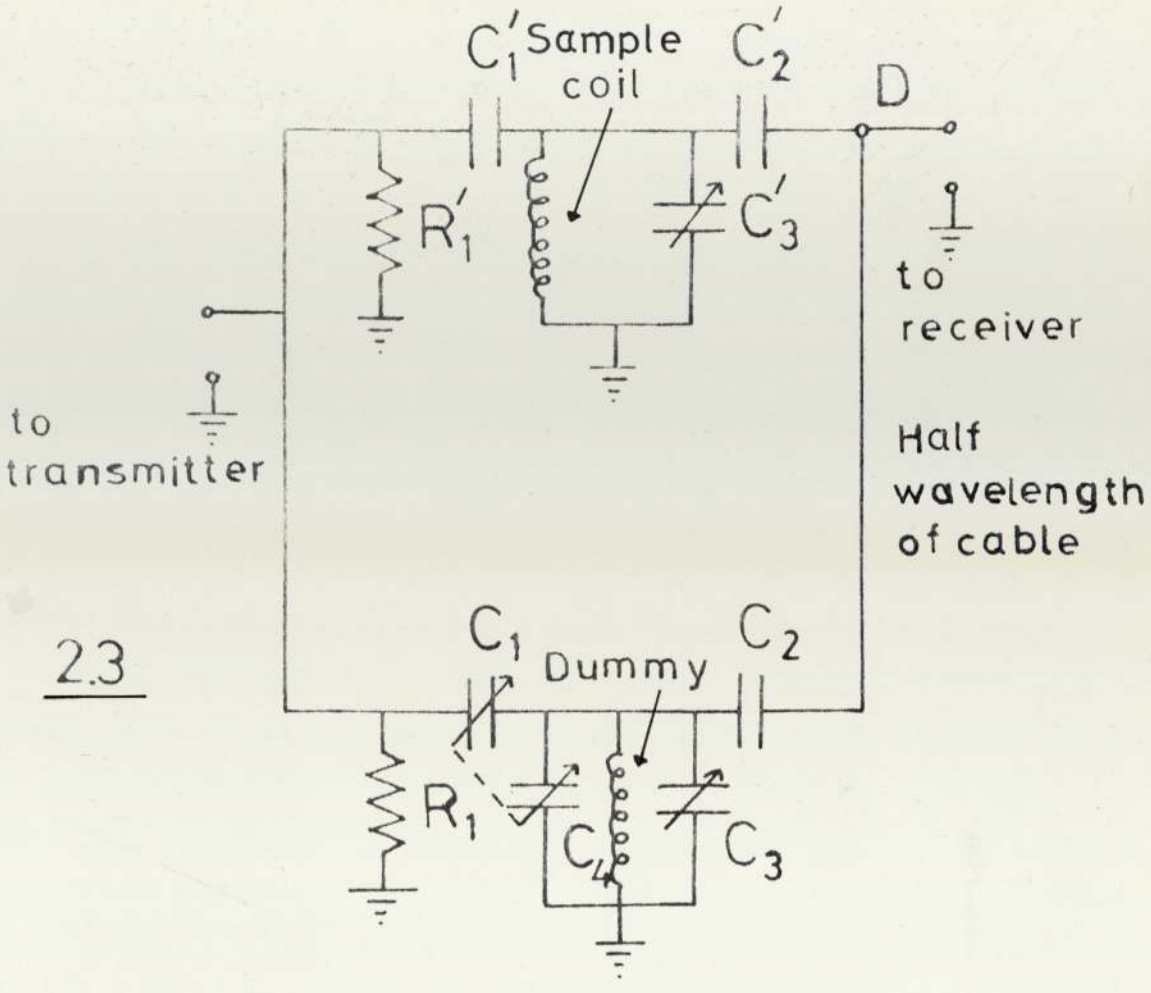
2.5 The Radiofrequency Oscillator

As this makes use of a novel system of operation it will be discussed in some detail. The radiofrequency signal for proton resonance studies is derived from a thermostatted quartz crystal-controlled oscillator operating at 5.000MHz with a high harmonic content. It is necessary both to thermostat the crystal and also to have a final automatic gain control in the circuit because the r.f. power fed to the probe must be both frequency stable (to 1 part in 10^8 or 10^9 per minute) and also at a constant level. The second harmonic (15MHz) is selected and further multiplied to 60.000 MHz. In order to obtain the very stable base line necessary for slow sweep rates the R10 spectrometer uses a single side-band (S.S.B.) mode of operation. A separate crystal-controlled oscillator (of 2kHz, which is multiplied to 4kHz in the phase sensitive detector) provides a signal which is used to amplitude modulate the main 60.000 MHz signal. Thus three signals are obtained, 59.996 MHz, the carrier at 60.000 MHz and 60.004 MHz; the lower side-band and the carrier frequencies are then rejected in the following manner. The single side-band unit consists of two suppressed carrier modulators, each of which is fed with the 60.000 MHz r.f. signal and with a 4kHz signal, the two 4kHz signals being $\frac{\pi}{2}$ rad out of phase with each other. In each unit the 60.000 MHz signal is split and fed via contraconducting diodes onto the primary winding of a transformer, the 4kHz signal being fed to the centre tap. The diodes are arranged so that they are alternatively conducting and cut-off by each half cycle of the 4kHz signal, thus

the carrier signal is always averaged to zero whilst both upper and lower side-bands remain. The lower side-band is suppressed as follows; the two 4kHz signals to the suppressed carrier modulators are $\frac{\pi}{2}$ rad out of phase with each other and by de-tuning the transformer primaries in the two halves of the circuit further $\pm \frac{\pi}{4}$ rad phase shifts are obtained relative to each other. Thus when the outputs of the two channels are recombined the components of the lower side-band subtract and those of the upper side-band add together thus leaving only the upper side-band signal. This signal is then fed, after further amplification and automatic gain control to the input of a twin-T bridge.

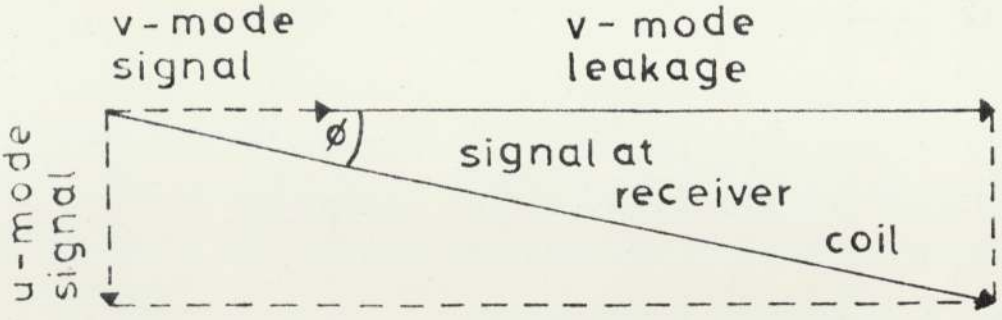
2.6 The Probe and Detector System

The probe assembly consists of the air turbine for sample spinning, the receiver coil, the linear sweep coils and the pre-amplifier. The critical part is the probe itself which is made from a non-magnetic material such as aluminium and must be very accurately located to ensure that the receiver coil is in the most homogeneous part of the main magnetic field. The r.f. coil is wound on a vertical glass former and consists of a few turns of copper wire. Purcell, Torrey and Pound[6] in their first n.m.r. experiment used a single coil method of detection in conjunction with a bridge circuit[18,35]. A bridge circuit is versatile and may be used in two ways: i) the very large transmitter signal may be balanced out and then the small absorption or dispersion signal appears as an out-of-balance e.m.f. across the bridge or ii) the bridge may be partially off-balanced so that some of the transmitter signal is leaked through in phase with the absorption mode signal so as to swamp the dispersion mode signal (figure 2.2). In high resolution work the twin-T bridge has been found to be particularly satisfactory[36] since, because of audio frequency modulation and phase sensitive detection, this enables the



2.3

Radio-frequency bridge circuit diagram.



2.2

Suppression of the u-mode (χ') component of the magnetization vector by adding in-phase leakage to the v-mode (χ'') component.

bridge to be completely balanced; any signal resulting in off balance of the bridge being detected in the a.f. circuit. A circuit of this type is used in the R10 spectrometer. The bridge circuit consists of two almost identical tuned LC circuits in parallel, connected to the same r.f. oscillator, one circuit containing the sample coil and the other a dummy coil (figure 2.3). An extra electrical half wave-length of cable is inserted in one circuit and the outputs are connected at point D and fed to a receiver circuit[18, 37]. This half wave-length of cable reverses the phase of the sample output with respect to the dummy output at point D, hence the voltages are subtracted. For a balanced circuit the only voltage which reaches the receiver would be that induced by the magnetic nuclei. This output is then fed (at 60.004 MHz) into a r.f. amplifier where it is amplified and combined with the carrier frequency (60.000MHz), thus giving a resultant 4kHz signal, the phase and amplitude of which contain complete information about both the absorption and dispersion components of the n.m.r. signal. This signal is then fed to an audio phase sensitive detector which is also supplied with a 4kHz reference signal (derived from that supplying the S.S.B. unit) whose phase may be varied by a phase rocking network to give a d.c. output of either the absorption or dispersion signal mode.

2.7 Spectral Presentation

The d.c. output from the phase sensitive detector is then fed to an oscilloscope or a pen recorder. The phase detector gives a very stable base-line because, until a nuclear signal is encountered, the steady d.c. signal is reduced to zero by means of a y-axis back-off system. The chart recorder is arranged such that its x-axis corresponds to the field sweep of the spectrometer. For the oscilloscope the field sweep is derived from the x-axis of the oscilloscope and for either recording mode the detector output is connected to the y-axis which

thus monitors the intensity of the n.m.r. signal. By passing the signal through a circuit containing a d.c. amplifier connected across a condenser, an integral of the absorption spectrum may be obtained.

2.8 Calibration of Spectra

The spectrometer uses pre-calibrated chart paper, but for the work described herein much more accuracy is required and it is necessary to use an audio side-band technique for measuring line frequencies. In the R10 the r.f. is modulated by a known frequency to give an inverted representation of the portion of the spectrum under observation displaced to either side of the original by the modulation frequency. Internal or external references may be used, and in either case by using a remote single sharp line from the reference and suitably varying the modulation frequency, a series of inverted sharp lines of accurately known frequency may be drawn around the portion of the spectrum of interest. The exact position of all lines relative to this reference may then be obtained by interpolation. The advantage of this method is that all changes in field drift are accounted for and it is not necessary to rely on the accuracy of the pre-calibrated charts. The frequencies used, derived from a Muirhead-Wigan D890-A oscillator, were checked to an accuracy of $\pm$ 0.01 Hz using a Venner 3336 counter.

2.9 The Variable Temperature Probe

The normal probe described above operates at the temperature of the magnet enclosure and elaborate precautions are taken to ensure that as little thermal disturbance as possible occurs in the region of the probe assembly. There are, however, many applications of variable temperature studies, and in particular such studies have been made in this thesis in order to obtain thermodynamic parameters of complex formation. This has required the use of the variable temperature probe, the particular model available with the R10 allowing any temperature from 173K to 473K to be readily obtained and automatically maintained; temperatures 40K

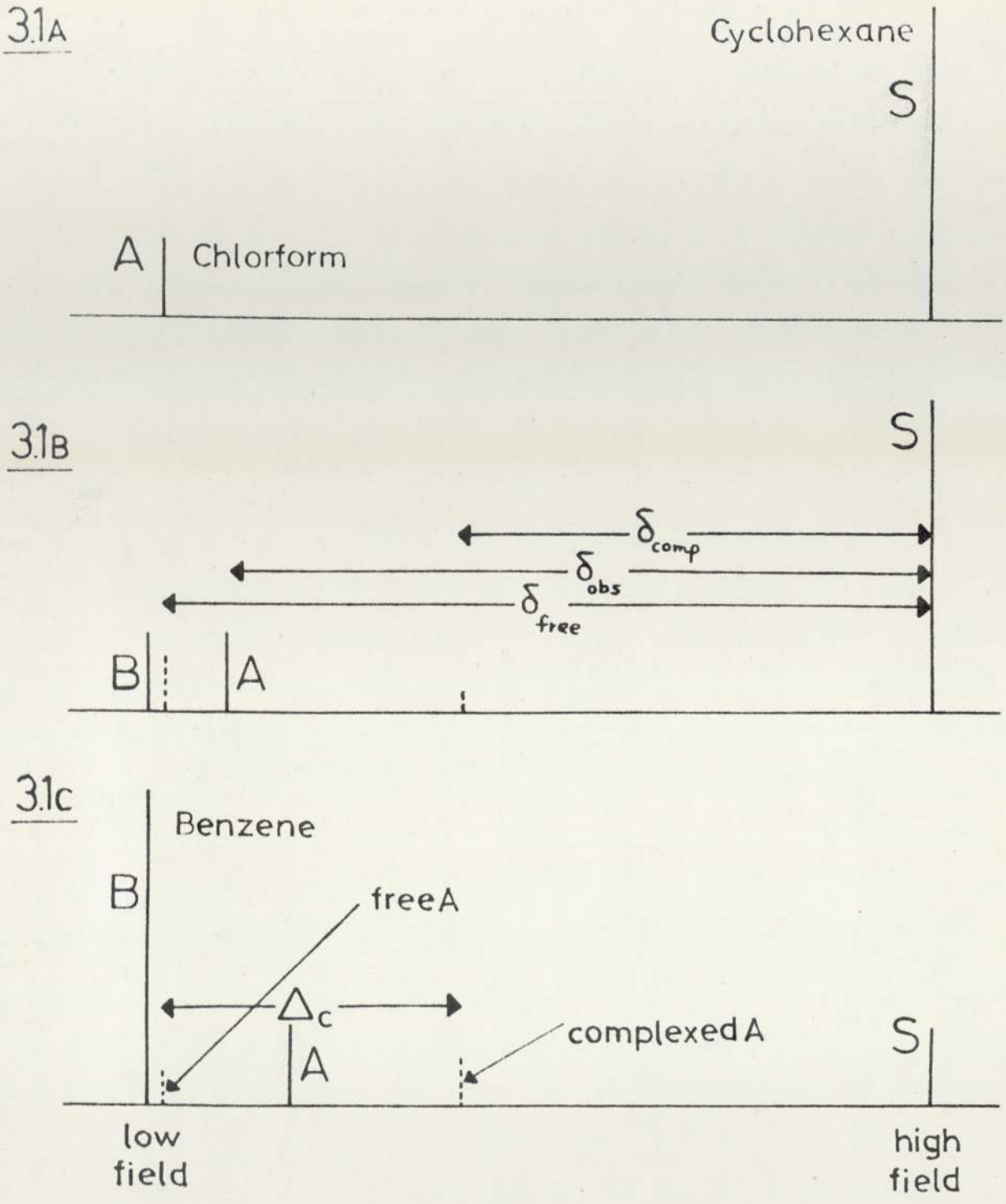
below the lower limit being obtained by careful manual control. The probe contains a small dewar flask which is positioned in the magnet gap and replaces the standard assembly, effectively insulating the magnet from the environment of the sample tube. This, in turn, is surrounded by a water jacket maintained at 306.6K which completes the thermal isolation of the magnet from the sample. To raise the temperature of the sample, air is drawn in through a large electrically heated copper block and passed to the probe, this minimizes any temperature gradients in the air stream. To reach temperatures below that of the magnet a supply of liquid nitrogen droplets and gas, boiled from the liquid, is mixed with dry air and the mixture heated, as above, to obtain the desired temperature. Within 5 mm of the r.f. coil is a platinum resistance thermometer which monitors the sample temperature in order than automatic correction, to the pre-set temperature, can be made. Very steady temperatures can be achieved repetitively with this device and this feature makes it particularly useful in the determination of thermodynamic data. In order to determine the temperature to 0.1K an independant copper-constantan thermocouple is incorporated in the probe and the e.m.f. it produces can be monitored by means of a potentiometer, calibrated by the use of a standard Weston cell, and reference to an e.m.f.-temperature table.

CHAPTER 3

A Critical Examination of the Thermodynamics of Complex Formation

3.1 Introduction

The formation of intermolecular complexes in solution has received considerable study; in particular the properties of charge-transfer complexes, hydrogen bonded species, and various dipole-induced dipole complexes have been examined by a number of instrumental methods[38-41]. These have included dipole moment studies[42-43] and a variety of spectroscopic techniques, especially ultra-violet[44-45], infra-red[46-48] and nuclear magnetic resonance[30-33,49-62]. In most cases the complexes are so short lived that the spectroscopic parameters are time-average values. From these it should be possible to obtain limiting values for the pure molecular complex (extinction coefficient in u.v. measurements and limiting chemical shift in n.m.r. studies) which should be independent of the method of determination and also of the choice of concentration scale. As an example, consider the dipole-induced dipole interaction between chloroform and benzene, in the inert solvent cyclohexane (see Chapter 7), as investigated by n.m.r. The relative concentrations must be varied in order to obtain an alteration in a measurable n.m.r. parameter, and it may be seen, from figures 3.1A, 3.1B and 3.1C, that as the ratio of benzene to chloroform increases so the chemical shift of chloroform with respect to cyclohexane is shifted markedly upfield, due to increasing formation of the complex. Since this shift variation is a direct function of the proportion of chloroform complexed (due to chemical exchange, see section 1.11) it is possible, by measuring this variation in a series of samples, to obtain an equilibrium quotient, K_i, for the interaction and also a limiting value for the complex shift, Δ_c (c referring to the complex), which should be independant of the concentration scale (i) used. It should be clearly understood that two assumptions must be made in order to facilitate this work. Firstly, it is assumed that only 1 : 1



Typical spectra for the three-component system Chloroform (A) - Benzene (B) - Cyclohexane (S); showing the variation in the chemical shift of chloroform with respect to cyclohexane (δ_{obs}) as the ratio of benzene to cyclohexane is varied. This is achieved by keeping the amount of chloroform fixed and varying the relative proportions of benzene and cyclohexane. The chemical shifts of chloroform in the free and complexed states (δ_{free} and δ_{comp}) are also shown together with the excess shielding in the complex ($\Delta_c = \delta_{comp} - \delta_{free}$).

complexes are formed between the solute (in this case chloroform) and the interacting solvent (benzene) and secondly, since there is no evidence for charge transfer complexes between the molecular types considered herein[31], it may be assumed that the π -electron circulation in the aromatic molecule is unchanged in the complex and hence the shielding of the solute can be used to calculate the geometry of the complex, as is discussed in section 5.8. Nevertheless, thermodynamic and spectroscopic properties of molecular complexes have been reported which do depend on the concentration units used to analyse the data[45,50,53]; furthermore, negative equilibrium quotients are known[52] as well as variations with the choice of inert solvent[50], (and reference material in n.m.r. studies[54,63]) and because of interactions with the solvent system[64-65]. Studies of molecular complexes at a single temperature should result in a value for the equilibrium quotient for the interaction, and also some indication of both the stoichiometry and stereochemistry of the complex[32,55]; measurements at a series of temperatures should lead to various theromodyanmic parameters (ΔH^o, ΔG^o and ΔS^o of complex formation), and variations in ΔH^o with temperature should indicate changes in the stoichiometry of the complex[32,66]. Such information is clearly important, but much of the literature data is obtained by inconsistent methods and may well be thermodynamically invalid. It has been suggested that only data which have been cross-checked by the use of an additional method should be considered to be reliable[53], but it would seem more important to decide upon a valid data evaluation procedure, a range of component concentration, and a concentration scale which gives the thermodynamically soundest and most consistent data.

Two major data evaluation techniques are applicable to n.m.r. studies, namely variants of the Benesi-Hildebrand (BH) procedure[44-45,67-68] which was originally derived for use in u-v studies and iterative

procedures based on the Creswell and Allred [62] method. The thermodynamics of these methods will be studied in detail, to try and decide under which experimental conditions these may be used correctly and further to attempt to find which is the most sensible concentration scale to use. The correlation of the thermodynamic parameters of complex formation with stereochemistry and stoichiometry of the complexes will also be considered. Other points to be examined include the variation of the free chemical shift of the solute (δ_{free}) with change of solvent, and the effect of varying the nature of the inert solvent on the values of K and Δ_c obtained. Two problems associated with these studies namely a) the method of referencing the chemical shifts and correcting for medium screening effects and b) the choice of a suitable inert solvent/reference for three component studies, will be considered in Chapters 4 and 7 and for the present discussion they will be assumed to have been resolved.

3.2 The Basic N.M.R. Measurements

In order to investigate the formation of weak molecular complexes of the type

$$A + B \rightleftharpoons A\cdots B$$

for which the equilibrium quotient, K, is given by

$$K = \frac{[AB]}{[A][B]} \qquad 3,1$$

in either a two component mixture or as a solution in an inert solvent, it is necessary to assume that some measurable property, P, of A is modified, by complex formation, from P_{free} to $P_{complex}$ and that the value of P actually observed is given by

$$P_{obs} = {}^{n_{AB}}/_{n_A} P_{complex} + {}^{n_A - n_{AB}}/_{n_A} P_{free} \qquad 3,2$$

where n_A is the total number of moles of A present initially and n_{AB} is the number of moles of complex at equilibrium. Equation 3,2 may be rearranged to give

$$P_{obs} = {}^{n_{AB}}/_{n_A}\left(P_{complex} - P_{free}\right) + P_{free} \qquad 3,3$$

which may be written in either of the forms

$$P_{obs} = {}^{n_{AB}}/_{n_A}\Delta_c + P_{free} \; ; \; \Delta_{obs} = P_{obs} - P_{free} = {}^{n_{AB}}/_{n_A}\Delta_c \qquad 3,4 - 3,5$$

It is not normally possible to measure the ratio $\frac{n_{AB}}{n_A}$ directly, hence Δ_c and the thermodynamic properties describing complex formation must be obtained either by the use of a suitable form of equation 3,5 and the graphical technique due originally to Benesi and Hildebrand[44] or by the use of equation 3,4 and the data processing method originally proposed by Creswell and Allred[62]. In n.m.r studies P_{free}, P_{obs} and $P_{complex}$ are equated with δ_{free}, δ_{obs} and δ_{comp} as shown in figure 3.1. In order to determine Δ_c (i.e. $\delta_{comp} - \delta_{free}$) it is necessary to vary the ratio of A to B as shown in this figure. This is normally done by using a three component mixture in which the concentration of A is kept constant and very small whilst the ratio of B to inert solvent S is varied to give the required variation in B/A. As the figures show, a series of δ_{obs} values (relative to cyclohexane) are then determined which may be used to obtain values for K and Δ_c.

3.3 The Benesi-Hildebrand (BH) Extrapolation Method of Determining Equilibrium Parameters

The BH method[44] depends upon an ability a) to construct an equilibrium quotient for the interaction $A + B \rightleftharpoons A\cdots B$, the value of which is independant of the concentration of B over an appreciable concentration range, and b) to use the quotient to obtain an expression for the fraction of A complexed, all terms in which are known. Neglecting activity coefficients K may be expressed either by

$$K_x = {}^{x_{AB\,eq}}/_{x_{A\,eq} \cdot x_{B\,eq}} \qquad 3,6$$

where $x_{AB\,eq}$, $x_{A\,eq}$ and $x_{B\,eq}$ are the mole fractions of AB, A and B at equilibrium, or by

$$K_c = {}^{C_{AB\,eq}}/_{C_{A\,eq} \cdot C_{B\,eq}} \qquad 3,7$$

where $C_{AB\ eq}$, $C_{A\ eq}$ and $C_{B\ eq}$ are the volume concentrations at equilibrium, and similarly for K_m on the molal concentration scale. This scale is not generally considered in much detail because the molality of B approaches infinity as x_B tends to unity, hence no meaningful equilibrium quotient can be obtained over this range. It should be noted that

$$K_c = K_x V_m \qquad 3,8$$

where V_m is the mean molar volume of the mixture in m^3. Considering the three component system, which is illustrated in figure 3.1, it is evident that at equilibrium, if the numbers of moles of A, B and S are denoted by the symbols n_A, n_B and n_S, and the numbers of moles of complex by n_{AB} then

$$K_x = \frac{n_{AB}(n_A + n_B + n_S - n_{AB})}{(n_A - n_{AB})(n_B - n_{AB})} \qquad 3,9$$

$$K_c = \frac{n_{AB} V_m}{(n_A - n_{AB})(n_B - n_{AB})} = \frac{n_{AB}\{(n_A - n_{AB})\bar{V}_A + (n_B - n_{AB})\bar{V}_B + n_S\bar{V}_S + n_{AB}\bar{V}_{AB}}{(n_A - n_{AB})(n_B - n_{AB})} \qquad 3,10$$

where $\bar{V}_A$, $\bar{V}_B$, $\bar{V}_S$ and $\bar{V}_{AB}$ are the partial molar volumes of A, B, S and AB. On assuming that n_A (and thus n_{AB}) is very small compared with the total number of moles in the system and also that n_{AB} is very much smaller than n_B (these assumptions have been criticised by Baker and Davis[69], but are necessary in order to obtain a plottable equation) it may be seen that

$$K_x \cong \frac{n_{AB}(n_B + n_S)}{(n_A - n_{AB})\, n_B} \quad , \quad K_c \cong \frac{n_{AB}(n_B\bar{V}_B + n_S\bar{V}_S)}{(n_A - n_{AB})\, n_B} \qquad 3,11 - 3,12$$

Thus

$$n_{AB}/n_A = \frac{K_x n_B}{n_B + n_S + K_x n_B} \quad , \quad n_{AB}/n_A = \frac{K_c n_B}{n_B\bar{V}_B + n_S\bar{V}_S + K_c n_B} \qquad 3,13 - 3,14$$

It then follows from equations 3,5 and 3,13 that

$$1/\Delta_{obs} \cong \frac{n_B + n_S}{n_B K_x \Delta_c} + 1/\Delta_c \cong \frac{1}{x_B K_x \Delta_c} + 1/\Delta_c \qquad 3,15$$

and from equations 3,5 and 3,14 that

$$1/\Delta_{obs} \cong \frac{n_B\bar{V}_B + n_S\bar{V}_S}{n_B K_c \Delta_c} + 1/\Delta_c \cong \frac{1}{C_B K_x \Delta_c} + 1/\Delta_c \qquad 3,16$$

equations 3,15 and 3,16 being analogous to the Benesi-Hildebrand equation. The BH method depends upon plotting $^1/\Delta_{obs}$ against $^{n_B+n_S}/n_B$ or $^1/C_B$, such a plot being independant of B. Should this requirement hold, the plots will be straight lines which are independant of $^{n_B}/n_B+n_S$ or C_B, hence values of K_x, K_c and Δ_c which are likewise independant of concentration should be obtained. In certain circumstances it may be better to follow the suggestion of Scott[45] and plot $^{n_B}/(n_{B+}n_S)\Delta_{obs}$ against $^{n_B}/n_B+n_S$ or $^{C_B}/\Delta_{obs}$ against C_B, which again yield straight lines which may be evaluated to give values for K_x, K_c and Δ_c. Such a procedure is particularly useful when $^{n_B}/n_B+n_S$ (or C_B) is very small, the normal BH plot then being difficult to use.

Trotter and Hanna[53] consider that if K is independant of concentration over a particular range on one scale, then over this range linear plots will be obtained from the BH procedure on all three concentration scales. Hence the linearity or otherwise of a BH plot on any particular concentration scale merely indicates that K is or is not independant of concentration over the plotted range, and is not a validification of the use of any particular scale. They show this for Benesi and Hildebrand's original data[44] for the interaction between iodine and benzene in n-heptane where BH plots on the mole fraction, molar and molal scales are all linear but the absorbancy of the complex is respectively 18,000, 13,500 and 9,800. It should be pointed out that the use of the BH plot over a wide concentration range, as is often advocated in the literature, will be shown to give misleading results and it will not therefore be considered until the thermodynamics of the procedure have been fully elucidated. This examination will cover all three concentration scales in order to decide which gives the most

reliable data evaluation; and it will also include a consideration of the possible concentration ranges over which the BH equation may be used.

3.4 The Thermodynamics of the BH Method

a) $n_A < n_B$ and $n_B \ll n_S$

The equilibrium quotient will obviously be independant of concentration if the concentrations of all the solute species A, B and AB are very small since the solution will then be ideal and the Henry activity coefficients of all species will be unity. It may be represented by

$$K = {}^{a_{AB}}/_{a_A \cdot a_B} \qquad 3,17$$

where $a_{AB} = \gamma^{II}_{AB}\, x_{AB}$ is the activity of species AB and similarly for a_A and a_B. Under the above conditions all the activity coefficients are unity hence

$$K = {}^{x_{AB}}/_{x_A \cdot x_B} \times {}^{\gamma^H_{AB}}/_{\gamma^H_A \cdot \gamma^H_B} = {}^{x_{AB}}/_{x_A \cdot x_B} \qquad 3,18$$

The chemical potentials of each species at equilibrium may then be represented by

$$\mu_i = \mu_i^{\ominus} + RT \ln x_i \qquad 3,19$$

where

$$\mu_i^{\ominus} = \lim_{x_i \to 0} (\mu_i - RT \ln x_i) \qquad 3,20$$

$$\mu_i = \mu_i^{c} + RT \ln C_i \qquad 3,21$$

where

$$\mu_i^{c} = \mu_i^{\ominus} + RT \ln V_m \qquad 3,22$$

V_m being the mean molar volume (in m^3) of the solution

$$\mu_i = \mu_i^{m} + RT \ln m_i \qquad 3,23$$

where

$$\mu_i^{m} = \mu_i^{\ominus} + RT \ln m_s \qquad 3,24$$

m_s being the molar mass (in kg) of species S. Statistical thermodynamics indicates that equations 3,19, 3,21 and 3,23 will be valid when each species i is so dilute that each molecule of i is completely surrounded by molecules of solvent S. If the concentrations of A, B and AB are so low that these equations hold then the equilibrium quotients may be written as

$$RT\ln K_x = RT\ln \frac{x_{AB\,eq}}{x_{A\,eq}\cdot x_{B\,eq}} = \mu_A^{\ominus} + \mu_B^{\ominus} - \mu_{AB}^{\ominus} = -\Delta G^{\ominus} \qquad 3,25$$

where $\Delta G^{\ominus}$ is the standard free energy change at infinite dilution, i.e. the free energy change resulting from the formation of one mole of complex (each molecule of which is completely surrounded by S) from one mole of A and one mole of B (both completely surrounded by S). It follows from equations 3,21 and 3,22 that

$$RT\ln K_c = \mu_A^c + \mu_B^c - \mu_{AB}^c = -\Delta G^{\ominus} + RT\ln V_m = -\Delta G^c \qquad 3,26$$

and from equations 3,23 and 3,24 that

$$RT\ln K_m = \mu_A^m + \mu_B^m - \mu_{AB}^m = -\Delta G^{\ominus} + RT\ln m_s = -\Delta G^m \qquad 3,27$$

Therefore even under these conditions K_c and K_m depend upon V_m and m_s respectively. Clearly the stipulated conditions that a) the concentration of A should be very much smaller than that of B (required for the BH approximation) and b) the concentration of B shall, notwithstanding a), be itself very small are not easy to satisfy and little work has been done under these conditions because of experimental difficulties. It is therefore necessary to consider the effect of adding rather more B to the system, in particular on equations 3,19, 3,21 and 3,23.

b) $n_A \ll n_B$ and $n_B < n_S$

If rather more B is present than in a) there will be only slight changes in the values of $\mu_A^{\ominus}$ and $\mu_{AB}^{\ominus}$ because there will now be a finite chance that some positions around the molecules are occupied by B, but μ_B will now be given by

$$\mu_B = \mu_B^{\theta} + RT\ln\gamma_B^H + RT\ln x_B \qquad 3,28$$

where γ_B^H is the Henry activity coefficient of B. K_x will, therefore, be given by

$$RT\ln K_x = \mu_A^{\theta\prime} - \mu_{AB}^{\theta\prime} + \mu_B^{\theta} + RT\ln\gamma_B^H \qquad 3,29$$

where $\mu_A^{\theta\prime}$ and $\mu_{AB}^{\theta\prime}$ are the new values of μ_A^{θ} and μ_{AB}^{θ}. Clearly K_x is no longer independant of the concentration of B. The effect on equations 3,26 and 3,27 is even more complicated, firstly V_m will no longer be independant of the concentration of B and will acquire a new value V_m' for each value of C_B so that K_c will be given by

$$RT\ln K_c = \mu_A^{\theta\prime} - \mu_{AB}^{\theta\prime} + \mu_B^{\theta} + RT\ln\gamma_B^H + RT\ln V_m' \qquad 3,30$$

and will obviously depend upon C_B. Secondly equation 3,24 will no longer hold and must be replaced by

$$\mu_i^m = \mu_i^{\theta} + RT\ln\frac{m_S}{1 + m_S m_B} \qquad 3,31$$

and will obviously depend on m_B, so that K_m will be given by

$$RT\ln K_m = \mu_A^{\theta\prime} - \mu_{AB}^{\theta\prime} + \mu_B^{\theta} + RT\ln\gamma_B^H + RT\ln\frac{m_S}{1 + m_S m_B} \qquad 3,32$$

It is quite feasible, however, that certain terms in equations 3,30 and 3,32 may cancel each other out and it is then possible that K_c and K_m may prove to be independant of the concentration of B over a greater concentration range than K_x. This would explain why Hanna et.al.[52] and Kuntz et. al.[50] have reported more consistent results when using equation 3,16 rather than equation 3,15, i.e. when $1/\Delta_{obs}$ is plotted against $1/C_B$ rather than against $^{n}B+^{n}S/n_B$. It is apparent, however, that thermodynamically the use of the BH procedure under the above concentration conditions is invalid; hence another, more suitable, concentration range is required for use in n.m.r. studies.

c) $n_B \gg n_S$ and $n_S \gg n_A$

The particular problem with n.m.r. investigations is that the method is very insensitive to small changes in the observable property, P_{obs},

hence sensible responses are only obtained when the concentrations of both reagents are 'high'. This is the case where complex formation between molecules such as halogenated alkanes and alkenes and benzene or the methylbenzenes has been studied by n.m.r. Such interactions have been investigated by a number of workers using a variety of experimental procedures,[31-33, 55-56, 59-62] and they have generally used solutions containing the complexing species A at about mole fraction 0.01 to 0.015 and mole fractions of B ranging from about 0.1 to 0.9. Self-consistent data was obtained using the Creswell and Allred[62] data evaluation method (section 3.9) but as this may equally well be criticised it is reasonable to see if the BH method may be used with the concentration of A at 0.01 m f and that of B at 0.9 m f. Initially only the effect of increasing the concentration of B will be examined. Consideration of the chemical potential of B indicates that if it may be supposed that the relatively small amounts of A and AB in the mixture have little effect on the fugacity of B (f_B) then μ_B will depend only on the relative amounts of B and S. Typical plots of f_B against n_B/n_B+n_S are shown in figures 3.2A and 3.2B; the chemical potential of B being described over the whole concentration range by

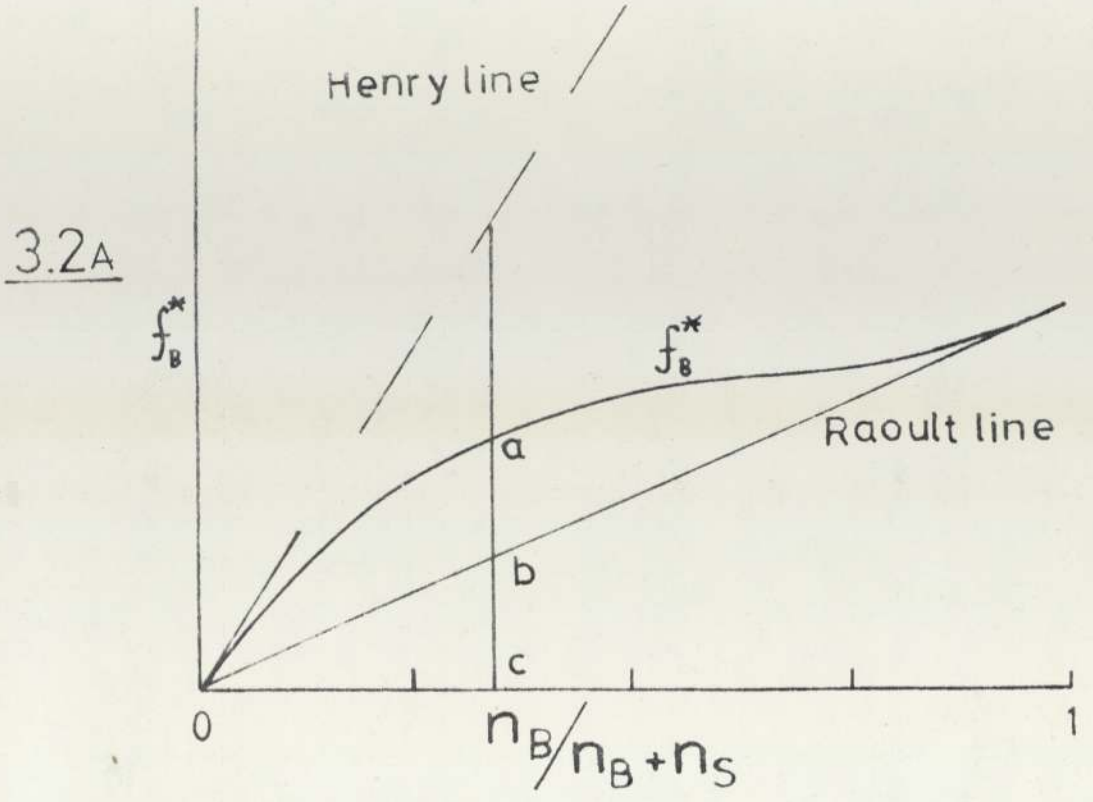
$$\mu_B = \mu_B^o + RT \ln \gamma_B^R x_B \qquad 3,33$$

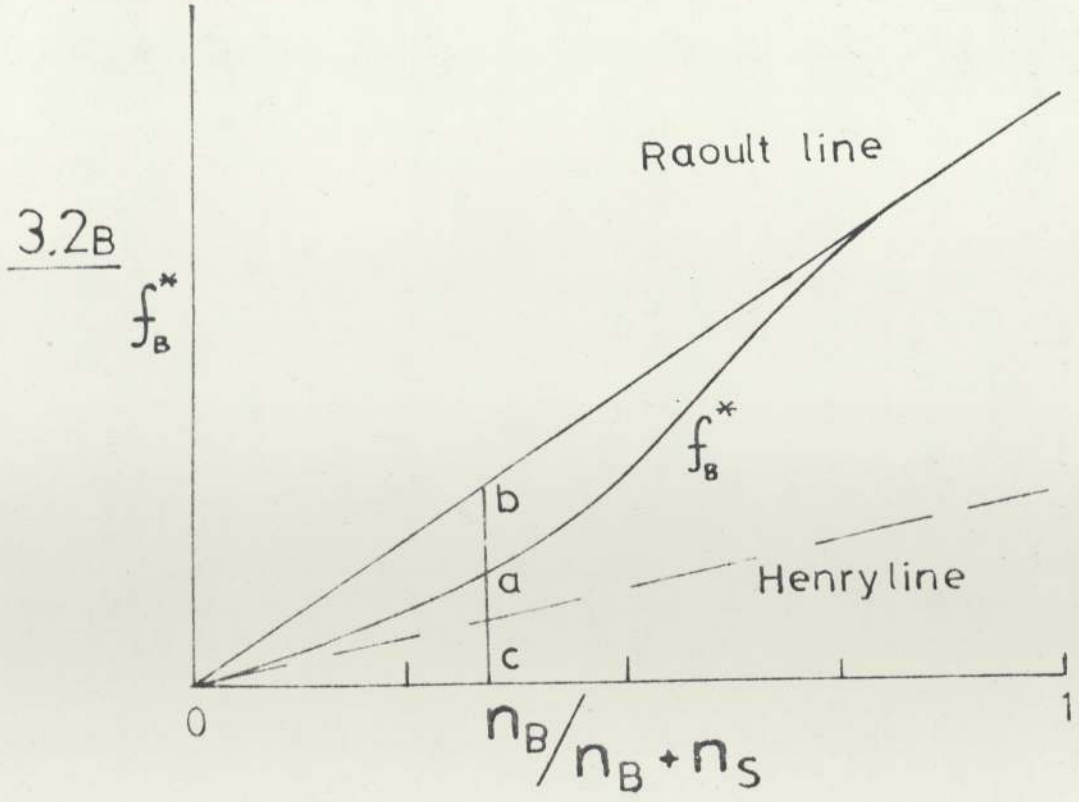
where μ_B^o is the chemical potential of pure B, x_B is the ratio n_B/n_B+n_S and γ_B^R is the Raoult activity coefficient and is given by the ratio ac/bc in the above figures. From both figures it is clear that as x_B approaches unity so does the value of γ_B^R; hence there are two concentration ranges over which reasonably accurate activity coefficient-free expressions for the chemical potential of B may be obtained,

a) the range over which x_B is small when

$$\mu_B = \mu_B^{\ominus} + RT \ln x_B \qquad 3,34$$

and which has already been discussed (section 3.4 a)) and b) the range





Typical plots of the fugacity of B (f_B^*) against the mole ratio of B to S (n_B/n_B+n_S). The Raoult activity coefficient is given by ac/bc.

over which x_B approaches unity when

$$\mu_B = \mu_B^o + RT \ln x_B \qquad 3,35$$

Because of the criticisms that have been levelled against the mole fraction scale[49-50] it is worth attempting to construct an equation for μ_B in terms of the molarity of B. Since x_B and C_B are given, assuming that n_A is negligibly small, by

$$x_B = n_B/n_B + n_S \; ; \; C_B = n_B/n_B\bar{V}_B + n_S\bar{V}_S \qquad 3,36 - 3,37$$

it follows that on combining equations 3,36 and 3,37

$$x_B = \frac{n_B\bar{V}_B + n_S\bar{V}_S}{n_B + n_S} C_B = V_{BS} C_B \qquad 3,38$$

where V_{BS} is the mean molar volume of the mixture of B and S. Thus it follows from equations 3,35 and 3,38 that as long as x_B is approaching unity, μ_B may be described by

$$\mu_B = \mu_B^o + RT \ln V_{BS} + RT \ln C_B = \mu_B^c + RT \ln C_B \qquad 3,39$$

It is evident from equation 3,39 that μ_B^c will only be independant of the ratio n_B/n_S if V_{BS} is independant of composition, which is true only if the molar volumes of B and S are the same. On the molality scale, as x_B approaches unity m_B approaches infinity, hence μ_B^m will not be considered. It is apparent therefore, that the BH procedure may be used, as n_B/n_B+n_S approaches unity, to give an equilibrium quotient which is activity coefficient free; by working on the mole fraction scale K_x and Δ_c are, from thermodynamic considerations, independant of S, but by working on the molarity scale K_c and Δ_c will depend both on the nature of S and also on the concentrations used in the determination of Δ_{obs} (excepting the special case when $\bar{V}_B = \bar{V}_S$).

d) $n_B \gg n_S$ and $n_S > n_A$

The other major problem associated with the BH method as applied to n.m.r. is that the concentration of A (the interacting solute) needs to be very much greater (it has usually been in the range 0.01 to 0.015 mf)

than Benesi and Hildebrand[44] used in their original work (where the concentration of iodine was 1.6×10^{-2} mol m^{-3}). This raises the problem that the assumption has been made that three-component thermodynamics are an extension of two-component thermodynamics. Such an assumption may well be valid when the concentration of A is extremely small, as has been the case in the above considerations. It is necessary to consider, therefore, whether the concentrations of A used still make the BH method valid. In fact a) do two-component thermodynamics hold at the above concentrations of A and hence b) does the equation

$$\mu_A = \mu_A^{\ominus} + RT \ln x_A \qquad 3,40$$

also remain valid and c) is the value of $\mu_A^{\ominus}$ independant of the composition of the environment? It is impossible to answer a) and b) and it must be assumed that these are true whilst at the same time attempting to keep the concentration of A to a minimum (it is suggested that for a solute containing only one proton, e.g. $CHCl_3$, this might be 0.005 mf). As regards c) it is possible to make the following predictions : If the forces between A and B and A and S are much the same it is expected that each molecule of A will be surrounded by some molecules of B (say b) and some molecules of S (say s) and then the value of $\mu_A^{\ominus}$ will be given by

$$\mu_A^{\ominus} = \mu_A^{o} + w = \mu_A^{o} + Lb\omega'_{A,B} + Ls\omega'_{A,S} \qquad 3,41$$

where L is Avogadro's constant and $w'_{A,B}$ and $w'_{A,S}$ are defined as

$$\omega'_{A,B} = \varepsilon_{A,B} - \tfrac{1}{2}\left(\varepsilon_{A,A} + \varepsilon_{B,B}\right) \qquad 3,42$$

$$\omega'_{A,S} = \varepsilon_{A,S} - \tfrac{1}{2}\left(\varepsilon_{A,A} + \varepsilon_{S,S}\right) \qquad 3,43$$

$\varepsilon_{A,B}$ and $\varepsilon_{A,S}$ are the energies required to bring together one molecule of A and B or A and S from an infinite separation and $\varepsilon_{A,A}$, $\varepsilon_{B,B}$ and $\varepsilon_{S,S}$ are the corresponding energies for like pairs. It is expected that the ratio b/s would be related to the ratio n_B/n_S and that the

value of $\mu_A^{\ominus}$ would be similarly dependant. However, the solutions of interest are rather different from this in that it is known that the forces between A and B are strong, but that S has been selected so that the forces between A and S are weak. Thus it is reasonable to suppose that, although when n_S is very much greater than n_B, molecules of A will still have as nearest neighbours some molecules of B and some of S (so that $\mu_A^{\ominus}$ will depend on the ratio $^{n}B/n_S$); when n_B is much greater than n_S molecules of B will preferentially cluster around A and exclude all molecules of S from the immediate vicinity. When this occurs

$$\mu_A^{\ominus} = \mu_A^{o} + zL\omega'_{A,B} \qquad 3,44$$

(where z is the number of molecules of B surrounding each molecule of A), and is in principle independant of $^{n}B/n_S$. However, equation 3,44 is approximate because as long as some molecules of S are present, these must dilute the solution and z cannot be constant as the ratio $^{n}B/n_S$ varies. To a first approximation $\mu_A^{\ominus}$ will be constant and μ_A may be described by equation 3,40, but more exactly the variation in z will mean that even on the mole fraction scale K_x and Δ_c will not be independant of the nature of S. If the expressions for μ_A are considered in terms of C_A and m_A then, from equations 3,21 and 3,22

$$\mu_A = \mu_A^{c} + RT\ln C_A \qquad 3,45$$

where

$$\mu_A^{c} = \mu_A^{\ominus} + RT\ln V_{BS} \qquad 3,46$$

V_{BS} being the molar volume of the mixture of B and S. μ_A^{c} will only be independant of the ratio $^{n}B/n_S$ if the molar volumes of B and S are the same. Similarly from equations 3,23 and 3,24

$$\mu_A = \mu_A^{m} + RT\ln m_A \qquad 3,47$$

where

$$\mu_A^{m} = \mu_A^{\ominus} + RT\ln m_{B,S} \qquad 3,48$$

where $m_{B,S}$ is the mean molar mass of the mixture of B and S and μ_A^{m} is independant of the ratio $^{n}B/n_S$ only if the molar masses of B and S are the same. It therefore appears that the mole fraction concentration scale is the correct one to use, but that the equilibrium quotient so obtained is

dependant on the nature of S due to the variation of z in equation 3,44. It also follows, from this equation, that the closer that the experimental data can be obtained to $x_B = 1.0$, the more likely will equation 3,44 be independant of the ratio $^nB/n_S$, and K_x and Δ_c will similarly become more independant of the nature of S. This variation with the nature of S will be discussed in detail in section 3.8c). Finally, it should be pointed out that small variations in the mole fraction of A, have been found experimentally to have little effect on the chemical shifts obtained. For example the shift of chloroform (at mole fractions varying from 0.02 to 0.0025) in pure cyclohexane has been investigated at 220MHz, and a dilution shift of approximately 1Hz (0.005 ppm) obtained. Thus over the maximum possible range of solute concentration actually used (say 0.005 to 0.01 mf) the shift (at 60MHz) would only be 0.15Hz which is within experimental error. Similar conclusions were obtained from dilution studies in pure benzene.

3.5 Criticism of the BH Method

Most literature use of the BH plot is open to severe censure because a wide concentration range is normally used whereas it has been shown in the previous section that the method is only valid over two very narrow ranges a) when n_A, n_{AB} and n_B are all very small and thus n_S large and b) when n_A and n_{AB} are very small and n_B very large. Furthermore the method has often been used on the molarity scale where the resultant K_c and Δ_c have been shown always to depend upon the concentration and nature of the inert solvent. A criticism that has been levelled against the BH method is that it leads to different values of K_x if different inert solvents are used[50] and evidence in favour of using equation 3,16 rather than equation 3,15 has been that the values of K_c obtained in different solvents are closer together than the corresponding K_x values. However, there is no thermodynamic justification for these conclusions and they probably result from applying the method over an invalid range. Certainly, Kuntz et al's[50]

conclusions, in which they state that the BH equation gives a good indication of the average properties of the complex especially when considered on the molarity scale, are not supported. Indeed, the value of K_x given by equation 3,29 (i.e. over the concentration range where n_B is of the same order of magnitude as n_S) would be expected to depend on the nature of S, simply because the values of $\mu_A^{\theta\prime}$, $\mu_{AB}^{\theta\prime}$, μ_B^{θ} and γ_B^{H} are so dependant. The fact that in some cases K_c appears to have much the same value in different solvents may be quite accidental since it is probably due to fortuitous cancelling of terms in equation 3,26. Because $K_c = K_x V_m$ it follows that values of K_c in two solvents i and j may be very close if K_{xi}/K_{xj} is much the same as V_{mi}/V_{mj}. It would, therefore, appear that criticisms levelled at the mole fraction equilibrium quotient, K_x, on the basis of BH evaluations of K_x and K_c in different solvents may be spurious. Clearly, in view of these comments, it is necessary to examine a system using different inert solvents over a thermodynamically valid concentration range and evaluate the data on both the mole fraction and molarity scales in order to provide confirmation of the thermodynamic predictions. This will be reported in section 3.8 c)

3.6 The Meaning of an Equilibrium Quotient at High Concentration of the Interacting Species

It is apparent from the comments in section 3.4 d) that a new equilibrium quotient K_x', given by

$$K_x' = x_{AB\,eq} / x_{A\,eq} \cdot x_{B\,eq} \qquad 3,49$$

is required which is reasonably independant of the value of x_B as long as a) the initial mole fraction of A is very small and b) x_B is close to unity. This quotient will not be the same as the infinite dilution equilibrium quotients, K_x and K_c, since from equations 3,35 and 3,40 it follows that

$$RT \ln K_x' = \mu_A^{\theta} - \mu_{AB}^{\theta} + \mu_B^{o} = -\Delta G^{*} \qquad 3,50$$

Therefore as x_B approaches unity it is expected that a plot of $^1/\Delta_{obs}$ against $^1/x_B$ (strictly against $^{n_B+n_S}/n_B$) should give a straight line. From the slope of the line and the value of the intercept at any value of $^1/x_B$, values of K_x' and Δ_c may be obtained. Likewise, a plot of $^1/\Delta_{obs}$ against $^1/C_B$ should give a straight line from which values of K_c' and Δ_c are obtained. This later procedure would be expected to be less reliable than the first but, due to cancelling of terms, the $^1/C_B$ plot could give a straight line over a larger concentration range. Comparison of equation 3,50 with equation 3,25 shows that equation 3,25 contains the term μ_B^θ i.e. the chemical potential of B at infinite dilution in S (hence each molecule of B is surrounded by molecules of S), whereas equation 3,50 contains the term μ_B^o which is the chemical potential of pure B (hence each molecule of B is entirely surrounded by other molecules of B). Also, the values of μ_A^θ and μ_{AB}^θ in the two equations are not the same; those in equation 3,25 refer to circumstances in which each molecule of A and AB is surrounded by molecules of S. Finally, it should be pointed out that neither ΔG^θ from equation 3,25 nor ΔG^* from equation 3,50 are the same as the free energy change which would result from the formation of L isolated molecules of AB from L isolated molecules of A and L isolated molecules of B.

3.7 Analysis of Experimental Data by the BH Method

Very few papers related to the problems surrounding complex formation as studied by n.m.r. give detailed experimental results and it is usually impossible to assess the concentration range of B or the concentration of A to which the results apply. However, Hanna and Ashbaugh have investigated the interaction between 7,7,8,8 - tetracyanoquinomethane (A) with various aromatics (B) in dioxan[52], using a constant concentration of A of 0.008 mol kg^{-1} and concentrations of B in the range 0.4 to 2.0 mol kg^{-1}. Their plot of $^1/\Delta_{obs}$ against $^1/m_B$

appears to give very good straight lines through the lowest values of m_B, but departures from these lines are evident at the highest values of m_B. In order to test the currently accepted ideas further, preliminary use is made of experimental data obtained by other workers[31-32,60-61,70] in this laboratory who have studied interactions between chloroform[31,70], ethylene chloride[60], methyl iodide[61] and vinylidine chloride[32] (A) with benzene (B) in the inert solvent cyclohexane (S). The data are far from satisfactory, consideration of the chloroform-benzene system shows that the mole fraction of A is probably too high (about 0.01 mf) and the highest value of $^{n}B/n_{B}+n_{S}$ is only 0.9042[70]. This latter point is very important and further measurements at higher $^{n}B/n_{B}+n_{S}$ values would be highly desirable. Nevertheless, the chloroform-benzene system was analysed[71] both by the normal BH plot[44] and secondly by the suggested Scott modification[45]. The first gave values of $^{1}/K'_{x}\Delta_{c}$ of 0.00843 and $^{1}/\Delta_{c}$ of 0.01094 and the second gave the figures 0.00845 and 0.01090. These results correspond to the values K'_{x} = 1.29 and Δ_{c} = 91.6 Hz. Similar plots were made of $^{1}/\Delta_{obs}$ against $^{1}/C_{B}$ and of $^{C}B/\Delta_{obs}$ against C_{B}, yielding an average value of K'_{c} = 1.6 x $10^{-4}m^{3}mol^{-1}$ and Δ_{c} = 81.0Hz. These results may be compared in the following way; if K'_{x} was the true equilibrium quotient corresponding to A and AB at infinite dilution in pure benzene and K'_{c} the corresponding quotient in terms of volume concentrations, then K'_{c}/K'_{x} would be equal to the molar volume of benzene (9.04 x $10^{-5}m^{3}mol^{-1}$). In fact the value of this ratio is 1.24 x $10^{-4}m^{3}mol^{-1}$, the discrepancy giving some indication of the errors in K_{x}' or K_{c}'. The other systems have been examined in less detail by this author and the results are recorded in table 3.1 for the mole fraction plot together with the literature values (by the Creswell and Allred method[62]. (see section 3.9)).

Table 3.1

Comparison between K_x' and Δ_c by a BH plot and K and Δ_c by the Creswell and Allred method (literature values).

Solute	highest value of $^nB/n_B+n_S$	B H method K_x'	B H method Δ_c (Hz)	literature value K	literature value Δ_c (Hz)
chloroform	0.9042	1.29	91.6 [71]	1.14	97.2 [70]
ethylene chloride	0.8910	1.50	57.4	0.96	70.2 [60]
methyl iodide	0.9028	0.72	73.3	0.70	74.4 [61]
vinylidene chloride	0.7910	0.65	62.9	0.50	75.6 [32]

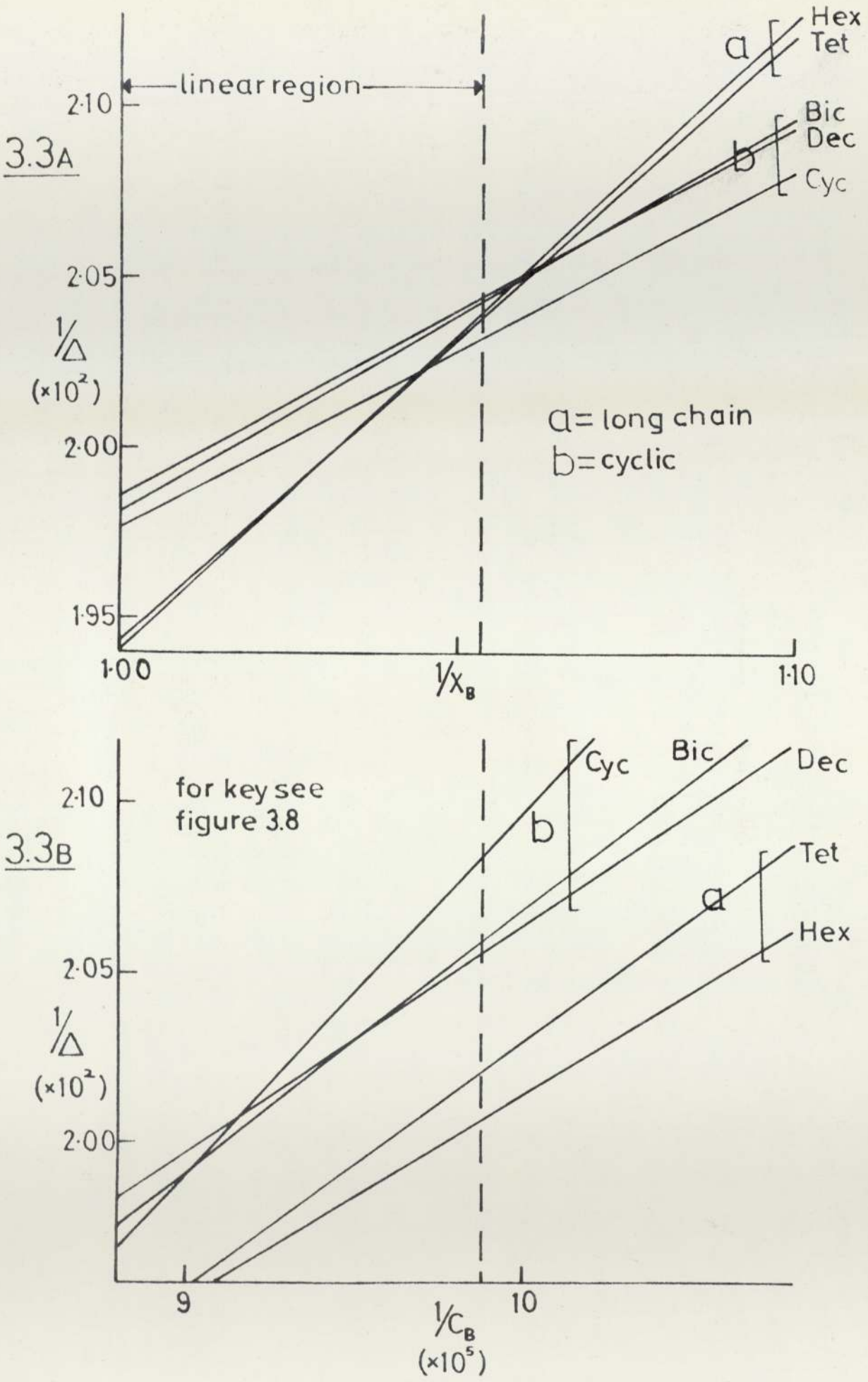
It is clear from the highest values of $^nB/n_B+n_S$ that the BH plots have been constructed over an invalid concentration range, and as a result curves are obtained. The results are included only to show that comparisons between the BH values and the Creswell and Allred values are certainly meaningless over such concentration ranges. They do, however, indicate that in carrying out a BH type evaluation, it is necessary to have experimental points of considerably higher mole fraction of B in order to be able to accurately construct the best line and hence obtain reliable values for K and Δ_c. It is equally obvious that it is necessary to examine a particular system much more thoroughly in order to illustrate the validity of the thermodynamic arguments in favour of the mole fraction scale over the molarity scale and also to substantiate the claim that the BH method is invalid over such a wide concentration range as has been used both above and by other workers.

3.8 Investigation of the Chloroform (A) - Benzene (B) Interaction in a Variety of Inert Solvents (S) by the BH Procedure

a) The Basic Measurements

In view of the problems encountered above, a critical examination has been made of the chloroform-benzene system over the concentration range for benzene (B) of 0.85 mf to 0.99 mf; the opportunity was taken to limit the chloroform (A) concentration to 0.005 mf and to utilize a number of inert solvents, of widely differing molar volumes, in order

to illustrate the respective variation of K_x' and K_c'. The solvents used were cyclohexane, cis-decalin, bicyclohexyl, tetradecane and hexadecane having molar volumes of 1.099, 1.560, 1.865, 2.633 and 2.962 x 10^{-4} m^3 mol^{-1} respectively. Cyclohexane was chosen because it is known to be inert (section 7.3) and the other cyclic solvents because of their similarity to cyclohexane. The two long chain solvents were chosen, because they were also believed to be inert and, moreover, because of their large molar volumes. The composition of the whole of each series is given in table 3.2 (the samples below $x_B = 0.85$ being required for the Creswell and Allred evaluation (section 3.9) and also to provide a value for δ_{free} of chloroform by means of a graphical extrapolation). The parameters used in the BH plots are recorded in table 3.3, where it will be noted that both the ratios $1/x_B$ and n_B+n_S/n_B are included. The mole fraction evaluation is initially performed using $1/x_B$ and the calculated results for K_x', K_c', Δ_c and K_c'/K_x' are given in table 3.4. It is immediately apparent that the mole fraction scale gives far more consistent results than the molarity scale for the three cyclic inert solvents (cyclohexane, cis-decalin and bicyclohexyl). Equally, for the two long-chain inert solvents (tetradecane and hexadecane) the results on the mole fraction scale are closer together than on the molarity scale, but they differ markedly from those obtained for the cyclic solvents; overall the molarity scale results are slightly more consistent but they definitely show a trend towards a higher K_c' value as the molar volume of the inert solvent increases. It is noticeable that both sets of results also show a marked dependance on the nature of S despite the prediction that as x_B tends to unity, the value of K_x' obtained should be independant of this parameter (section 3.4 c)). This point will be discussed in section 3.8c). The BH plots over the range $x_B = 0.90 - 1.00$, $C_B \cong 9.0 - 11.1 \times 10^3$ mol m^{-3} are shown in figures 3.3A and 3.3B for the five inert solvents, but it should be noted that the results reported in table 3.4 are obtained from a computer line-fitting procedure. This is used because of the



BII plots on the mole fraction and molarity scales for the chloroform-benzene interaction in various solvents.

Table 3.2

The composition of the systems studied in the investigation into the effect of the inert solvent on the parameters of complex formation; and the measured chemical shifts relative to benzene as the reference.

Sample No.	n_A ($\times 10^4$ mol)	n_B ($\times 10^2$ mol)	n_S ($\times 10^3$ mol)	x_B	C_B($\times 10^{-3}$ mol m^{-3})	δ_{obs} (Hz)
a) Chloroform (A) - Benzene (B) - Cyclohexane (S)*						
49/1	0.8980	0.2764	25.015	0.09918	0.919	16.82
49/2	1.1183	0.4160	12.589	0.24673	2.352	28.11
49/3	0.9307	0.6309	12.456	0.33456	3.169	32.66
49/4	1.0429	1.0271	12.489	0.44922	4.447	39.44
49/5	1.5295	1.5295	12.499	0.54729	5.526	43.58
49/6	0.9223	1.1813	6.2778	0.64966	6.692	47.50
49/7	0.7473	1.0956	3.3158	0.76367	8.052	51.44
49/6	1.1342	1.0018	1.7697	0.84179	9.032	53.91
49/9	0.9214	1.4353	1.2226	0.91609	9.974	55.44
49/10	0.8127	1.5673	1.0211	0.93429	10.208	56.15
49/11	0.8141	1.9047	1.0121	0.94571	10.355	56.50
49/12	0.9206	1.1952	0.5000	0.95281	10.460	56.48
49/13	0.9382	1.6172	0.4886	0.96519	10.619	57.14
49/14	0.8963	1.6314	0.3462	0.97398	10.734	57.23
49/15	0.9298	1.6520	0.2009	0.98252	10.849	57.38
49/17	0.8762	1.6585	0.0782	0.99010	10.949	57.72
b) Chloroform (A) - Benzene (B) - cis-Decalin (S)*						
48/1	1.0395	0.0332	12.014	0.02670	0.174	9.74
48/2	1.7884	0.0739	11.626	0.05889	0.390	11.99
48/3	1.8462	0.1081	10.123	0.09493	0.639	14.18
48/4	2.3664	0.3329	15.348	0.17602	1.226	20.10
48/5	1.4718	0.8516	15.378	0.35422	2.677	30.78
48/6	1.7482	1.2634	10.789	0.53539	4.450	39.91
48/7	0.9977	1.8207	6.1726	0.74377	6.958	48.82
48/8	2.1193	1.7794	3.1626	0.84059	8.398	52.57
48/9	1.3386	2.6686	2.8866	0.89832	9.288	54.48
48/10	0.9164	1.5661	1.4403	0.91089	9.506	55.22
48/11	1.4911	2.7866	1.4361	0.94617	10.113	56.29
48/12	1.7181	1.3646	0.1667	0.97579	10.716	57.06
48/13	1.1316	2.3797	0.1654	0.98842	10.888	57.55

Table 3.2 (cont'd.)

Sample No.	n_A ($\times 10^4$ mol)	n_B ($\times 10^2$ mol)	n_S ($\times 10^3$ mol)	x_B	C_B ($\times 10^{-3}$ mol m^{-3})	δ_{obs} (Hz)
c) Chloroform (A) - Benzene (B) - Bicyclohexyl (S)* ø						
52/1	1.8571	0.1845	12.2210	0.12527	0.751	16.00
52/2	0.7305	0.2562	9.8884	0.20456	1.233	20.54
52/3	1.2925	1.1188	11.3360	0.49388	3.587	36.60
52/4	1.4492	2.0291	8.0815	0.71153	6.107	46.75
52/5	1.5003	3.4625	8.5583	0.79904	7.389	49.73
52/6	1.5723	3.4936	5.0314	0.87069	8.612	53.21
52/7	1.8236	4.0791	3.8425	0.91019	9.361	54.71
52/8	1.8747	3.9754	2.8212	0.92964	9.755	55.34
52/9	0.9231	2.0955	1.0564	0.94803	10.137	55.99
52/10	1.0061	5.4165	1.5951	0.96964	10.578	56.85
52/11	1.9024	4.5961	0.8951	0.97693	10.769	57.31
52/12	1.6159	4.7219	0.4504	0.98720	10.995	57.43
d) Chloroform (A) - Benzene (B) - Tetradecane (S)+						
50/0	0.7707	0.6291	6.8746	0.08298	0.335	10.80
50/00	0.8687	0.2095	8.0296	0.20517	0.907	17.39
50/1	1.0136	0.5968	5.5071	0.51555	2.980	33.21
50/2	0.9625	1.2073	4.9314	0.70600	5.036	43.18
50/3	1.4333	2.3477	5.5879	0.80378	6.373	47.75
50/4	1.1493	2.1666	2.8296	0.88035	7.979	51.77
50/5	0.9767	1.1686	1.4296	0.88442	8.112	52.10
50/6	0.7849	0.9746	0.9981	0.90052	8.475	52.64
50/7	1.3721	1.6904	1.0472	0.93452	9.315	54.53
50/8	0.8695	1.1810	0.4651	0.95535	9.867	55.79
50/9	0.6274	2.5045	0.4812	0.97874	10.456	56.51
50/10	1.5271	2.9200	0.3840	0.98195	10.608	56.78
e) Chloroform (A) - Benzene (B) - Hexadecane (S)+						
51/0	1.1610	0.0871	6.0262	0.12423	0.465	12.85
51/00	0.6902	0.2316	4.3787	0.34241	1.532	23.02
51/1	1.8630	0.4359	4.0593	0.50658	2.705	31.65
51/2	1.4349	1.2444	5.3125	0.69518	4.592	41.79
51/3	1.3001	1.7766	4.2607	0.80184	6.172	47.36
51/4	1.9652	3.0950	4.2078	0.87542	7.624	51.26
51/5	0.8486	1.5088	1.5856	0.90032	8.199	52.57
51/16	1.2063	1.4487	1.1769	0.91780	8.686	53.59
51/7	0.8670	1.2880	0.7595	0.93835	9.225	54.73
51/8	0.8921	1.8103	0.6152	0.96255	9.916	55.92
51/9	0.8435	1.4534	0.3498	0.97099	10.206	56.32
51/10	1.0245	2.6421	0.3116	0.98457	10.617	56.98

Table 3.3

Parameters used in the BH plots on the mole fraction and molarity scales.

Sample No.	$1/x_B$	$\frac{n_B+n_S}{n_B}$	$\Delta = \delta_{obs} - \delta_{free}$ (Hz)	$1/\Delta$ ($\times 10^2$)	$1/C_B$ ($\times 10^5$ m^3 mol^{-1})	$\Delta = \delta_{obs} - \delta_{free}$ (Hz)	$1/\Delta$ ($\times 10^2$)
a) Chloroform (A) - Benzene (B) - Cyclohexane (S)*							
49/9	1.09160	1.08518	48.16	2.0764	10.026	48.24	2.0730
49/10	1.07033	1.06516	48.76	2.0509	9.796	48.71	2.0530
49/11	1.05741	1.05314	49.11	2.0362	9.657	49.01	2.0404
49/12	1.04953	1.04183	49.31	2.0208	9.559	49.23	2.0313
49/13	1.03607	1.03022	49.67	2.0133	9.417	49.56	2.0178
49/14	1.02672	1.02122	49.90	2.0040	9.316	49.80	2.0080
49/15	1.01779	1.01216	50.11	1.9956	9.217	50.04	1.9984
49/17	1.01000	1.00416	50.31	1.9877	9.133	50.26	1.9897
b) Chloroform (A) - Benzene (B) - cis-Decalin (S)*							
48/9	1.11319	1.10817	47.12	2.1222	10.767	47.06	2.1249
48/10	1.09782	1.09197	47.61	2.1004	10.520	47.62	2.1000
48/11	1.05689	1.05154	48.81	2.0488	9.888	48.89	2.0454
48/12	1.02481	1.01232	49.65	2.0141	9.332	49.80	2.0080
48/13	1.01172	1.00695	49.99	2.0003	9.184	50.02	1.9992
c) Chloroform (A) - Benzene (B) - Bicyclohexyl (S)* ø							
52/7	1.09867	1.09420	47.13	2.1218	10.683	47.26	2.1160
52/8	1.07569	1.07165	48.00	2.0833	10.251	41.98	2.0842
52/9	1.05482	1.05041	48.75	2.0513	9.865	48.65	2.0555
52/10	1.03131	1.02945	49.53	2.0190	9.454	49.38	2.0251
52/11	1.02361	1.01947	49.77	2.0092	9.286	49.68	2.0129
52/12	1.01297	1.00954	50.07	1.9972	9.095	50.02	1.9992
d) Chloroform (A) - Benzene (B) - Tetradecane (S)+							
50/4	1.13591	1.13060	45.57	2.1944	12.532	45.80	2.1834
50/5	1.13068	1.12233	45.90	2.1786	12.328	46.05	2.1716
50/6	1.11046	1.10241	46.44	2.1533	11.800	46.65	2.1436
50/7	1.07007	1.06195	48.33	2.0691	10.735	48.35	2.0683
50/8	1.04674	1.03938	49.37	2.0255	10.135	49.29	2.0288
50/9	1.02172	1.01921	50.46	1.9818	9.563	50.31	1.9877
50/10	1.01838	1.01315	50.60	1.9763	9.427	50.57	1.9775

Table 3.3 (cont'd.)

Sample No.	$1/x_B$	$\frac{n_B+n_S}{n_B}$	$\Delta\delta_{obs}-\delta_{free}$ (Hz)	$1/\Delta$ ($\times 10^2$)	$1/C_B$ ($\times 10^5$ m^3 mol^{-1})	$\Delta\delta_{obs}-\delta_{free}$ (Hz)	$1/\Delta$ ($\times 10^2$)
e) Chloroform (A) - Benzene (B) - Hexadecane (S)$^+$							
51/4	1.14231	1.13767	45.06	2.2193	13.117	45.10	2.2173
51/5	1.11071	1.10509	46.37	2.1566	12.197	46.45	2.1529
51/6	1.08956	1.08123	47.38	2.1106	11.513	47.50	2.1053
51/7	1.06570	1.05896	48.50	2.0619	10.840	48.52	2.0610
51/8	1.03891	1.03399	49.73	2.0109	10.085	49.72	2.0113
51/9	1.02987	1.02407	50.12	1.9952	9.798	50.17	1.9932
51/10	1.01567	1.01180	50.76	1.9701	9.419	50.76	1.9701

* δ_{free} is found to be 7.40 Hz)
+ δ_{free} is found to be 6.20 Hz) by a graphical extrapolation
as explained in section 3.8 b)

ø In the calculation of the results it was assumed that the cis-isomer of bicyclohexyl had been used and the values of V_S and V_S/V_B given in table 3.6 are therefore relevant to this isomer. The corresponding values for the trans-isomer are $V_S = 19.3552 \times 10^{-5}$ m^3 mol^{-1}, $V_S/V_B = 2.1418$, these being very similar to those for the cis-isomer. If a mixture of isomers has in fact been used this will only have a slight effect on the values of K_x', K_x^{CA} and Δ_c^x given in tables 3.8, 3.10 and on page 76b.

Table 3.4

Results of the BH plots on the mole fraction (both using $1/x_B$ (1) and n_B+n_S/n_B (2)) and molarity concentration scales for the Chloroform-Benzene interaction. *

Solvent System	K_x' (1)	K_x' (2)	K_{c4}' ($\times 10^4$ m^{3}mol^{-1})	K_c'/K_x' ($\times 10^4$m^{3}mol^{-1}) (1)	K_c'/K_x' ($\times 10^4$m^{3}mol^{-1}) (2)	Δ_c^x (Hz) (1)	Δ_c^x (Hz) (2)	Δ_c^c (Hz)
Cyclohexane	1.382	1.125	1.017	0.74	0.90	87.1	95.2	95.4
cis-Decalin	0.911	1.288	3.110	3.41	2.41	105.6	88.9	64.8
Bicyclohexyl	0.951	0.890	1.752	1.84	1.97	103.5	106.9	76.1
Tetradecane	0.332	0.072	1.666	5.02	23.14	205.7	660.0	79.2
Hexadecane	0.330	0.046	2.288	6.93	49.74	206.8	1179.7	71.7

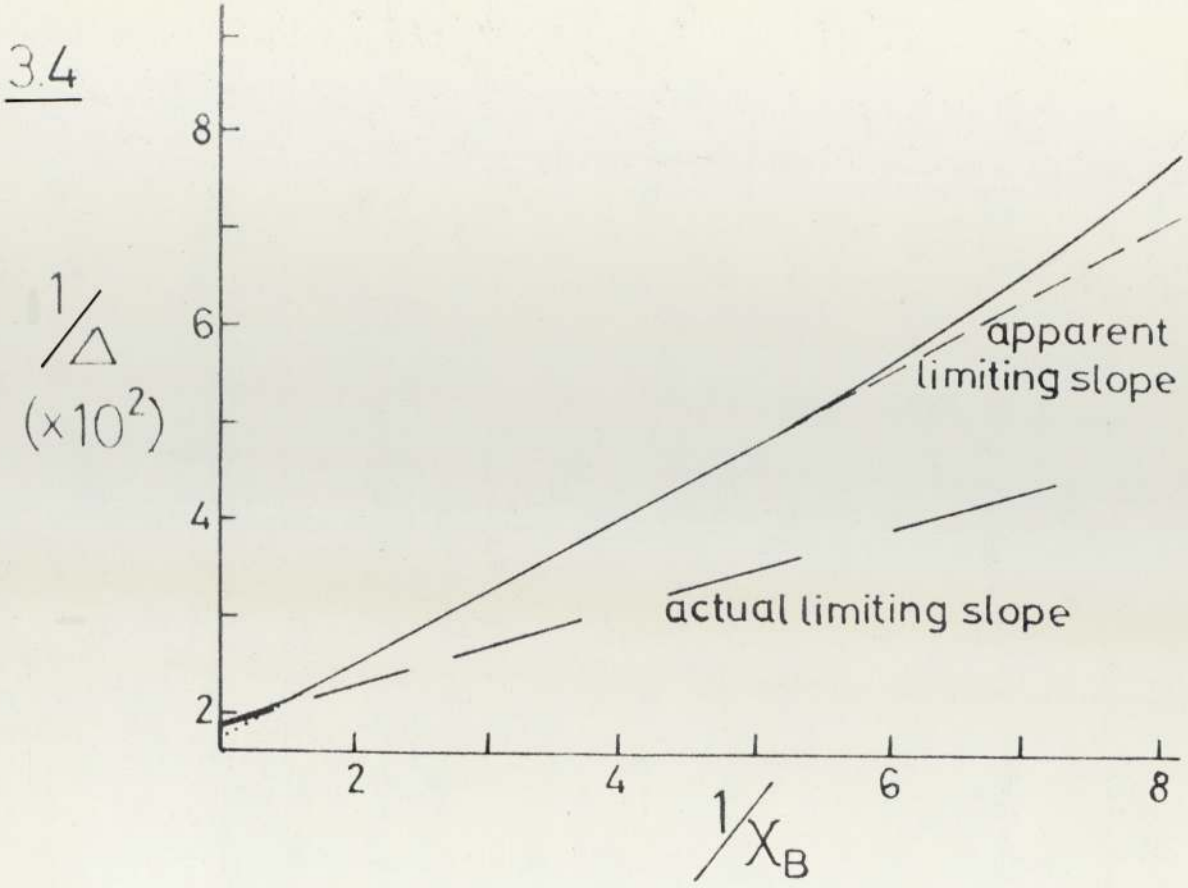
* The validity of the experimental procedure used to evaluate the results given in this table, and in table 3.8, is discussed further in an addendum (see page 76a).

difficulty in visually deciding on the linearity or otherwise of the $^1/\Delta_{obs}$ against $^1/x_B$ (or $^1/C_B$) plot, and hence in determining the slope of the line at any point. The points are fitted to a quadratic equation which is differentiated to provide the slope of the tangent at any value of x_B or C_B. Whilst the plots shown in figures 3.3A and 3.3B appear to be reasonably linear over the range x_B = 0.95 - 1.00, C_B = 10 - 11.06x10^3 mol m^{-3}, slight curves are indicated by the computer evaluation. This serves to emphasize the serious errors possible using a purely visual 'best-line' technique. Figures 3.4 and 3.5 show typical BH plots over a much larger concentration range (more nearly that used in the literature) and it is immediately apparent that such plots lead to grossly erroneous conclusions about the linearity, slope and intercept at the point x_B = 1.00 (or C_B = 11.06x10^3 mol m^{-3}). Values of K_x' and Δ_c are also recorded in table 3.4 from the BH plot of $^1/\Delta_{obs}$ against $^{n_B+n_S}/n_B$ (as is in fact required by the BH approximation), and it will be seen that they are little different from those obtained from a $^1/x_B$ plot. Therefore, it can be seen that although the BH evaluation was performed over the correct concentration range the results are extremely poor and it is necessary to consider if certain factors have been neglected. Two which are immediately apparent are i) the fact that δ_{free} has been seen to vary with solvent, hence the determination of Δ at high aromatic concentrations using a value of δ_{free} obtained in pure inert solvent is incorrect and ii) the results indicate that the nature of S may be important even on the mole fraction scale. These factors will be considered separately.

b) The Variation of δ_{free} of Chloroform With Change of Solvent

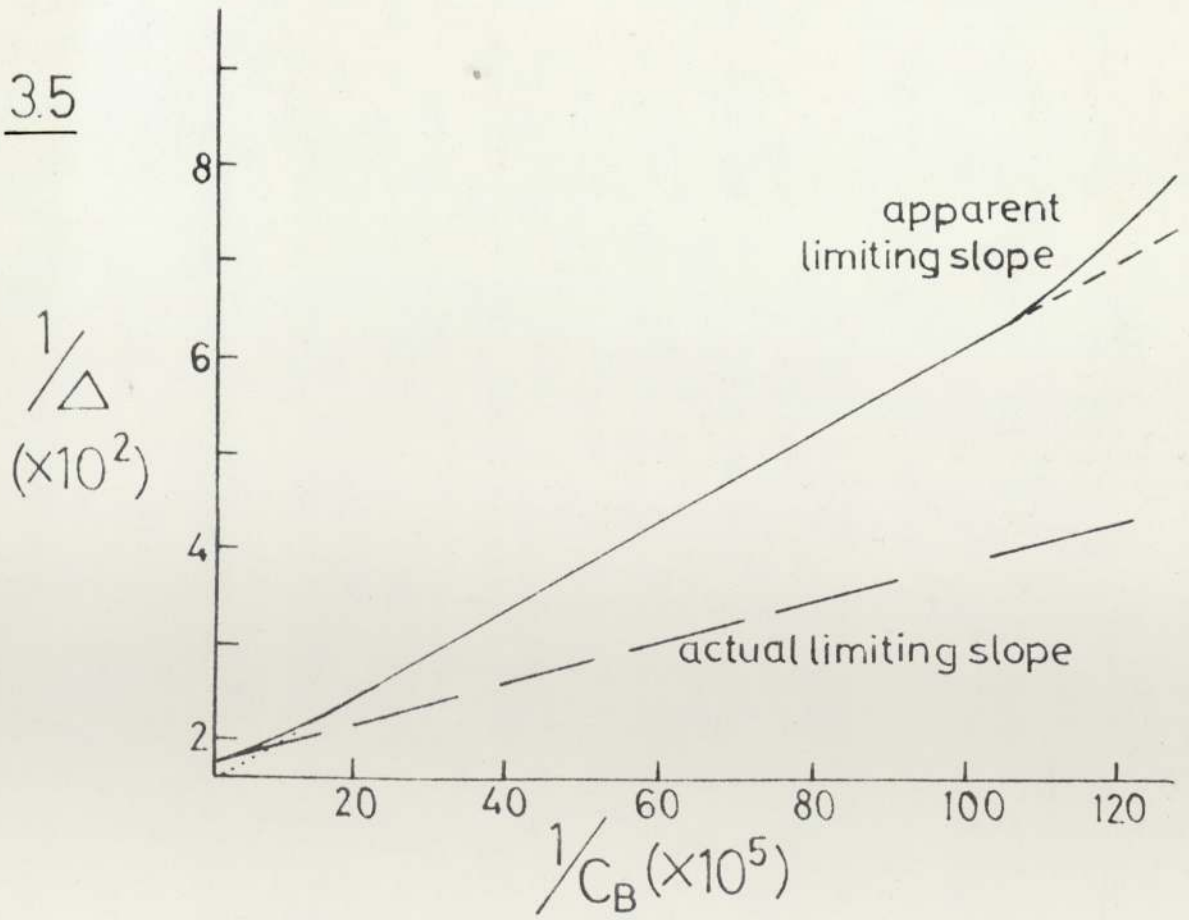
It is apparent from plots of the experimentally observed shifts (recorded in table 3.2) against either x_B or C_B that the free chemical shift of chloroform in the inert solvents (δ_{free}) is dependant on the nature of the solvent. For the solvents cyclohexane, cis-decalin and

3.4



Typical literature BH type plot showing how errors may originate - mf scale.

3.5



Typical literature BH type plot showing how errors may originate - molarity scale, (on same horizontal scale as 3.4).

bicyclohexyl the δ_{free} value is 7.4 Hz, whereas in tetradecane and hexadecane it is 6.2 Hz. It therefore follows that the chemical shift of chloroform in pure benzene may well be different and hence the use, in the previous section, of a single value to represent δ_{free} throughout a concentration series is strictly incorrect. This is a point which has been neglected in all previous work although it has been recognized for some time in this laboratory. Assuming that the variation of δ_{free} with solvent is a mole fraction function, it must be possible to include this parameter when deriving an expression for the variation of δ_{obs} with constituent mole fraction. The total screening experienced by the solute in any situation is

$$\sigma_A^{TOT} = \frac{n_{AB}}{n_A}\left(\sigma_A + \sigma_C + x_B\sigma_A^B + x_S\sigma_A^S\right) + \frac{n_A - n_{AB}}{n_A}\left(\sigma_A + x_B\sigma_A^B + x_S\sigma_A^S\right) \quad 3,51$$

where σ_A is the basic screening of isolated A, σ_C is the fully complexed screening of A and σ_A^B and σ_A^S are the screening effects on A due to solvents B and S, it being assumed that the effects of B and S on the complexed and free A are the same. Likewise the screening experienced by the aromatic solvent (which is acting as reference) is given by

$$\sigma_B^{TOT} = \sigma_B + x_B\sigma_B^B + x_S\sigma_B^S \quad 3,52$$

Combination of equations 3,51 and 3,52 gives

$$\delta_{obs} = \sigma_A^{TOT} - \sigma_B^{TOT} = \sigma_A - \sigma_B + \frac{n_{AB}}{n_A}\sigma_C + x_B\left(\sigma_A^B - \sigma_B^B\right) + x_S\left(\sigma_A^S - \sigma_B^S\right) \quad 3,53$$

which may be written in the form

$$\delta_{obs} = \delta'_{free} + \frac{n_{AB}}{n_A}\Delta_C + x_B E + x_S F \quad 3,54$$

where Δ_C has been equated with δ_C, δ'_{free} is the chemical shift of A with respect to B in the absence of any solvent effects, E is the nett effect of the aromatic solvent on δ'_{free} and F similarly for the inert solvent. Because $x_B = 1 - x_S$, (i.e. the amount of solute is ignored) equation 3,54 may be written in the following form

$$\Delta_{obs} = \delta_{obs} - \left(\delta'_{free} + F\right) = \frac{n_{AB}}{n_A}\Delta_C + x_B q \quad 3,55$$

since $\delta'_{free} + F$ is the measured free shift of A in the inert solvent (obtained by extrapolation) and η is the variation in the solvent shift in changing from pure aromatic to pure inert, i.e. E - F. Assuming that η may be measured it is possible to rewrite equation 3,55 in the BH form:

$$1/(\Delta_{obs} - x_B\eta) = 1/x_B K\Delta_c + 1/\Delta_c \qquad 3,56$$

Hence, revised values of K and Δ_c may be obtained. It will be shown in section 7.3 that cyclohexane is inert and also that benzene may be considered as an excellent probe since its shift is little affected by any interactions in which it may take part. Since for any system $\delta'_{free} + F$ is a measurable quantity it is only necessary to obtain the value of η. A convenient way of achieving this for the benzene-cyclohexane solvent system is to measure the shift between these two species in a series of samples of differing mole fraction and to extrapolate the resultant line to obtain the shifts corresponding to infinitely dilute benzene in cyclohexane and also infinitely dilute cyclohexane in benzene. This may be done by reference to figure 7.4 from which subtraction of these two values leads to a value for η^{BZ-CY} (=E-F) of $\sim$ - 2Hz. It should be noted that the experimental line is not quite straight, but as a first approximation η may be taken to be linear with mole fraction. Furthermore, cyclohexane and benzene have been used as respective solutes at infinite dilution in the other rather than chloroform and it is obvious that dispersion forces and reaction fields will differ in the two cases; nevertheless the method offers a reasonable value for η. It follows therefore that the δ_{free} values of chloroform are 7.4 Hz in cyclohexane, cis-decalin and bicyclohexyl and 6.2 Hz in tetradecane and hexadecane; this yields a value of 5.4 Hz for $\delta'_{free} + E$ (i.e. the chemical shift of infinitely dilute chloroform in benzene with respect to benzene) and a value for η^{BZ-TET}_{BZ-HEX} of - 0.8 Hz. Using these values of η the mole fraction BH

plots were re-evaluated (using the ratio $^{n}B/n_{B}+n_{S}$). The values of $^{1}/\Delta$ used are obtained by the use of the left hand side of equation 3,56 and the data in table 3.3; the results are recorded in table 3.5.

Table 3.5

Results of the BH plots on the molefraction scale (using the ratio $^{n}B/n_{B}+n_{S}$), allowance being made for the variation δ_{free} with solvent composition, for the Chloroform-Benzene interaction.

Solvent System	Cyclohexane	cis-Decalin	Bicyclohexyl	Tetradecane	Hexadecane
K_x'	1.042	0.708	0.805	0.121	0.050
Δ_c (Hz)	102.7	125.8	117.3	380.1	1104.9

It may be seen, by comparison with the results designated (2) in table 3.4, that making allowance for the variation of δ_{free} with solvent composition has little effect on the values of K_x' and Δ_c. It is therefore necessary to consider the nature of S.

c) The Effect of the Nature of the Inert Solvent

It can be seen from tables 3.4 and 3.5 that the mole fraction scale results are considerably dependant on the nature of S despite the thermodynamic predictions to the contrary. Hence it seems reasonable to postulate that the effect may be a statistical one, i.e. dependant on the chance the solute has of interacting with either an active or inactive solvent molecule. Basically the effect of the inert solvent should simply be to dilute the amount of aromatic in relation to the amount of solute and hence alter the chance of forming a complex, thereby changing the observed chemical shift. Ideally therefore the inert solvent should have all the properties of the aromatic except for the π-system (i.e. should be the same size and shape, and have the same molar volume). Therefore, if all the molecules with which a solute comes into contact

during the time of the n.m.r. experiment are considered, dilution with a truly inert solvent could be illustrated by figure 3.6. In this figure, one aromatic molecule has been replaced by one inert solvent molecule. In practice the size, shape and molar volume of the inert solvents used vary markedly, cyclohexane is indeed rather similar to benzene in these respects but not so hexadecane, for example. The molar volumes at 306.6K (except for bicyclohexyl for which data are only available at 293K) are recorded in table 3.6 for benzene (V_B) and

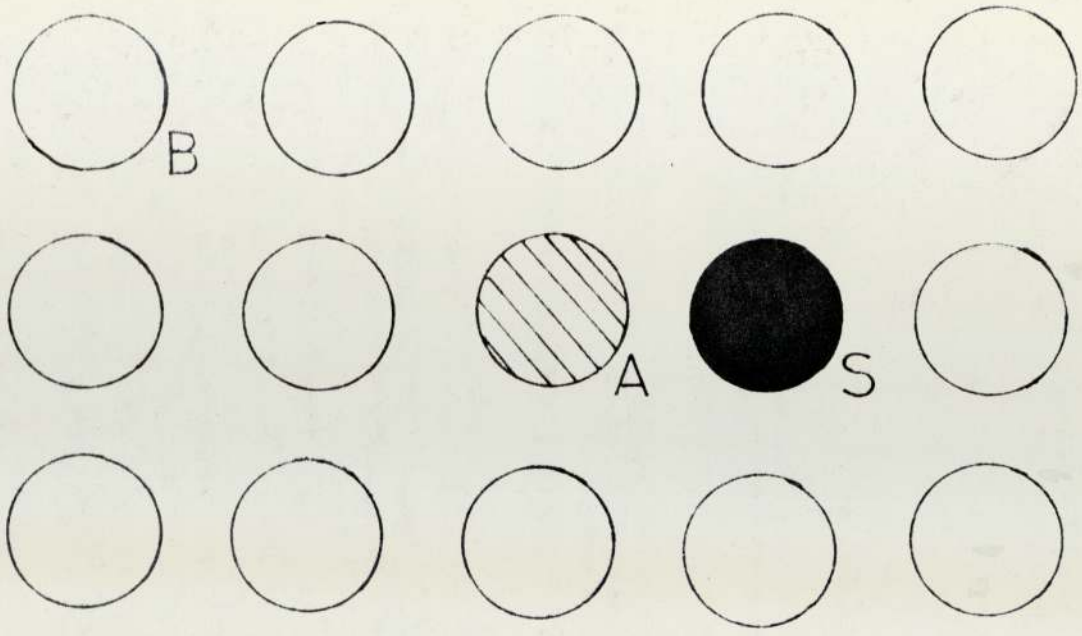
Table 3.6

Molar volumes (V_B and V_S) and the ratio V_S/V_B for a number of solvents at 306.6K (* 293K).

Solvent	V_B or V_S ($\times 10^5 m^3 mol^{-1}$)	V_S/V_B
Benzene	9.0369	-
Cyclohexane	10.9901	1.2162
cis-Decalin	15.5956	1.7258
Bicyclohexyl	18.6508 *	2.0980 *
Tetradecane	26.3298	2.9136
Hexadecane	29.6128	3.2769

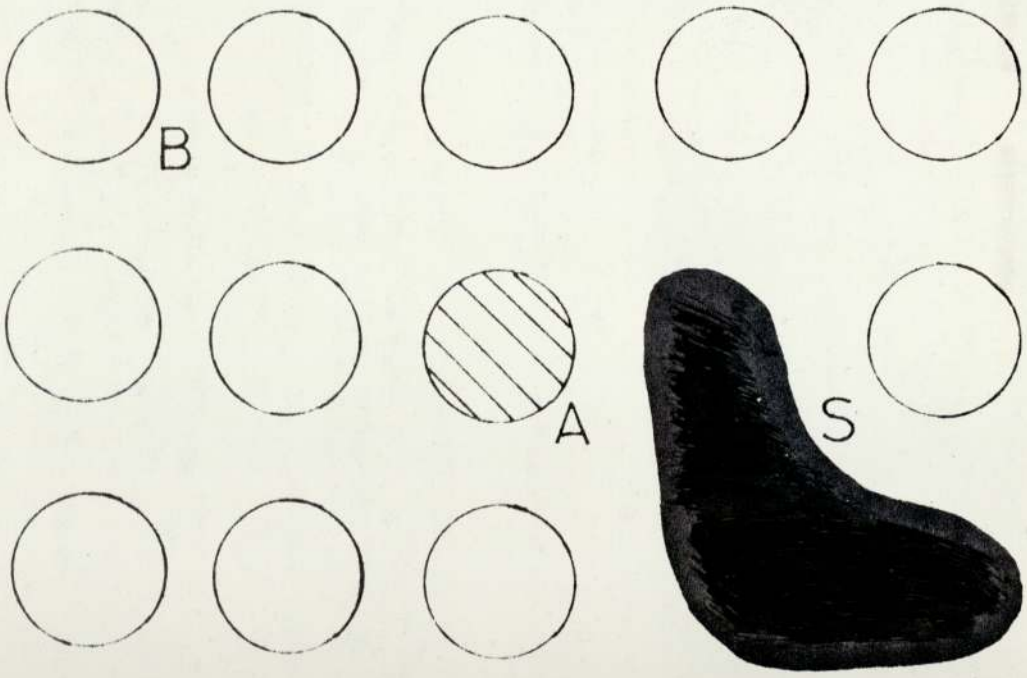
the inert solvents (V_S), together with the ratio V_S/V_B. If the theoretical, inert solvent shown in figure 3.6 is replaced by, say, a hexadecane molecule it follows that, due to the bulk of hexadecane, less benzene molecules can contact the solute during the time of the n.m.r. experiment and dilution may therefore be illustrated by figure 3.7. Therefore, in the microscopic system surrounding a solute molecule the hexadecane solvent molecule has three times the dilution effect of the ideal inert solvent; however, in the macroscopic system only one 'inert' molecule has been added in each case and hence the macroscopic mole fraction is the same in each case. The only way to emulate the

3.6



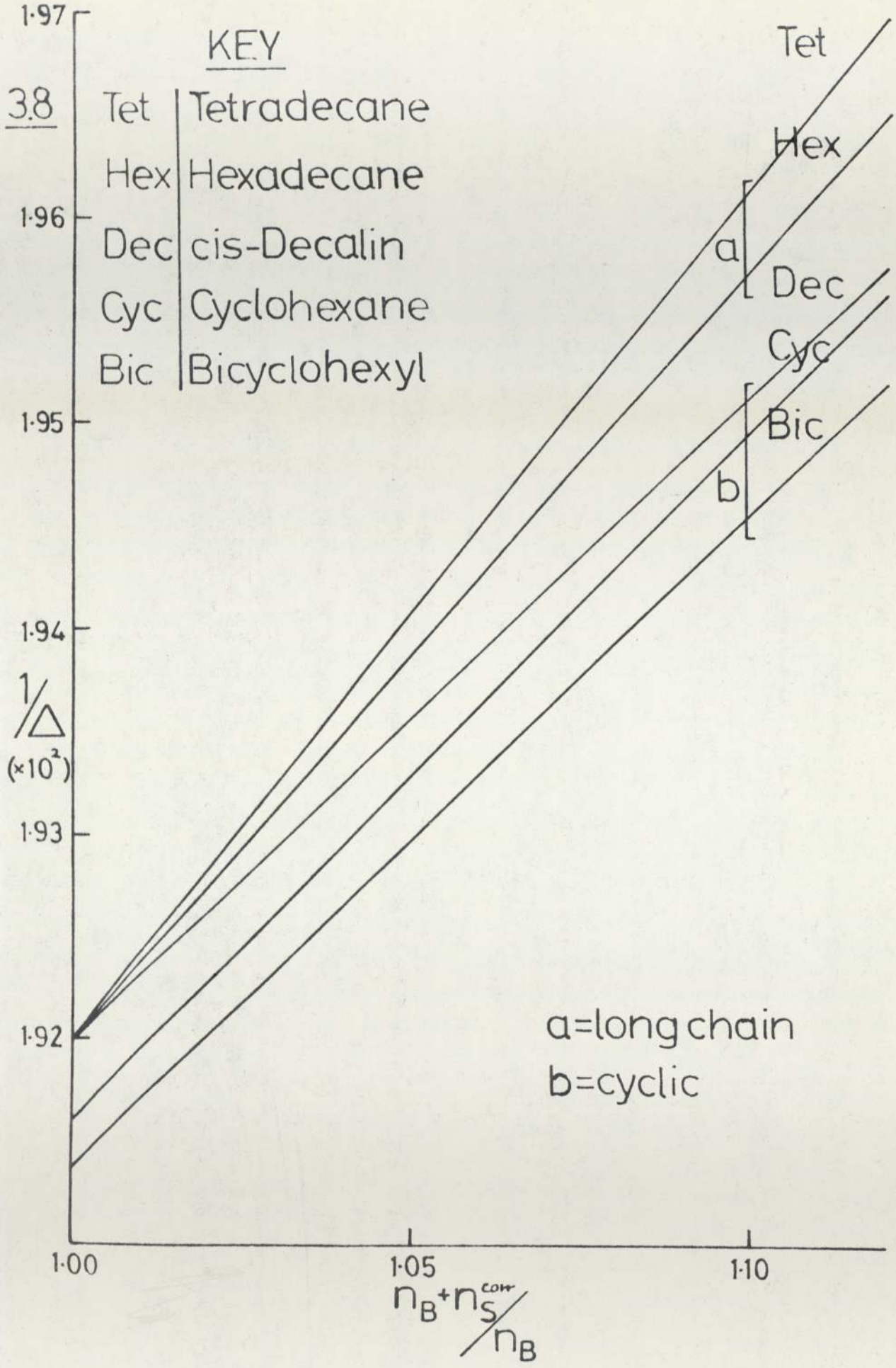
Hypothetical dilution of an A(solute) - B(aromatic solvent) mixture by S(inert solvent). S being similar in size, shape and molar volume to B.

3.7



Actual dilution of an A(solute) - B(aromatic solvent) mixture by S(inert solvent). S in this instance being Hexadecane which is extremely dissimilar in size, shape and molar volume to B. The B to S mole ratio of the macroscopic system being the same as in figure 3.6.

microscopic system on the macroscopic scale is to alter the actual number of moles of inert solvent into the apparent number of moles of benzene which have been replaced. This is achieved by multiplying the number of moles of inert solvent, in each sample, by the ratio V_S/V_B, thus producing the number of 'benzene-equivalent' moles, and then recalculating the ratio $^nB/n_B+n_S$. The values obtained in this way are recorded in table 3.7 and the results from new BH plots in table 3.8, the plots being shown in figure 3.8 (as the lines curve virtually to $^nB/n_B+n_S^{corr} = 1.0$ the tangents to the curves at this point are shown). These results include both the modification to $^nB/n_B+n_S$ and also the modification for the variation of δ_{free} with solvent. Examination of the results (which are again from a computer curve fitting procedure) immediately shows that they are far more consistent, especially Δ_c. The tetradecane and hexadecane results are slightly different from those in the other three solvents for two reasons i) the use of the molar volume ratio to correct for the difference in size between the two solvents (inert and active) can only be approximate for such large molecules as these since they in fact are really equivalent to three benzene molecules (say) plus the spaces between them; the spaces not been taken into account in the correction and ii) the correction to the mole ratio is so large that only a few points are available in the range of $^nB/n_B+n_S^{corr}$ from 0.90 to 1.00 hence there may possibly be a larger extrapolation error. Therefore it would appear that it is important to consider the relative sizes (in terms of molar volume) of the solvents on the mole fraction scale despite the thermodynamic evidence that this may not be necessary. However, as discussed in section 3.4d) it was assumed that z (the number of molecules of benzene surrounding a solute molecule) in equation 3,44 was constant as the ratio $^nB/n_S$ varied, and this resulted in the statement that K_x' was independant of the nature of S. Nonetheless, it is apparent that, despite the preferential clustering of benzenes around a solute molecule because of their stronger interaction, the size of S is an



BH plot corrected for molar volume variation for the chloroform–benzene interaction - mole fraction scale.

Table 3.7

Parameters used in BH plots of the Chloroform-Benzene interaction in different inert solvents, allowing both for the bulk of S and the variation of δ_{free} with S.

Sample Number	$n_B/n_{B+n_S}^{corr}$	$n_{B+n_S}^{corr}/n_B$	Δobs(Hz)	$-x\varsigma$(Hz)	Δ(Hz)	$^1/\Delta(x10^{-2})$
a) Chloroform (A) - Benzene (B) - Cyclohexane (S)						
49/11	0.93920	1.06463	49.10	1.90	51.00	1.9608
49/12	0.95159	1.05087	49.40	1.92	51.32	1.9486
49/13	0.96457	1.03673	49.68	1.94	51.62	1.9372
49/14	0.97484	1.02581	49.87	1.96	51.83	1.9294
49/15	0.98545	1.01477	50.03	1.98	52.01	1.9227
49/17	0.99430	1.00573	50.15	1.99	52.14	1.9179
-	1.00000	1.00000	50.20	2.00	52.20	1.9157
b) Chloroform (A) - Benzene (B) - cis-Decalin (S)						
48/11	0.91832	1.08895	48.90	1.90	50.80	1.9685
48/12	0.97933	1.02111	49.85	1.98	51.83	1.9294
48/13	0.98815	1.01200	49.96	1.99	51.95	1.9249
-	1.00000	1.00000	50.08	2.00	52.08	1.9201
c) Chloroform (A) - Benzene (B) - Bicyclohexyl (S)						
52/9	0.90435	1.10577	48.89	1.90	50.79	1.9689
52/10	0.94181	1.06179	49.54	1.94	51.48	1.9425
52/11	0.96075	1.04085	49.81	1.96	51.77	1.9316
52/12	0.98038	1.02001	50.05	1.98	52.03	1.9220
-	1.00000	1.00000	50.25	2.00	52.25	1.9139
d) Chloroform (A) - Benzene (B) - Tetradecane (S)						
50/8	0.89708	1.11473	49.53	0.77	50.30	1.9891
50/9	0.94699	1.05598	50.45	0.78	51.23	1.9520
50/10	0.96309	1.03832	50.71	0.79	51.50	1.9417
-	1.00000	1.00000	51.28	0.80	52.08	1.9201
e) Chloroform (A) - Benzene (B) - Hexadecane (S)						
51/8	0.89980	1.11136	49.70	0.77	50.47	1.9814
51/9	0.92691	1.07885	50.17	0.78	50.95	1.9627
51/10	0.96279	1.03865	50.77	0.79	51.56	1.9395
-	1.00000	1.00000	51.28	0.80	52.08	1.9201

Table 3.8

Results of the BH plots on the mole fraction scale (using $^{n}B/n_{B}+n_{S}^{corr}$) for the Chloroform-Benzene interaction in different inert solvents, corrected (1) for both the bulk of the inert solvent and the variation in δ_{free} with solution composition and (2) for just the inert solvent's bulk.

Inert Solvent	$K_x'^{corr}$ (1)	(2)	K_c' ($\times 10^4 m^3 mol^{-1}$) †	$K_c'/K_x'^{corr}$ ($\times 10^4 m^3 mol^{-1}$) (1)	(2)	Δ_c^x (Hz) (1)	(2)	Δ_c^c (Hz) †
Cyclohexane	3.372	3.860	1.017	0.302	0.263	67.7	63.2	95.4
cis-Decalin	3.768	3.984	3.110	0.825	0.781	65.9	62.7	64.8
Bicyclohexyl	4.008	4.328	1.752	0.437	0.405	65.3	61.9	76.1
Tetradecane	2.503	2.540	1.666	0.666	0.656	72.9	71.5	79.2
Hexadecane	2.876	2.884	2.288	0.795	0.794	70.2	69.1	71.7

† from table 3.4, included for comparison purposes.

important factor even at very high concentrations of B and therefore the thermodynamic assumptions ensuing from equation 3,44 are not supported.

The above considerations on the different dilution effects of the various solvents are inherent in the molarity scale results (these are also included in table 3.8 for comparison purposes). That this is so may be seen as follows: A mole fraction corrected for the bulk of the inert solvent may be written $\frac{n_B}{n_B+n_S \cdot V_S/V_B}$ or $\frac{n_B V_B}{n_B V_B + n_S V_S}$ whereas the corresponding concentration in mol m^{-3} is given by $^{n}B/n_B V_B + n_S V_S$; thus the number of moles of inert solvent is always weighted by its molar volume on the molarity concentration scale, and does not require a further correction. Furthermore, since

$$K_x'^{corr} = \frac{n_{AB}(n_B + n_S \cdot V_S/V_B)}{(n_A - n_{AB})n_B} = \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB})n_B V_B} \qquad 3,57$$

making the usual BH assumptions[44], and K_c' may be written approximately as

$$K_c' = \frac{n_{AB}\left[(n_A - n_{AB})V_A + (n_B - n_{AB})V_B + n_S V_S + n_{AB}(V_A + V_B)\right]}{(n_A - n_{AB})n_B}$$

$$= \frac{n_{AB}(n_A V_A + n_B V_B + n_S V_S)}{(n_A - n_{AB})n_B} \qquad 3,58$$

it is apparent that a) when the amount of A is somewhat larger than negligible the best approximation to K_c' is as given above, i.e. C_B is the true concentration of B in the total moles of solution; hence in tables 3.4 and 3.8 there is only one value for K_c' and Δ_c^c, b) if n_A is small, the ratio $K_c'/K_x'^{corr}$ should be equal to V_B over a wide concentration range; hence the ratio in table 3.8 should equal 9.0369×10^{-5} $m^3 mol^{-1}$ * whereas c) the ratio K_c'/K_x' should only equal V_B when n_S is negligible, i.e. in the limit when x_B tends to unity. Finally it should be pointed out that because mixtures are being studied partial molar volumes should strictly be used, but these are not readily available. Because the correction to the original values of K_x' for the variation of δ_{free} had little effect (see section 3.8 b)), and also because the correction is difficult to apply accurately, the BH evaluations on the mole fraction scale were repeated with this correction omitted and the results are recorded (designated (2)) in table 3.8. Whilst these are not quite so consistent it may be seen that the use of the correct BH evaluation, with the inclusion of the allowance for the bulk of the inert solvent, enables quite reliable results to be obtained, on the mole fraction scale, for the five inert solvents studied. This suggests that the above approach is correct and it is proposed that this may well be the ultimate way of calculating K_x and Δ_c for these weak molecular interactions in three component solutions; by working at very high aromatic concentrations the method should also be applicable to two component studies as well. In summary the method proposed is a BH plot on the mole fraction scale over the range $n_B/n_B n_S^{corr} = 0.90 - 1.00$

* The experimental values for this ratio (table 3.8) are further considered in an addendum (page 76a).

where the numbers of moles of S are changed into 'equivalent moles' of benzene with, if possible, a correction for the variation of δ_{free} with composition being applied (although as shown above this has only a minor effect).

3.9 The Creswell and Allred Data Evaluation Method

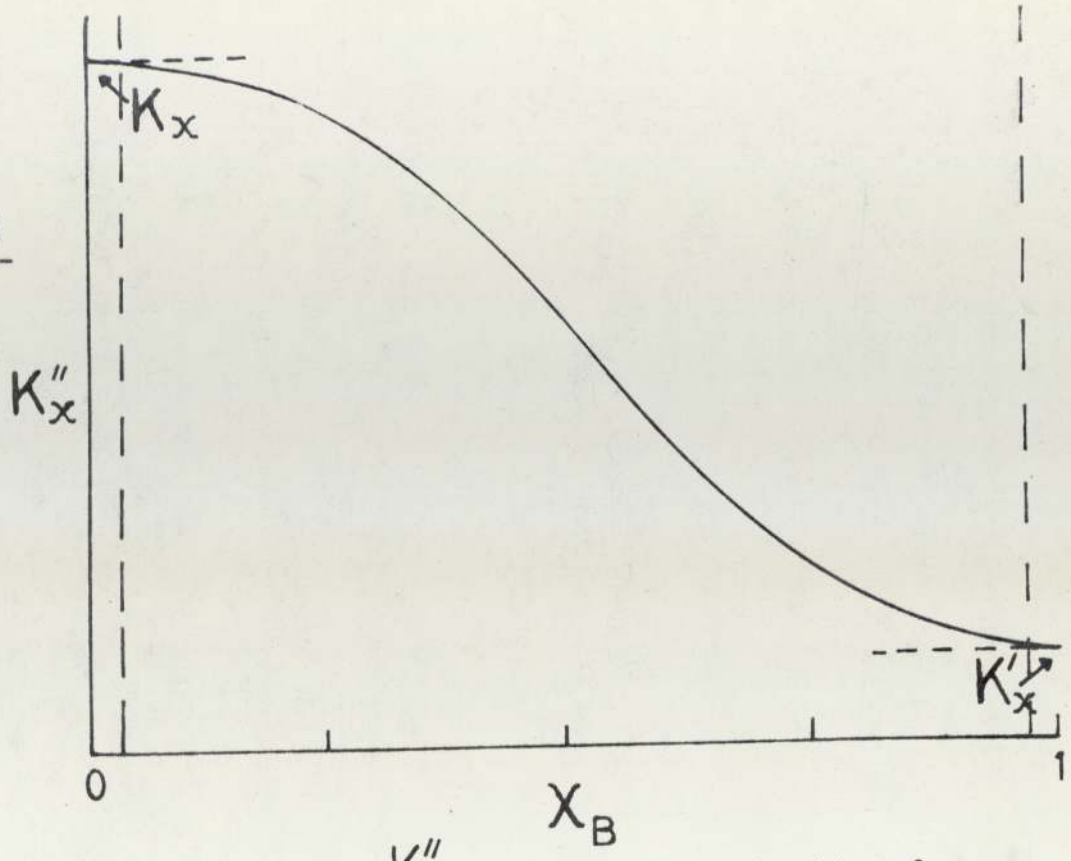
The Creswell and Allred method[62] of data processing makes use of equation 3,4 and an equilibrium quotient given by equation 3,9. These authors suggest that a plot of P_{obs} against $^{n}AB/n_{A}$ should give a straight line, hence they calculate $^{n}AB/n_{A}$ for assumed values of K_x and suppose that the correct value of K_x is obtained when a straight line ensues. A computer program to facilitate this iterative calculation has been published by Groves et.al.[70]; modifications are available for use in two-component and self-association studies. Creswell and Allred used the method to process data obtained from solutions of chloroform (at mole fraction 0.015) in mixtures of benzene and cyclohexane from x_B=0.0 to x_B=0.98; this method, which has been used in many subsequent investigations, being equivalent to obtaining values of Δ_c and K_x from

$$\delta_{obs} = \Delta_c \left[\frac{(K_x+1)(n_A+n_B) + n_S \pm \sqrt{\left(([K_x+1][n_A+n_B]+n_S)^2 - 4K_x(K_x+1)n_A n_B\right)}}{2(K_x+1)n_A} \right] + \delta_{free} \qquad 3,59$$

It is only strictly valid if used a) over a concentration range in which both n_A and n_B are very small compared with n_S, so that all three Henry activity coefficients γ^{H}_{A}, γ^{H}_{B} and γ^{H}_{AB} may be assumed to be close to unity, or b) over a range in which n_A is very much smaller than n_B, but x_B is close to unity. In this case γ^{H}_{A} and γ^{H}_{AB} are assumed to be unity (and μ^{o}_{A} and μ^{o}_{AB} independant of $^{n}B/n_{S}$) and γ^{R}_{B} close to unity. It should be apparent, therefore, that neither the method nor the results obtained have any exact meaning when used over the whole concentration range from x_B=0.0 to x_B=1.0. This statement is so much at variance with the work of many authors and Homer and Cooke[32, 55-58] in particular,

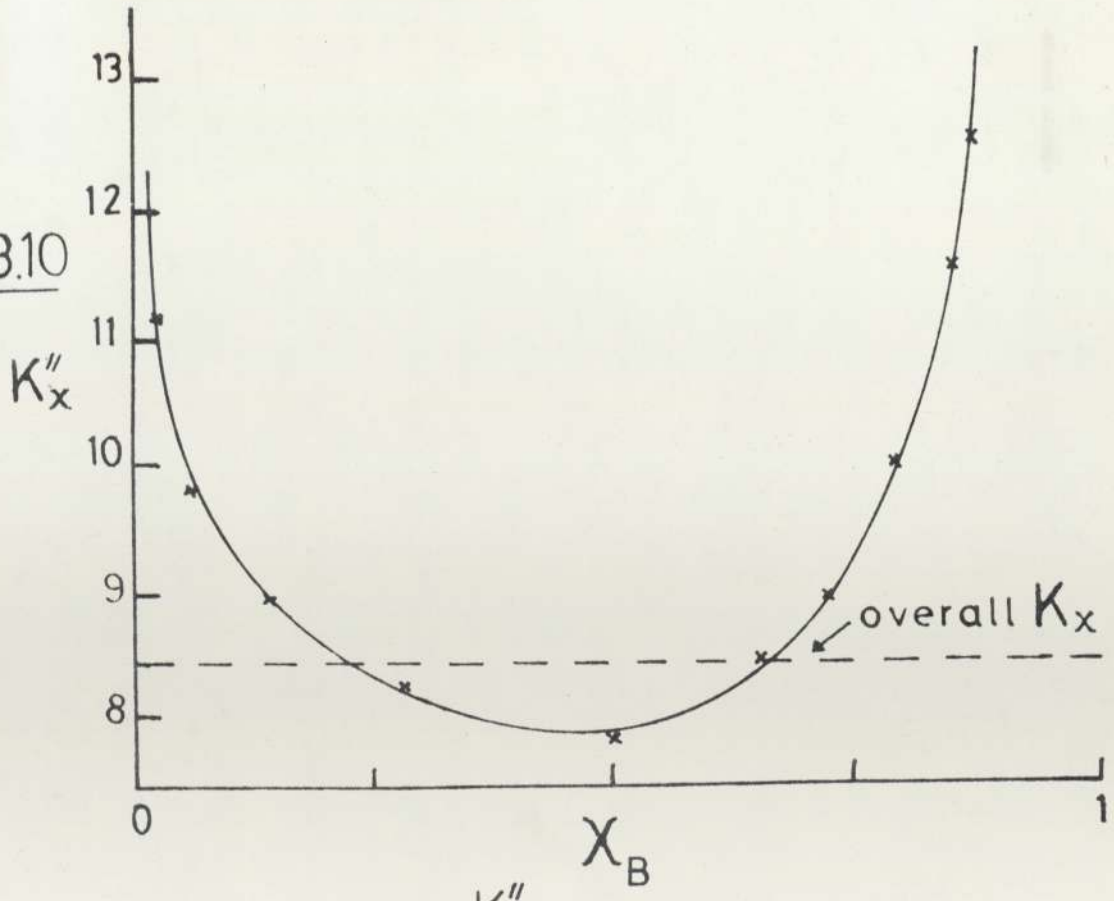
who have apparently obtained sensible equilibrium quotients, thermodynamic data and structures for the complexes that they studied, and who have also obtained good correlation between these equilibrium quotients and interaction energies[32, 56-57] that some explanation is required. This may possibly be provided as follows: In the discussion on the BH method (sections 3.4 and 3.6) two equilibrium quotients K_x and K_x', both being independant of activity coefficients and constant over closely defined ranges, were considered. It has been calculated[71] that for the chloroform-benzene-cyclohexane system, K_x ($x_B \rightarrow 0$) would be about 1.7 times greater than $K_x'(x_B \rightarrow 1.0)$, this being based on the assumption that the concentration of A is infinitesimal and that μ_A° and μ_{AB}° are independant of $^{n}B/n_S$. Between these two extremes there is a quotient K_x'' which is dependant on x_B and on the relevant activity coefficients, and it is postulated[71] that a plot of K_x'' against x_B would be of the shape shown in figure 3.9 (K_x and K_x' being special cases of K_x'' as x_B tends to zero and unity respectively). If it is assumed that this shape holds for other solutes in benzene-cyclohexane mixtures then it is possible to try and evaluate what the Creswell and Allred K_x means. The argument may be quantified using the nitroform-benzene-cyclohexane system studied by Homer and Huck;[31,33] a series of K_x'' values were obtained for this system by using an iterative procedure over small portions of the concentration range. Sets of three consecutive measurements were used in the evaluations, and the δ_{free} value was included in each case in order to fix one end of the δ_{obs} v $^{n}AB/n_A$ plot, and so improve the accuracy of the evaluation. The values of K_x'' obtained, together with the average mole fraction of B in each case (the average of the set of three points), are recorded in table 3.9;

3.9



Postulated plot of K''_x against the mole fraction of aromatic, X_B, showing the two linear regions K_x and K'_x.

3.10



Experimental plot of K''_x against mole fraction of aromatic, X_B, for the nitroform - benzene - cyclohexane system.

Table 3.9

The average mole fraction ($\overline{x_B}$) and the equilibrium quotient (K_x'') for the series of evaluations, of the nitroform-benzene interaction data[31], by the Creswell and Allred method.

K_x''	8.47	11.19	9.81	8.96	8.29	7.89	8.50	8.97	10.00	11.50	12.56
$\overline{x_B}$	whole range	0.03	0.06	0.14	0.28	0.50	0.65	0.72	0.79	0.85	0.87

they are plotted in figure 3.10 against $\overline{x_B}$. Although the plot is rather dissimilar to the hypothetical plot, given in figure 3.9, this may possibly be due to inaccuracies in the evaluation, and also to the rather crude 'average x_B' used to plot the results. It therefore appears possible that the overall K_x is in fact an average of all the K_x'' values, i.e.

$$\overline{K_x} = \sum_i K_x'' \partial x_{B_i} \Big/ \sum_i \partial x_{B_i} \qquad 3,60$$

which is the area under the curve (of the K_x'' against x_B plot) divided by the length x_B. Although $\overline{K_x}$ may appear to be an arbitary constant it does have a significance as follows. The chemical potentials of A, AB and B may all be described by equation 3,33 over any part of the concentration range. Thus

$$RT\ln K_x'' = \mu_A^o + \mu_B^o - \mu_{AB}^o + RT\ln \frac{\gamma_B^R \cdot \gamma_A^R}{\gamma_{AB}^R} \qquad 3,61$$

where $\mu_A^o + \mu_B^o - \mu_{AB}^o$ describes the true equilibrium constant for the formation of pure AB from pure A and pure B and is equal to $RT\ln K_x^{true}$. Therefore

$$RT\ln K_x'' = RT\ln K_x^{true} + RT\ln \frac{\gamma_B^R \cdot \gamma_A^R}{\gamma_{AB}^R} \qquad 3,62$$

Since the concentrations of A and AB are small it is reasonable to suppose that the ratio $\gamma_A^R / \gamma_{AB}^R$ is fixed, despite the variation in the concentration of B, and therefore

$$K_x'' = K_x^{true} C \gamma_B^R \qquad 3,63$$

where C is the ratio $\gamma^{R}_{A} / \gamma^{R}_{AB}$. Hence K_x^{CA} (i.e. $\overline{K_x}$) is given as follows

$$K_x^{CA} = \frac{\sum_i K_x'' \partial x_{B_i}}{\sum_i \partial x_{B_i}} = K_x^{true} \frac{C \sum_i \gamma^R_{B_i} \partial x_{B_i}}{\sum_i \partial x_{B_i}} \qquad 3,64$$

which may be written simply in the form

$$K_x^{CA} = K_x^{true} . C \, \overline{\gamma}^R_B \qquad 3,65$$

It is reasonable to suppose that in a given solvent system, such as benzene-cyclohexane, $\overline{\gamma}^R_B$ will be the same irrespective of the solute, thus in a series with this common solvent system the evaluated K_x^{CA} will be K_x^{true} multiplied by a common factor. Therefore the linearity of the ln K_x^{CA} against interaction energy plot of Homer and Cooke[32,56-57] will not be affected. Similarly ΔH^o as calculated from K_x^{CA} will be the same as that calculated from K_x^{true} since a plot of ln K_x against $1/T$ is required (section 3.10), and it follows from equation 3,65 that

$$\ln K_x^{CA} = \ln K_x^{true} + \ln C \overline{\gamma}^R_B \qquad 3,66$$

Thus both plots will have the same slope and the value of ΔH^o will be unaffected.* Possible confirmation of these ideas, on the thermodynamics of the Creswell and Allred method, is provided by the Homer and Cooke[32,56-57] plot of $\log_{10} K_x$ against interaction energy where one straight line is provided by the solvent pair benzene-cyclohexane, and a second line by the higher methyl benzenes-cyclohexane (any changes due to changes in the individual methyl benzenes tends to be lost due to the high equilibrium quotients obtained, but there is a definite change in slope at the expected point), this change in slope being due to the alteration in the value of $\overline{\gamma}^R_B$ caused by the change of solvent system.

It is worth attempting at this point to see if the BH evaluated K_x' can be similarly related to K_x^{true} and hence give meaningful thermodynamic data. It follows from equations 3,44 and 3,50 that

*assuming $\overline{\gamma}^R_B$ to be temperature independant.

$$RT\ln K_x' = \mu_A^o + \mu_B^o - \mu_{AB}^o + zL\left(\omega_{A,B}' - \omega_{AB,B}'\right) \qquad 3,67$$

which, on making the initial assumption that z is a constant over the BH evaluation range, may be written

$$\ln K_x' = \ln K_x^{true} + C' \qquad 3,68$$

Therefore, plots of ln K_x' against $^1/T$ will have the same slope, and identical values of ΔH^o will be obtained. Furthermore the values of ΔH^o obtained by both the Creswell and Allred[62] and BH[44] procedures should be the same. It has, however, been shown (section 3.8c)) that the nature of S has a considerable influence on the values of K_x' and Δ_c obtained by the BH procedure (i.e. the actual value of z in equations 3,44 and 3,67 is solvent dependant). Therefore, it seems reasonable that equation 3,68 is only valid when values of K_x' corrected for solvent bulk are used. It also seems reasonable to suppose that the nature of S will have an even larger effect on the K_x^{CA} and Δ_c values obtained from a Creswell and Allred type study, since the value of $\overline{\gamma}_B^R$ will be dependant on S even though B may be constant.

The chloroform-benzene interaction has been investigated, therefore, by the Creswell and Allred procedure[62], in the five solvents used in section 3.8 and the data evaluated both with and without correcting the number of moles of S to 'equivalent moles' of benzene. The results are recorded in table 3.10.

Table 3.10

K_x^{CA} and Δ_c obtained for the Chloroform-Benzene interaction in different inert solvents, both with and without correcting n_S to 'equivalent moles' of benzene.

Inert Solvent	uncorrected		corrected	
	K_x^{CA}	Δ_c (Hz)	K_x^{CA}	Δ_c (Hz)
Cyclohexane	1.099	96.5	1.552	83.0
cis-Decalin	0.559	140.8	1.697	80.1
Bicyclohexyl	0.397	178.3	1.928	76.9
Tetradecane	0.034	1561.3	2.015	76,4
Hexadecane	0.0	-	2.027	76.4

The data used in the uncorrected evaluations are recorded in table 3.2, and the values of n_S^{corr} used in the corrected evaluations may be obtained by multiplying the values of n_S contained in this table by the relevant ratio of V_S/V_B from table 3.6. Since the effect of the change of δ_{free} with solvent is small, this correction has been neglected. It is immediately apparent that a considerable improvement in the values of K_x^{CA} and Δ_c is obtained when corrected values of n_S are used; therefore such a correction is essential before making use of any data regarding an A-B interaction taking place in an inert solvent S. It is suggested, therefore, that the change in slope of the $\log_{10} K_x^{CA}$ against interaction energy plot of Homer and Cooke[32, 56-57] when the aromatic is altered may be due, at least in part, to the alteration in the molar volume of the aromatic molecule, which necessitates a change in the value of n_S^{corr}; although confirmation of this supposition will require recalculation of their data.

3.10 Stoichiometry of Complex Formation

In work on haloform and pseudo-haloform complexes with benzene[31, 33, 70], 1 : 1 complexes were assumed with some justification based on cryoscopic data[72]. However, in work on other types of complex this assumption is no longer justifiable and must be established. A procedure which has been used for this purpose[49, 52, 73-75] is to plot $^1/\Delta_{obs}$ against $^1/x_B$ (i.e. a BH type plot[44]) it being assumed that if a straight line is obtained then complex formation may be represented by

$$A + B \rightleftharpoons A\cdots B$$

Apart from the criticisms made above about the validity of BH plots over a wide concentration range it has been demonstrated[76] that the linearity of BH type plots is not a good test for demonstrating the presence of only 1 : 1 complexes. The more exact way of demonstrating the presence of a single complex is by the constancy of ΔH^o with temperature[66]. ΔH^o may be obtained from the equilibrium quotient data (considering a

general K_x) in the following way, it is known that

$$\Delta G^\circ = - RT\ln K_x \qquad 3,69$$

The temperature dependance of free energy is given classically by the Gibbs-Helmholtz equation which may be written

$$\left[\frac{\partial(\Delta G^\circ/T)}{\partial(1/T)}\right]_p = \Delta H^\circ \qquad 3,70$$

Thus, combination of equations 3,69 and 3,70 gives

$$-R\left[\frac{\partial \ln K_x}{\partial(1/T)}\right]_p = \Delta H^\circ \qquad 3,71$$

hence a plot of ln K_x against $^1/_T$ should give a slope of $-\,^{\Delta H^\circ}/_R$ at any temperature T, a linear plot indicating the constancy of ΔH° with temperature. Homer and Cooke[55] have applied this to a number of complexes formed between benzene and some substituted ethylenes; despite using the Creswell and Allred[62] procedure for evaluating K_x (as discussed in section 3.9 this should only affect the value of the intercept of a ln K_x against $^1/_T$ plot and not the slope), they obtained virtually linear plots which they took to confirm the presence of 1 : 1 molecular complexes. Any higher complexes of the type A_nB_m ($n \geqslant 1 \leqslant m$, $n \neq m$) would be expected to form by consecutive associations and hence in such cases each ΔH° will differ and the ln K_x against temperature plot for an assumed 1 : 1 complex will not be linear. The above procedure has since been applied to many other systems. More recently, Baker and Wilson[77] have proposed that a plot of $\log_{10}\left(^{\delta_{obs}}/_{\delta_{comp}-\delta_{obs}}\right)$ against $\log_{10}(C_B)$ should give a straight line of slope n, where n is the number of molecules of benzene complexed with each molecule of solute, the intercept being $\log_{10}K_c$. The derivation of this model contains a number of dubious assumptions and it also uses the molarity scale over a wide concentration range; despite these points the validity of the procedure was checked by considering the accepted 1 : 1 interactions between benzene and nitroform, chloroform and bromoform, widely different values of n being obtained[78]. It is clear, therefore, that this procedure does not supersede the use of the constancy of ΔH° with

T as a measure of 1 : 1 complex formation.

Both ΔG^{o} and ΔH^{o} [31-32, 56-57, 79] for complex formation have, in the past, been used to measure the 'strength' of the interaction between solute and aromatic. It should be clearly understood that both cannot be valid in as much as the equilibrium constant (and hence ΔG^{o}) and the enthalpy of complex formation (ΔH^{o}) are independant parameters[80], and hence, at a particular temperature T, the complex with the higher equilibrium quotient does not necessarily have the higher ΔH^{o} of formation. It is possible to produce a realistic model of complex formation which is consistent with ΔG^{o} providing a measure of the 'strength' of the complex. This has been critically examined by Homer and Cooke[32, 56-57], who have related interaction energies to the equilibrium quotient for complex formation. Since interaction energies are found to vary with temperature (via an interaction distance which is temperature dependant) they must be directly compared with ΔG^{o} at any temperature and not with the invariant ΔH^{o}.

3.11 A Model for Complex Formation

It is envisaged that the electric field of the dipolar molecule has a large gradient in the vicinity of the positive end of the dipole (usually the hydrogen atom)[81], and that this field polarizes the π-electron system of the aromatic ring, thus forming the basis for electrostatic bonding between the molecules. It is also assumed that the solute molecule approaches the aromatic molecule (usually benzene) with its dipolar axis aligned along the aromatic six fold symmetry axis [31-33,55]. This is to enable there to be the maximum interaction between the two molecules, and is contrary to a fallacious assumption[30] that the solute dipolar axis should lie parallel to the plane of the aromatic ring. This latter assumption, which is based on the fact that benzene is twice as polarizable in the molecular plane ($\alpha_{11}=12.3\times10^{-30}m^{3}$) than normal to it ($\alpha_{\perp}=6.35\times10^{-30}m^{3}$)[82], ignores the angular dependance of the interaction

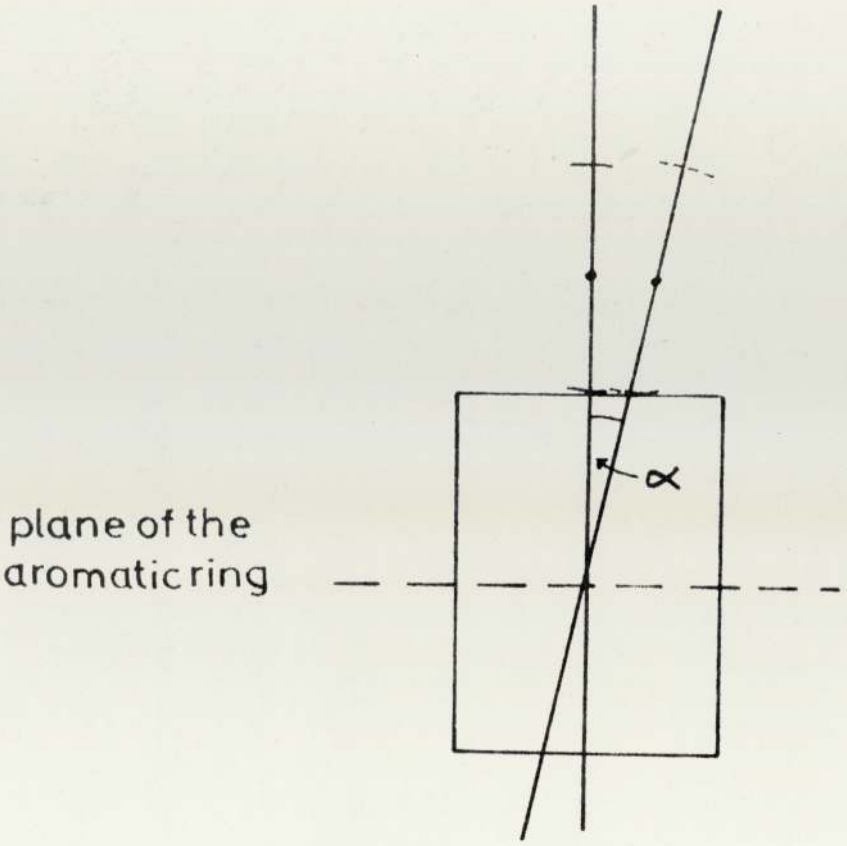
via a $3\cos^2\theta - 1$ term which in fact favours the alignment along the six fold axis. The model as now considered allows the solute dipolar axis not only to align along the aromatic six-fold axis but also at small angles to it. Therefore the envelope of possible orientations is a cone with a small semi-angle α. As the temperature increases the energy of the complex will increase and more orientations will be possible, hence α will increase and a larger cone will be obtained. Consequently it is expected that the entropy of the complex should increase; however, this is difficult to prove or disprove becaue the experimentally determined quantity is ΔS^o which is known to be negative and is defined as

$$\Delta S^o = S^o_{AB} - S^o_A - S^o_B \qquad 3,72$$

where S^o_{AB}, S^o_A and S^o_B are the entropies of the complex and free solute and solvent respectively. Certainly the entropy of each species will increase with increasing temperature, probably at much the same rate. Therefore, if the complex had a rigid structure, it would seem reasonable to postulate that the entropy of the complex would increase less quickly than the sum of the entropies of A and B, hence ΔS^o would rapidly become more negative. However, if the above flexible model is correct the entropy of the complex should increase more rapidly than that of either A or B individually, hence ΔS^o should either go more negative very slowly or even tend to become less negative. This hypothesis may be checked using results obtained by Huck[31] for the interactions between nitroform and benzene and some methyl benzenes (these being the strongest complexes studied and hence the most likely to show this variation). It should be realized that as a Creswell and Allred[62] data evaluation procedure was used to obtain the equilibrium quotients, these are not the correct values (as discussed in section 3.9); therefore, whilst ΔH^o should be absolutely correct, the ΔG^o values will be wrong. It is expected therefore that although the ΔS^o variation with temperature will indicate the trend followed by the true value,

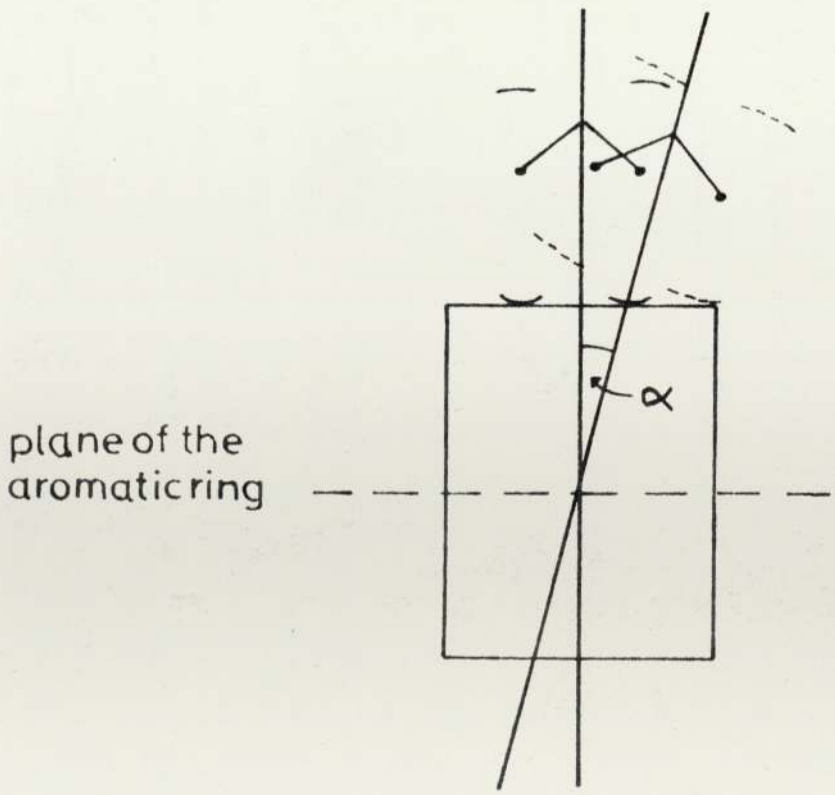
numerically it will also not be correct. The values of ΔS^{o}, calculated assuming that ΔH^{o} does not vary with the temperature, are recorded in table 3.11. It may be seen the ΔS^{o} is almost constant with temperature which appears to confirm that the flexible model is valid. Further indirect evidence may be obtained from the screenings, recorded in table 3.12, both for the nitroform complexes discussed above and also for some complexes formed between the haloforms and substituted ethylenes with benzene and substituted benzenes. It may be seen that the screenings of the haloforms and pseudo-haloforms just decrease with increasing temperature whereas those of the substituted ethylenes increase with increasing temperature. It may be seen from figures 3.11 and 3.12 that as the temperature increases and hence also the semi-angle of the possible orientations of the solute dipolar axis there is a greater chance that the haloform proton will lie off this axis, but at the same distance from the plane of the ring, and hence be slightly less shielded. Whereas, for the substituted ethylenes, the structure will twist as shown and result in one proton lying approximately on the six-fold axis and the other slightly further away from this axis than anticipated from the fixed model. Hence, since the screening variation is greatest along the six-fold axis, a slight increase in screening is indicated, as is found experimentally. Therefore, this model explains the observed screenings for both types of solute and also explains how the interaction energy[32, 56-57] decreases with increasing temperature due to the slight increase in the angle between the solute dipolar axis and the aromatic six fold axis. Hence it is apparent, from table 3.11, that ΔG^{o} is the correct thermodynamic quantity related to the 'strength' of the interaction.

3.11



Proposed structure for a haloform-benzene complex, showing effect of tilting as the temperature is raised. ∝ is the semi-angle of the cone of possible orientations.

3.12



Proposed structure for a substituted ethylene-benzene complex showing effect of tilting as the temperature is raised. ∝ is the semi-angle of the cone of possible orientations.

Table 3.11

Variation of ΔS^{o}, ΔH^{o} and ΔG^{o} for Nitroform-Aromatic Complexes †

T(K)	ΔS^{o} (J $mol^{-1} K^{-1}$)	ΔH^{o} (kJ mol^{-1})	ΔG^{o} (kJ mol^{-1})
Nitroform-Benzene			
279.1	- 24.99	- 13.18	- 6.20
287.0	- 24.97		- 6.01
297.8	- 25.04		- 5.72
306.6	- 25.00		- 5.52
313.8	- 25.02		- 5.33
Nitroform-Mesitylene			
276.7	- 30.99	- 18.83	-10.25
287.0	- 31.01		- 9.93
298.8	- 31.02		- 9.56
306.6	- 30.98		- 9.33
313.8	- 30.97		- 9.11
Nitroform-Durene			
277.6	- 30.55	- 20.29	-11.81
286.5	- 30.45		-11.57
296.7	- 30.38		-11.28
306.6	- 30.25		-11.02
314.0	- 30.23		-10.80
Nitroform-Hexamethylbenzene			
276.7	- 43.62	- 27.75	-15.68
288.2	- 43.91		-15.09
296.9	- 43.92		-14.71
306.6	- 43.87		-14.30
314.1	- 43.91		-13.96

† based on data provided by Huck[31]

Table 3.12

Additional screening (Δ_c) experienced by the complexes indicated at various temperatures[31-32, 58].

T(K)	Δ_c (ppm)	T(K)	Δ_c (ppm)
Nitroform-Benzene		Bromoform - p-Xylene	
279.1	2.00	276.9	1.96
287.0	1.90	287.1	1.80
297.8	1.90	297.8	1.73
306.6	1.86	306.6	1.78
313.8	1.81	312.9	1.81
Nitroform-Mesitylene		cis-1,2-Dichloroethylene-Benzene	
276.7	2.20	277.2	1.32
287.0	2.17	285.9	1.30
298.8	2.04	295.7	1.32
306.6	2.00	306.6	1.33
313.8	1.94	314.7	1.37
Nitroform-Durene		1.1-Dichloroethylene-Benzene	
277.6	2.39	276.8	1.29
286.5	2.31	285.9	1.26
296.7	2.24	296.1	1.28
306.6	2.15	306.6	1.26
314.0	2.14	314.9	1.35
Nitroform-Hexamethylbenzene		Methylene Iodide-Benzene	
276.7	2.52	275.8	1.52
288.2	2.54	285.3	1.51
296.9	2.50	295.0	1.53
306.6	2.38	306.6	1.53
314.1	2.40	315.0	1.57
Chloroform- p-Xylene			
276.8	1.62		
287.0	1.60		
298.1	1.59		
306.6	1.49		
313.9	1.54		

3.12 Conclusions

This chapter has attempted to show the conditions under which true equilibrium quotients, for the interactions studied, would be obtained. It is apparent that this is either when A, B and AB are all at infinite dilution in an inert solvent or when A and AB are likewise at infinite dilution in a solution mainly consisting of B. However, in neither case does the equilibrium quotient (K_x or K_x') correspond to the Creswell and Allred overall K_x^{CA}. It would appear that the 'equilibrium quotient' calculated by this method does have a certain validity however, when the solvent system (interacting and inert) is constant throughout a given series. In such cases perfectly reliable and self-consistent qualitative comparisons are possible for different interactions, and the thermodynamic parameters obtained may also be used (ΔH^o will be much the same and ΔG^o will vary by a common factor from the true value). It has also been shown that the equilibrium quotients obtained on the mole fraction scale (K_x' and K_x^{CA}) are dependant on the nature of S unless the quantity of inert solvent present is modified to allow for the difference in size between itself and the interacting (aromatic) solvent, which it is diluting. If this is allowed for, K_x' and K_x^{CA} are then independant of the nature of S; whereas the use of other concentration scales results in equilibrium quotients which are dependant both on the amount and nature of S.

Addendum

The values of K_x', Δ_c^x, K_c' and Δ_c^c given in tables 3.4 and 3.8 were obtained by using a computer curve-fitting procedure to evaluate BH plots based on 'best-line' values of the experimental data. These may, therefore, include a subjective error depending on the 'best-line' selected. In order to overcome this problem Whitney[195] has used a computer to determine this 'best-line' (permitting up to a quadratic line shape) through the experimental points and then to evaluate the values of K and Δ_c, by the BH procedure, in the normal way. These results are given in the table and they serve to confirm the conclusions reached in section 3.8c) that consistent K_x' and Δ_c^x values may be obtained when a correction is made allowing for the nature of the inert solvent. It was stated in section 3.4c) that values of K_c' and Δ_c^c would be expected to vary in different solvents and this statement is still valid when experimental values over a finite concentration range are evaluated. However, in the present work, the limiting slopes of the $^1/\Delta$ against ^{1}/concentration curves are considered and therefore the situation corresponds to that discussed in section 3.7 where it was stated that the limiting value of the ratio $K_c'/K_x'^{corr}$ should be the molar volume of the aromatic solvent (benzene = 0.904×10^{-4} m^3 mol^{-1}). It may be seen from the table that this was found to be so, and further, that for the reaction between chloroform and benzene in benzene the following values are obtained $K_x' = 1.7 \pm 0.2$, $K_c' = 1.55 \pm 0.2 \times 10^4$ m^3 mol^{-1} and $\Delta_c = 80 \pm 4$ Hz at 60.004 Hz.

Table

Results of the BH plots for the Chloroform-Benzene interaction in different inert solvents (obtained by Whitney[195]); (1) including a correction for both the bulk of the inert solvent and the variation of δ_{free} with solution composition and (2) including a correction just for the inert solvent's bulk.

Inert Solvent	$K_x'^{corr}$ (1)	(2)	K_c' ($\times 10^4 m^3 mol^{-1}$)	$K_c'/K_x'^{corr}$ ($\times 10^4 m^3 mol^{-1}$) (1)	(2)	Δ_c^x (Hz) (1)	(2)	Δ_c (Hz)
Cyclohexane	1.366	1.479	1.340	0.981	0.906	90.5	84.3	84.3
cis-Decalin	1.680	1.734	1.562	0.929	0.901	83.4	79.3	79.1
Bicyclohexyl	1.886	1.935	1.738	0.922	0.898	80.3	76.5	76.3
Tetradecane	1.671	1.672	1.782	1.066	1.064	83.3	82.0	77.0
Hexadecane	1.694	1.701	1.630	0.962	0.957	83.8	82.4	80.7

CHAPTER 4

A New Procedure for Investigating Molecular Interactions in Solution

4.1 Introduction

In the study of transient complexes by means of nuclear magnetic resonance spectroscopy[30], various types of experimental procedure have been used. In all cases these suffer from a number of disadvantages in that certain approximations are involved in the evaluation of the experimental data. Particularly well studied have been interactions between simple molecules (solute) and benzene and other aromatic molecules (solvent)[30-33, 55]. Such studies are made possible by the anisotropy in the magnetic susceptibility of the aromatic molecule which modifies the screening and hence the chemical shift of the nuclei of the solute with which it specifically interacts. Experimental procedures using two-[72], three-[62,83] and four-[49]component liquid mixtures have been used in the past or are in current use and in each case the solute-solvent ratio has been varied over a series of samples for which the solute chemical shift (usually ^1H) has been measured. The variations in this with solvent concentration have been attributed to specific effects, in the complex, of the magnetic anisotropy of the aromatic molecule. It is true to say that these methods have never been used properly from a thermodynamic viewpoint (see chapter 3); and, furthermore, they suffer from certain disadvantages. The purpose of this chapter is to devise a new procedure which will enable molecular interaction studies to be carried out over a valid thermodynamic range, and even more importantly to overcome many of the disadvantages of the other methods, which will now be considered. The two-component method[72] requires the measurement of chemical shifts relative to a normal external reference and these can be subject to significant error due to the difficulty in accurately correcting for bulk medium effects. Also there is a possibility of solvent or solute self-association occurring and this has, as in the other methods, either been ignored or the assumption made that the two mechanisms of complex formation and self-association are independent;

if this is done it is then possible to correct the amounts of solute and solvent for any self-association (studied independantly) which may be occurring and, by assuming that the self-associated species are inert[84-85], evaluate the parameters for complex formation. The three-component studies can be divided into two types. The first of these[83] employs a very small quantity of a reference compound, such as tetramethylsilane (TMS), and varying solute-solvent ratios, as in the two-component method; disadvantages are that errors may arise from the assumptions that the reference compound is inert and that the self-association of the other species is negligible. The second type uses a constant, low concentration of solute in order to avoid the effects of self-association, and achieves different solute-solvent ratios by varying the aromatic concentration via the addition of a second solvent, which also acts as a reference, and which is assumed to be inert[62]. A fourth method has also been used which essentially involves the addition of ca. 0.5 per cent of a reference compound to systems similar to those used in the second three-component method[49]. Of the four methods, probably the third would appear normally to offer the best prospects of accuracy, and this has often been used. Nevertheless if, for example, both ^{1}H and ^{19}F shift variations with aromatic concentration are to be determined for a given solute, it is evident, in view of the suggestion that the binding in the complexes may be solute local dipole-aromatic induced dipole in nature[32, 56-57], that it may be difficult to find a fluorine containing reference compound suitable for any of the internally referenced procedures. This is because an essentially non-polar compound such as perfluorocyclohexane has strong local dipoles and could well specifically interact with benzene. Therefore, in order to carry out investigations on such systems it is necessary to revert to experimental procedures employing an external reference. Although there are apparently many disadvantages to this, one advantage which may emerge, if it can be done, is that real two

component systems can be investigated which are amenable to thermodynamic analysis.

4.2 Theory of the New Procedure

It is possible to devise suitable experimental conditions, for which it is necessary to adapt the normal external referencing procedure, to accommodate various problems, the most significant of which arise from the effects of constituent self-association and screening by the medium. Investigations of this type usually employ a cylindrical sample vessel containing a co-axial reference capillary. For simplicity only this procedure will be considered, and furthermore it will be assumed that the reference vessel is also perfectly cylindrical. To study complex formation it is necessary to measure the difference between the chemical shifts of a particular solute nucleus in the free and various complex equilibrium situations. This can be done by arranging that in the annulus, X, of a cylindrical sample tube is contained the solute, A, in a complexing aromatic solvent, B, and that in a co-axial capillary, Y, is contained the solute in some non-interacting solvent, S. Neglecting all bonding interactions other than that involved in complex formation, the solute in the capillary will be entirely free whereas the state of that in the annulus will be governed, for a sample j, by the mole fraction equilbrium expression (neglecting activity coefficients):

$$K_x = \frac{n_{AB_j}(n_{A_j} + n_{B_j} - n_{AB_j})}{(n_{A_j} - n_{AB_j})(n_{B_j} - n_{AB_j})} \qquad 4,1$$

if 1:1 complex formation occurs according to

$$A + B \rightleftharpoons A\cdots B,$$

n_{A_j} and n_{B_j} are the number of moles of A and B initially present and n_{AB_j} is the number of moles of complex formed at equilibrium, in sample j; the fraction of the solute complexed is n_{AB_j}/n_{A_j}, with the remainder free. Thus, in the annulus and capillary, the solute will be differently shielded due to the effect of complex formation and, in addition, different medium screening effects. The corresponding shift can be measured directly, but from this must be abstracted the specific screening contribution due

to the aromatic molecule in the complex. If the absolute screening constant for a particular nucleus in the solute is σ, then the screening in the medium (σ_M) is defined by

$$\sigma_M = \sigma + \sigma_a + \sigma_b + \sigma_E + \sigma_w \qquad 4,2$$

where σ_a, σ_b, σ_E and σ_w have their usual significance[86]. When solute-aromatic interaction occurs an additional term, σ_{comp}, representing the screening contribution of the aromatic to the solute must be included in equation 4,2. The various medium screening terms and their variation with solution composition will be discussed in detail in chapter 5, where it is shown that the dispersion force screening (σ_w) and electric field screening (σ_E) appear to be mole fraction functions of solution composition. Similarly bulk susceptibility effects (σ_b) are found to be almost linearly additive as a function of the volume fraction of each of the components. Finally it is shown that constituent magnetic anisotropy contributions in mixtures (σ_a) are normally not linearly additive mole - or volume fraction functions of the pure constituent anisotropy screenings and such screenings have therefore to be individually determined as described in chapter 6.

With the above comments, concerning the medium screening effects, in mind it is possible to derive expressions representing the actual screening of the nucleus in the solute, both in the annulus and capillary. It is evident that this is most conveniently done by considering the effects on the solute of the appropriate contributions from anisotropy, bulk susceptibility and initially composite dispersion force and reaction field screening effects for each constituent in solution. The relevant values for the complex are, of course, inaccessible and it becomes necessary to assume that the bulk properties of the components in solution are independant of whether or not they are bound in a complex. The appropriate contributions of each component are then governed by the quantities of the materials initially present. It must also be assumed

that the configuration of the solute, and hence the absolute screening σ, is the same in both the free and complexed situations. Assuming that all the vessels are perfectly cylindrical and denoting the capillary by the suffix Y and the annulus by the suffix X it is apparent that for a single material, σ_X and σ_Y, the total screenings in the annulus and capillary respectively, are given by

$$\sigma_X = \sigma + \sigma_{aX} + \sigma_{EX} + \sigma_{\omega X} + \frac{1}{6}\chi_{vX} \qquad 4,3$$

$$\sigma_Y = \sigma + \sigma_{aY} + \sigma_{EY} + \sigma_{\omega Y} + \frac{1}{6}\chi_{vY} \qquad 4,4$$

where χ_v is the volume susceptibility. If both the annulus and capillary contain mixtures, then the values of σ_{aX} and σ_{aY} must be individually determined; σ_E and σ_w are initially assumed to be mole fraction additive and the volume susceptibility screenings are assumed to be volume fraction additive. Therefore, on combining the σ_w and σ_E screening terms into a composite screening of the form

$$\sigma^A = \sigma_E^A + \sigma_w^A \qquad 4,5$$

and similarly for σ^B and σ^S it is possible to rewrite equations 4,3 and 4,4, representing the overall screening of the solute A in the two situations, as follows:

$$\sigma_X^A = \sigma + \sigma_{aX}^A + x_A\sigma^A + x_B\sigma^B + \frac{1}{6}\left[\phi_A\chi_{vA} + \phi_B\chi_{vB}\right] \qquad 4,6$$

$$\sigma_Y^A = \sigma + \sigma_{aY}^A + x'_A\sigma^A + x_S\sigma^S + \frac{1}{6}\left[\phi'_A\chi_{vA} + \phi_S\chi_{vS}\right] \qquad 4,7$$

where x_A, x'_A, x_B and x_S are the initial mole fractions of A, B and S; ϕ_A, ϕ'_A, ϕ_B and ϕ_S the corresponding volume fractions and χ_{v_A}, χ_{v_B} and χ_{v_S} the corresponding volume bulk susceptibilities. It is assumed that A and B form a complex such that at any time there is the fraction n_{AB}/n_A of species A complexed and the fraction $\frac{n_A - n_{AB}}{n_A}$ of species A free; also it is assumed that the specific screening of the complex is σ_{comp}, the other screenings being as for the free state. Therefore, if the samples are deliberately prepared with $x_B = x_S = x$ and hence $x_A = x'_A$, equations 4,6 and 4,7 now become, for a sample j,

$$\sigma^{A}_{X_j} = \sigma + \sigma^{A}_{aX_j} + \frac{n_{A_j} - n_{AB_j}}{n_{A_j}}\left[\chi_{A_j}\sigma^{A} + \chi_j\sigma^{B} + \frac{1}{6}\left\{(1-\phi_{B_j})\chi_{VA} + \phi_{B_j}\chi_{VB}\right\}\right]$$

$$+ \frac{n_{AB_j}}{n_{A_j}}\left[\chi_{A_j}\sigma^{A} + \chi_j\sigma^{B} + \frac{1}{6}\left\{(1-\phi_{B_j})\chi_{VA} + \phi_{B_j}\chi_{VB}\right\} + \sigma_{comp}\right] \qquad 4,8$$

$$\sigma^{A}_{Y_j} = \sigma + \sigma^{A}_{aY_j} + \chi_{A_j}\sigma^{A} + \chi_j\sigma^{S} + \frac{1}{6}\left\{(1-\phi_{S_j})\chi_{VA} + \phi_{S_j}\chi_{VS}\right\} \qquad 4,9$$

Equation 4,8 may be simplified to give

$$\sigma^{A}_{X_j} = \sigma + \sigma^{A}_{aX_j} + \chi_{A_j}\sigma^{A} + \chi_j\sigma^{B} + \frac{1}{6}\left\{(1-\phi_{B_j})\chi_{VA} + \phi_{B_j}\chi_{VB}\right\} + \frac{n_{AB_j}}{n_{A_j}}\sigma_{comp} \qquad 4,10$$

The difference between equations 4,9 and 4,10 ($\sigma^{A}_{Xj} - \sigma^{A}_{Yj}$) is equivalent to the measured chemical shift, $\delta_{obs\ j}$, for the solute in the two different situations in the sample tube. Thus the observed chemical shift is given by

$$\delta_{obs_j} = \chi_j(\sigma^{B} - \sigma^{S}) + \sigma^{A}_{aX_j} - \sigma^{A}_{aY_j} + \frac{1}{6}\left\{(\phi_{S_j} - \phi_{B_j})\chi_{VA} + \phi_{B_j}\chi_{VB} - \phi_{S_j}\chi_{VS}\right\} + \frac{n_{AB_j}}{n_{A_j}}\sigma_{comp} \qquad 4,11$$

If no complex formation occurs this equation reduces to

$$\delta'_{obs_j} = \chi_j(\sigma^{B} - \sigma^{S}) + \sigma^{A}_{aX_j} - \sigma^{A}_{aY_j} + \frac{1}{6}\left\{(\phi_{S_j} - \phi_{B_j})\chi_{VA} + \phi_{B_j}\chi_{VB} - \phi_{S_j}\chi_{VS}\right\} \qquad 4,12$$

Consequently, if for each one of a series of samples having different mole fractions x_j (corresponding to n_{Aj}, n_{Bj} and n_{Sj}) the chemical shift difference between the solute in the annulus and capillary is determined and plotted against x_j, for convenience, the shift difference between the resulting line and the correspondingly plotted absolute reference line (from equation 4,12) can be represented by

$$\Delta_j = \delta_{obs_j} - \delta'_{obs_j} = \frac{n_{AB_j}}{n_{A_j}}\Delta_c \qquad 4,13$$

where σ_{comp} has been equated with the aromatic induced shift, Δ_c. If the line corresponding to equation 4,12 can be accurately constructed, then the procedure described above automatically corrects for any medium effects. Also, since the solute is contained at the same mole fraction in both the annulus and capillary, solute self-association ideally affects equations 4,11 and 4,12 to the same extent, and the effect on solute screening would not be detected. However, since in the annulus, complex

formation occurs, the efficiency of the procedure for correcting for solute self-association may be reduced, as well as the operative value of n_{Aj} (in equation 4,1) being modified. As is discussed in chapter 6 the experimentally determined anisotropy screenings include the dispersion force screening as well. There will, however, remain a residual dispersion screening to be taken into account, this arising from the use of cyclohexane as the solute in the experimental determination of the anisotropy (and dispersion) screening, whereas in this new procedure different solutes are used. This does not change either of equations 4,11 and 4,12 but equation 4,5 must be redefined as

$$\sigma^A = \sigma_E^A + \sigma_{\omega'}^A \qquad 4,14$$

where $\sigma_{w'}^A$ is the residual dispersion screening acting on A. σ^A is neither obtainable theoretically or experimentally but differences in this screening are assumed to be very small and equated to zero.

4.3 The Procedure to be Adopted

In order to make use of this new procedure it is necessary to be able to construct the line corresponding to equation 4,12 so that the observed chemical shifts between the solute in the two situations may be corrected for medium screening effects. To do this it is necessary to consider the nature of the various screening effects and particularly their variation with mixture composition. Because of the complexity of these screenings, the implementation of the new procedure will be delayed until chapter 7, after the discussion on these points. These are examined in detail in chapter 5 and the assumptions made above regarding their mole - or volume fraction additivity are given detailed justification. Because of the conclusions reached there it is necessary to study the composite anisotropy screening $(\sigma_a + \Delta\sigma_w)$ separately and values relevant to the systems to be examined for complex formation are given in chapter 6. In the course of the experimental determination of $\sigma_a + \Delta\sigma_w$, screening corrections are obtained which

enable the line corresponding to equation 4,12 to be obtained and the new procedure implemented. This implementation is considered in detail in chapter 7 where the procedure is used to determine values of the equilibrium quotient, K, and excess shielding, Δ_c for a number of known 1 : 1 complexes; as well as to investigate the inertness of various solvents and references. Finally, investigations at a variety of temperatures are reported in chapter 9; these results are used to obtain thermodynamic parameters which are compared with corresponding data obtained by using a conventional three-component procedure[62].

CHAPTER 5

A Critical Examination of the Chemical Shift

5.1 Introduction

Because of the new externally referenced procedure described in chapter 4 it is necessary to examine the various contributory factors to the chemical shift in some detail. The actual field, B_i, experienced by a nucleus (i) placed in a strong external magnetic field differs slightly from the static applied field, B_o, and may be represented by

$$B_i = B_o(1 - \sigma_i) \qquad 5,1$$

where σ_i is the nuclear screening and is a measure of the secondary fields which are induced both within the molecule containing the resonant nucleus and also in its neighbours (see section 1.9). Therefore a chemical shift between two such nuclei i and j is defined by

$$\delta_{ij} = B_i - B_j / B_o = \sigma_j - \sigma_i \qquad 5,2$$

It is possible to write σ as the sum of intermolecular and intramolecular terms, so that the total screening of nucleus A may be represented by

$$\sigma_A = \sigma_A^{intra} + \sigma_A^{inter} \qquad 5,3$$

It is extremely difficult to calculate the magnitude of either of these terms directly; for example, the earliest attempt to calculate σ_A^{intra} was by Lamb[87] who considered that the magnetic screening of a nucleus resulted from induced electronic currents in a free atom that had no orbital or spin angular momentum. This proved unsuitable even for isolated molecules and Ramsey[88-89], using a second order perturbation treatment, was the first to derive a theoretical expression for the screening in such systems. However, for calculations involving any but the smallest molecules this is still unsuitable and it seems reasonable therefore, especially when dealing with large molecules, to use simple physical models to obtain approximate calculations of chemical shifts.

Saika and Slichter[90] were the first to suggest splitting the total intramolecular screening of a nucleus into a number of individual contributions, each having classical significance, when they divided the nuclear screening into three separate atomic contributions as follows -

a) the diamagnetic correction for the atom in question,

b) the paramagnetic term for the atom in question, corresponding to the Lamb[87] equation,

c) contributions from other atoms.

Since it was evident that treatment of the intramolecular screenings in the classical sense is beneficial this was also applied to the intermolecular screenings. It is now generally accepted that the total nuclear screening may be divided into nine contributions[9,86] representing intramolecular and intermolecular screenings, wherein the terms in equation 5,3 become

$$\sigma_A^{intra} = \sigma_{AA}^{dia} + \sigma_{AA}^{para} + \sum_{B \neq A} \sigma_{AB} + \sigma_A^{deloc} \qquad 5,4$$

$$\sigma_A^{inter} = \sigma_a + \sigma_b + \sigma_\omega + \sigma_E + \sigma_A^{specific} \qquad 5,5$$

A contribution to the measured chemical shift between two nuclei is obtained from differences in any of these terms. Each of the individual terms, which will be discussed in sections 5,2 and 5,3, has classical significance and can be evaluated with at least a certain degree of accuracy. However, for the present work where the chemical shift between a common solute in different environments is required, the assumption may be made that the intramolecular screening of such a solute is identical in the two cases; hence it is only necessary to consider intermolecular screenings. If an external reference is being used to study molecular interactions in solution, as required for the procedure described in chapter 4, it is particularly important to have a complete understanding of the various intermolecular screening contributions, especially their variation with mixture composition and temperature. Whilst each of the screening terms will therefore be discussed in turn,

emphasis will be placed on the intermolecular screenings.

5.2 The Intramolecular Screening Effects

a) The Diamagnetic Term, σ^{dia}_{AA}

σ^{dia}_{AA} arises from diamagnetic currents induced on atom A and it corresponds to term a) proposed by Saika and Slichter[90]. The magnitude of σ^{dia}_{AA} depends upon the electron density around the nucleus of A and its effect through equation 5,1 (as with all the other screenings) is proportional to the applied field. The moment induced through the rotation (with the Larmor precessional frequency, $\frac{eB_o}{2mc}$) of the electrons about a nucleus produces a screening at that nucleus, which for those atoms having spherically symmetrical electron distributions is wholly diamagnetic whereas for those having unsymmetrical electron distributions there is also a paramagnetic contribution to the screening.

b) The Paramagnetic Term, σ^{para}_{AA}

σ^{para}_{AA} arises as a consequence of the mixing, of the ground and excited electronic states of an atom[91-92], induced by the applied field, B_o. A simple physical representation is that this screening arises from local fields induced at the resonant nucleus. If these fields are axially symmetric, with respect to the applied field, there is no paramagnetic screening term, but if they are not axially symmetric there is a hindrance to the Larmor precession of the electrons about the resonant nucleus which results in a σ^{para}_{AA} screening. Pople[93] has shown that an excited state contributes to the local paramagnetic current on an atom only if it corresponds to the transfer of an electron between p and d orbitals, hence σ^{para}_{AA} is zero when the electrons localized on A are in a pure s state.

c) The Interatomic Screening Term, σ_{AB}

σ_{AB} arises from the neighbour anisotropy effect[94] and corresponds in part to the third term of Saika and Slichter[90]. When atoms, other than A in the molecule, having different principal components of magnetic

susceptibility χ_i, are placed in a strong magnetic field, B_i in the i direction, different magnetic moments $\chi_i B_i$ are induced along the principal axes of the substituent, and these induced dipoles produce secondary fields at nucleus A. The magnitude of the screening produced by these fields is entirely dependant on the nature of B, and may be positive or negative depending on whether the induced currents on B are diamagnetic or paramagnetic in character and also on the orientation of the AB radial vectorwith respect to the applied field.

d) The Delocalized Electron Screening, σ_A^{deloc}

σ_A^{deloc} arises from additional induced interatomic currents which flow around closed conjugated loops such as in benzene, where the six mobile π-electrons appear to behave like charged particles that are free to move in a circular wire. Thus, on applying a magnetic field, B_o perpendicular to the plane of the ring, these electrons circulate with an angular frequency $eB_o/2mc$ giving a total current (i) of

$$i = 3e^2B_o/4\pi mc \qquad 5,6$$

This electron current induces a secondary field at the centre of the aromatic ring which is in opposition to the applied field. The lines of force of this secondary field follow circular paths at right angles to the plane of the ring, and thus the applied field is reinforced at the positions of the aromatic protons which are consequently deshielded. This is also relevant to studies of complex formation, and will be discussed further in section 5.8.

5.3 An Introduction to Intermolecular Screening Effects

Intermolecular screening effects have received study in considerable detail recently[8,10,30,86,95-96], and many authors have used the term solvent effects for these screenings. For a qualitative interpretation this is adequate since it is then only necessary to consider the effect of a change of solvent on a solute chemical shift. However, on a quantitative basis such considerations are inadequate because it then becomes imperative to make allowance for the effect of every molecule in the solution

(including any solute molecules present) on the chemical shift of the solute. Such studies have usually resulted from an interest in a single one of the intermolecular screening effects and there has thus arisen the problem of separating the particular effect considered from all the remaining screening contributions. The bulk magnetic susceptibility screening (σ_b) may easily be evaluated[8], but the other three screenings (σ_a, σ_w and σ_E) have proved more troublesome. Buckingham[97] has provided the theory for the electric field effect (σ_E) and this, with later refinements which take better account of molecular shape[98], has given a good basis for estimating σ_E. Howard, Linder and Emerson[99] have tried to develop a similar theory for the van der Waals (dispersion) contribution (σ_w) and have achieved qualitative success. More recently Raynes et.al.[100-102] have produced an improved quantitative description of the screening due to dispersion forces. Similarly, with regard to σ_a a qualitative picture of the anisotropy effect was gained by Buckingham et. al.[86] and by Stephen[103]. Homer[104] has provided a quantitative measurement of anisotropy screening and a mathematical treatment has been attempted by Schug[95] and Becconsall[105-107]. In almost every case the basic assumption has been made that a single solvent species acts on an isolated solute molecule; thus neither the effect of mixed solvents nor of other solute molecules has normally been considered. Where predictions regarding the variation of these screenings as a function of composition and temperature have been made they are generally without experimental substantiation. Thus, in the following discussion on intermolecular screening effects, predictions or theories relating them to the composition and temperature of solutions will be emphasized.

5.4 Bulk Magnetic Susceptibility, σ_b

The bulk susceptibility screening (σ_b) usually arises from the diamagnetic polarization of solvent molecules in an applied field. Solvent molecules at large distances from a resonant nucleus behave as

if they formed a continuum having the macroscopic properties of the solvent. Thus the bulk polarization of the solvent produces an additional field at the resonant nucleus which contributes to its screening constant σ. To calculate the magnetic field that would act on a resonant nucleus due to the bulk solution (i.e. assuming that there are no short range interactions) consider a macroscopic spherical cavity (figure 5.1), small relative to the size of the whole sample, hollowed out of the medium surrounding the active molecule. If the primary magnetic field is B_o, then the field B_i in the medium is uniform and parallel to B_o if the bulk sample is in either a spherical or cylindrical vessel. The application of classical magnetostatics leads to the results

$$\text{sphere: } B_i = B_o\left[3/(\chi_v+3)\right] = B_o\left[1/(1+\tfrac{1}{3}\chi_v)\right] \qquad 5,7$$

$$\text{cylinder: } B_i = B_o\left[2/(\chi_v+2)\right] = B_o\left[1/(1+\tfrac{1}{2}\chi_v)\right] \qquad 5,8$$

where χ_v is the volume susceptibility of the medium. The effective field in the cavity is

$$B_c = B_i\left[(\chi_v+3)/3\right] = B_i\left[1+\tfrac{1}{3}\chi_v\right] \qquad 5,9$$

Thus from equations 5,1, 5,7 and 5,9 it may be seen that

$$\sigma_b(\text{sphere}) = \frac{B_o - B_c}{B_o} = \frac{B_o - [1+\frac{1}{3}\chi_v][1/(1+\frac{1}{3}\chi_v)]B_o}{B_o} = 0 \qquad 5,10$$

and from equations 5,1, 5,8 and 5,9 that

$$\sigma_b\ (\text{cylinder}) = \frac{B_o - B_c}{B_o} = \frac{B_o - [1+\frac{1}{3}\chi_v][1/(1+\frac{1}{2}\chi_v)]B_o}{B_o} = \frac{1}{6}\chi_v \qquad 5,11$$

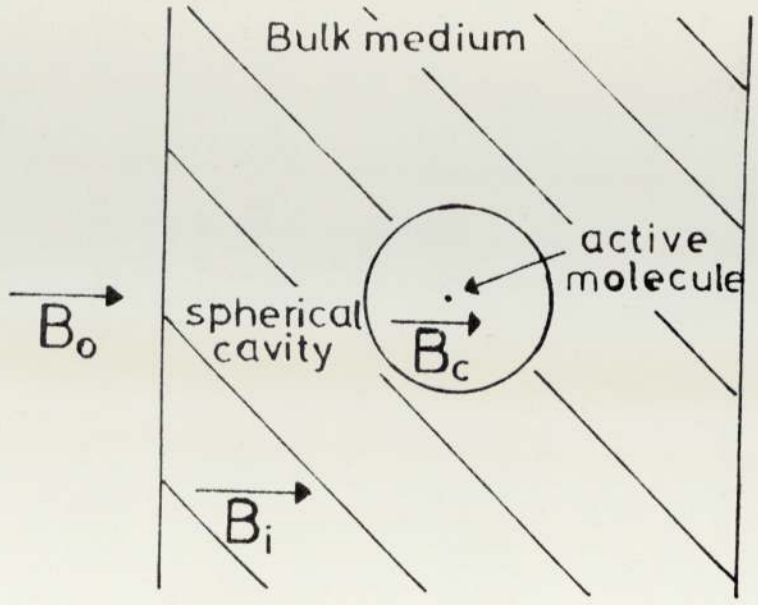
on neglecting terms in χ_v^2. These are the results originally obtained by Dickinson[108].

From equation 5,11 it follows that for cylindrical vessels

$$\delta_{corr}^{s-r} = \delta_{obs}^{s-r} + \frac{1}{6}\left(\chi_r - \chi_s\right) \qquad 5,12$$

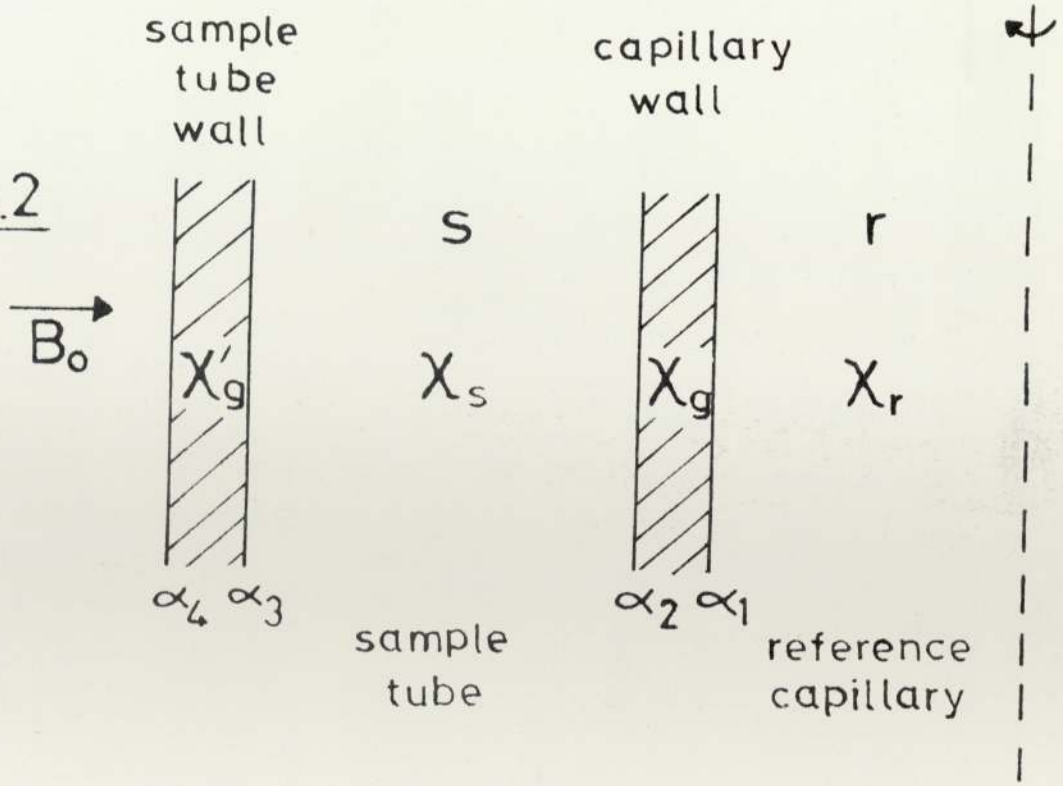
where s and r refer to sample and reference as illustrated in figure 5.2. Similar results have been obtained by Frost and Hall[109] who considered the sample vessels in terms of shape factors for each surface (α_i) and the susceptibilities of the glass of the main tube (χ'_g) and

5.1



Macroscopic spherical cavity, hollowed out of the bulk medium, surrounding the active molecule. B_o is the applied magnetic field and B_i and B_c are the magnetic fields in the bulk sample and spherical cavity respectively.

5.2



Symbols used in Frost and Hall's calculation of the bulk susceptibility screening(σ_b).

capillary (χ_g). Thus, by reference to figure 5.2 where a cylindrical sample tube with a cylindrical capillary is considered, it follows that

$$\sigma_s = \sigma + \alpha_4 \chi_g' - \alpha_3 \chi_g' + \alpha_3 \chi_s - \tfrac{1}{3}\chi_s \qquad 5,13$$

$$\sigma_r = \sigma + \alpha_4 \chi_g' - \alpha_3 \chi_g' + \alpha_3 \chi_s - \alpha_2 \chi_s + \alpha_2 \chi_g - \alpha_1 \chi_g + \alpha_1 \chi_r - \tfrac{1}{3}\chi_r \qquad 5,14$$

$$\sigma_s - \sigma_r = -\tfrac{1}{3}\chi_s + \alpha_2 \chi_s - \alpha_2 \chi_g + \alpha_1 \chi_g - \alpha_1 \chi_r + \tfrac{1}{3}\chi_r \qquad 5,15$$

where s refers to the sample solution and r to the reference solution. For a perfectly cylindrical reference vessel $\alpha_1 = \alpha_2 = {}^1/2$ and thus

$$\sigma_s - \sigma_r = \delta_{sr} = -\tfrac{1}{3}\chi_s + \tfrac{1}{2}\chi_s - \tfrac{1}{2}\chi_r + \tfrac{1}{3}\chi_r \qquad 5,16$$

and since $\delta^{s-r}_{corr} = \delta^{s-r}_{obs} - \delta_{sr}$ it follows that δ^{s-r}_{corr} is given by equation 5,12 which is thus identical to the result obtained by Dickinson[108], (for a spherical reference $\alpha_1 = \alpha_2 = {}^1/3$ and $\delta_{sr} = 0$, which again parallels Dickinson's result).

In general, mixture volume bulk susceptibilities have been considered to be additive as a function of the volume fractions of the mixture constituents[8, 110] thus

$$\chi_{mixt} = \sum_i \phi_i \chi_i \quad , \qquad 5,17$$

where ϕ_i is the volume fraction and χ_i the volume susceptibility of constituent i of the mixture. Broersma[111] has, however, investigated the volume susceptibilities of mixtures and, despite the relative insensitivity of the inductance technique[112] that he used in part, found that some mixtures showed nonlinear variations of volume susceptibility with component volume fraction. Mixtures such as ethanol-water and acetic acid-water, which are known to have large volume changes on mixing, were found to deviate by about 4.0 per cent from additivity in their volume susceptibilities, but these were exceptional. Table 5.1 compares the reduced excess volume of mixing (ρ) of the ethanol-water system with for a number of systems which have been investigated in the course of work reported herein.

Table 5.1

System	V^{excess} ($\times 10^6$ m^3 mol^{-1})	ϱ ($\times 10^2$)
Ethanol-water	- 1.4[113]	- 3.66
Acetone-chloroform	- 0.19[114]	- 0.25
Benzene-cyclohexane	~	+ 0.61[115-116]
Benzene-ethylene chloride	+ 0.24[117]	+ 0.29
Benzene-bromobenzene	Negligible[118]	Negligible
Chloroform-methyl iodide	Negligible[119]	Negligible
nHexane - n-Heptane	Negligible[120]	Negligible

The reduced excess volume change on mixing may be defined by

$$\varrho = \frac{V^{excess}}{\frac{1}{2}(V_1^{\,o}+V_2^{\,o})} \qquad 5,18$$

where V^{excess} is the volume change on mixing equimolar quantities of the components to form one mole of the mixture and $V_1^{\,o}$ and $V_2^{\,o}$ are the molar volumes of components 1 and 2. It is clear from table 5.1 that systems such as those studied herein will deviate by much less than 4.0 per cent from additivity, and in fact most mixtures of organic compounds show deviations from linearity of the volume susceptibility as a function of mixture composition of no more than 0.5 per cent, thus implying a maximum deviation of ca. $1/6(0.04 \times 10^{-6})$ or 0.36Hz at 60MHz. It therefore appears justified to state that equation 5,17 only holds exactly when there is no volume change on mixing and that the generally applicable expression is

$$\chi_{mixt} = \sum_i \bar{\phi}_i \chi_i \qquad 5,19$$

where $\bar{\phi}_i$ is the partial molar volume fraction of constituent i of the mixture. Nevertheless, Broersma's work[111] would appear to show that, unless there is reason to believe that there has been a considerable volume change on mixing, equation 5,17 may safely be used. In correcting for σ_b, tables of volume

susceptibilities provided by Emsley et. al.[9] have frequently been used but it would appear that this is unsatisfactory since χ_v is temperature dependant (via a density term). The molar susceptibility, χ_M, should in fact be used and the volume susceptibility at any particular temperature calculated using the equation

$$\chi_v^{(t)} = \frac{\chi_M \rho^{(t)}}{M} \qquad 5,20$$

where M is the molecular weight and $\rho^{(t)}$ the density of the compound at temperature t. Values of χ_M are most satisfactorily obtained from the Landolt-Börnstein tables of diamagnetic susceptibilities[121] and density variations with temperature from Timmermans compilations[122-123] since these refer to the original literature. Thus, it is possible, within the accuracy indicated above, to correct experimental chemical shifts for σ_b for any combination of solution composition and temperature.

5.5 Electric (or Reaction) Field Screening, σ_E

A uniform electric field distorts an atom in an S state giving a reduction in the shielding coefficient of magnitude proportional to E_z^2, since the symmetry of the atom requires that a change in the direction of E should not affect σ. However, a particular nucleus in a molecule may not be at a centre of inversion and σ may then be proportional to E_z and well as E_z^2. When E is an applied field then its average value at a particular nucleus will be zero if the molecules are in a liquid or gaseous state, but if E arises from a polar group within the molecule the E_z may not be zero. Thus, forming an X - H bond gives an increase in charge between the two nuclei and an electric field applied along the bond direction will draw this excess charge away from the hydrogen nucleus, thereby decreasing its shielding coefficient. The magnitude of the decreases is[97]

$$\sigma_E = -2 \times 10^{-5} - 2 \times 10^{-12} E_z - 10^{-18} E_z^2 \qquad 5,21$$

A polar molecule in solution polarizes the surrounding medium and the nuclei in the molecule experience a reaction field, R, whose value is independant of the random motion of the molecules; if the molecule is symmetrical the resultant mean field is in the direction of the dipole moment of the molecule. Buckingham[97] has used a value for R obtained by Onsager[124]; the solute molecule is considered to be a sphere of radius r with a point dipole μ at the centre, and the solvent is considered as a continuous medium of dielectric constant ε_r, thus

$$R = \frac{2(\varepsilon_r - 1)(n^2 - 1)}{3(2\varepsilon_r + n^2)\alpha}\mu \qquad 5,22$$

where n is the refractive index of the pure solute and α is the polarizability of the sphere and is equal to $\left(\frac{n^2+1}{n^2+2}\right) r^3$. Diehl and Freeman[98] have accounted for the shape of the solute molecules using

$$R = \frac{\mu}{abc} \cdot 3\,\xi_a\left[1+(n^2-1)\xi_a\right]\left[\frac{\varepsilon_r - 1}{\varepsilon_r + \left(n^2\xi_a/(1-\xi_a)\right)}\right] \qquad 5,23$$

where the dipole acts from the centre of a non-spherical cavity with semi-axes a, b, c and ξ_a is a shape factor for the solute which can be deduced by the method of Ross and Sack[125]. It has been shown[104] that equation 5,23 gives a better fit with experiment than equation 5,22, but since values of σ_E are usually required for comparison purposes little error is introduced by using 5,22 which has the virtue of being easier to use.

In mixtures electric field screenings are believed to be mole fraction additive[86], but in any case, in the measurements reported herein, shift differences are always used and, as an approximation, differences in electric field screenings (even if operative) on a common solute are ignored.

5.6 Anisotropy in the Magnetic Susceptibility, σ_a

The anisotropy screening (σ_a) is most clearly seen in the large differential shifts often found between solutes in aromatic and non-aromatic solvents. These are caused by a modification to the magnetic

field at the solute nucleus, which is in principle calculable from a knowledge of the distrubution of magnetization in the sample. Qualitatively these shifts may be explained in terms of the large diamagnetic anisotropy of an aromatic molecule which arises from the circulation of the aromatic π-electrons (ring current effect[126]). The distribution of orientations of solvent molecules surrounding a solute molecule may be non random at small distances because of the latter's presence and this may result in a time-averaged non-zero susceptibility tensor which leads to a screening at the nucleus of the solute molecule[127]. Possible causes of this nonrandomness, which have recently been discussed, include electric dipolar interactions[128-133], size and shape of the solute[134-136] and steric crowding in condensed aromatics[137]. Where polar solutes are present specific collision complexes of finite lifetime may be obtained due to particularly strong attractive forces, and in these cases only that part of the screening attributable to nonrandom orientations may be considered to constitute σ_a (i.e. the anisotropy screening is present in addition to any screening due to complex formation[138]). Normally, theoretical predictions on the magnitude of σ_a only consider nonpolar solutes and then σ_a is assumed to be dependant on the shapes of the constituent molecules of the solution. Buckingham et.al.[86] have given an 'order-of-magnitude' approximation for this shape effect, describing σ_a by the following expression

$$\sigma_a = -\frac{n}{4\pi}\left[\chi_{\parallel} - \chi_{\perp}\Big/3R^3\right](3\cos^2\theta - 1) \qquad 5,24$$

where n is the number of molecules in the relevant range of R, $\chi_{\parallel}$ and $\chi_{\perp}$ are the molar magnetic susceptibilities parallel and perpendicular to the molecular axis, R is the distance from the centre of the anisotropic molecule to the centre of the resonating nucleus and θ is the angle between the axis of the solvent molecule and the line joining the solvent and the nucleus under consideration. Two limiting cases of this basic

equation were given, for disc and rod shaped solvents respectively.

$$\sigma_a(\text{disc}) \cong - n\Delta\chi/6\pi R^3 \qquad 5,25$$

$$\sigma_a(\text{rod}) \cong + n\Delta\chi/12\pi R^3 \qquad 5,26$$

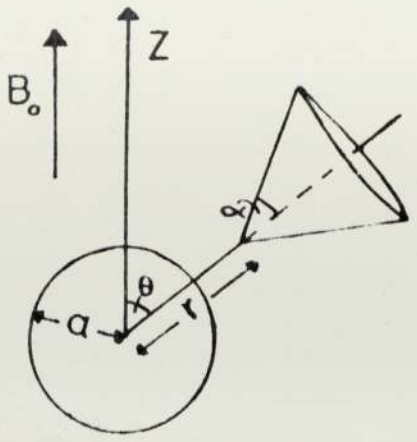
where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$. Similarly, Stephen[103] has given a statistical mechanical calculation in which the solute is treated as a point, and he obtained similar equations. Stephen[103] was the first to suggest that anisotropy screenings were dependant on the contact of the anisotropic molecule with the molecule containing the resonant nucleus since restricted rotation prevented averaging of the susceptibility to zero. Abraham[139] has derived a rather less qualitative equation, based on an idea (of a proton moving over a cylindrical surface encasing the anisotropic molecule) introduced by Bothner-By and Glick[140], which defines σ_a as

$$\sigma_a = 10^{42} \cdot \frac{1}{6\pi} \Delta\chi \frac{r-h}{(r+2h)(r^2+h^2)^{3/2}} \qquad 5,27$$

where the anisotropic molecule is a cylinder of effective radius r (pm) and height 2h (pm) with different magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ along and perpendicular to the cylinder axis. Equation 5,27, however, only provides an estimate of the screening contribution from a single anisotropic molecule. Schug[95] has expanded Abraham's ideas but as his approach is based on some apparently erroneous concepts (which will be considered later) his theory will not be discussed in detail.

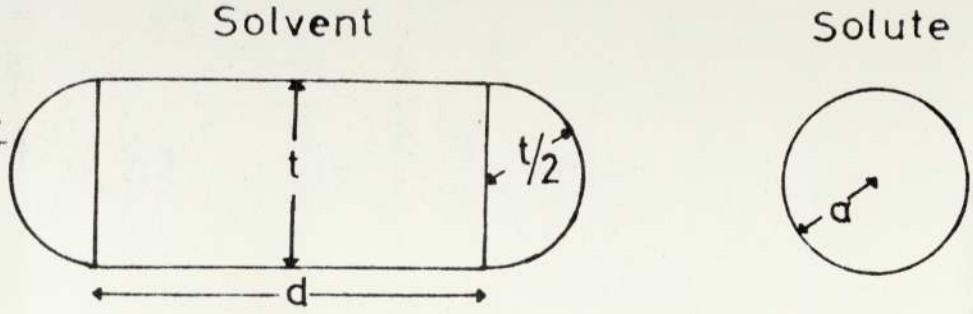
Becconsall has recently expanded the suggestion of Stephen[103], that σ_a is a contact phenomenon, so as to give a much better calculation of σ_a[105-107]. His model is based on setting up cones of permitted orientations of the axis of symmetry of the solvent molecule in relation to the solute molecule, the semi-angle of the cone being dependant on the dimensions of the solute and solvent molecules and on the separation distance. By reference to figures 5.3 and 5.4 it may be seen that for the particular example of a solute which is a sphere of radius a, and of a solvent which is a disc having a thickness t with parallel flat faces of diameter d and semi-circular end profiles of radius $t/2$, the semi-angle

5.3



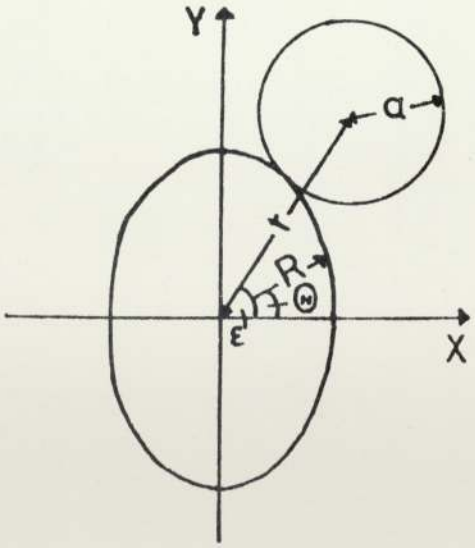
Cone of permitted orientations for a solvent molecule about a spherical solute molecule of radius a.

5.4



Dimensions of the solvent and solute used in the calculation of σ_a.

5.5



Orientation restriction for a general solvent molecule represented by R = F(Ⓝ).

of the cone α may be given by

$$\alpha = \cos^{-1}\left(\frac{a + t/2}{r}\right) \qquad 5,28$$

for $a + t/2 \leqslant r \leqslant \left(a^2 + \frac{d^2 + t^2}{4} + at\right)^{\frac{1}{2}}$ and

$$\alpha = \sin^{-1}\left(\frac{r^2 + (d^2 - t^2)/4 - a^2 - at}{rd}\right) \qquad 5,29$$

for $\left(a^2 + \frac{(d^2 + t^2)}{4} + at\right)^{\frac{1}{2}} < r \leqslant a + \frac{1}{2}(d + t)$, whilst for $r > a + \frac{1}{2}(d + t)$ there will be no restriction on the orientations of the solvent molecules. Becconsall also assumed that the probability distribution for the orientation of the solvent molecular symmetry axis was uniform throughout the solid angle of the cone, and, with the restriction on the angle of contact between solute and solvent molecules, this means that the solute experiences a screening, due to any anisotropy in the solvent's magnetic susceptibility, from those solvent molecules within the contact distance, but from those solvent molecules outside this distance σ_a averages to zero.

Values of σ_a for a general solvent were obtained by considering it to be represented by an axially symmetric convex solid body whose surface may be given by

$$R = F(\Theta) \qquad 5,30$$

where R is the radius from the centre of symmetry and Θ is the angle between the radius vector and the symmetry axis. A rectangular co-ordinate system was set up with its origin at the centre of the solvent molecule and its x-axis lying along the symmetry axis of the molecule (figure 5.5). The y-axis was chosen so that the centre of the solute molecule lay in the xy plane, thus the condition that a point on the surface of the 'solvent molecule' at $x = R\cos\Theta$, $y = R\sin\Theta$ also lay on the surface of the 'solute molecule' centered at $x = r\cos\varepsilon$, $y = r\sin\varepsilon$ was

$$[F(\Theta)\cos\Theta - r\cos\varepsilon]^2 + [F(\Theta)\sin\Theta - r\sin\varepsilon]^2 = a^2 \qquad 5,31$$

For arbitary values of r and ξ equation 5,31 will in general have two real roots $\textcircled{H}_1$ and $\textcircled{H}_2$ or none. The condition that the surfaces touch is that the two real roots $\textcircled{H}_1$ and $\textcircled{H}_2$ are equal, and for a given separation r between centres the value of ξ which makes the two roots converge is the semi-angle α of the allowed orientations.

The solvent anisotropy contribution to the screening constant, assuming $F(\frac{\pi}{2}) > F(0)$, is

$$\sigma_a = -\frac{\rho(\chi_{ax} - \chi_{br})}{3} \int_{a+F(0)}^{a+F(\frac{\pi}{2})} \frac{\cos\alpha(1+\cos\alpha)}{r}\, dr \qquad 5,32$$

and if $F(0) > F(\frac{\pi}{2})$ it is found that

$$\sigma_a = +\frac{\rho(\chi_{ax} - \chi_{br})}{3} \int_{a+F(\frac{\pi}{2})}^{a+F(0)} \frac{\cos^2\alpha}{r}\, dr \qquad 5,33$$

This model gave a good qualitative correlation between the value of σ_a and the radius of the solute, but the answers obtained were about twice those actually observed. Becconsall[105-107] has postulated that this may be due to neglect of weak attractive dispersion forces between the solute and solvent which are believed to pull the edges of the solvent molecules towards the surface of the solute (i.e. so as to favour those orientations of the solvent molecular axis that are furthest from the radial orientation); this would invalidate the assumption of a uniform distribution through the permitted solid angle, and would act in such a way as to reduce σ_a. The extreme case is that the solvent is always on the edge of the cone and σ_a has been recalculated with this assumption;[106-107] excellent correlation between theory and experiment being obtained.

The anisotropy screening, allowing for dispersion forces between solute and solvent molecules, may be calculated as follows[107]. The interaction forces which produce a locally non-random distrubution of solvent molecule orientations must be of comparatively short range and it may be assumed that their effects are confined to a shell around the solute molecule whose thickness is of the same order of magnitude as the molecular

dimensions. This solvent shell is treated as a continuum over a long period of time. Using a reference frame which is fixed on the solute molecule, sharing its translational and rotational motions, the magnetic effects of the solvent are represented by a time-averaged volume magnetic susceptibility tensor χ_v, which is determined by the solute-solvent interaction forces for each point in the shell. The approximate exclusion surface presented to a benzene solvent molecule is considered to be the envelope of the atomic exclusion spheres of the solute, which have radii $(a_i + {}^{t}/_{2})$, a_i being the van der Waals radius of the ith atom in the solute molecule and t being the thickness of the benzene molecule. The susceptibility tensor, χ_v, is assumed to be axially symmetric, the symmetry axis being the normal from the nearest point on the exclusion surface, i.e. along the radius vector from the nearest exclusion sphere. The anisotropy can then be expressed as a scalar $(\chi_{vr} - \chi_{v\theta})$, where χ_{vr} and $\chi_{v\theta}$ are the susceptibilities along the radius vector and perpendicular to it respectively. The anisotropy is assumed, for simplicity, to be constant along a given radius vector, and to be a function of the nature and radius of the nearest exclusion sphere. With these assumptions σ_{ai} may be defined as

$$\sigma_{ai} = -\frac{1}{4\pi}\int^{\text{shell}} (\chi_{vr} - \chi_{v\theta})_j \frac{3\cos^2\theta_{ij} - 1}{3r_i^3}\, dv \qquad 5,34$$

where $(\chi_{vr} - \chi_{v\theta})_j$ is the anisotropy appropriate to the exclusion sphere (the j th) nearest the volume element dv, and θ_{ij} is the angle between the vectors from the ith nucleus and the jth exclusion sphere centre to dv, r_i being the distance from that nucleus.

None of the above theories have been concerned with mixtures, but as it would appear that the anisotropy screening is a molecular interaction effect it might be expected that the total σ_a be given as

$$\sigma_a = \sum_i x_i \sigma_a^i \qquad 5,35$$

where x_i is the mole fraction of the ith component of the mixture whose anisotropic screening is given by σ_a^i. Schug[95] has, however,

developed Abraham's[139] ideas to include mixtures. He assumed that the nucleus under observation sampled the entire available volume outside the exclusion surface of each anisotropic molecule. The exclusion surface that he used was a cylinder and this necessitates an arbitrary compromise in choosing its dimensions since if its length and diameter are equal, σ_a is zero and σ_a is positive for a short cylinder and negative for a long one. Schug particularly stressed that this method accounts for the effects of all anisotropic molecules in the system (and not just the nearest neighbours as in Abraham's approach[139]); and in doing so used the fact that all liquid solutions are completely random in nature[141] and hence the anisotropy shift is directly proportional to the volume fractions of the anisotropic species. This would appear to be at variance with the idea that σ_a is a function of molecular shape and that σ_a of mixtures is a molecular parameter. Furthermore he stated[95] that the anisotropy screening of any anisotropic species is independant of the nature, size and shape of the molecule under study, and is entirely dependant on the concentrations and characteristics of the anisotropic species. Therefore he postulated that the anisotropy shift of every proton in solution should be identical; this is at variance with Becconsall's ideas[105-107] on the concept of σ_a, and also the experimental indications of Homer et. al.[63, 104, 142] that σ_a is in fact dependant on the nature of the molecule under study. Furthermore, only one special class of mixtures are completely random (perfect mixtures[143]), normally there are forces between all molecules which preclude a completely random arrangement. Critical examination of Schug's plots of σ_a versus constituent volume fraction[95] clearly show deviations, from the straight lines plotted, which would appear to indicate curvature rather than random scatter. The above considerations suggest that the variation of σ_a with mixture composition may be more complex than supposed,especially as the weak attractive forces between unlike solvent molecules should be different from those between like

molecules; and may well be more important than the solute-solvent attractive forces (whose neglect was acknowledged by Becconsall[105]) in determining the variation of σ_a with mixture composition. Hence the variation of σ_a has been the subject of a detailed examination (Chapter 6). With regard to the variation of σ_a with temperature Becconsall[105, 107] has indicated that this should occur because the dispersion forces, which control the σ_a screening, were believed to be temperature dependant[86,144]; therefore as these became weaker, on increasing the temperature, he predicted that the distribution of solvent molecules about the solute would become more random, hence σ_a would increase. This variation has been examined experimentally and reported in chapter 8.

5.7 Dispersion or van der Waals Screening, σ_w

σ_w arises from dispersion forces which exist when any two molecules come together. Interactions between molecules perturb their electronic structure and the resultant distortion leads to a solvent dependant nuclear screening constant. The screening due to dispersion interactions is believed to result from fluctuating electric fields originating in both molecules. However, as the effect on the solute is being examined it is the fluctuating electric field of the solvent molecule which contributes to the σ_w screening. Although the average magnitude of this field, $\bar{F}$, is zero over a period of time, the time average value of its square, $\bar{F}^2$, is not zero. This causes an expansion of the electric cloud of the solute proton and therefore a reduction in the screening. Thus[103,145]

$$\sigma_w = - C\bar{F}^2 \qquad 5,36$$

where C is a parameter depending only on the solute molecule. There are two ways of determining $\bar{F}^2$. That of Howard, Linder and Emerson[99] treats the solute as being surrounded by a continuous dielectric medium, giving the dispersion screening as

$$\sigma_w = \frac{3}{4} hg\phi \left[\nu_1\nu_2/\nu_1+\nu_2\right] \qquad 5,37$$

where ν is a mean absorption frequency (1 refers to solvent, 2 to solute) deduced from

$$\nu = -\left[mc^2/\pi hL\alpha\right]\chi_M \qquad 5,38$$

α being the optical polarizability and χ_M the molar diamagnetic susceptibility of the appropriate solution component. ϕ is a constant characteristic of the nuclear species and g is given by

$$g = \left[(2n^2-2)/(2n^2+1)\right]/a^3 \qquad 5,39$$

where n is the refractive index of the solvent, and a is the radius of the solute which can be deduced from its molar volume. Lumbroso et. al[146] consider that this does not give good agreement with experimentally determined values, and subsequent improvements in the theory by de Montgolfier[147] leads to little better agreement with experiment. The second approach to $\overline{F}^2$ involves treating the solute's environment as consisting of a discrete number of solvent molecules and Rummens et. al.[148] have presented both a binary 'collision gas' model and a 'cage' model of estimating σ_w in this case. Their approach allows $\overline{F}^2$ to be different at different parts of the solute; however, this only gives reasonable answers for small molecules. In general, calculated values of σ_w are relatively small but Raynes et. al.[100] has apparently measured real dispersion screenings which are large, although in many cases differences in σ_w when using the same solute are small; and he has made the point that dispersion screening theory is far from understood.

Nearly all measurements made by Raynes et. al.[100] were using solutes and solvents having highly anisotropic bonds in them and it would seem possible that when such molecules are in contact some measure of restricted rotation of one or more of these bonds could cause a σ_a screening which has been measured and equated with the σ_w screening. It appears, therefore, that these two screenings are very difficult to separate

experimentally and it is suggested that they be combined into one measurable parameter. Assuming that Becconsall's[105-107] ideas are correct it would appear that this parameter consists of three separate terms; a genuine σ_a due to contact within the anisotropic shell surrounding the solute, a σ_w term arising within this shell and again due to molecular contact and finally a σ_w term from solvent molecules outside this shell (this term would be small due to the fall off in the magnitude of σ_w via a r^{-6} term). Therefore a solute molecule in an anisotropic solvent would experience all three screenings, whilst in an isotropic solvent it would only experience a genuine σ_w effect. However, even if the solvent is superficially isotropic it may still give a σ_a effect, e.g. tetranitromethane [100], which is isotropic solely because of the free rotation of the nitro groups about the carbon-nitrogen bond. It appears certain that within the contact shell of a solute molecule the rate of rotation of at least one nitrogroup will be reduced and a transient σ_a will be obtained. In the experimental determination of the $\sigma_a + \sigma_w$ screening a 'probe' solute is used in both the 'unknown' solvent and in a carbon tetrachloride reference capillary (this being a genuine isotropic molecule) hence a $\sigma_a + \Delta\sigma_w$ screening is in fact obtained which accurately reflects changes in mixture composition and temperature.

5.8 The Screening due to Specific Interactions, $\sigma_A^{specific}$

This is an additional screening obtained when molecules (of the same or different molecular species) participate in an interaction for a finite time, thus forming a complex. A complex of this type can exist in a variety of forms such as hydrogen bonded, charge transfer, dipole-dipole or dipole-induced dipole. In general, because the time of the n.m.r. experiment is long, only a time average position for the free and complexed molecules is observed (see figure 3.1),,the chemical shift being dependant on the relative amounts of each (see section 1.11).

The type of complex considered herein is the solute dipole-aromatic solvent induced dipole type where considerable chemical shift changes occur due to the presence of the conjugated π-system of the aromatic ring. The main interest in these is to obtain structural and thermodynamic parameters relating to their formation. In order to determine the structures of these complexes it is necessary to assume that their stoichiometry is 1 : 1 and that the solute dipolar axis is aligned along the aromatic six-fold axis (but see section 3.11). An important aspect in the study of these complexes is that $\sigma_A^{specific}$ is concentration dependant hence it can be experimentally determined using a concentration series.

In order to determine the precise magnitude of the induced magnetic field in the vicinity of the ring, arising from the π-electron circulation (Musher[149-150] has strongly criticized the idea of a ring current, but it is a useful concept when considering aromatic screenings) a convenient model must be developed since a rigorous treatment involving consideration of the shape of the π-orbitals would be extremely complicated. Pople[126], following Pauling[151] considered the π-electrons to move in the carbon plane and to produce a ring current (I) of

$$I = \frac{ne^2 B_o \cos\theta}{4\pi mc} \qquad 5,40$$

where n is the number of circulating π-electrons and $\cos\theta$ is a term allowing for the time-averaged orientation of the ring with respect to the B_o direction.

The aromatic ring current is equivalent to a point magnetic dipole ($\bar{m}$), acting at the ring centre, given by

$$\bar{m} = \frac{ne^2a^2 B_o \cos\theta}{4mc^2} \qquad 5,41$$

where a is the aromatic ring radius. This causes a magnetic field at the aromatic proton, distance R from the centre of the ring (expressed as a screening) of

$$\sigma_{HOR} = -\frac{ne^2a^2\cos^2\theta}{4mc^2R^3} \qquad 5,42$$

Substituting n = 6, $\cos^2\theta$ = 1/3, R = 246.5 pm and a = 139.5 pm, σ_{HOR} is calculated to be - 1.83 ppm which may be compared with the experimental value of - 1.48 ppm[152] for the aromatic proton (when compared with the proton screening in a non aromatic cyclic diene:- 1 : 3 cyclohexadiene, which is similar to benzene in all respects except for a circulating π system). Johnson and Bovey[152], in more elegant calculations, have shown that by taking two current carrying loops of the radius of the aromatic ring to represent the circulating electrons, the calculated shifts for a wide range of aromatics are in good agreement with the experimental values when the separation of the loops is 0.918 ring radii (128 pm). This would appear to indicate that a two loop model of electron circulations can be considered reliable when estimating π -electron screening effects in the plane of the ring. It is reasonable, therefore, to extend the use of this model for the calculation of screenings in the direction of the six-fold symmetry axis of the ring. By the use of simple electromagnetic theory the following expression may be obtained for the screening effect of the two loops along the six-fold axis, at a distance R from the plane of the aromatic ring

$$\sigma_{VERT} = \frac{ne^2a^2\cos\theta}{4mc^2}\left[\frac{1}{((R-d)^2+a^2)^{3/2}} + \frac{1}{((R+d)^2+a^2)^{3/2}}\right] \qquad 5,43$$

To obtain a screening at any general position around an aromatic ring it is possible to use tables provided by Emsley et. al.[9], based on Johnson and Bovey's calculations[152]. Experimental values of the induced chemical shift may be obtained by the methods outlined in chapter 3 and these may be used in conjunction with the above tables of aromatic screenings to obtain structures for the complex.

5.9 Conclusions

In the above sections all the various screening terms have been considered, their importance depending on whether the chemical shifts are measured internally (when differences between the screenings are small) or externally (when these differences are large). The new procedure, for investigating molecular interactions in solution[59], discussed in chapter 4 employs an external reference, therefore the foregoing is valuable in the elucidation of the screening corrections required for this. From the above discussions on the various intermolecular screening effects it is apparent that only σ_b can be accurately evaluated; this is particularly true as the variation of these effects with mixture composition is required. It may be seen by reference to the theory of the new procedure (section 4.2) that the chemical shift of the same solute in different environments is required. However, because this solute is of necessity interacting, in one half of the system, with the aromatic to form a complex, it is impossible to measure the σ_a, σ_w and σ_E screenings of the aromatic on the solute. It is therefore necessary to use a non-complexing 'probe' which is non-polar to obtain approximate values for these screenings, hence no value or even estimate of the σ_E screening is possible. Nevertheless, since the shift of the same polar solute in two different environments is required it is reasonable to assume that $\Delta\sigma_E$ is zero. Furthermore it is possible to estimate the composite anisotropy screening $(\sigma_a + \Delta\sigma_w)$ by use of the 'probe' and this will be described in the following chapter. There remains a residual $\Delta\sigma_w'$ screening which arises due to use of a 'probe' which differs from the solute used in the new procedure, but this should be small and is combined with the σ_E screening, as shown in equation 4,14, differences in which are equated to zero. The combination of the ideas expressed in this chapter with the results obtained in chapter 6 enables the new procedure[59], described in chapter 4, to be evaluated and this is discussed in chapter 7.

CHAPTER 6

The Variation of 'Neighbour Anisotropy' Screening with Composition of Mixtures, and its Relationship to the Thermodynamics of Solutions

6.1 Introduction

It was shown in chapter 4 that the new externally referenced procedure[59], derived to overcome many of the problems associated with previously used methods, required a knowledge of the medium screening corrections for its implementation. Theoretical aspects of these were considered in detail in chapter 5 where particular attention was paid to their expected variation with mixture composition. It was shown, in section 5.3, that the screening of nuclei in molecules situated in liquid media was affected, in the absence of specific intermolecular interactions, by four factors which constitute the intermolecular (or medium) screening. The overall screening in such cases is given by

$$\sigma_{TOTAL} = \sigma + \sigma_a + \sigma_b + \sigma_E + \sigma_W \qquad 6,1$$

where the terms have the significance detailed in sections 5,4 - 5,7. For accurate correction of externally referenced chemical shifts a knowledge of the magnitude of all the screening terms is required. It was shown that the bulk susceptibility[8] (section 5.4) screening could be accurately evaluated, but that the electric field[97] (section 5.5), magnetic anisotropy[105-107] (section 5.6) and dispersion[100] (section 5.7) screenings could only be calculated approximately. However, since both the last two screenings are influenced by steric and anisotropic effects[100,105-107], they may be considered to have a common origin as molecular contact phenomena, certainly they are difficult to separate experimentally[100]. Consequently, these two screenings are more exactly described by a joint term[63] ($\sigma_a + \Delta\sigma_W$) which needs to be determined experimentally; the method employed and the results obtained being discussed in detail in this chapter.

The new procedure described in chapter 4 depends upon measuring

the chemical shift of the same solute in an aromatic solvent and separately in an inert solvent, at the same mole fraction in the annulus and capillary respectively. This results in the measurement of a shift corresponding to δ_{obsj} in equation 4,11 and in order to determine K and Δ_c by this new procedure, a value must be obtained which corresponds to δ'_{obsj} in equation 4,12. In other words information must be obtained about each of the four solvent screenings given in equation 6,1. The appropriate value of σ_b is immediately calculable[8] and as explained in section 5,9 σ_E must be overlooked. However, by the use of a suitable inert 'probe' compound it is possible to obtain the appropriate $\sigma_a + \Delta\sigma_w$ parameters. It will be shown later, (section 7.2), that the shift δ'_{obsj} of equation 4,12 may be obtained directly by the measurement of two chemical shifts; however, the $\sigma_a + \Delta\sigma_w$ screenings were determined separately as a matter of interest.

6.2 The Experimental Procedure for Determining the Anisotropy Screening

The variation of $\sigma_a + \Delta\sigma_w$ was determined in the first instance for systems relevant to those chosen to test the new procedure[59]. These had been selected because they had been studied by conventional three-component methods[82] and found to form complexes with a 1 : 1 stoichiometry and furthermore data was available for comparison purposes. The systems selected were those between benzene and separately chloroform[31,70], ethylene chloride[60], methyl iodide[61] and vinylidene chloride[55]; also the possible interactions between benzene and separately TMS and cyclohexane were studied because the new method offers a way of determining if they are inert to benzene. Therefore all these systems were investigated in order to determine the variation of their $\sigma_a + \Delta\sigma_w$ screening with mixture composition, and similar investigations were carried out on samples containing cyclohexane in place of benzene since these provide the external references for the new procedure. The composite anisotropy screenings of some other systems have also been studied as a matter of

interest and these will be referred to later.

The indirect method employed[104] requires that a solution containing a low concentration (c.a. 0.005 mf) of an isotropic solute (having no strong local dipoles) dissolved in the anisotropic mixture, be placed in the annulus surrounding a precision capillary containing the same concentration of the solute in carbon tetrachloride (acting as an isotropic reference). The solute originally chosen by Homer[104] was tetramethylsilane (TMS); however, as the work of Laszlo et. al.[54] showed that this may specifically interact with benzene, a highly anisotropic solvent in common use, cyclohexane was instead used as solute in these investigations. Although cyclohexane is anisotropic this is unlikely to affect the measurements made since it is only present at very low concentrations and it will be shown in chapter 7 that it does not specifically interact with benzene. Cyclohexane was thus added, at a constant low concentration, to each of a series of samples of similar compositions to those to be used for testing the new procedure (i.e. two series for each system, one containing benzene plus the interacting solute and one containing cyclohexane and the same solute). Each sample gave rise to two cyclohexane resonance lines which could be identified by their relative intensities, (the smaller line arising from the capillary). The screenings of the solute (cyclohexane) in each situation may be written as

$$\sigma^{CY}_{ANN_j} = \sigma + \sigma^{AB}_{a\,ANN_j} + x_{A_j}\left(\sigma^{A}_{E} + \sigma^{A}_{\omega}\right) + x_{B_j}\left(\sigma^{B}_{E} + \sigma^{B}_{\omega}\right) + \frac{1}{6}\left[\phi_{A_j}\chi_{vA} + \phi_{B_j}\chi_{vB}\right] \qquad 6,2$$

$$\sigma^{CY}_{CAP_j} = \sigma + \sigma^{CCl_4}_{a\,CAP_j} + \sigma^{CCl_4}_{E_j} + \sigma^{CCl_4}_{\omega_j} + \frac{1}{6}\chi_{v\,CCl_4} \qquad 6,3$$

where $\sigma^{CCl_4}_{a\,CAP}$ is zero (because CCl_4 is isotropic) and, since cyclohexane is non polar, σ^{A}_{E}, σ^{B}_{E} and $\sigma^{CCl_4}_{E}$ are also zero. Therefore the measured chemical shift $(\sigma^{CY}_{ANN} - \sigma^{CY}_{CAP})_j$, after correction for σ_b is equal to $\sigma_a + \Delta\sigma_w$ e.g.

$$\delta^{CY}_{j(AB)} = \sigma^{CY}_{ANN_j} - \sigma^{CY}_{CAP_j} = \sigma^{AB}_{a\,ANN_j} + x_{A_j}\sigma^{A}_{\omega} + x_{B_j}\sigma^{B}_{\omega} - \sigma^{CCl_4}_{\omega_j} \qquad 6,4$$

It should be pointed out that the residual screening given by equation 4,14 arises in the following manner. The corresponding chemical shift to that given in equation 6,4,for the AS system, is $\delta^{CY}_{j(AS)} = \sigma^{AS}_{aj} + \sigma^{AS}_{wj} - \sigma^{CCl_4}_{wj}$. Therefore, the shift difference $\delta^{CY}_{j}(AB) - \delta^{CY}_{j}(AS)$ (where A is at the same mole fraction in each) which constitutes the composite anisotropy screening for a sample j in the new procedure is given by

$$\delta_{j(AB-AS)} = \sigma^{AB}_{a_j} - \sigma^{AS}_{a_j} + \sigma^{AB}_{w_j} - \sigma^{AS}_{w_j} \qquad 6,5$$

the term $\sigma^{CCl_4}_{wj}$ cancelling out; where σ^{AB}_{wj} and σ^{AS}_{wj} refer to the dispersion screening of an AB or AS mixture on cyclohexane. In practice the new procedure requires that this screening acts on A, hence there arises a small residual σ'_w screening due to the differing effects of A and cyclohexane as 'probe', which may be defined as

$$\sigma'^{(AB)}_{w_j} = \sigma^{(AB)}_{w_j} \text{ on cyclohexane} - \sigma^{(AB)}_{w_j} \text{ on } A, \qquad 6,6$$

and similarly for $\sigma'^{(AS)}_{wj}$. Since differences between $\sigma'^{(AB)}_{wj}$ and $\sigma'^{(AS)}_{wj}$ are required, $\Delta\sigma'_{wj}$ should be extremely small and as explained in section 5,9 may be neglected. The σ_E term in equation 4,14 arises because, unlike cyclohexane, A is presumably polar, but again differences in σ_E acting on a common solute are required and this is assumed to be zero.

In order to make use of the familiar equation for correction for the bulk susceptibility screening as required in the above discussion, it is necessary to use perfect cylinders; those used being precision drawn capillaries (2 mm o.d.). They were tested by inserting each capillary, filled with TMS, into a sample tube which also contained TMS, deviations from perfect cylindrical uniformity of the capillary would then have shown either as a broadening of the TMS signal or even as a second discrete signal.

6.3 The Experimental Variation of Mixture Anisotropy with Sample Composition

The systems appropriate to the investigations required for the

testing of the new procedure outlined in chapter 4 were studied by the method outlined above. However, before discussing the results in this context it is intended to diverge and discuss them for their own interest. The experimentally measured shifts (δ^{A}_{obs}) are shown as a function of the mole fraction of one component in figure 6.1. The corresponding curves corrected for volume bulk susceptibility on a simple volume additivity basis are shown in figure 6.2, and, with the assumption of the linearity of this correction, indicate the variation of mixture anisotropy, σ_a (more exactly $\sigma_a + \Delta\sigma_w$, the combined real anisotropy and difference in dispersion screening) with solution composition. The corrected results indicate that mixed-medium anisotropy screenings are not linearly additive mole fraction functions of the pure constituents; moreover they are not linearly additive volume fraction functions (figure 6.3). The full results are tabulated in table 6.1, and values of the molar susceptibility, χ_M, molecular weight, M, and density, ρ, used in the calculation of the σ_b screenings for all the systems studied, are recorded in table 6.2. The volume bulk susceptibility, χ_v, is given by equation 5,20 and its value may be obtained at any temperature t from table 6.2. The bulk susceptibility correction to the measured shift is then given by

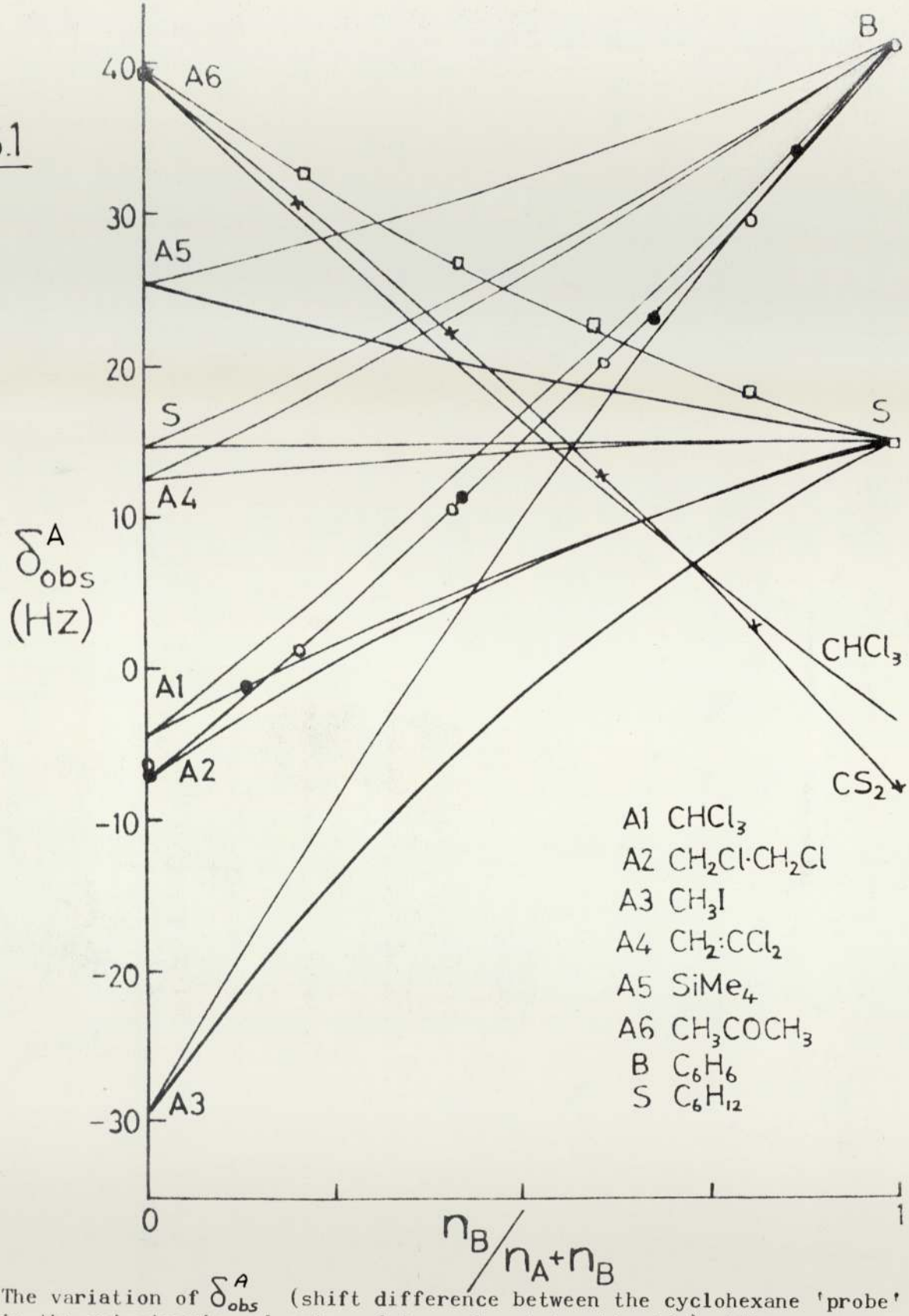
$$\delta^{r-s}_{corr}(\Delta\sigma_b) = -\frac{10^6}{6}\left(\phi_A\chi_{v_A} + \phi_B\chi_{v_B} - \chi_{v\,CCl_4}\right) ppm \qquad 6,7$$

where ϕ_A and ϕ_B are the volume fractions of components A and B in the mixture and χ_{VA} and χ_{VB} are the corresponding volume bulk susceptibilities; $\chi_{V\,CCl_4}$ being that for the carbon tetrachloride reference. The anisotropy screening may then be obtained from

$$\Delta^{s-r}(\sigma_a + \Delta\sigma_w) = \delta^{s-r}_{obs}(\Delta\sigma_b + \sigma_a + \Delta\sigma_w) + \delta^{r-s}_{corr}(\Delta\sigma_b) \qquad 6,8$$

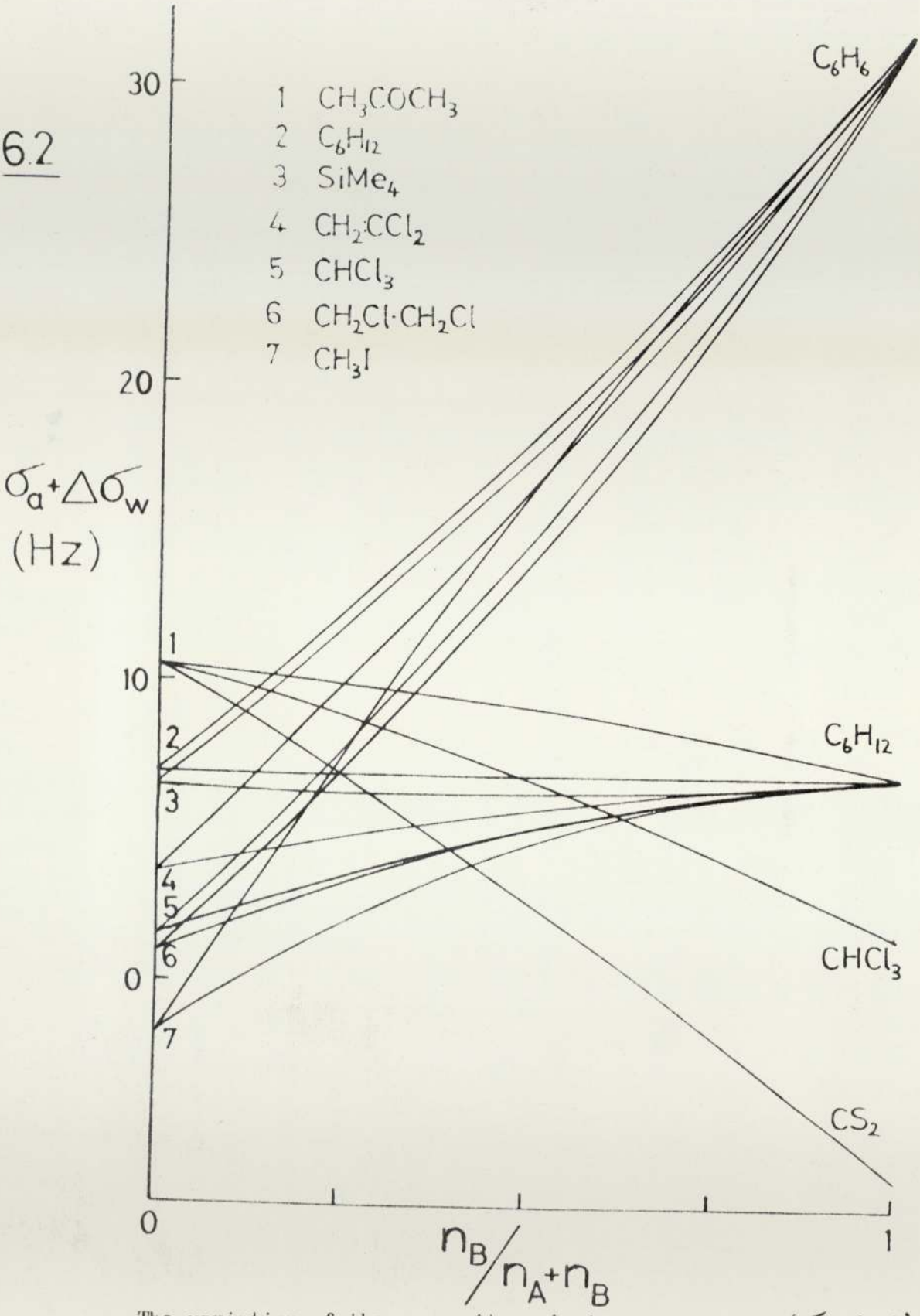
The significance of the apparent deviations from linearity of the curves shown in figure 6.2, depends upon the assumption that bulk susceptibility corrections to the screening can be made in a linearly

6.1



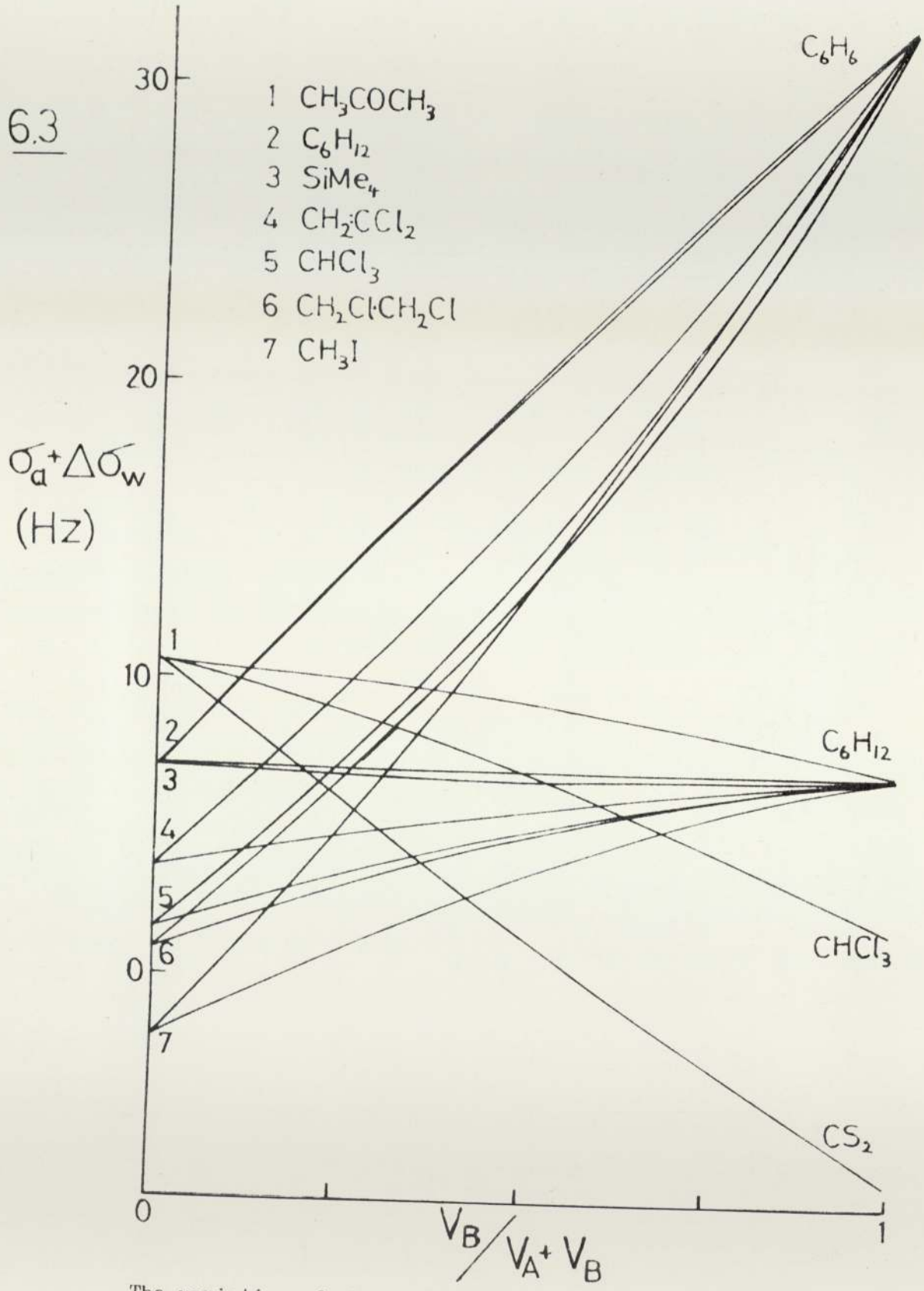
The variation of δ^A_{obs} (shift difference between the cyclohexane 'probe' in the anisotropic solvents and in carbon tetrachloride) with constituent mole ratio in several mixtures. The curves are the best lines through the experimental points of which representative examples are given for the ethylene chloride-benzene (O), acetone-carbon disulphide (X) and acetone-cyclohexane (□) systems. The reproducibility of the curves is demonstrated by the ethylene chloride-benzene system (O and ●). The curves are labelled to correspond to figure 7.5.

6.2



The variation of the composite anisotropy screening ($\sigma_a+\Delta\sigma_w$) with constituent mole ratio ($^{n_B}/_{n_A+n_B}$) for the mixtures studied.

6.3



The variation of the composite anistropy screening ($\sigma_a + \Delta\sigma_\omega$) with constituent volume ratio ($V_B / V_A + V_B$) for the mixtures studied.

Table 6.1

Corrected and uncorrected 'anisotropy shifts' as a function of mixture composition.

Sample No.	$n_A/n_A + n_B(n_S)$	$V_A/V_A + V_B(V_S)$	δ^A_{obs} $(\Delta\sigma_b + \sigma_a + \Delta\sigma_w)$ (Hz)	δ_{corr} $(\Delta\sigma_b)$ (Hz)	Δ $(\sigma_a + \Delta\sigma_w)$ (Hz)
a) Acetone (A) - Chloroform (B)					
39/1	1.0000	1.0000	†	- 28.63	(10.47)
39/2	0.7888	0.7744	29.91	- 20.80	9.11
39/3	0.5881	0.5676	21.28	- 13.62	7.66
39/4	0.3944	0.3744	12.55	- 6.91	5.64
39/5	0.1959	0.1830	3.76	- 0.29	3.47
39/6	0.0000	0.0000	- 4.49	6.07	1.58
b) Acetone (A) - Carbon Disulphide (S)					
25/1	1.0000	1.0000	†	- 28.63	(10.47)
25/2	0.8004	0.8308	30.98	- 23.54	7.44
25/3	0.6016	0.6488	22.82	- 18.05	4.77
25/4	0.3984	0.4477	12.88	- 12.00	0.88
25/5	0.2013	0.2357	2.99	- 5.62	- 2.63
25/6	0.0000	0.0000	- 8.13	1.48	- 6.65
c) Acetone (A) - Cyclohexane (S)					
24/1	0.9779	0.9679	**	-	-
24/2	0.8004	0.7323	32.93	- 22.93	10.00
24/3	0.5954	0.5010	27.45	- 18.02	9.43
24/4	0.3931	0.3064	22.62	- 13.90	8.72
24/5	0.1961	0.1427	18.50	- 10.42	8.08
24/6	0.0000	0.0000	14.51	- 7.39	7.12

Table 6.1 (cont'd.)

Sample No.	$n_A/n_A + n_B(n_S)$	$V_A/V_A + V_B(V_S)$	δ^{A}_{obs} $(\Delta\sigma_b+\sigma_a + \Delta\sigma_w)$ (Hz)	δ_{corr} $(\Delta\sigma_b)$ (Hz)	Δ $(\sigma_a+\Delta\sigma_w)$ (Hz)
d) Chloroform (A) - Benzene (B)					
31/1	1.0000	1.0000	- 4.53	6.07	1.54
31/2	0.7905	0.7728	3.77	2.64	6.41
31/3	0.5985	0.5734	12.36	- 0.38	11.98
31/4	0.3782	0.3542	22.50	- 3.69	18.81
31/5	0.1908	0.1755	31.54	- 6.39	25.15
31/6	0.0000	0.0000	41.22	- 9.04	32.18
e) Chloroform (A) - Cyclohexane (S)					
32/1	0.9961	0.9948	- 4.47	6.00	1.53
32/2	0.7947	0.7418	*	-	-
32/3	0.6009	0.5278	*	-	-
32/4	0.3965	0.3278	8.82	- 2.98	5.84
32/5	0.2015	0.1578	11.78	- 5.27	6.51
32/6	0.0000	0.0000	14.74	- 7.39	7.35
f) Cyclohexane (A) - Benzene (B)					
23/1	1.0000	1.0000	14.66	- 7.39	7.27
23/2	0.8026	0.8317	19.04	- 7.67	11.37
23/3	0.6048	0.6504	24.04	- 7.97	16.07
23/4	0.4019	0.4497	29.11	- 8.30	20.81
23/5	0.1993	0.2324	34.81	- 8.66	26.15
23/6	0.0031	0.0038	41.41	- 9.04	32.37
g) Cyclohexane (A) - Cyclohexane (S)					
-	all compositions		14.74	- 7.39	7.35

Sample No.	$n_A/n_A + n_B(n_S)$	$V_A/V_A + V_B(V_S)$	δ^A_{obs} $(\Delta\sigma_b + \sigma_a + \Delta\sigma_w)$ (Hz)	δ_{corr} $(\Delta\sigma_b)$ (Hz)	Δ $(\sigma_a + \Delta\sigma_w)$ (Hz)
h) Ethylene Chloride (A) - Benzene (B)					
22/1	1.0000	1.0000	- 7.25	8.08	0.83
22/2	0.7931	0.7729	1.90	4.19	6.09
22/3	0.5876	0.5585	10.90	0.52	11.42
22/4	0.3943	0.3662	20.10	- 2.77	17.33
22/5	0.1928	0.1749	30.15	- 6.05	24.10
22/6	0.0000	0.0000	41.50	- 9.04	32.46
i) Ethylene Chloride (A) - Cyclohexane (S)					
21/1	0.9920	0.9890	- 7.05	7.91	0.86
21/2	0.7912	0.7345	0.00	3.97	3.97
21/3	0.5858	0.5081	4.35	0.47	4.87
21/4	0.3917	0.3198	8.25	- 2.44	5.81
21/5	0.1927	0.1484	12.00	- 5.09	6.91
21/6	0.0000	0.0000	14.75	- 7.39	7.36
j) Methyl Iodide (A) - Benzene (B)					
29/1	1.0000	1.0000	- 29.53	28.19	- 1.34 Ø
29/2	0.7961	0.7323	- 12.90	18.22	5.32
29/3	0.6004	0.5129	2.55	10.05	12.60
29/4	0.3636	0.2771	20.10	1.27	21.37
29/5	0.1651	0.1218	31.89	- 4.51	27.38
29/6	0.0000	0.0000	42.26	- 9.04	33.22
k) Methyl Iodide (A) - Cyclohexane (S)					
30/1	0.9872	0.9781	- 29.41	27.41	- 2.00 Ø
30/2	0.7885	0.6824	- 16.05	16.89	0.84
30/3	0.5781	0.4412	- 4.26	8.31	4.05
30/4	0.4005	0.2780	*	-	-
30/5	0.1916	0.1202	9.49	- 3.11	6.38
30/6	0.0000	0.0000	14.73	- 7.39	7.34

Sample No.	$n_A/n_A + n_B(n_S)$	$V_A/V_A + V_B(V_S)$	δ^A_{obs} $(\Delta\sigma_b + \sigma_a + \Delta\sigma_w)$ (Hz)	δ_{corr} $(\Delta\sigma_b)$ (Hz)	Δ $(\sigma_a + \Delta\sigma_w)$ (Hz)
l) Tetramethylsilane (A) - Benzene (B)					
35/1	1.0000	1.0000	25.39	- 18.33	7.06
35/2	0.7879	0.8523	28.25	- 16.96	11.29
35/3	0.5841	0.6857	30.22	- 15.41	14.81
35/4	0.4103	0.5194	33.72	- 13.87	19.85
35/5	0.1997	0.2793	37.19	- 11.64	25.55
35/6	0.0000	0.0000	41.83	- 9.04	32.79
m) Tetramethylsilane (A) - Cyclohexane (S)					
34/1	0.9964	0.9972	25.39	- 18.30	7.09
34/2	0.7799	0.8190	23.19	- 16.35	6.84
34/3	0.6036	0.6604	21.12	- 14.61	6.51
34/4	0.3965	0.4563	19.08	- 12.38	6.70
34/5	0.1977	0.2394	16.50	- 10.01	6.49
34/6	0.0000	0.0000	14.41	- 7.39	7.02
n) Vinylidene Chloride (A) - Benzene (B)					
27/1	1.0000	1.0000	12.56	- 8.90	3.66
27/2	0.7985	0.7801	17.95	- 8.93	9.02
27/3	0.5864	0.5594	23.69	- 8.97	14.72
27/4	0.3936	0.3676	28.50	- 8.99	19.51
27/5	0.2034	0.1861	34.95	- 9.02	25.93
27/6	0.0000	0.0000	41.49	- 9.04	32.45
o) Vinylidene Chloride (A) - Cyclohexane (S)					
28/1	0.9948	0.9930	12.57	- 8.89	3.68
28/2	0.6630	0.5916	13.31	- 8.29	5.02
28/3	0.5835	0.4976	13.85	- 8.14	5.71
28/4	0.3840	0.3146	14.32	- 7.87	6.45
28/5	0.1982	0.1540	14.53	- 7.62	6.91
28/6	0.0000	0.0000	14.73	- 7.39	7.34

Table 6.1 (cont'd.)

* the two cyclohexane peaks were superimposed, hence no shift was measurable; since the cyclohexane concentration is so high in the main tube the peak is broad and the chemical shift between the two peaks cannot be equated to zero.

† as above this could not be measured due to superimposition of two peaks, however two separate lines can be extrapolated to this point and a chemical shift of 39.10 Hz is indicated, and this is used to obtain a $\sigma_a + \Delta\sigma_w$ for pure acetone.

ø the reason for this discrepancy is discussed in the text.

** this could not be measured because the cyclohexane peak is beneath the main acetone peak.

Table 6.2

Molar diamagnetic susceptibilities[9,121], molecular weights and densities[122-123] of the compounds used in these studies.

the densities are recorded in the form $\rho = -At + B$ kg m^{-3}, t being the temperature above 273.16K.

Compound	χ_M ($x - \frac{10^{12}}{4\pi}$ m^3 mol^{-1})	M* ($x10^3$ kg mol^{-1})	A	B ($x10^{-3}$)
Acetone	33.80[111]	58.08067	1.126	0.8125
Benzene	54.85[153]	78.11472	1.070	0.9001
Bromobenzene	78.92[154]	157.01575	1.338	1.5217
Carbon Disulphide	42.29[155]	76.13915	1.480	1.2927
Carbon Tetrachloride	66.60[111]	153.82315	1.944	1.6327
Chloroform	59.30[111]	119.37812	1.878	1.5264
Cyclohexane	68.13[156]	84.16254	0.944	0.7974
Ethanol	33.60[111]	46.06952	0.862	0.8064
Ethyl Bromide	54.74[154]	108.97115	2.024	1.5014
Ethylene Chloride	59.62[157]	98.96018	1.441	1.2816
Ethyl Iodide	68.53[154]	155.96655	2.240	1.9807
n-Heptane	85.24[111]	100.20557	0.854	0.7005
n-Hexane	74.05[111]	86.17848	0.906	0.6770
Methyl Iodide	57.2[158]	141.93946	2.815	2.3350
Nitrobenzene	61.80[111]	123.11185	0.984	1.2231
Tetramethylsilane	74.8[159]	88.22624	1.042	0.6634[161]
Vinylidene Chloride	49.2[160]	96.94424	1.500	1,2480[162-163]

* using the 1961 Table of Atomic Weights[163]

additive manner and also upon the relationship between the experimental error and the magnitude of the deviation. It is realized that the deviations from linearity in terms of the anisotropy shift are relatively small, and that the apparent non linearity of the lines could arise from extremely fortuitous accumulation of experimental errors. The reproducibility of the ethylene chloride-benzene curve has been investigated, therefore, to eliminate this possibility. The absolute position and reproducibility of such a curve could be considerably influenced by a) not achieving thermal equilibrium for each sample, b) variable contributions to the measured shifts caused by different non co-axial arrangements of the capillaries and c) differences in solute concentration between the samples. The first of these was minimized by ensuring that the samples remained in the probe until they were at thermal equilibrium before the shift measurements were made. The effect on the measured shifts of tilting a capillary was investigated and found to be negligible[164]. The shift variation with solute concentration was investigated by determining the anisotropy screening of an ethylene chloride (A) - benzene (B) mixture at the fixed mole ratio $({}^{n}A/n_{A}+n_{B})=0.5816$, with different solute concentrations. The results are tabulated in detail in table 6.3 and it is evident from these that small variations in the cyclohexane concentration around that nominally used (0.005 mf) have little effect on the screenings obtained; nevertheless the concentration used should be as low as possible. It will be noted that the correction for $\Delta\sigma_{b}$ is applied in two ways, these being a) including the volume fraction of cyclohexane in the calculation of the bulk susceptibility screening - labelled (1) in table 6.3, and b) excluding cyclohexane and using the volume ratios $V_{A}/V_{A}+V_{B}$ and $V_{B}/V_{A}+V_{B}$ in the same calculation - labelled (2) in table 6.3, since in the procedure used to determine the composite anisotropy screening this small amount of 'probe' has been neglected. It is clearly more exact to include every constituent of the solution in the calculation

Table 6.3

The variation in anisotropy screening with alteration in solute (e.g. cyclohexane) concentration, of a representative ethylene chloride-benzene sample.

Sample No.	$n_S/n_A+n_B+n_S$	$V_S/V_A+V_B+V_S$	$\delta^{s-r\,A}_{obs}$ $(\Delta\sigma_b+\sigma_a+\Delta\sigma_w)$ (Hz)	δ^{r-s}_{corr} $(\Delta\sigma_b)$(Hz)		Δ^{s-r} $(\sigma_a+\Delta\sigma_w)$ (Hz)	
				(1)	(2)	(1)	(2)
22/31	0.0065	0.0088	11.07	0.37	0.43	11.44	11.50
22/32	0.0108	0.0140	11.11	0.31	0.43	11.42	11.54
22/33	0.0224	0.0290	11.10	0.20	0.43	11.30	11.53
22/34	0.0269	0.0347	10.92	0.15	0.43	11.07	11.35

(1) The $\Delta\sigma_b$ correction is obtained by using the exact volume fractions of the mixture, i.e. including the small amount of cyclohexane.

(2) The $\Delta\sigma_b$ correction is obtained by using the volume ratios V_A/V_A+V_B i.e. excluding the small amount of cyclohexane.

---

but it should be noted that the screening variations of two component mixtures are being measured using a cyclohexane 'probe' and it seems valid, therefore, to make the de facto assumption that this 'probe' is completely inert and has no effect on the mixture. Nevertheless, it is apparent from table 6.3 that, when the concentration of S used is as low as 0.005 mf, the results corrected by either of procedures a) and b) given above are about the same and it is considered valid to ignore this concentration of S in the bulk susceptibility corrections.

The screenings (either $\Delta\sigma_b+\sigma_a+\Delta\sigma_w$ or $\sigma_a+\Delta\sigma_w$) should strictly be plotted against mole or volume ratio ($n_A/n_A+n_B(n_S)$ or $V_A/V_A+V_B(V_S)$) not mole or volume fraction ($n_A/n_A+n_B+n_{probe}$, or $V_A/V_A+V_B+V_{probe}$). In other words the amount of the 'probe' is ignored because it is only present to sample a particular solution. In systems composed of solute (A) and aromatic (B) exactly correct screenings corresponding to a particular mole ratio of A and B are obtained, but in systems composed of solute (A) and cyclohexane (S)

the total amount of cyclohexane present in the solution is included in the calculation of the A to S mole ratio, whereas in practice a small amount should have been considered as 'probe' and the mole ratio adjusted accordingly. Therefore the AS and AB plots for a given system will differ slightly at the point corresponding to pure A since the AS line includes a correction for the amount of 'probe' and the AB line does not. However, the discrepancy is not serious except for the methyl iodide system where, because of its large χ_v value, the small dilution effect of cyclohexane is noticeable. This discrepancy has been checked for this system and after allowing for 0.05 mf of cyclohexane as 'probe' the methyl iodide-cyclohexane line was re-examined. It was found that the curvature was unaffected but that the magnitude of the $\sigma_a + \Delta\sigma_w$ screening was slightly altered. It was further considered that any effect that this would have on the new procedure (chapter 4) would be within experimental error even for this particular interaction.

The general reproducibility of the experimental procedure for determining the composite anisotropy screening has been examined by remeasuring the variation in this screening for the ethylene chloride-benzene system, using as low a cyclohexane 'probe' concentration (0.005 mf) as possible. It is considered that the 'probe' has two effects i) on the mole ratio used in plotting the results, for systems composed of A and S (examined above), and ii) on the values obtained for $\sigma_a + \Delta\sigma_w$, for systems composed of A and B, via the correction for the bulk susceptibility screening. This is examined by making two $\Delta\sigma_b$ corrections, as before, to the ethylene chloride-benzene system. The data recorded in table 6.4A is uncorrected for the bulk susceptibility screening of the 'probe', whereas that recorded in table 6.4B has this correction included. Curves are obtained for plots of δ^{A}_{obs} and Δ against $^{n}B/n_A+n_B$ which are almost completely coincident with the curves originally obtained (see figures 6.1 and 6.2). Also the two sets of

Table 6.4

Remeasurement of the anisotropy screening of the ethylene chloride-benzene to check the general reproducibility of the system.

Sample No.	n_A/n_A+n_B	V_A/V_A+V_B	x_S	ϕ_S	δ^A_{obs} (σ_a + $\Delta\sigma_b$ + $\Delta\sigma_w$) (Hz)	δ_{corr} ($\Delta\sigma_b$) (Hz)	Δ (σ_a + $\Delta\sigma_w$) (Hz)
a) Ethylene chloride (A) - Benzene (B) excluding 'probe' (A)							
22/08	1.0000	1.0000	-	-	- 6.90	8.08	1.18
22/04	0.8847	0.8720	-	-	- 1.68	5.89	4.21
22/06	0.5674	0.5380	-	-	12.30	0.17	12.47
22/09	0.3050	0.2804	-	-	24.43	- 4.22	20.21
22/05	0.1124	0.1010	-	-	35.17	- 7.29	27.88
b) Ethylene chloride (A) - Benzene (B) including 'probe' (B)							
22/08	1.0000	1.0000	0.0059	0.0081	- 6.90	7.96	1.06
22/04	0.8847	0.8720	0.0069	0.0093	- 1.68	5.78	4.10
22/06	0.5674	0.5380	0.0113	0.0146	12.30	0.08	12.38
22/09	0.3050	0.2804	0.0054	0.0067	24.43	- 4.24	20.19
22/05	0.1124	0.1010	0.0058	0.0071	35.17	- 7.30	27.87

results shown above are very close and practically within experimental error, certainly neglect of correcting for the 'probe' does not alter the 'curvature' of these results in any way. It is suggested, however, that any future measurements on the anisotropy screening of AS mixtures should be made by adding 0.005 mf of cyclohexane to a known mixture, thus making the AB and AS systems identical in this respect and eliminating effect i) above.

6.4 The Effect of Deviations from Additivity of σ_b on the Variation of Anisotropy with Composition

The possibility of deviations in the volume fraction additivity

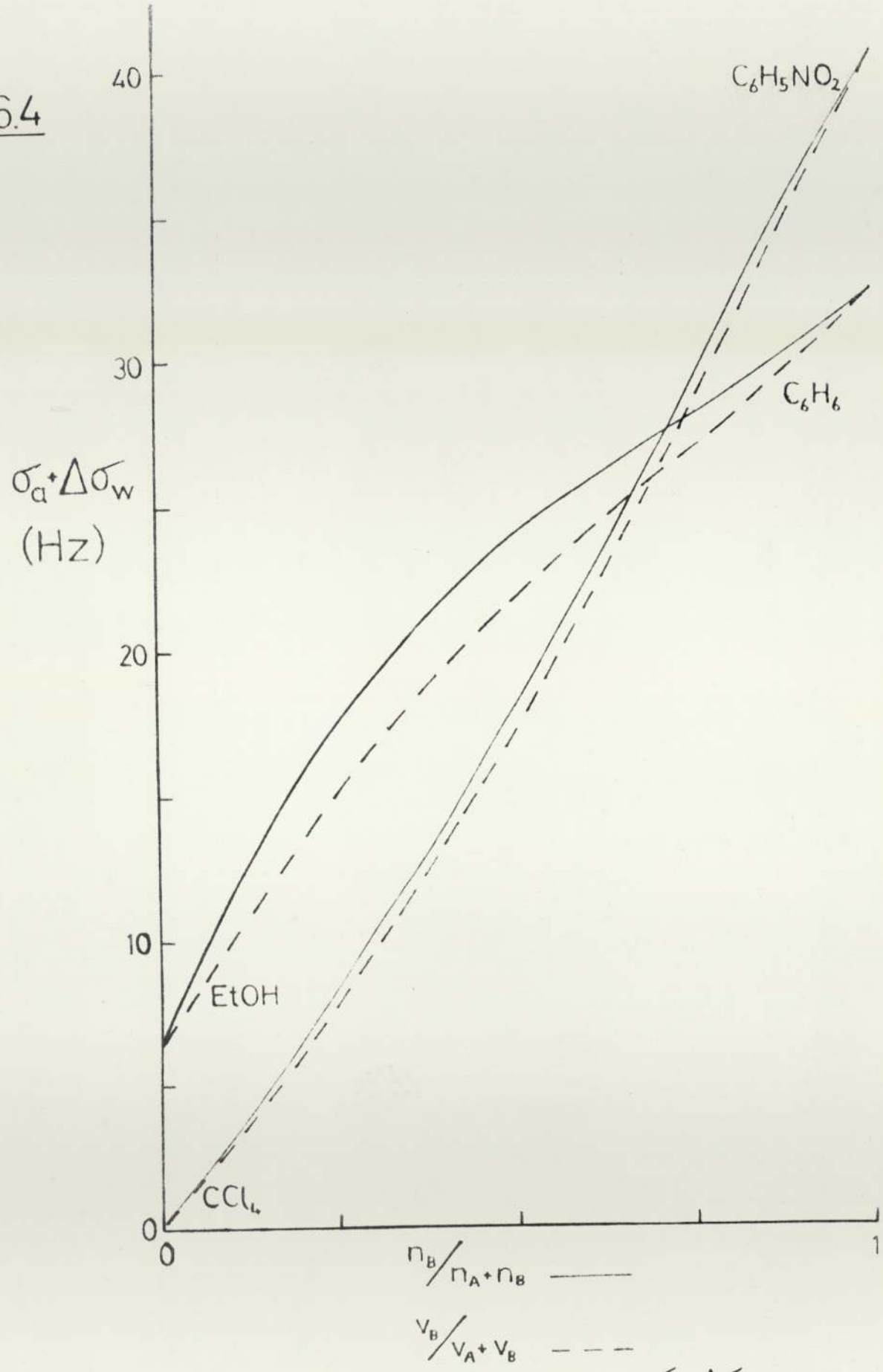
of volume bulk susceptibility has been discussed in section 5.4, and it was concluded that for systems measured here volume fraction additivity could be assumed. It is possible to demonstrate unambiguously that anisotropy screenings of mixtures are not necessarily linear mole- or volume fraction functions of the solution constituents by reference to the ethanol-benzene and carbon tetrachloride-nitrobenzene systems which were found, by Broersma[111], to show insignificant deviations from linear variation of their volume susceptibilities with volume fraction. The anisotropy screenings of these mixtures are shown plotted against $^{n}B/n_{A}+n_{B}$ and $^{V}A/V_{A}+V_{B}$ in figure 6.4 and the data is recorded in table 6.5.

Table 6.5

The variation of the anisotropy screening of ethanol-benzene and carbon tetrachloride-nitrobenzene mixtures with solution composition. A linear volume bulk susceptibility correction being valid[111].

Sample No.	$^{n}A/n_{A}+n_{B}$	$^{V}A/V_{A}+V_{B}$	δ^{A}_{obs} $(\Delta\sigma_{b}+\sigma_{a}+\Delta\sigma_{w})$ (Hz)	δ_{corr} $(\Delta\sigma_{b})$ (Hz)	Δ $(\sigma_{a}+\Delta\sigma_{w})$ (Hz)
a) Ethanol (A) - Benzene (B)					
41/1	1.0000	1.0000	20.08	- 14.02	6.06
41/2	0.7961	0.7190	28.88	- 12.62	16.26
41/3	0.6099	0.5061	33.34	- 11.55	21.79
41/4	0.3959	0.3005	36.60	- 10.53	26.07
41/5	0.1891	0.1326	38.99	- 9.69	29.30
41/6	0.0000	0.0000	41.55	- 9.04	32.51
b) Carbon Tetrachloride (A) - Nitrobenzene (B)					
42/6	1.0000	1.0000	0.00	0.00	0.00
42/5	0.7827	0.7736	9.31	- 2.31	7.00
42/4	0.5981	0.5853	18.32	- 4.24	14.08
42/3	0.3865	0.3741	29.34	- 6.40	22.94
42/2	0.2060	0.1975	39.90	- 8.20	31.70
42/1	0.0000	0.0000	51.11	- 10.22	40.89

6.4



The variation of the composite anisotropy screening $\sigma_a + \Delta\sigma_w$ with constituent mole ($n_B/n_A + n_B$) or volume ($V_B/V_A + V_B$) ratio for the systems ethanol-benzene and carbon tetrachloride-nitrobenzene.

For the ethanol-benzene system the work of Broersma[111] allows a simple linear volume susceptibility correction to be made, despite this curves are still obtained for the anisotropy plots against mixture composition and it may therefore be concluded that such screenings need not be linear functions of mixture composition. For the carbon tetrachloride-nitrobenzene system the relatively small deviation from linearity (of 0.4 per cent) of the volume susceptibility versus volume fraction plot could result in a maximum deviation of + 0.3 Hz from linearity for an anisotropy versus $^{n}B/n_{A}+n_{B}$ or $^{V}B/V_{A}+V_{B}$ plot. This may be compared with the experimental variations (assuming a linear volume bulk susceptibility correction) of + 2.6 Hz and +3.0 Hz on the respective plots. Therefore, this represents a genuine deviation of 2.3 Hz on the $^{n}B/n_{A}+n_{B}$ plot and 2.7 Hz on the $^{V}B/V_{A}+V_{B}$ plot, which is very considerably in excess of any possibility of experimental error.

6.5 The Variation of the Mixture Anisotropy with Solution Composition

Becconsall[105] has predicted the separate magnetic anisotropy screening effect of benzene on a number of solute molecules and obtained fairly good agreement with experimental values, (see section 5.6). He suggested that the main source of error in his initial calculations could be due to neglect of weak attractive dispersion forces across the small gaps between the solute and solvent molecules which would favour those orientations of the solvent molecular axis that are furthest from the radial orientation, i.e. the assumption of a random orientation of solvent molecules is invalid. On the basis of his work the effects of dispersion forces between unlike solvent molecules in the effective anisotropy shell must be recognized when discussing the anisotropy screening ($\sigma_a + \Delta\sigma_w$) of mixtures. Such forces could impose further restrictions on the permitted orientation of one or both of the solvent molecular types relative to those in their pure states. These restrictions will depend on the magnitude of the various interactions, the composition of the

effective shell, the molecular arrangement within it and also on the shape of the solvent molecules in the mixture. It is clear, therefore, that the composite anisotropy plus dispersion force screenings of mixed solvents need not change in a simple linear manner particularly if specific interactions between the solvents occur. Of course, if this explanation is correct then the solvent anisotropy effect should be temperature dependant (σ_w is accepted to be[86]); investigations reported in Chapter 8 show that this is so, but generally in the opposite manner to that predicted by Becconsall[105] for the magnetic anistropy.

6.6 A Correlation Between the Thermodynamics of Solutions and their Anisotropy Screening

Linear variations of the anisotropy screening of mixed solvents as a function of composition can, on the basis of the above suggestions, only be expected when all the interactions between an effective anisotropic solvent molecule and all of its neighbours are the same and allow a uniform distribution of its orientations in the permitted cone (see section 5.6). For this to be possible it is expected that there must be no specific interactions between solvent molecules (as these would tend to prevent random distribution), that the dispersion interactions between them must be the same whether the interacting species are alike or unlike, and that they must have similar shape. These resemble the requirements for the formation of a perfect mixture, for which the molar quantities of mixing[165-167], at constant temperature and pressure are given by

$$\Delta_m G^P = x_1 RT \ln x_1 + x_2 RT \ln x_2 \qquad 6,9$$

$$\Delta_m S^P = -x_1 R \ln x_1 - x_2 R \ln x_2 \qquad 6,10$$

$$\Delta_m H^P = \Delta_m U^P = 0;\ \Delta_m V^P = 0;\ \Delta_m A^P = \Delta_m G^P \qquad 6,11 - 6,13$$

The superscript P describes the perfect mixture and x_1 and x_2 are the mole fractions of the two components. Equation 6,9 means that both components of the mixture obey Raoult's law and that their chemical potentials may be described by

$$\mu_i = \mu_i^{\circ} + RT \ln x_i \qquad 6,14$$

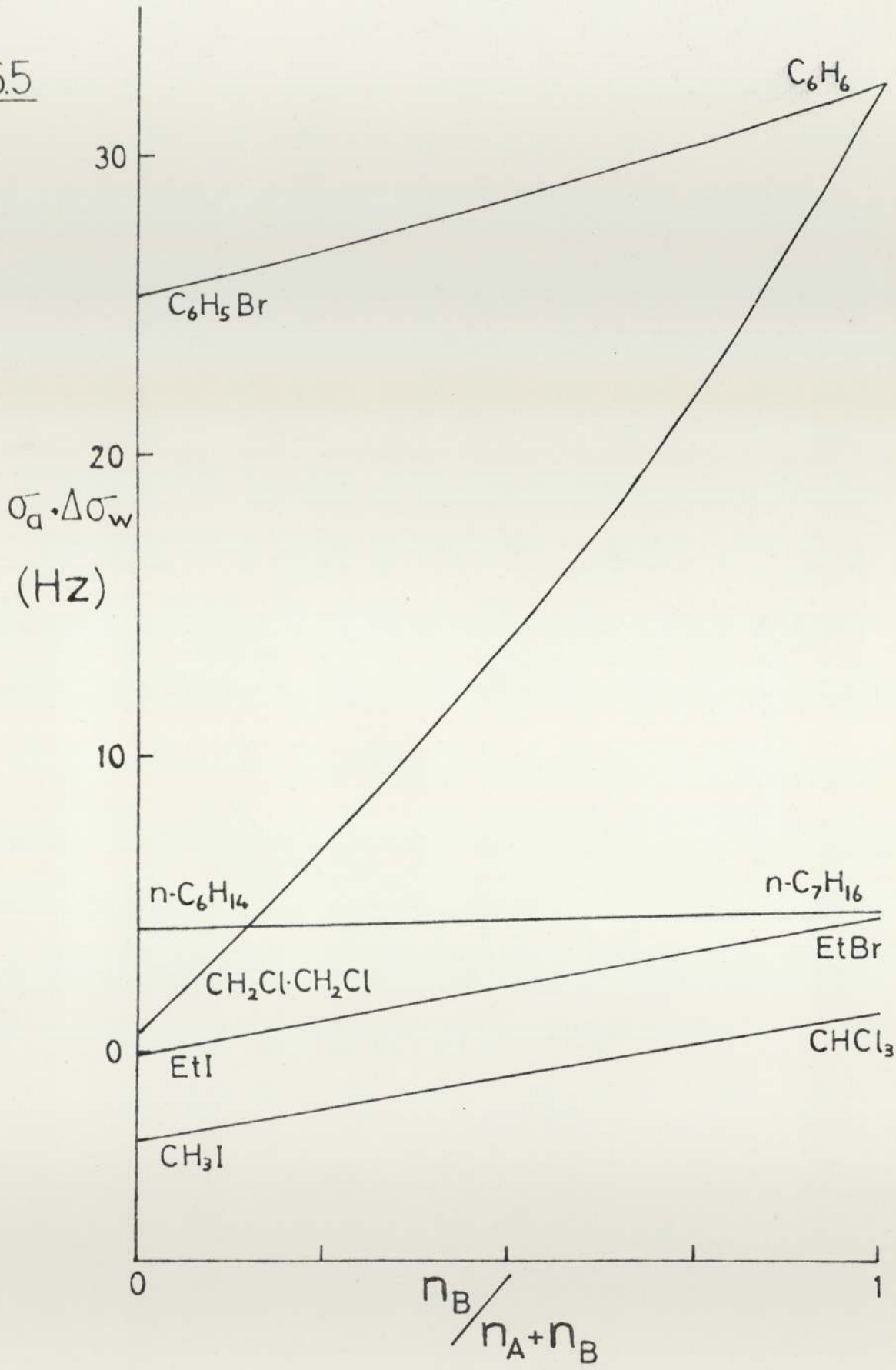
where μ_i° is the chemical potential for the pure liquid at the same temperature and pressure. Equation 6,12 means that the mixing process may also be described as one at constant temperature and volume. It is well known that these equations may be given a theoretical foundation by the use of the methods of statistical thermodynamics with the assumptions[166] that a) the size and shape of the molecules of the two species are similar, b) the molecular distribution in the mixture is completely random, and c) the intermolecular forces between a pair of unlike molecules is the same as the arithmetic mean of the forces between the two pairs of like molecules i.e.[143]

$$\omega' = \varepsilon_{12} - \tfrac{1}{2}\left(\varepsilon_{11} + \varepsilon_{22}\right) = 0 \qquad 6,15$$

where ε_{11} is the free energy required to bring together two molecules of component 1, each originally isolated in space, to a position they would occupy as 'nearest neighbours' in the pure liquid, ε_{22} is the corresponding quantity for component 2 and ε_{12} that corresponding to the formation of an unlike pair 1,2 so that when two liquids are mixed w' is proportional to the free energy required to separate the 1,1 pairs in one liquid and the 2,2 pairs in the second and to form 1,2 pairs in the mixture. The requirements a) to c) above are essentially equivalent to those suggested earlier for mixed solvents likely to show linear variations in the anisotropy screenings as a function of solvent composition. It might be expected, therefore, that this feature should be exhibited by solvent systems which are perfect mixtures.

No known mixture is perfect except that in which the molecules differ only by isotopic substitution, but some mixtures are known which approach perfect behaviour very closely, e.g. n-hexane - n-heptane[120], ethyl bromide-ethyl iodide[167], methyl iodide-chloroform[119] (all perfect c.a. 303K) and bromobenzene-benzene[118] (perfect at 353K). The anisotropy screening variations of these systems have been studied and the resulting data are presented in figure 6.5 (where $\Delta(\sigma_a + \Delta\sigma_w)$ is plotted against n_B/n_A+n_B) and table 6.6, these show that the lines are very close to the expected linearity. For these systems the simple linearly varying correction employed for the volume susceptibility screening is absolutely valid and therefore the lines shown are meaningful. Within experimental error all of the systems, except bromobenzene-benzene, provide straight lines. In the latter case it is not surprising, at first sight, that a shallow curve is obtained since the temperature at which the anisotropy measurements were made was considerably different from that at which the system was reported to be perfect. However, it is difficult to see how the perfectness of mixtures may vary with temperature since it is unlikely that the requirements for such mixtures, as detailed above, are so dependant. Certainly the existence or otherwise of a specific interaction is unlikely to be critically dependant on temperature and the sizes and shapes of the molecules are again virtually temperature independant. Finally, although dispersion forces are temperature dependant[86,144], their variation for similar molecules should be very similar. Therefore, the thermodynamic justification for the statement that a mixture is perfect at only one temperature is open to question, especially for the bromobenzene-benzene system. It appears reasonable that bromobenzene could interact with benzene to form a specific complex. Complex formation between benzene and chlorobenzene has been reported[168] and it is known (chapter 10) that chlorobenzene forms a self-association complex. It is thus possible that similar

6.5



The variation of the composite anistropy screening($\sigma_a+\Delta\sigma_w$) with mole ratio ($n_B/n_A + n_B$) of one component in perfect and imperfect mixtures which obey Raoult's Law.

Table 6.6

The variation of the anisotropy screening with solution composition for some perfect mixtures.

Sample No.	n_A/n_A+n_B	V_A/V_A+V_B	δ^{Λ}_{obs} $(\Delta\sigma_b+\sigma_a+\Delta\sigma_w)$ (Hz)	δ_{corr} $(\Delta\sigma_b)$ (Hz)	Δ $(\sigma_a+\Delta\sigma_w)$ (Hz)
a) Bromobenzene (A) - Benzene (B)					
26/1	1.0000	1.0000	17.42	7.99	25.43
26/2	0.7912	0.8168	21.98	4.88	26.86
26/3	0.5946	0.6331	26.32	1.75	28.07
26/4	0.3989	0.4384	31.06	- 1.56	29.50
26/5	0.1985	0.2256	36.50	- 5.18	31.32
26/6	0.0000	0.0000	41.75	- 9.02	32.73
b) n-Hexane (A) - n-Heptane (B)					
36/1	1.0000	1.0000	19.77	-15.47	4.30
36/2	0.7974	0.7797	19.40	-15.03	4.37
36/3	0.6051	0.5780	19.20	-14.63	4.57
36/4	0.3944	0.3679	18.81	-14.21	4.60
36/5	0.1991	0.1818	18.54	-13.84	4.70
36/6	0.0000	0.0000	18.21	-13.47	4.74
c) Chloroform (A) - Methyl Iodide (B)					
40/6	1.0000	1.0000	- 4.83	6.07	1.24
40/5	0.8147	0.8499	- 8.64	9.40	0.76
40/4	0.6034	0.6621	- 14.05	13.55	- 0.50
40/3	0.4084	0.4706	- 18.96	17.79	- 1.17
40/2	0.2252	0.2723	- 24.29	22.17	- 2.12
40/1	0.0000	0.0000	*	-	-
d) Ethyl Bromide (A) - Ethyl Iodide (B)					
37/1	1.0000	1.0000	- 0.60	5.20	4.60
37/2	0.8068	0.7950	- 4.33	8.23	3.90
37/3	0.6070	0.5893	- 8.78	11.24	2.46
37/4	0.4048	0.3871	- 12.40	14.23	1.83
37/5	0.2014	0.1898	- 16.14	17.14	1.00
37/6	0.0000	0.0000	- 20.34	19.93	- 0.41

* not measurable due to superimposition of methyl iodide and cyclohexane peaks

behaviour may occur between bromobenzene and benzene, which of necessity implies that the system cannot be perfect, even though Raoult's law is apparently obeyed. In other words a fortuitous cancellation of terms in the thermodynamic expressions is obtained. The other 'perfect' systems studied appear to be much more likely to be perfect since they are of similar sizes and shapes and they would appear to be inert to each other.

Under the experimental conditions employed in the above investigations the addition of cyclohexane may cause deviations of the main solvent system from perfect behaviour. However, its concentration is so low that the effect should be negligible. The observation of straight lines for perfect mixtures (figure 6.5) suggests that the short-range solute-solvent interactions, although operative, are less important in causing deviations from linearity of the other mixtures (figure 6.2) than the similar solvent-solvent effects in the anisotropically effective solvent shell. This arises because in a perfect mixture all solvent-solvent interactions are the same and hence they have no effect on the arrangement of molecules within the anisotropically effective shell around a solute molecule; whereas in an imperfect mixture solvent-solvent interactions can affect the orientations of molecules within this shell. In both cases, however, solute-solvent interactions are operative, and these must of necessity be imperfect; despite this, perfect mixtures give linear variations of $\sigma_a + \Delta\sigma_w$ with mixture composition, and imperfect mixtures gives non-linear variations. This would seem to indicate that neglect of solute-solvent dispersion interactions does not provide a full explanation of the discrepancy between the predicted and measured solvent magnetic anisotropy screening provided by Becconsall's original approach[105]. It should also be noted that in the case of supposedly perfect mixtures the overall $\sigma_a + \Delta\sigma_w$ variation with composition is small and this may well be a characteristic of such systems because of the close similarity of the mixture

components. However, it should be clear that this does not mask any curvature since, for example, the ethylene chloride-cyclohexane line (figure 6.2), which has a similar range of $\sigma_a + \Delta\sigma_w$ variation, has a maximum deviation from linear additivity of 1.4 Hz, whereas for the perfect mixtures any deviation is within experimental error.

The curves shown in figure 6.2 arise from mixtures which are believed to be imperfect, these being mixtures with some or all of their molar quantities of mixing differing from those given in equations 6,9 to 6,13[165]. They are usually classified in terms of their excess quantities of mixing. The excess free energy of mixing is defined by equation 6,16 and the excess entropy of mixing by equation 6,17 and so on

$$G^E = \Delta_m G - \Delta_m G^P \; ; \; S^E = \Delta_m S - \Delta_m S^P \qquad 6,16 - 6,17$$

It is possible that the values of some of the excess functions may be zero. The most important classes of imperfect mixtures are a) those for which G^E and H^E are finite but S^E is zero or very close to zero, b) those for which G^E and S^E are finite but H^E is zero or close to zero and c) those for which G^E is zero or close to zero, but S^E and H^E are finite. Those of class a) are sometimes called simple or regular mixtures[165]. They may be accounted for by a statistical model in which the distribution of the molecules is almost completely random, but in which the value of $w' = \varepsilon_{12} - 1/2(\varepsilon_{11} + \varepsilon_{22})$ is other than zero, i.e. the departure from the equations of the perfect mixture is due almost entirely to a finite energy of interaction between the molecules of different species. Those of class b) are sometimes called athermal mixtures[165], in these the interaction energies are negligibly small and the departure from perfect behaviour is due almost completely to the nonrandom arrangements in the mixture. The solvent mixtures giving rise to all of the curves shown in figure 6.2 (except the ethylene chloride-benzene system), belong to one of these two classes of mixtures.

The acetone-chloroform system has also been studied as this is representative of systems showing negative deviations from Raoult's law; the experimental data are presented in table 6.1 and figures 6.1 and 6.2. Whilst it may be shown by classical thermodynamics that all the above systems are imperfect[165-166], it is more difficult to demonstrate that the mixtures belonging to class c) are imperfect. Such mixtures appear to obey Raoult's law so that G^E is zero but both H^E and S^E are finite; since

$$G^E = H^E - TS^E \qquad 6,18$$

it follows that in such mixtures H^E and TS^E must be of the same sign and of almost the same value. Ethylene chloride-benzene mixtures fall into this class and such mixtures were thought, for many years, to be perfect since they appear to obey Raoult's law[169] although Baud[170] had shown H^E to be finite. These results were confirmed by Coulson et. al.[117] and discussed further by Herington[171]. It is of interest that although Raoult's law is obeyed the lines in figures 6,2 and 6,5, for this system, show considerable curvature, suggesting, as for the other solvent systems referred to in table 6.1 and figure 6.2, that this is indeed imperfect. It appears possible that similar behaviour occurs in the bromobenzene-benzene system discussed above, although the departure from perfect behaviour is apparently not so marked. This system has been little discussed in the literature so only n.m.r. evidence is available to indicate the existence of this possibility. However, comparable systems such as chlorobenzene-benzene have been shown to be imperfect[144].

In view of the apparent success of the explanations concerning the linearity or otherwise of the mixed solvent anisotropy screening variations with composition, it would appear reasonable to suppose that the differences in the behaviour of the various binary mixtures described above would be paralleled by differences in their behaviour found by the traditional methods of thermodynamics. Since, for the

perfect mixtures studied, the second differential of $\Delta(\sigma_a+\Delta\sigma_w)$ with respect to $^{n}A/n_A+n_B$ proves to be zero it was hoped to establish a correlation between this and the sign of one (or more) of the excess thermodynamic quantities of mixing (in particular, perhaps with the excess entropy of mixing at constant volume). Unfortunately, as may be seen by reference to table 6.7, where some of the excess thermodynamic quantities of mixing for a number of systems studied are recorded, no such correlation is evident.

6.7 Conclusions

It has been shown that the composite anisotropy $(\sigma_a+\Delta\sigma_w)$ screening of two component mixtures need not be a linearly additive function of either the mole fractions or the volume fractions of the components. Furthermore, it was seen that when near perfect mixtures are studied the screening appears to be mole fraction additive, whereas that for imperfect mixtures is always non-additive. Therefore, it is believed that this method of measuring anisotropies of mixtures may afford a simple means of determining whether a mixture is perfect. Despite the apparent correlation between the linearity or otherwise of the $\Delta(\sigma_a+\Delta\sigma_w)$ plots against mole fraction it was not possible to correlate the deviations from additivity with any of the excess thermodynamic quantities of mixing for the imperfect mixtures. Finally, composite screening values $(\Delta\sigma_b+\sigma_a+\Delta\sigma_w)$ have been obtained for the two component mixtures used in the new procedure[59] for investigating molecular interactions (chapter 4), and these may be used directly as will be indicated in chapter 7.

Table 6.7

Various excess thermodynamic quantities of mixing for some of the systems studied (at mole fraction 0.5).

System	Temperature (K)	G^E_p	A^E_p	TS^E_p	TS^E_v	H^E_p	U^E_v	V^E ($\times 10^6$ $m^3 mol^{-1}$)	Sign of the second differential
Acetone-Carbon Disulphide[172]	308.33	1046[165]	1038[165]	414[114]	80[114]	1460[114]	1117[114]	1.06[178]	-
Acetone-Chloroform[172]	308.33	-556	-556[165]	-1297[114]	-1249[114]	-1766[114]	-1829[114]	- 0.19[114]	-
Bromobenzene -Benzene	297.5	v.small[118]	*	*	*	29[175]	114[175]	- 0.014[118]	+ (slightly)
Chloroform -Benzene	298.16	-167[173]	*	*	- 209[173]	- 420[173]	*	*	+
Cyclohexane -Benzene	293.16 303.16 313.16	310[115+] 300[179]	310[115+]	425[115+]	204[115+]	820[176] 735[115+]	517[115+]	0.66[115+]	+
Ethylene Chloride[172] -Benzene	298.16	26[172]	26[172]	35[172]	- 58[172]	63[177]	- 33[172]	0.24[117]	+
Ethylene Chloride -Cyclohexane	298,16	600[174]	*	*	*	*	*	*	-

J mol^{-1}

\+ these refer to an equimolal mixture, hence other values are provided where possible

* no data available

CHAPTER 7

The Use of the New Procedure to Investigate Molecular Interactions in Solution

7.1 Introduction

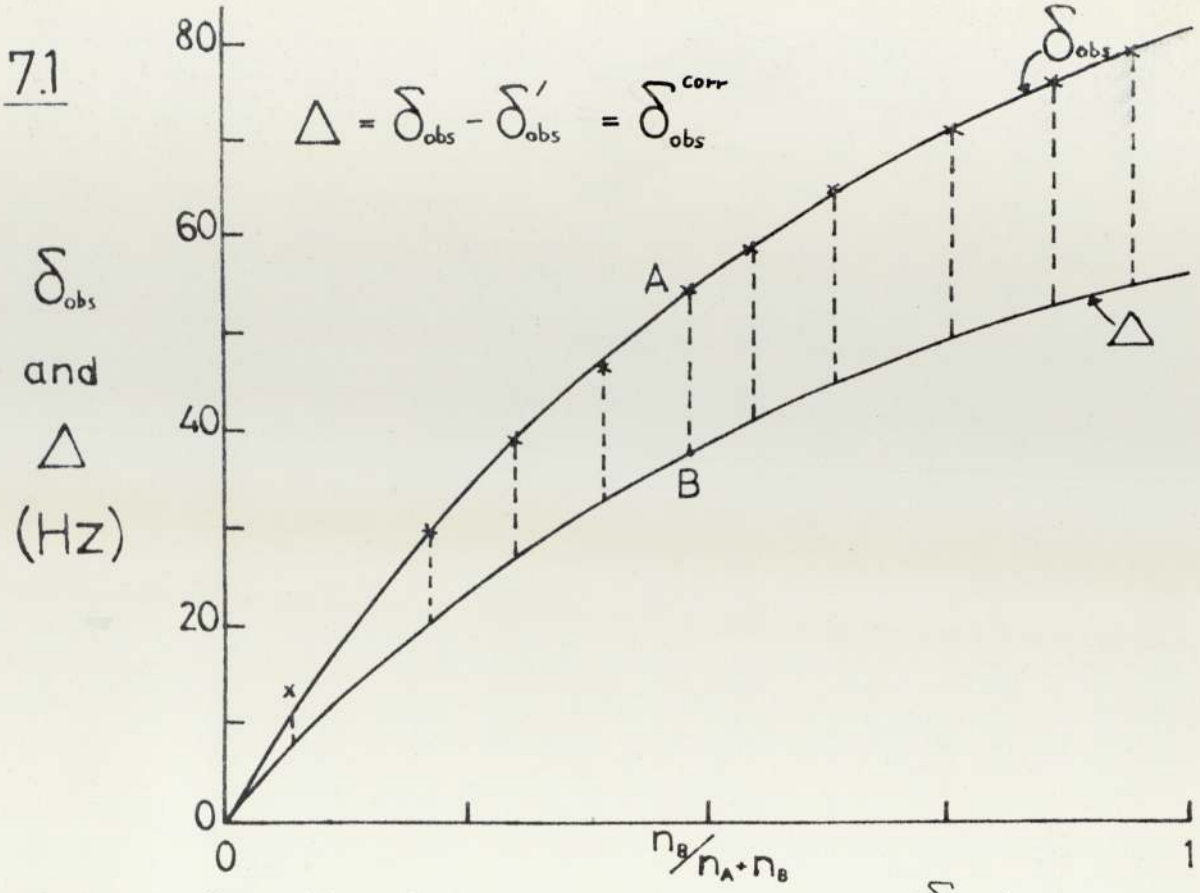
A new procedure derived partly as a result of the thermodynamic considerations detailed in chapter 3 and also as a result of the desire to overcome the problems associated with the choice of inert solvent and reference material has been described in detail in chapter 4. It was shown that the use of this procedure require a knowledge of the variation of the solute chemical shift in the absence of specific interactions; in other words the variation of equation 4,12 with mixture composition. This required a detailed knowledge of the various medium screening effects and in particular their variation with mixture composition; as a result these were considered theoretically in chapter 5. For the procedure the total screening effect of the medium is required but it was found to be of interest to study the composite anisotropy screening separately. In point of fact a line corresponding to equation 4,12 can be obtained by the use of the uncorrected results $(\Delta\sigma_b+\sigma_a+\Delta\sigma_w)$, shown in figure 6.1, as discussed in section 7.2. These results are used both for convenience and to avoid introducing unnecessary errors in trying to correct for $\Delta\sigma_b$ separately.

7.2 The Experimental Procedure

For each interacting system studied a series of ten samples of differing mole fraction of solute was prepared in accordance with the procedure outlined in section 4.2; the mole fraction of the solute in any particular sample being the same in the interacting (contained in the annulus) and inert (contained in the capillary) solvents. Because the shapes of the capillaries are important both in the susceptibility correction and in the new procedure (i.e. the $\Delta\sigma_b$ correction was obtained using perfectly cylindrical capillaries hence these are also

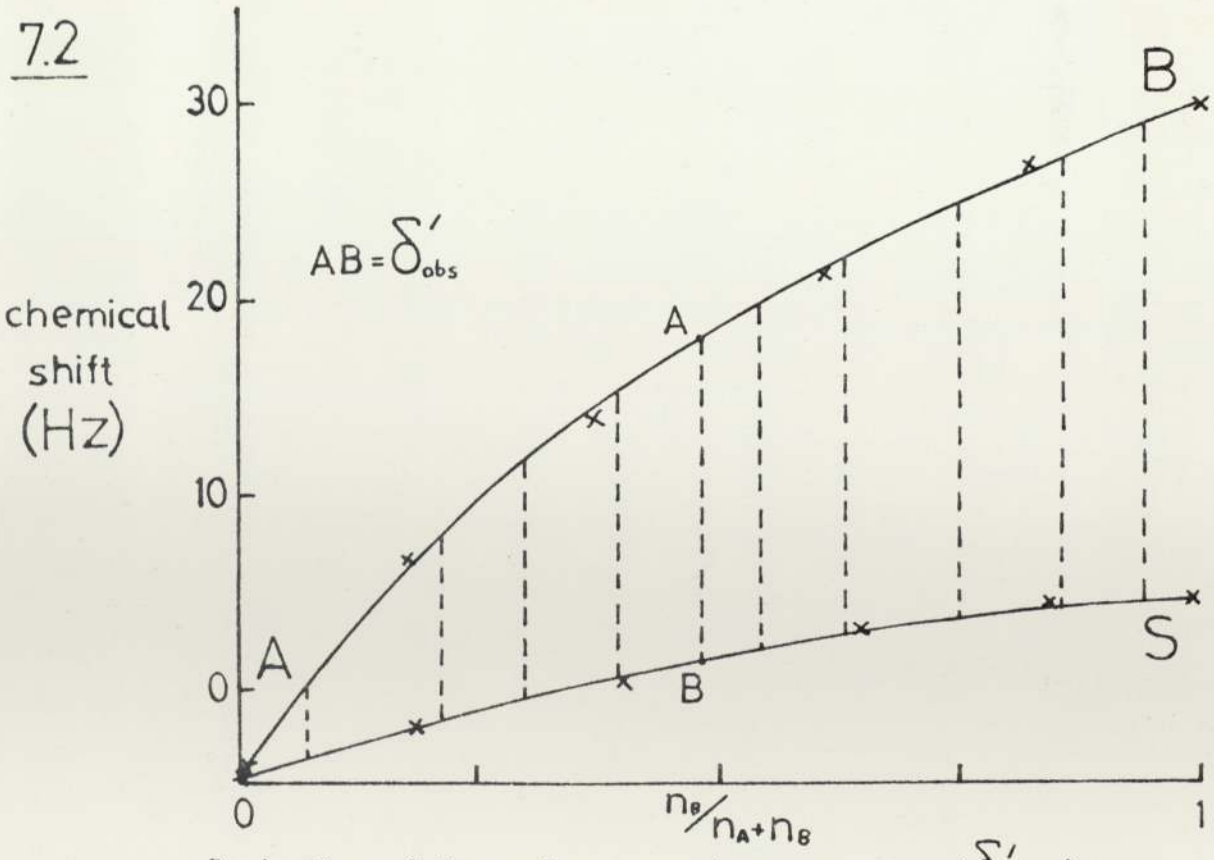
required for the new procedure if the measured screening corrections are to be applicable) precision drawn, 2 mm o.d. capillaries were used; these being tested as described in section 6.2. Each sample of a particular series gave rise to two solute resonances which could be identified on relative intensity grounds. Each shift was measured six times in order to minimize random errors and the average shift value was taken to represent δ_{obs}. In order to implement the new procedure the reference line corresponding to equation 4,12 is normally required. However, it is less involved and eventually more precise to correct the experimentally measured shifts corresponding to equation 4,11 for both volume bulk susceptibility and composite anisotropy screenings. To do this for each contributing effect individually would be difficult and prone to considerable error for two reasons. Firstly, both screenings are known to often show non linear variations with mixture composition[63] and secondly, whilst the former is temperature dependant[8] little is known about the temperature dependance of the latter;[100,105] hence correcting for these screenings at the probe temperature would prove difficult. Nevertheless these difficulties are easily overcome by using the uncorrected 'anisotropic shifts' versus mole fraction curves given in chapter 6 (figure 6.1), for the solvent mixtures used in the present investigations. Both the volume bulk susceptibility and composite anisotropy screenings can then be corrected for in one step without incurring accumulative errors; as well as accommodating, for both, the effects of their dependence on temperature and mixture composition. The overall procedure employed, which is graphical, is as follows. The experimental chemical shifts for complex formation are plotted against n_B/n_A+n_B (figure 7.1) and the best curve is drawn. Then the relevant 'uncorrected anisotropy' curves, from figure 6.1, are selected for the systems A - S and A - B (see figure 7.2) and at the exact mole ratio of each of the original measurements shown in figure 7.1, the difference in the chemical shift between the A - S and A - B lines is graphically measured to give δ'_{obs}. The δ'_{obs} values are then subtracted from

7.1



Correction of the observed chemical shifts (δ_{obs}) for medium screening (δ'_{obs}) as a function of composition.

7.2



Derivation of the medium screening correction (δ'_{obs}) at the mixture compositions used to obtain the observed chemical shifts (δ_{obs}) given in figure 7.1.

the curve representing δ_{obs} against $^{n}B/n_{A}+n_{B}$ giving a new curve of δ^{corr}_{obs} against $^{n}B/n_{A}+n_{B}$ (figure 7.1) which represents the shifts corrected for the composite anisotropy and volume bulk susceptibility screening effects. If this is done it follows that the operative form of equation 4,11 becomes

$$\delta^{corr}_{obs\,j} = \frac{n_{AB_j}}{n_{A_j}}\Delta_c + \chi_j\left[\left(\sigma^{B}_{E}+\sigma^{B}_{\omega'}\right)-\left(\sigma^{S}_{E}+\sigma^{S}_{\omega'}\right)\right] \qquad 7,1$$

where x_j is equated to $^{n}Bj/n_{Aj}+n_{Bj}$; which if no complex formation occurs, reduces to

$$\delta^{corr'}_{obs\,j} = \chi_j\left[\left(\sigma^{B}_{E}+\sigma^{B}_{\omega'}\right)-\left(\sigma^{S}_{E}+\sigma^{S}_{\omega'}\right)\right] \qquad 7,2$$

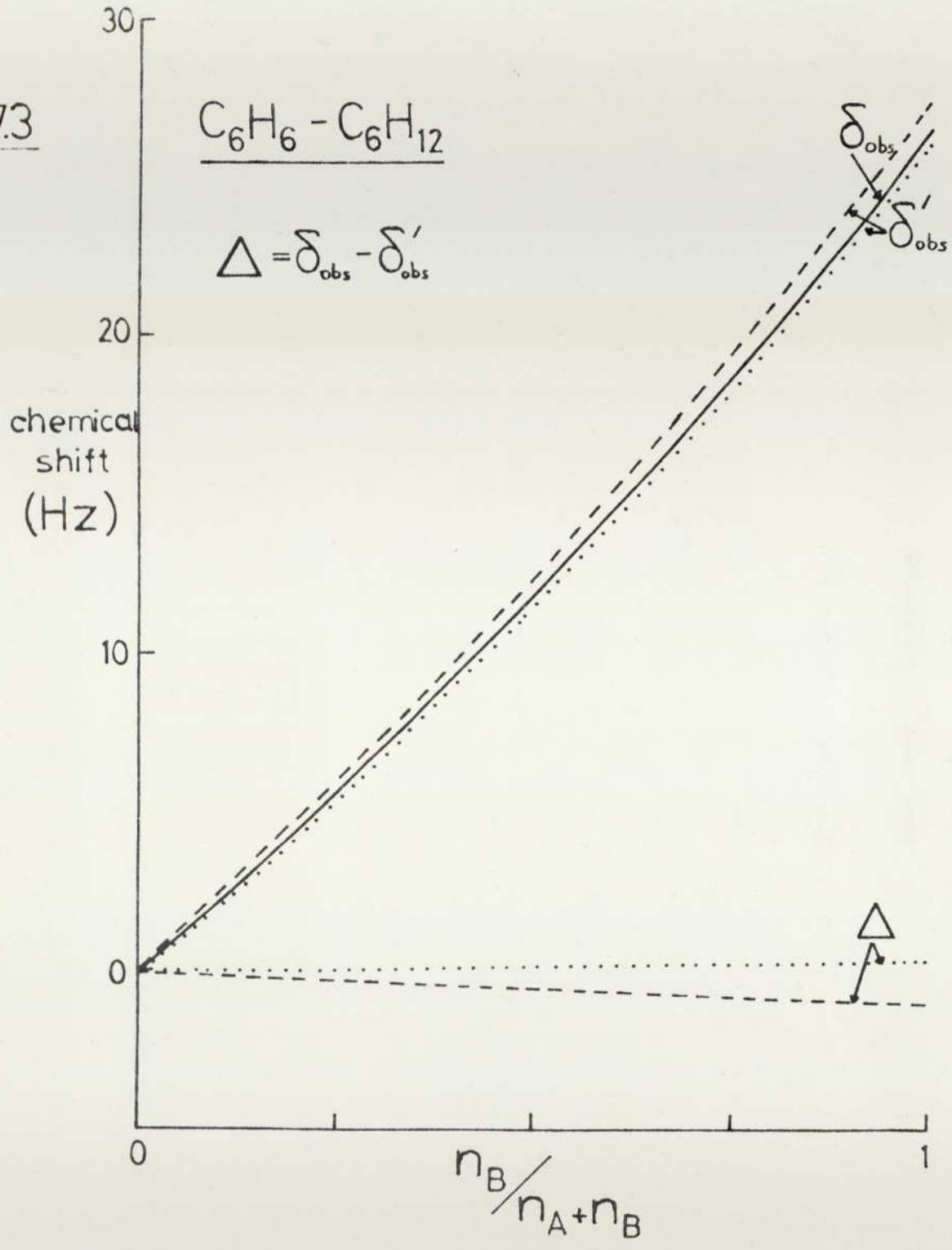
which corresponds to equation 4,12. It is assumed, on the basis of reasonable arguments put forward in chapter 5, that $\delta^{corr'}_{obs\,j}$ is always zero and therefore Δ_j of equation 4,13 may be equated to $\delta^{corr}_{obs\,j}$ of equation 7,1. These corrected results may then be used to evaluate the equilibrium quotients and Δ_c values for the systems studied. If 1 : 1 complex formation occurs the plots of equation 7,1 against $^{n}B/n_{A}+n_{B}$ should be concave with respect to the $\delta^{corr}_{obs} = 0$ line, in order to give a limiting shift.

7.3 Experimental Verification of the Inertness of Cyclohexane

An essential requirement of the above procedure is the need for an inert material to act as a non-interacting solvent in the equilibrium studies and also as a reference 'probe' in the screening correction determinations. Compounds which have been used in the past as inert solvents include carbon tetrachloride, cyclohexane and TMS; however carbon tetrachloride has recently been shown (by thermodynamic considerations) to complex with benzene[80] and TMS also appears to interact with this solvent[54]. No evidence is available to indicate if cyclohexane is inert to aromatic compounds but in view of the fact that it has no strong local dipoles (the importance of which is discussed fully in reference 32) it seems highly probable that this is in fact so;

certainly it has been used extensively in the past without apparent error. For an initial attempt to investigate the possibility of an interaction between cyclohexane and benzene it was proposed to use the new procedure[59]. Hence samples containing various amounts of cyclohexane and benzene, referenced by capillaries containing pure cyclohexane were to be prepared and the chemical shifts between the two cyclohexane peaks measured (δ_{obs}). However, it was realized that this would do no more than test the experimental accuracy of the procedure. This was because the δ'_{obs} values for this system (i.e. corresponding to equation 4,12) would be obtained as the difference in the chemical shift differences between cyclohexane in a series of cyclohexane-benzene mixtures and 0.005 mf cyclohexane in carbon tetrachloride, and between pure cyclohexane and the same reference. Since the effect of the carbon tetrachloride should cancel out it is a requirement of the procedure that δ_{obs} should equal δ'_{obs} in this particular case. Nevertheless, for this purpose alone the idea was persued and the experimental results are recorded in table 7.1 and shown in figure 7.3. Since Δ is always very close to zero the experimental validity of the procedure is demonstrated. In order to demonstrate the inertness of cyclohexane to benzene properly it is necessary to determine the variation of the medium screening effects with composition using a genuinely inert 'probe'. The 'probe' chosen was benzene; although this may seem a surprising choice it has the advantage that the chemical shift of benzene is very little affected by complex formation even when there is a strong interaction (e.g. benzene-nitroform[31,33]). Therefore a series of benzene-cyclohexane mixtures was prepared each containing a capillary containing 0.005 mf benzene in cyclohexane,(acting as reference). In order to obtain shifts relevant to the interaction the chemical shifts between the cyclohexane peaks were measured (δ_{obs}), then to obtain the medium screening corrections the chemical shifts between the benzene

7.3



The observed chemical shifts (δ_{obs}) for the cyclohexane-benzene interaction together with the medium screening contribution (δ'_{obs}) and the corrected shifts (Δ), as a function of the mole ratio of benzene ($n_B/n_A + n_B$); using both benzene (-----) and cyclohexane (·····) as the reference 'probe' (see text).

Table 7.1

Initial investigation of the inertness of cyclohexane; concentrations used and measurements made.

Sample No.	n_B/n_A+n_B	n_B ($x10^2$ mol)	n_A ($x10^2$ mol)	δ_{obs} (Hz)		δ'_{obs} (Hz)	$\Delta(=\delta_{obs}-\delta'_{obs})$ (Hz)
Cyclohexane (A) - Benzene (B)				*	†		
17/1	0.1172	0.3162	2.3807	3.27	2.80	2.60	0.20
17/2	0.2625	0.7868	2.2099	6.69	6.20	6.00	0.20
17/3	0.4169	0.9091	1.2715	10.43	10.00	9.70	0.30
17/4	0.5028	0.9271	0.9168	12.36	12.20	11.90	0.30
17/5	0.6094	0.9405	0.6026	15.09	15.00	14.70	0.30
17/6	0.7090	1.7493	0.7178	17.84	17.65	17.45	0.20
17/7	0.8050	2.2928	0.5555	20.59	20.50	20.35	0.15
17/8	0.9025	4.1778	0.4514	23.66	23.65	23.50	0.15
17/9	0.9510	4.6477	0.2393	25.30	25.45	25.15	0.30
17/10	0.9708	6.0472	0.1818	26.25	26.25	25.80	0.45

* experimental observed shift values.

† representing the best curve through the above experimental shift values.

Table 7.2

Use of benzene as the 'probe' in investigations on the inertness of cyclohexane.

Sample No.	n_B/n_A+n_B	n_B ($x10^2$ mol)	n_A ($x10^2$ mol)	δ_{obs} (Hz)	δ'_{obs} (Hz)	$\Delta(=\delta_{obs}-\delta'_{obs})$ (Hz)
Cyclohexane (A) - Benzene (B)						
46/11	0.2930	0.4223	1.0191	6.75	6.87	- 0.12
46/6	0.4508	1.4162	1.7255	10.50	11.05	- 0.55
46/9	0.5153	1.2873	1.2106	12.20	13.22	- 1.02
46/12	0.6147	2.7875	1.7476	14.85	15.60	- 0.75
46/8	0.7564	2.5809	0.8315	18.80	19.83	- 1.03
46/13	0.8156	2.5502	0.5768	20.60	21.60	- 1.00
46/3	0.9361	2.4186	0.1650	24.30	25.17	- 0.87
46/7	1.0000	1.0000	0.0000	26.40	27.27	- 0.87

peaks were measured (δ'_{obs}). Since these two peaks correspond to identical samples, direct subtraction gives Δ (the residual shift). Values of δ_{obs}, δ'_{obs} and Δ together with sample composition are given in table 7.2; δ_{obs} and Δ are also shown plotted, in figure 7.3, against $^{n}B/n_{A}+n_{B}$. It may be seen that a residual shift of less than - 1Hz is obtained. This line appears to be virtually straight and as the shifts are very small it would appear that the deviation from $\Delta = 0$ is due to the residual effects of neglecting the $\Delta\sigma_{E} + \Delta\sigma'_{w}$ screenings, specific interactions being unlikely. It will be shown (section 7.7) that the residual benzene - TMS line has a maximum deviation of - 3Hz, from $\Delta = 0$, which is considerable larger than that for cyclohexane-benzene and it is also curved. It would, therefore, appear that cyclohexane is considerably more inert than TMS, but that a slight interaction with benzene cannot be completely ruled out. A further check on the inertness of cyclohexane is available, and this is obtained by measuring the shift difference between benzene and cyclohexane and TMS respectively, in straightforward two component mixtures, over a range of concentrations. The concentrations used and the shifts obtained are shown in table 7.3, and a plot of these results (figure 7.4) clearly shows that considerably larger shifts are obtained in the benzene-TMS situation and the curvature is also much greater. The cyclohexane-benzene shift variation is almost linear with mole fraction as would be expected if the shift variation is in fact due to residual $\Delta\sigma_{E}+\Delta\sigma'_{w}$ screenings. Therefore it seems reasonable to conclude that cyclohexane is inert and it may therefore be used both as an inert solvent in molecular interaction studies and also as a 'probe' in the determination of medium screening effects.

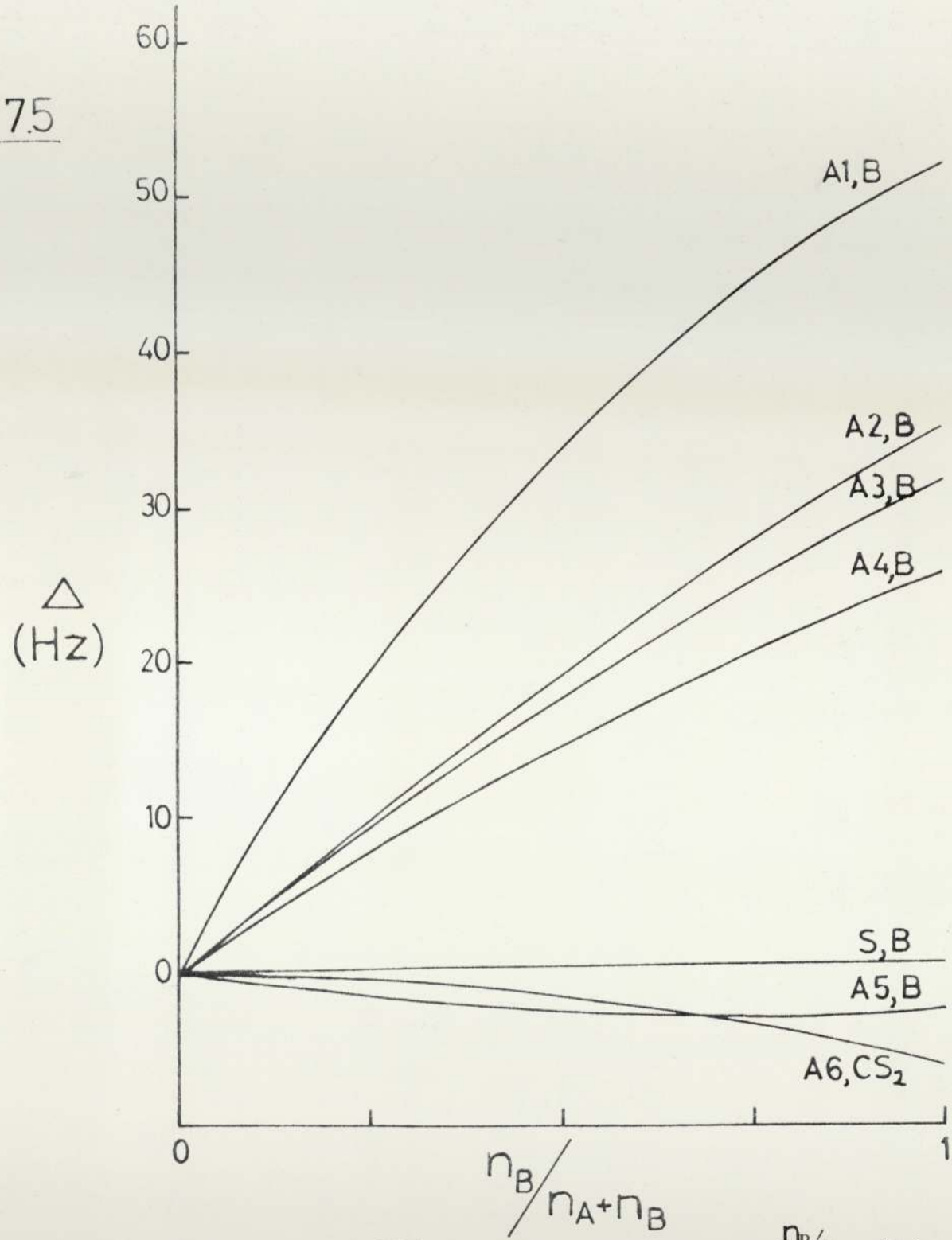
Table 7.3

Shift variation, with mixture composition, for a series of benzene-cyclohexane and benzene-TMS mixtures, measured with respect to benzene.

Sample No.	n_B/n_A+n_B	$n_B(x10^2 mol)$	$n_A(x10^2 mol)$	δ^{A-B}_{obs}(Hz)
a) Cyclohexane (A) - Benzene (B)				
46/1	0.0921	0.2323	2.2913	346.32
46/11	0.2930	0.4223	1.0191	345.62
46/2	0.5488	1.2929	1.0630	344.95
46/22	0.7696	2.5889	0.7751	344.66
46/3	0.9361	2.4186	0.1650	344.83
b) TMS (A) - Benzene (B)				
47/1	0.0261	0.0637	2.3719	433.36
47/11	0.2627	0.4406	1.2365	431.60
47/2	0.4875	1.0237	1.0763	430.10
47/22	0.8046	2.2876	0.5556	429.00
47/3	0.9459	3.0007	0.1716	428.76

7.4 Experimental Results

In order to test the procedure given in section 7.2, four solute-solvent systems, for which evidence exists that 1:1 molecular complex formation occurs, have been investigated. These are those in which benzene complexes with chloroform[31,70], ethylene chloride[60], methyl iodide[61] and vinylidene chloride[55]. In addition, the same procedure has been used to investigate possible interactions between benzene and TMS and acetone and carbon disulphide, where multiple interactions may occur because the solutes concerned have more than one possible site of attack; these will be discussed in detail in section 7.7. The results obtained are recorded in table 7.4, together with the δ_{obs} values for the best curve through the experimental results; these latter are corrected for medium screening (δ'_{obs}) and both δ'_{obs} and Δ (the corrected results) are also recorded in table 7.4 The results are shown plotted after correction for medium screening, in figure 7.5. Deviation from the mole fraction axis ($\Delta = 0$) in figure 7.5 is indicative of solute-aromatic interactions. If 1:1 molecular complex formation occurs, the curves of interest should be concave with respect to this axis in order that a limiting complex shift can be obtained, as would be the case for any A_nB_m complex.



Shift variation (Δ) with solution composition ($^{n_B}/_{n_A + n_B}$) after correction for medium screening effects by the use of the relevant curves given in figure 6.1. The curves may be identified as follows : A1 - $CHCl_3$, A2 - $CH_2Cl.CH_2Cl$, A3 - CH_3I, A4 - $CH_2:CCl_2$, A5 - $SiMe_4$, A6 - CH_3COCH_3, B - C_6H_6 and S - C_6H_{12}.

Table 7.4

Two component interaction studies; composition of samples and shifts obtained.

Sample No.	n_B/n_A+n_B	n_A ($\times 10^2$ mol)	n_B ($\times 10^2$ mol)	δ_{obs} (Hz)		δ'_{obs} (Hz)$^{\phi}$	$\Delta(=\delta_{obs}-\delta'_{obs})$ (Hz)
a) Chloroform (A) - Benzene (B)				*	‡		
X18/0	0.0000	1.0000	0.0000	0.00		0.00	0.00
X18/1	0.1026	1.3778	0.1576	12.18	10.05	1.30	8.75
X18/2	0.2988	1.4962	0.6376	27.80	27.80	5.05	22.75
X18/3	0.4945	1.3496	1.3201	43.95	43.60	9.75	33.85
X18/4	0.5987	0.9942	1.4831	51.23	51.20	12.70	38.50
X18/5	0.7013	0.6612	1.5527	58.12	58.50	15.80	42.70
X18/6	0.7942	0.3722	1.4361	64.87	64.90	18.85	46.05
X18/7	0.8890	0.2134	1.7089	71.26	71.40	22.40	49.00
X18/8	0.9435	0.1454	2.4297	75.61	75.15	24.40	50.75
X18/9	0.9748	0.0351	1.3597	77.24	77.20	25.60	51.60
X18/10	0.9904	0.180	1.8511	77.68	78.10	26.15	51.95
b) Ethylene Chloride (A) - Benzene (B)							
45/0	0.0000	1.0000	0.0000	0.00		0.00	0.00
45/1	0.1062	2.0550	0.2441	4.88	5.05	1.25	3.80
45/2	0.2442	3.4059	1.1002	12.09	12.25	3.35	8.90
45/3	0.3838	1.1042	0.6877	20.27	20.40	5.95	14.45
45/4	0.5004	1.0102	1.0119	27.65	27.60	8.55	19.05
45/5	0.5930	1.2216	1.7801	33.38	33.60	11.10	22.50
45/6	0.6966	0.7274	1.6705	40.56	40.40	14.30	26.10
45/7	0.8096	0.7868	3.3457	48.32	48.10	18.20	29.80
45/8	0.8974	0.3202	2.8011	54.37	54.30	21.85	32.45
45/9	0.9492	0.3188	5.9529	58.03	58.00	24.25	33.75
45/10	0.9693	0.1530	4.8290	59.55	59.50	25.25	34.25
c) Methyl Iodide (A) - Benzene (B)							
15/0	0.0000	1.0000	0.0000	0.00		0.00	0.00
15/1	0.1027	4.1041	0.4699	5.66	5.65	1.85	3.80
15/2	0.2499	1.4366	0.4787	13.73	14.00	4.60	9.40
15/3	0.4028	1.0675	0.7199	23.10	23.10	8.10	15.00
15/4	0.5011	0.4625	0.4645	28.16	29.00	11.10	17.90
15/5	0.6545	0.6463	1.2240	†	38.10	15.95	22.15
15/6	0.7042	0.2281	0.5430	41.19	41.20	17.55	23.65
15/7	0.8007	0.3125	1.2552	47.28	46.95	20.65	26.30
15/8	0.9001	0.2442	2.2014	53.10	52.90	23.85	29.05
15/9	0.9503	0.2016	3.8541	55.83	55.85	25.35	30.50
15/10	0.9701	0.1010	3.2764	57.04	57.05	25.95	31.20

Table 7.4 (cont'd.)

Sample No.	n_B/n_A+n_B	n_A ($\times 10^{-2}$ mol)	n_B ($\times 10^{-2}$ mol)	δ_{obs} (Hz)		δ'_{obs} (Hz)ø	$(=\delta_{obs}-\delta'_{obs})$ (Hz)
d) Vinylidene Chloride (A) - Benzene (B)							
14/0	0.0000	1.0000	0.0000	*	0.00 ‡	0.00	0.00
14/1	0.1206	0.7533	0.1033	6.21	6.60	2.85	3.75
14/2	0.2379	2.7552	0.8601	12.96	13.00	5.65	7.35
14/3	0.4012	1.5359	1.0292	22.83	21.60	9.65	11.95
14/4	0.4999	1.2900	1.2896	26.94	26.90	12.20	14.70
14/5	0.6059	0.6285	0.9663	32.89	32.40	15.00	17.40
14/6	0.6855	1.1069	2.4123	36.60	36.40	17.20	19.20
14/7	0.8015	0.2230	0.9014	42.31	42.30	20.50	21.80
14/8	0.9007	0.2256	2.0462	47.18	47.40	23.65	23.75
14/9	0.9504	0.1326	2.5403	49.86	49.95	25.10	24.85
14/10	0.9703	0.0498	1.6269	51.14	51.00	25.75	25.25
e) TMS (A) - Benzene (B)							
33/0	0.0000	1.0000	0.0000	0.00		0.00	0.00
33/1	0.0989	1.5956	0.1752	1.60	1.65	2.35	- 0.70
33/2	0.2444	1.2583	0.4070	4.34	4.30	5.75	- 1.45
33/3	0.3893	1.0443	0.6659	7.28	7.20	9.25	- 2.05
33/4	0.4894	1.0286	0.9859	9.58	9.35	11.80	- 2.45
33/5	0.5840	0.7439	1.0445	11.47	11.55	14.30	- 2.75
33/6	0.6923	0.9452	2.1266	14.40	14.35	17.30	- 2.95
33/7	0.8027	0.4954	2.0154	17.28	17.55	20.55	- 3.00
33/8	0.9017	0.2720	2.4943	21.05	20.80	23.70	- 2.90
33/9	0.9482	0.2373	4.3471	22.73	22.45	25.25	- 2.80
33/10	0.9683	0.1717	5.2464	23.11	23.20	25.95	- 2.75
f) Acetone (A) - Carbon Disulphide (B)							
19/0	0.0000	1.0000	0.0000	0.00		0.00	0.00
19/1	0.0998	1.5316	0.1699	0.00	- 1.00	-0.85	- 0.15
19/2	0.2384	2.2211	0.6908	- 2.62	- 2.80	-2.45	- 0.35
19/5	0.6010	0.3330	0.5088	-10.93	-10.90	-8.60	- 2.30
19/7	0.7989	0.7041	2.7956	-18.62	-18.70	-15.45	- 3.25
19/10	0.9701	0.0342	1.0867	-27.40	-27.35	-21 45	- 5.90

† cyclohexane peak masked by methyl iodide resonance.

* experimentally observed solute chemical shift differences.

‡ values obtained from the best curve drawn through the * values.

ø obtained from the relevant curves given in figure 6.1.

7.5 Initial Treatment of Data for 1 : 1 Complex Formation

As mentioned above (section 7.2) the curves of interest, for the four systems which were expected to show specific solute-aromatic interactions, should significantly deviate from the mole fraction axis and be concave with respect to it. It may be seen, from figure 7.5, that this is indeed so thus indicating that a limiting complex shift can be obtained. Although it was shown in chapter 3 that the correct way of treating experimental data on molecular interactions was by using a BH type plot after correcting the amount of inert solvent for its molar volume difference from benzene, this is not of course directly applicable to two component studies. It will be shown in section 7.6 that this problem can be overcome and a BH type plot used. Before that is done, however, it was considered necessary to use an iterative procedure similar to that described by Groves et. al.[70], so as to obtain comparable data to those previously reported using a conventional three component procedure[62]. Values of the equilibrium quotients (K_x^{CA}) and excess shieldings (Δ_c), for the four systems studied, have been obtained and they are given in table 7.5

Table 7.5

Values of the equilibrium quotients (K_x^{CA}) and excess shielding (Δ_c) for all the systems studied, compared with the three-component values.

System	K_x^{CA}		Δ_c (ppm)	
	this method	three-component method	this method	three-component method
chloroform-benzene	1.4_4	1.15^{70}	1.32_6	1.620^{70}
ethylene chloride-benzene	0.4_1	0.96^{60}	2.00_6	1.174^{60}
methyl iodide-benzene	0.4_5	0.70^{61}	1.66_0	1.242^{61}
vinylidene chloride-benzene	0.6_2	0.50^{55}	1.09_3	1.259^{55}
TMS-benzene	14.5_7	-	-0.05_0	-

together with the corresponding results from three-component studies.

It may be seen that the results are reasonably consistent with those available from three-component studies, thus they validate, both theoretically and experimentally, the new procedure. It should be

noted that complete agreement is not expected between the two series of results for the reasons discussed in chapter 3. When evaluated over a wide concentration range the values of K_x^{CA} obtained can only be regarded as best-fitting average values of K_x^{CA} because the relevant activity coefficients will be varying with composition. It would be most unlikely that the average values obtained by the two methods would be the same because of different components in solution affecting the activity coefficients differently. This is especially the case for the 'solute' and complex, the concentrations of which are low in the three-component studies but at varying, and often high, concentrations in the two-component studies.

7.6 Use of the Limiting Benesi-Hildebrand Plot over a Thermodynamically Valid Concentration Range.

Equation 4,13 is obviously amenable to a Benesi-Hildebrand type treatment[44], but the experimental results given were obtained with a view to testing the new procedure in relation to the conventional Creswell and Allred[62] type procedure then in current use; and hence not with a BH plot in mind. Whilst these results are not really suitable for such treatment since the concentration range over which the data must be evaluated is much wider than that proposed for three-component mixtures, it is nonetheless true that in some samples the concentration of the aromatic is much higher than that of the solute so that the appropriate requirements for activity coefficients will be met. BH evaluations were, therefore, attempted; use being made of a computer curve-fitting procedure to obtain equations of the best curves through the experimental points. The slopes and intercepts to these curves at $^{n}B/n_A+n_B = 1.00$ being obtained from the equations; as a result values of K_x and Δ_c were obtained which had at least a reasonable thermodynamic basis. The data used for the BH plots is given in table 7.6, and the resulting values of K_x and Δ_c are contained in table 7.7. Use was not made of the molarity scale in these investigations because of the work reported in chapter 3

Table 7.6

Data for use in B-H type plots, for the four systems studied which show evidence for 1 : 1 molecular complex formation.

Sample No.	n_B/n_A+n_B	Δ (Hz)†	n_A+n_B/n_B	$1/\Delta$ ($x10^2$)	w *
a) Chloroform (A) - Benzene (B)					
X18/6	0.7942	46.00	1.2591	2.174	0.5
X18/7	0.8890	49.05	1.1249	2.039	0.8
X18/8	0.9435	50.70	1.0598	1.972	1.0
X18/9	0.9748	51.60	1.0259	1.938	1.2
X18/10	0.9904	52.00	1.0097	1.923	1.4
b) Ethylene Chloride (A) - Benzene (B)					
45/6	0.6966	26.20	1.4355	3.817	0.2
45/7	0.8096	29.90	1.2352	3.344	0.5
45/8	0.8974	32.45	1.1143	3.082	0.8
45/9	0.9492	33.75	1.0535	2.963	1.0
45/10	0.9693	34.27	1.0317	2.918	1.2
c) Methyl Iodide (A) - Benzene (B)					
15/6	0.7042	23.80	1.4201	4.202	0.4
15/7	0.8007	26.55	1.2489	3.770	0.6
15/8	0.9001	29.20	1.1110	3.424	0.8
15/9	0.9503	30.50	1.0523	3.276	1.0
15/10	0.9701	31.05	1.0308	3.222	1.2
d) Vinylidene Chloride (A) - Benzene (B)					
14/6	0.6855	19.20	1.4588	5.208	0.2
14/7	0.8015	21.75	1.2477	4.598	0.5
14/8	0.9007	23.80	1.1103	4.202	0.8
14/9	0.9504	24.80	1.0522	4.032	1.0
14/10	0.9703	25.20	1.0306	3.968	1.2

† These values differ slightly from those recorded in table 6.4 because it is essential to use points lying on a smooth curve (the Δ against n_B/n_A+n_B line) rather than specific points because the BH type plot is extremely sensitive to small changes in the values of $1/\Delta$ and n_A+n_B/n_B.

* A weighting factor used to increase the importance of those results of highest n_B/n_A+n_B.

Table 7.7

The values of K_x and Δ_c obtained, for the systems studied, by the use of a B-H type plot.

System	K_x	Δ_c (ppm)
Chloroform-Benzene	0.8_7	1.87_0
Ethylene Chloride-Benzene	0.5_1	1.73_7
Methyl Iodide-Benzene	0.2_5	2.62_8
Vinylidene Chloride-Benzene	0.3_3	1.72_7

Table 7.8

Data for the chloroform-benzene system after correction for the bulk of chloroform, assuming that 0.005 mf remains as solute.

Sample No.	n_A ($\times 10^2$ mol)	n_B ($\times 10^2$ mol)	n_S^{corr} ($\times 10^2$ mol)*	$n_B/n_{B+}n_S^{corr}$	Δ (Hz)
X18/6	0.0090	1.4361	0.3269	0.8146	-
X18/7	0.0096	1.7089	0.1835	0.9030	49.06
X18/8	0.0129	2.4297	0.1373	0.9465	50.70
X18/9	0.0070	1.3597	0.0254	0.9817	51.63
X18/10	0.0093	1.8511	0.0078	0.9953	51.96
-	0.0000	1.0000	0.0000	1.0000	52.05

* using the value $V_A/V_B = 0.9027$

showing that this scale is unreliable and unreasonable. As expected, the results given in table 7.7 are not the same as those obtained by the Creswell and Allred procedure[62] over the whole concentration range. Moreover, these results are in error in two ways, firstly, if it is considered that the solute is also acting as the diluant for the aromatic, no allowance has been made for the molar volume ratio, $^{V_A}/_{V_B}$, (i.e. n_A must be corrected to n_S^{corr}); and secondly there are far too few experimental points to obtain a reliable line. It seems reasonable to suppose that the solute does act as a diluent in much the same way as an inert solvent in three-component studies. Therefore the two-component results may be treated as follows. A small proportion (0.005 mf) of the solute is considered as the actual solute, n_A, whilst the remainder is considered to be inert diluent and is therefore converted into 'equivalent moles of aromatic' by multiplying by the molar volume ratio ($^{V_A}/_{V_B}$) thus giving 'n_S^{corr}'. Therefore a three-component treatment may now be applied.

This suggestion was followed up for the chloroform-benzene interaction, the data used being recorded in table 7.8. The values obtained were K_x = 1.68, Δ_c = 83.0 Hz, these being considerably nearer the results recorded in table 3.8 for this system, than those originally obtained (see table 7.7). It should also be noted that they are very close to the revised values recently obtained by Whitney[195], who made use of the above concept (see page 76a). Furthermore they are similar to corresponding values, obtained by the Creswell and Allred procedure[62], given in table 3.10. The other systems were not treated in the same way both because of a lack of sufficient data and also because results were not obtainable to provide the necessary comparison.

7.7 Interactions Other than 1 : 1

For the TMS-benzene system the curve representing Δ plotted against $^{n_B}/_{n_A+n_B}$ (figure 7.5) is found to curve back towards the

mole fraction axis when a large excess of benzene is present. Since this does not appear to be due to experimental error, it indicates that the equilibrium situation is more involved than for simple 1:1 molecular complex formation. Therefore the K_x^{CA} and Δ_c values quoted in table 7.5 were calculated using only those values of Δ for $n_B/n_A+n_B < 0.70$ and hence they should only be taken as an indication of the approximate values of the parameters pertaining to the assumed interaction. The value obtained for the equilibrium quotient appears to indicate that the interaction is strong and that TMS is a poor reference material for aromatic compounds. It is particularly interesting that the TMS-benzene results confirm those of Laszlo et. al.[54] who found an aromatic induced shift of c.a.-0.03 ppm for infinite dilution, which is close to the value reported herein of - 0.05 ppm for the fully complexed state. In addition, this value is in accordance with the findings of Homer et. al.[142] that composite anisotropy screenings of aromatic solvents measured using TMS as 'probe' are approximately 0.04 ppm lower than those obtained using cyclohexane as 'probe'. Homer et. al's observations may alternatively be explained in terms of the dependence of anisotropy on solute size[105, 107]; but it must be pointed out that the most consistent explanation is that TMS does indeed interact with aromatic molecules to form a complex.

The interaction between acetone and carbon disulphide has also been studied. The shape of the curve corresponding to equation 7,1 is inconsistent with that for the formation of a single specific complex as it curves away from the mole fraction axis (figure 7.5) and no limiting shift is obtained. It may be concluded that this is, in fact, due either to the occurance of multiple equilibria or to accumulative solvation and, furthermore, other systems resulting in lines of this shape may be interpreted on the same basis.

7.8 Modifications to the Proposed Procedure, for Future Use.

This procedure was designed to investigate complex formation and the inertness of solvents. If it is to be used properly (as discussed in sections 3.8 and 7.6) then a) more experimental points are required at values of $^{n}B/n_{A}+n_{B}$ near to unity and b) the number of steps in the procedure must be reduced. It is suggested that b) may be achieved as follows. A series of ten samples should be prepared each containing a given concentration of A in B in the annulus and the same concentration of A in S in the capillary; both samples should also have a very small amount of cyclohexane (preferably < 0.2 per cent) added as a medium screening 'probe'. The chemical shift between A in B and S respectively would then provide δ_{obs}, and the chemical shift between the cyclohexane peaks would provide δ'_{obs}; as these values relate to the same sample, $\delta_{obs} - \delta'_{obs}$ would directly provide Δ at the relevant mole fraction, $^{n}B/n_{A}+n_{B}$, no graphical evaluations being involved. For greatest accuracy a plot of Δ against $^{n}B/n_{A}+n_{B}$ would be required, and the 'best line' values for Δ used in the evaluation of K_x and Δ_c. In order to use the BH type procedure[44] all the samples should be concentrated in the range with $^{n}B/n_{A}+n_{B}$ varying from 0.9 to 1.0. The evaluation would then be by a BH plot using a curve-fitting procedure with a weighting favouring the highest aromatic concentrations. Over the appropriate range of $^{n}B/n_{A}+n_{B}$ ($\rightarrow 1.0$) the numerical values of δ_{obs}, δ'_{obs} and Δ should still be much the same as the values recorded in table 7.3 for the same systems. The major advantages of the revised procedure are a) the improvement in accuracy ensuing from the reduced number of experimental steps involved and b) the more accurate data available as a result of the elimination of the graphical correction for the medium screening effects. The only disadvantage is the loss of a strict two component solution, which might be relevant if the activity coefficients were known.

7.9 Conclusions

The method outlined above for the study of 1:1 molecular complex formation clearly gives approximate equilibrium quotient and aromatic induced shift data. It is also useful for studying more complicated interactions in solution and in a modified form it provides a means of testing the 'inertness' of solvents. It appears that there are certain advantages in employing the procedure as used above, these are a) it may offer a method for distinguishing between genuine complex formation and accumulative solvation, b) two component systems can be studied, for which activity coefficient data may be available and which will therefore enable, after variable temperature studies have been completed, more meaningful thermodynamic data to be evaluated, c) the shift referencing procedure enables nuclei other than ^1H to be studied and d) the difficulties in correcting for medium screening effects, normally required by an external referencing technique, are almost overcome, although the effects of self-association can, under certain circumstances, remain partially uncorrected. The main disadvantages of the system as used at present are that it a) has a data evaluation procedure which is essentially graphical in nature and this inherently limits the accuracy of the values of K_x and Δ_c and b) it has normally been used over the whole concentration range with consequent loss of thermodynamic validity. Both these criticisms would appear to be mitigated in the modified procedure proposed in section 7.8. A final source of difficulty is in the preparation of the two samples containing exactly the same mole fraction of A, errors in this will be difficult to correct for and they result in a large experimental scatter on the results obtained. Even in the modified procedure proposed in section 7.8 this is most easily overcome by using a final graphical treatment of the Δ values, to obtain 'best line' shifts which are then used in the appropriate data evaluation procedure.

CHAPTER 8

The Variation of the Composite Anisotropy Screening of Mixtures with Temperature.

8.1 Introduction.

It has been shown in chapter 7 that reasonable values are obtained for K_x and Δ_c, for a number of systems, using the new procedure[59] described in chapter 4. It was desirable, therefore, to examine these systems at various temperatures in order to obtain the thermodynamic parameters of complex formation and further test the realiability of the method. The proposed studies require that the medium screening corrections be obtained as a function of temperature. Since the variation of σ_b is easily obtained[8] and σ_E is not involved, and also because of the interest aroused in chapter 6 concerning the σ_a screening, it was decided to concentrate initially on the composite $\sigma_a + \Delta\sigma_w$ screening variation with temperature. The particular interest in this screening is that at standard probe temperatures the experimental measurements tie in with the theory of the anisotropy screening[105-107] (section 5.6), and correlate with the thermodynamics of binary liquid mixtures[165-166]. Therefore it was also of interest to attempt to predict the temperature dependance of this screening.

In chapter 6 it was shown that it was necessary to consider a joint $\sigma_a + \Delta\sigma_w$ screening and its variation with composition. This screening was interpreted in terms of a theoretical model provided by Becconsall[105-107], (which related to σ_a in pure liquids). It was not difficult to extend this to binary liquid mixtures and show that if these mixtures were not randomly arranged then the experimentally determined screenings would vary non-linearly with composition. Whilst fundamentally a $\sigma_a + \sigma_w$ term should be considered it was also shown in chapter 6 that because the dispersion term was actually measured with respect to carbon tetrachloride as reference, strictly a $\Delta\sigma_w$ term is obtained. There is considerable speculation as to which of the two terms

is the largest simply because they cannot normally be measured separately i.e. Raynes et. al.[100] have presumably obtained both. However, even if use is made of their values, $\Delta\sigma_w$ appears to be small, hence the composite screening is probably a number reasonably close to the true σ_a screening.

Becconsall[105] predicted that the magnetic anisotropy should be temperature dependent because of changes in the possible orientations within the anisotropically effective contact shell; these orientations being governed by various intermolecular forces between the molecules some of which are temperature dependant via density. Whilst dispersion forces are believed to be temperature independant[180] at constant density, it has been shown that the dispersion screening is temperature dependant[86] due to a distortion of the electronic environment about a nucleus caused by molecular 'buffeting'. Therefore is is to be expected that the composite anisotropy screening ($\sigma_a + \Delta\sigma_w$) should be temperature dependant and hence this variation has been experimentally measured. Furthermore an attempt has been made to calculate the dispersion part of this screening, in a pure substance, using the rather approximate theory of Howard, Linder and Emerson[99] in order to give some indication of the magnitude of the pure anisotropy screening and its variation with temperature; it should also be possible to obtain a guide to the variation of these effects with mixture composition.

8.2 The Experimental Conditions.

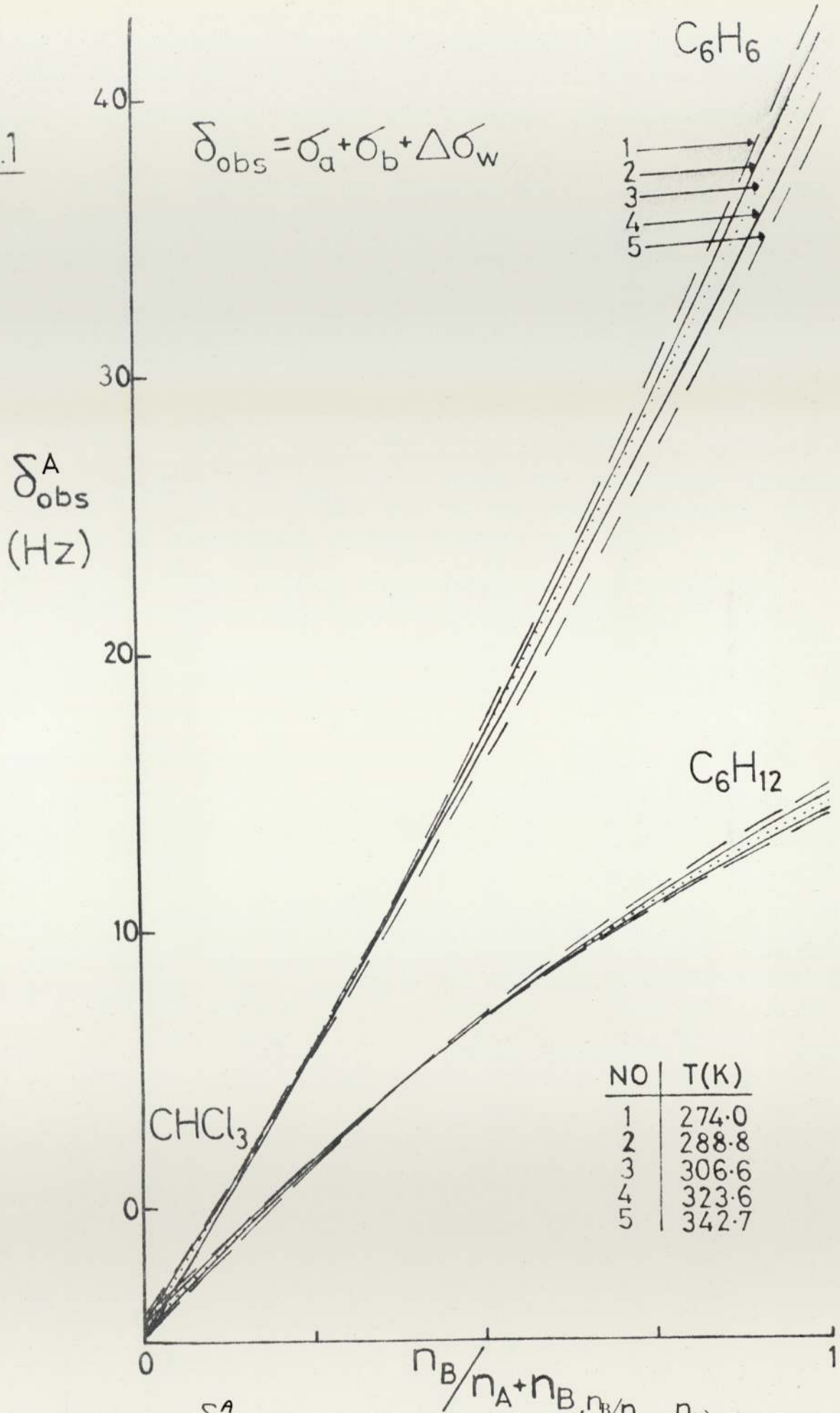
The procedure adopted was identical to that proposed in section 6.2, the same samples were used, and care was taken to obtain thermal equilibration at each temperature. The composite anisotropy screening variations were studied nominally at 273K (or 278K), 288K, 323K and 343K for all those systems relevant to the interaction studies reported in chapter 7. The temperatures deviated from these, by a few degrees, because of the need to use the precise temperatures relevant to the

interaction studies made using the new procedure[59] (see chapter 9). The acetone-carbon disulphide and acetone-chloroform systems were also investigated at a variety of temperatures; since these were not studied from an interaction point of view the opportunity was taken, in the investigation of $\sigma_a + \Delta\sigma_w$, to use as wide a temperature range as possible, i.e. between 256K and 323K. The results at the lower temperature should be particularly valuable because all the other systems could not be examined below 273K.

8.3 The Experimental Variation of the Composite Anisotropy Screening of Mixtures ($\sigma_a + \Delta\sigma_w$) with Temperature.

The experimentally measured chemical shifts between the cyclohexane 'probe' in the anisotropic medium and in the carbon tetrachloride reference, δ^A_{obs} ($\sigma_a + \Delta\sigma_b + \Delta\sigma_w$), and these shifts corrected for the bulk susceptibility screening, Δ ($\sigma_a + \Delta\sigma_w$) are recorded, in table 8.1, for each sample at the exact temperatures used for these systems in the appropriate molecular interaction studies. The exact volume ratio $V_A/V_A+V_B(V_S)$ at each temperature is shown and the samples are identified as in table 6.1. The corresponding values for the acetone-carbon disulphide and acetone-chloroform systems are shown in table 8.2. The volume susceptibility, χ_v, may be obtained at any temperature t by the use of data recorded in table 6.2 and equation 5,20, thus the volume bulk susceptibility screening (σ_b) may then be obtained from the use of equation 6,7 (ϕ_A and ϕ_B in this equation being equated with $^{V_A}/_{V_A+V_B}$ and $^{V_B}/_{V_A+V_B}$). It should be emphasized that the composite $\sigma_a + \Delta\sigma_w$ values quoted in table 8.1 are obtained by accommodating the variation of $\Delta\sigma_b$ via a density effect on both χ_v and the volume fraction. Typical plots at various temperatures, of the observed shifts, δ^A_{obs}, against the mole ratio $^{n_A}/_{n_A+n_B}$ are shown in figure 8.1 for the chloroform-benzene and chloroform-cyclohexane systems. These alone being depicted, for clarity, as representative of the others. Plots

8.1



The variation of δ^A_{obs} with constituent mole ratio ($n_B/n_A + n_B$) shown as a function of temperature for the representative mixtures indicated. The shift variations at 306.6K are included from figure 6.1 for completeness.

Table 8.1

The variation in the composite anisotropy screening, $(\sigma_a + \Delta\sigma_w)$, of mixtures with temperature.

Sample No.	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)
	274.0K			288.8K			323.6K			342.7K		
a) Chloroform (A) – Benzene (B)												
31/1	1.0000	- 4.43	2.01	1.0000	- 4.22	2.05	1.0000	- 4.28	1.59	1.0000	- 4.10	1.55
31/2	0.7727	6.43	9.27	0.7728	5.08	7.83	0.7731	5.25	7.78	0.7733	5.49	7.90
31/3	0.5733	12.44	12.11	0.5734	12.32	11.97	0.5738	12.54	12.14	0.5740	11.91	11.48
31/4	0.3540	22.99	19.19	0.3542	22.71	18.96	0.3545	22.43	18.80	0.3548	21.63	18.06
31/5	0.1753	32.42	25.78	0.1754	32.16	25.63	0.1756	31.08	24.81	0.1757	30.00	23.88
31/6	0.0000	43.05	33.63	0.0000	42.12	32.87	0.0000	39.96	31.11	0.0000	38.53	29.90
b) Chloroform (A) – Cyclohexane (S)												
32/1	0.9948	- 4.95	1.42	0.9948	- 4.63	1.57	0.9948	- 4.64	1.16	0.9948	- 4.41	1.18
32/2	0.7514	*	-	0.7516	*	-	0.7519	*	-	0.7521	*	-
32/3	0.5274	4.75	4.50	0.5276	5.45	5.18	0.5280	5.22	4.91	0.5283	5.07	4.74
32/4	0.3274	9.13	6.05	0.3276	9.26	6.23	0.3279	8.96	6.03	0.3282	8.73	5.86
32/5	0.1576	12.73	7.25	0.1577	12.29	6.91	0.1579	12.25	7.09	0.1580	11.70	6.67
32/6	0.0000	15.13	7.42	0.0000	14.96	7.40	0.0000	14.52	7.29	0.0000	14.14	7.10

Table 8.1 (cont'd.)

Sample No.	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)
	274.0K			289.1K			323.7K			343.0K		
c) Ethylene Chloride (A) - Benzene (B)												
22/1	1.0000	- 7.05	1.14	1.0000	- 6.93	1.21	1.0000	- 7.15	0.87	1.0000	- 7.20	0.76
22/2	0.7733	1.74	5.94	0.7731	1.77	5.97	0.7727	1.69	5.88	0.7724	1.72	5.90
22/3	0.5590	10.60	11.03	0.5588	10.62	11.09	0.5582	10.38	10.95	0.5579	10.26	10.88
22/4	0.3667	20.48	17.52	0.3665	20.27	17.40	0.3659	19.46	16.78	0.3656	19.12	16.55
22/5	0.1752	31.38	25.05	0.1751	30.72	24.52	0.1748	29.45	23.55	0.1745	28.81	23.08
22/6	0.0000	43.05	33.63	0.0000	42.22	32.98	0.0000	40.01	31.16	0.0000	38.61	29.98
d) Ethylene Chloride (A) - Cyclohexane (S)												
21/1	0.9890	- 6.70	1.32	0.9890	- 6.73	1.24	0.9890	- 7.03	0.83	0.9890	- 6.59	1.20
21/2	0.7349	0.00	3.98	0.7348	0.00	3.98	0.7343	0.00	3.97	0.7341	0.00	3.97
21/3	0.5086	4.89	5.27	0.5083	4.42	4.84	0.5078	4.39	4.91	0.5075	4.14	4.71
21/4	0.3202	8,87	6.25	0.3201	8.77	6.23	0.3196	8.30	5.95	0.3193	8.21	5.96
21/5	0.1587	12.31	6.97	0.1585	12.15	6.92	0.1583	11.62	6.66	0.1581	11.29	6.47
21/6	0.0000	15.13	7.42	0.0000	14.64	7.08	0.0000	13.78	6.56	0.0000	13.59	6.55

Table 8.1 (cont'd.)

Sample No.	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)
	279.4K			288.9K			323.5K			342.3K		
e) Methyl-Iodide (A) - Benzene (B)												
29/1	1.0000	- 27.90	1.29	1.0000	- 28.20	0.64	1.0000	- 30.42	- 2.85	1.0000	- 30.20	- 3.32
29/2	0.7322	- 12.70	6.17	0.7324	- 12.52	6.12	0.7326	- 12.65	5.17	0.7326	- 12.13	5.25
29/3	0.5128	2.76	13.17	0.5129	2.91	13.20	0.5130	2.43	12.26	0.5131	2.46	12.05
29/4	0.2770	20.87	22.19	0.2771	20.23	21.54	0.2772	†	-	0.2773	†	-
29/5	0.1217	†	-	0.1217	†	-	0.1218	30.22	25.80	0.1218	29.57	25.26
29/6	0.0000	42.91	33.56	0.0000	41.84	32.59	0.0000	39.88	31.03	0.0000	38.55	29.91
f) Methyl Iodide (A) - Cyclohexane (S)												
30/1	0.9781	- 28.08	0.30	0.9781	- 28.51	-0.47	0.9781	- 30.00	- 3.19	0.9781	- 31.35	- 5.21
30/2	0.6823	- 16.21	1.27	0.6823	- 16.19	1.08	0.6825	- 16.34	0.18	0.6826	- 15.58	0.53
30/3	0.4411	*	-	0.4411	*	-	0.4413	- 5.35	2.78	0.4414	- 4.40	3.53
30/4	0.2779	*	-	0.2779	*	-	0.2781	*	-	0.2782	*	-
30/5	0.1201	10.44	7.21	0.1202	9.89	6.70	0.1203	9.66	6.62	0.1203	9.14	6.18
30/6	0.0000	15.16	7.50	0.0000	14.64	7.08	0.0000	14.79	7.56	0.0000	13.93	6.89

Table 8.1 (cont'd.)

Sample No.	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)
	274.0K			289.0K			324.7K			343.5K		
g) TMS (A) - Benzene (B)												
35/1	1.0000	24.55	6.39	1.0000	24.66	6.42	1.0000	25.48	7.06	1.0000	ø	-
35/2	0.8506	27.38	10.53	0.8513	27.46	10.56	0.8532	27.64	10.62	0.8543	27.43	10.35
35/3	0.6829	29.87	14.48	0.6841	30.10	14.70	0.6874	29.59	14.16	0.6892	29.13	13.68
35/4	0.5161	33.06	19.13	0.5176	32.85	18.95	0.5213	31.84	18.00	0.5235	31.01	17.20
35/5	0.2767	37.34	25.51	0.2779	36.74	25.00	0.2809	35.10	23.57	0,2826	34.01	22.59
35/6	0.0000	43.05	33.63	0.0000	42.18	32.94	0.0000	39.84	31.00	0.0000	38.53	29.91
h) TMS (A) - Cyclohexane (S)												
34/1	0.9971	24.85	6.72	0.9972	25.17	6.96	0.9972	25.74	7.35	0.9972	ø	-
34/2	0.8170	22.67	6.42	0.8179	22.88	6.59	0.8202	22.93	6.52	0.8215	22.85	6.38
34/3	0.6574	21.11	6.53	0.6588	20.76	6.17	0.6622	20.97	6.33	0.6641	20.62	5.96
34/4	0.4530	ø	-	0.4545	ø	-	0.4582	18.68	6.33	0.4604	18.15	5.83
34/5	0.2370	16.81	6.62	0.2381	16.67	6.57	0.2409	16.30	6.39	0.2424	15.97	6.15
34/6	0.0000	15.03	7.32	0.0000	14.72	7.16	0.0000	14.33	7.12	0.0000	13.73	6.70

Table 8.1 (cont'd.)

Sample No.	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)
	278.9K			288.8K			323.9K			342.7K		
i) Vinylidene Chloride (A) - Benzene (B)												
27/1	1.0000	12.37	3.19	1.0000	12.44	3.36	1.0000	12.70	3.96	1.0000	13.00	4.46
27/2	0.7801	17.89	8.67	0.7801	18.09	8.97	0.7802	17.94	9.17	0.7802	17.76	9.20
27/3	0.5593	23.88	14.62	0.5594	23.63	14.47	0.5595	23.63	14.84	0.5595	23.03	14.45
27/4	0.3675	29.17	19.88	0.3675	29.00	19.81	0.3676	27.94	19.13	0.3677	27.34	18.74
27/5	0.1960	35.52	26.19	0.1961	35.06	25.84	0.1961	33.88	25.04	0.1962	33.03	24.41
27/6	0.0000	43.22	33.86	0.0000	41.83	32.58	0.0000	40.19	31.33	0.0000	38.95	30.32
j) Vinylidene Chloride (A) - Cyclohexane (S)												
28/1	0.9930	12.39	3.22	0.9930	12.30	3.23	0.9930	12.72	3.99	0.9930	13.12	4.59
28/2	0.5915	13.45	4.89	0.5915	13.83	5.37	0.5917	13.52	5.40	0.5918	13.53	5.60
28/3	0.4974	13.97	5.55	0.4975	14.19	5.87	0.4976	14.32	6.34	0.4977	13.71	5.92
28/4	0.3145	14.77	6.63	0.3146	14.55	6.51	0.3147	14.21	6.50	0.3148	13.98	6.47
28/5	0.1539	14.87	6.97	0.1540	14.30	6.50	0.1540	14.32	6.86	0.1541	14.04	6.77
28/6	0.0000	14.88	7.22	0.0000	14.86	7.30	0.0000	14.52	7.29	0.0000	14.14	7.10

Table 8.1 (cont'd.)

Sample No.	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)	$V_A/V_A+V_B(V_S)$	δ^A_{obs} (Hz)	Δ (Hz)
	279.4K			288.8K			323.8K			344.6K		
k) Cyclohexane (A) - Benzene (B)												
23/1	1.0000	14.88	7.22	1.0000	14.72	7.16	1.0000	14.16	6.94	1.000	13.95	6.93
23/2	0.8318	19.86	11.92	0.8317	-	-	0.8317	18.61	11.11	0.8317	17.99	10.70
23/3	0.6505	24.38	16.13	0.6504	23.87	15.72	0.6504	23.03	15.24	0.6504	22.44	14.86
23/4	0.4497	29.58	20.99	0.4497	29.11	20.62	0.4496	28.10	19.98	0.4496	27.50	19.60
23/5	0.2324	35.84	26.88	0.2324	35.66	26.80	0.2323	33.84	25.37	0.2323	32.77	24.53
23/6	0.0038	42.90	33.55	0.0038	42.49	33.25	0.0038	39.97	31.13	0.0038	38.79	30.18
l) Cyclohexane (A) - Cyclohexane (S)												
-	1.0000	14.88	7.22	1.0000	14.72	7.16	1.0000	14.16	6.94	1.0000	13.95	6.93

* could not be measured because the two cyclohexane peaks were virtually coincident.

† cyclohexane peak beneath one of the methyl iodide peaks.

ø could not be measured because one peak obscured beneath spinning side-bands of TMS.

Table 8.2

Variation of the observed chemical shifts, δ^{A}_{obs} $(\sigma_a + \Delta\sigma_b + \Delta\sigma_w)$, and the shifts corrected for volume bulk susceptibility, Δ $(\sigma_a + \Delta\sigma_w)$, as a function of composition and temperature.

Sample No.	V_A/V_A+V_B	δ^{A}_{obs} (Hz)	Δ (Hz)	V_A/V_A+V_B	δ^{A}_{obs} (Hz)	Δ (Hz)
	256K			323K		
a) Acetone (A) - Carbon Disulphide (B)						
25/1	1.0000	†	11.64	1.0000	†	9.96
25/2	0.8290	32.35	7.82	0.8314	30.58	7.32
25/3	0.6462	23.24	4.40	0.6500	22.97	5.10
25/4	0.4447	12.99	0.45	0.4481	13.12	1.23
25/5	0.2336	2.42	- 3.55	0.2366	3.12	- 2.45
25/6	0.0000	- 8.19	- 6.87	0.0000	- 7.82	- 6.34
b) Acetone (A) - Chloroform (B)						
39/1	1.0000	†	11.64	1.0000	†	9.96
39/2	0.7730	32.01	10.45	0.7749	29.26	8.66
39/3	0.5657	22.80	8.80	0.5683	20.77	7.24
39/4	0.3726	13.70	6.76	0.3752	11.93	4.99
39/5	0.1818	4.26	4.27	0.1834	3.63	3.23
39/6	0.0000	- 5.01	1.65	0.0000	- 4.76	1.12

† This could not be measured owing to the superposition of two peaks, however as there were two systems it was possible to extrapolate these to give a shift of 41.50 Hz at 256K and 38.25 Hz at 323K.

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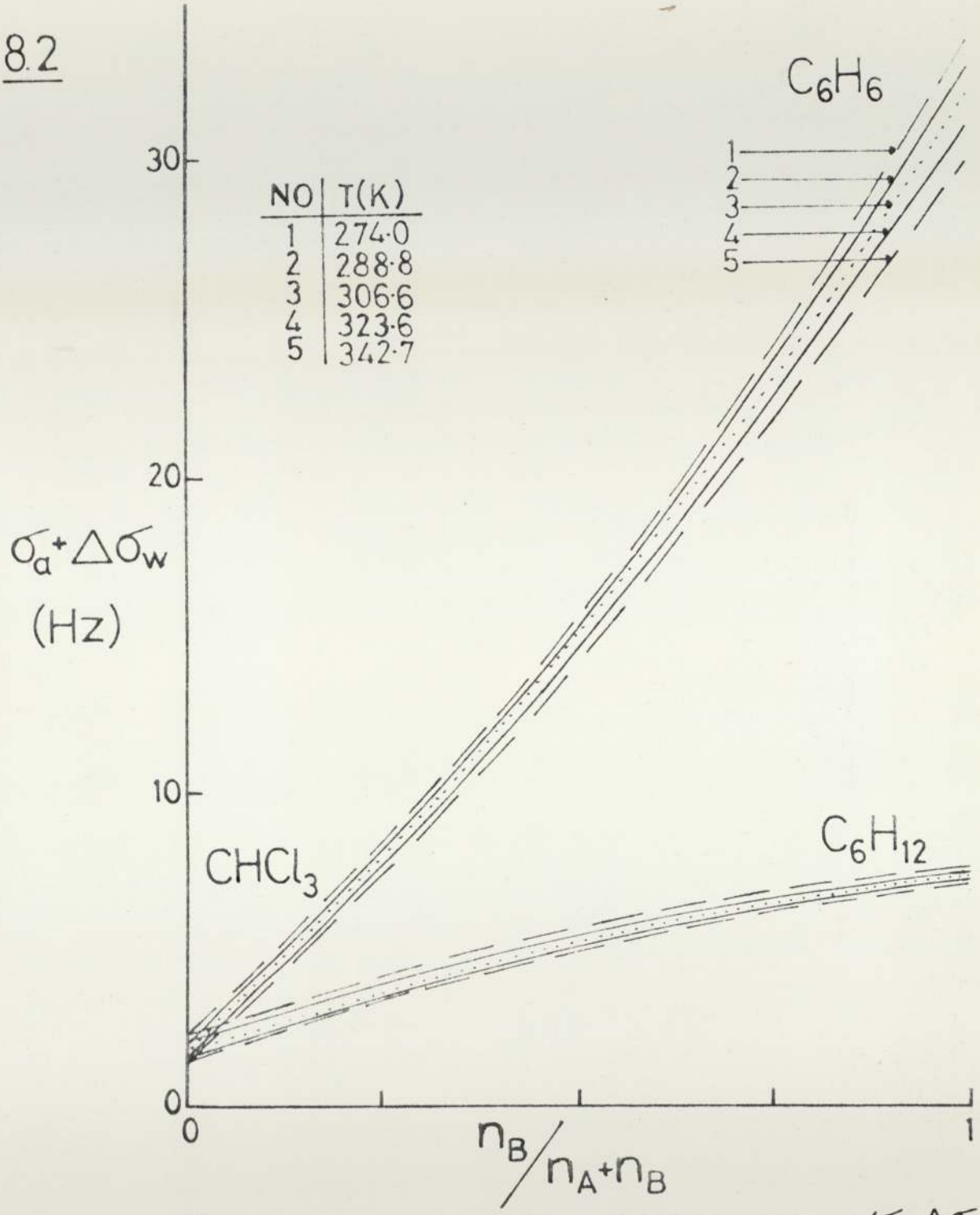
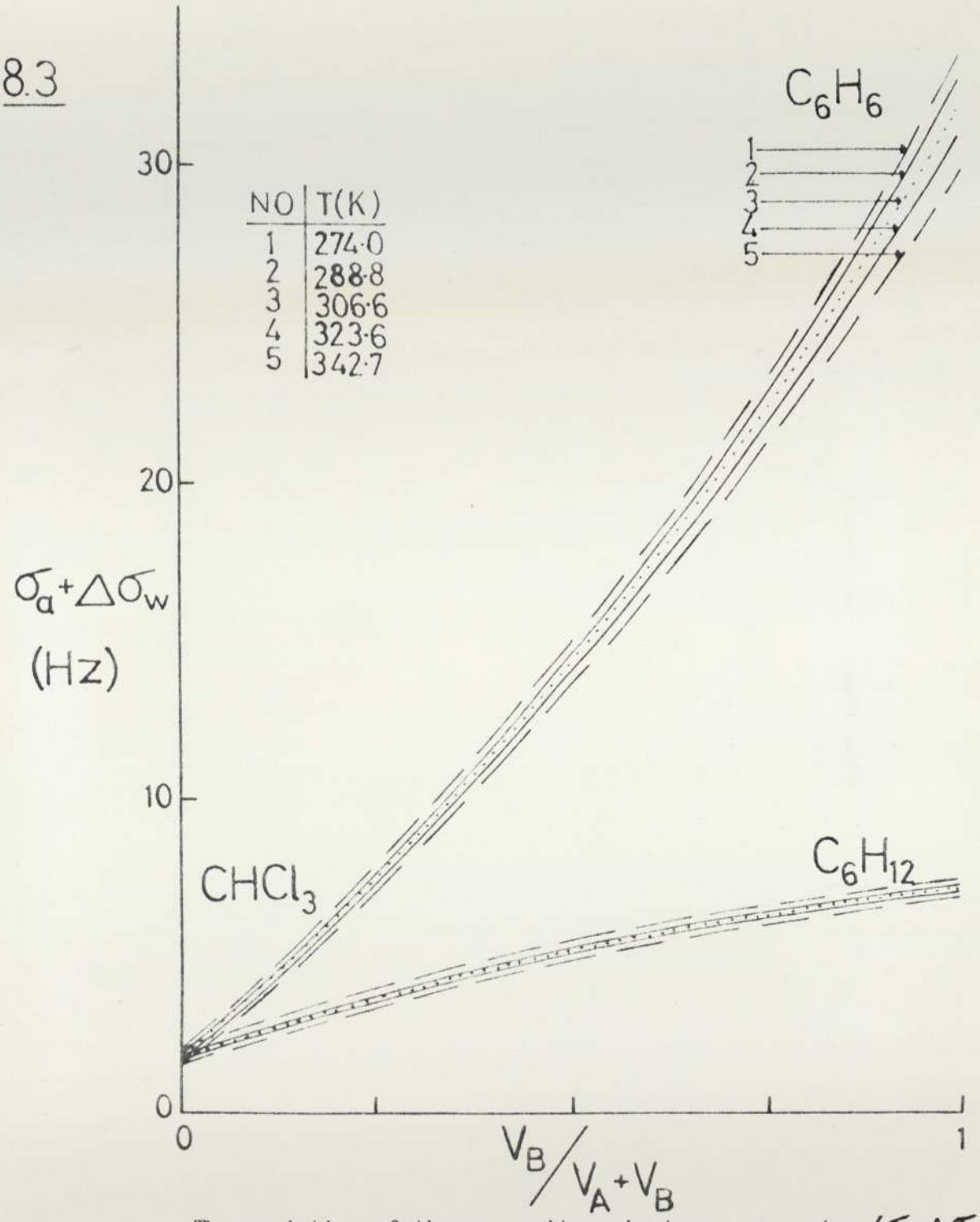
of these shifts after correction for bulk susceptibility Δ $(\sigma_a + \Delta\sigma_w)$ are shown in figure 8.2. It can be seen that at different temperatures these lines are curved, as found for one temperature in chapter 6. Plots of Δ may also be made against the volume ratio, V_A/V_A+V_B, and it may be seen from figure 8.3 that these are again curved and temperature dependant. These are all systems which were considered, in chapter 6,

8.2



The variation of the composite anisotropy screening ($\sigma_a+\Delta\sigma_w$) with constituent mole ratio ($n_B/n_A + n_B$) shown as a function of temperature for the representative mixtures indicated. The screening variations at 306.6K are included from figure 6.2 for completeness.

8.3



The variation of the composite anisotropy screening ($\sigma_a+\Delta\sigma_w$) constituent volume ratio ($^{V_B}/_{V_A + V_B}$) shown as a function of temperature for the representative mixtures indicated. The screening variations at 306.6K are included from figure 6.3 for completeness.

to be imperfect, therefore this is consistent with the thermodynamics of imperfect mixtures.

8.4 The Temperature Variation of the Dispersion Screening (σ_w) of Pure Materials and its Effect on the Temperature Variation of the Composite Anisotropy Screening ($\sigma_a + \Delta\sigma_w$).

Although this chapter is concerned with the variation of mixture screenings with composition and temperature, data are, of course, available for a number of pure liquids. In order to obtain a better understanding of these variations in mixtures it is reasonable to examine the variation of $\sigma_a + \Delta\sigma_w$ with temperature in pure substances initially.

Buckingham et. al.[86] have proposed that the dispersion screening on a solute 'probe' in a pure material occurs via two mechanisms. Their discussion of these may be summarized in the following way:

a) Interaction between the solute and the solvent (in its equilibrium configuration), causes a distortion of the electronic environment of the nucleus. This distortion is probably an expansion (since the electrons are attracted by the nuclei of neighbouring molecules), hence the diamagnetic screening is diminished thereby leading to resonance at lower field strengths. b) Departures from the equilibrium solvent configurations will lead to a 'buffeting' of the solute and hence to a time-dependant distortion of the electronic structure resulting in the symmetry of any X - H bonds in the solute being destroyed (they are normally axially symmetric), the proton shielding thereby being affected, They suggest that mechanism a) is temperature dependant via a density term and that mechanism b) is temperature dependant at constant density because of an increase in thermal motion causing larger departures from the solvent equilibrium configuration; thus an increased low-field shift is obtained. Of course, in practice, density and temperature both vary hence the variation of mechanism b) with temperature may well be complex and it is difficult to predict the overall variation of the

σ_w screening with temperature.

An alternative, but analogous, description of the two mechanisms may be considered as follows. In practice, molecules have translational, rotational, vibrational and electronic energies and small changes in temperature at or near room temperature may affect the translational energy of the molecules and also the vibrational or rotational energies, (the kinetic energy variation is approximately 3/2 RT and this will just about affect the rotational energy). Mechanism a) considers that the solute is in a continuum of solvent molecules which are fixed with respect to the solute such that they have no translational motion but they do have characteristic electronic, vibrational and rotational energies. The vibrational and rotational motions govern the dispersive contribution and, as shown above, the temperature dependence of these is considered negligible. Consequently, as the temperature varies, the only effect is to change the density; this alters the interaction distances and, for example, molecules come closer together as the temperature is reduced thus increasing σ_w. Mechanism b) considers the effect of temperature on the translational motion of the solvent molecules, which are now permitted to move in relation to the solute molecule. Therefore the solvent molecules will 'buffet' the solute and a σ_w screening will result. On increasing the temperature they will have greater translational energy, hence greater 'buffeting' will ensue and σ_w may be expected to increase (i.e. become more negative). However, the density will have decreased and the separation distances will have become greater thus decreasing σ_w. It is, therefore, difficult to decide which of these has the greater significance and the overall temperature dependance of σ_w based on the Buckingham model[86] cannot be decided theoretically, although combination of mechanisms a) and b) suggests that σ_w decreases on increasing the temperature.

An approximate calculation of σ_w is possible based on the theory of Howard, Linder and Emerson[99]. In order to obtain some indication

of the magnitude of σ_w and its variation with temperature, the dispersion screenings of pure benzene and separately pure carbon tetrachloride on cyclohexane were calculated at the temperatures used in the determination of $\sigma_a + \Delta\sigma_w$ for the benzene-cyclohexane system. From these results it should be possible to determine a) the approximate value of $\Delta\sigma_w$ and b) its temperature dependance. Thus it will be possible to estimate the variation of the magnetic anisotropy, σ_a, with temperature in a pure material (benzene). The basic equation for σ_w (equation 5,37) as proposed by Howard, Linder and Emerson[99] is discussed in detail in section 5.7, but in order to determine σ_w at different temperatures it is more convenient to make use of the Lorenz-Lorentz equation for molar refraction[99,181], which results in g (originally given as equation 5,39) being redefined as

$$g = \frac{n_1^2 + 2}{2n_1^2 + 1} \cdot \frac{8\pi L \alpha_1}{3V_1} \cdot \frac{1}{a_2^3} \qquad 8,1$$

substitution into equation 5,37 gives

$$\sigma_w = \oint \frac{n_1^2 + 2}{2n_1^2 + 1} \cdot \frac{2\pi L h \alpha_1}{M_1} \cdot \left(\frac{\nu_1 \nu_2}{\nu_1 + \nu_2}\right) \cdot \frac{1}{a_2^3} \cdot \rho_1 \qquad 8,2$$

where α_1 is now defined as

$$\alpha_1 = \frac{3}{4\pi L} \cdot \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \cdot \frac{M_1}{\rho_1} \qquad 8,3$$

where ε_r, is the dielectric constant of the solvent, and a_2^3 is defined by

$$a_2^3 = 3M_2 / \rho_2 L 4\pi \qquad 8,4$$

Since dispersion forces occur between both like and unlike molecules it is necessary to decide which interactions are relevant to the σ_w screening of the cyclohexane 'probe' in the two situations. The interactions in the benzene solution are a) benzene on benzene, b) benzene on cyclohexane, c) cyclohexane on benzene and d) cyclohexane on cyclohexane; and in the carbon tetrachloride solution they are a) carbon tetrachloride on carbon tetrachloride, b) carbon tetrachloride on cyclohexane,

c) cyclohexane on carbon tetrachloride and d) cyclohexane on cyclohexane. Interactions a) and c) clearly do not affect the σ_w screening of cyclohexane and since the concentration of cyclohexane in both solutions is very small and the same, effect d) may be neglected (it cancels out any way in the $\Delta\sigma_w$ term). Therefore it is necessary to calculate the σ_w screening of benzene and separately carbon tetrachloride on cyclohexane at each temperature. Subtraction of these two values gives an approximate value for the $\Delta\sigma_w$ portion of the composite anisotropy screening, $\sigma_a + \Delta\sigma_w$, of benzene at various temperatures. The parameters used in these calculations at 274K, 288K, 306.6K, 323K and 343K are given in tables 8.3, 8.4 and 8.5. The calculated σ_w screenings of benzene and carbon tetrachloride are given in table 8.6 and it may be seen that the variation of σ_w with temperature is in the most likely direction suggested by the ideas on the theory of this screening given above. The magnitude of this effect is shown in relation to measured values of δ^A_{obs} in table 8.7, where a value for the magnetic anisotropy, σ_a, portion of the composite anisotropy screening, $\sigma_a + \Delta\sigma_w$, is also given (assuming the validity of the above values for $\Delta\sigma_w$). It may be seen both that the numerical value of $\Delta\sigma_w$ is small and that its variation as a function of temperature is very small despite the fact that σ_w is much larger and is considerably dependant on temperature (the dispersion screening of pure benzene on cyclohexane varies from -6.6 Hz at 343K to -7.8 Hz at 274K). The magnitude of this variation has been confirmed by Symeonides[182] who obtained experimental σ_w values for TMS (from gas phase shifts relative to carbon tetrachloride) which varied from - 14 Hz to - 12 Hz over a 40K temperature range. Therefore, at least for a pure substance, the magnetic anisotropy, σ_a, appears to be temperature dependant. If the above calculation of $\Delta\sigma_w$ is accepted then the values for σ_a are large (see table 8.7) and of a similar magnitude to the values quoted by Raynes et. al[100] for the dispersion screenings of benzene acting on methane or

Table 8.3

Refractive index (n) of benzene, carbon tetrachloride and cyclohexane as a function of temperature.[122-123]

Compound	274K	288K	306.6K	323K	343K
Benzene	1.51384	1.50439	1.49268	1.48206	1.46926
Carbon Tetrachloride	1.47160	1.46305	1.45280	1.44334	1.43194
Cyclohexane	1.43666	1.42886	1.41680	1.40784	1.39704

Table 8.4

Dielectric constant (ε_r) of benzene, carbon tetrachloride and cyclohexane as a function of temperature.[122-123]

Compound	274K	288K	306.6K	323K	343K
Benzene	2.3185	2.2925	2.2560	2.2232	2.1835
Carbon Tetrachloride	2.2730	2.2450	2.2126	2.1825	2.1475
Cyclohexane	2.0531	2.0297	2.0010	1.9751	1.9439

Table 8.5

Physical constants in S.I. Units.[163]

$h = 6.6252 \times 10^{-34}$ J s^{-1} $\qquad$ $c = 2.99793 \times 10^{8}$ m s^{-1}

$L = 6.02474 \times 10^{23}$ mol^{-1} $\qquad$ $m = 9.1085 \times 10^{-31}$ kg

$\phi = -1 \times 10^{-11}$ kg^{-2} m^{2} s^{3} (ppm)

data for p, M and χ_M is given in table 6.2.

Table 8.6

The calculated dispersion screenings of pure benzene and pure carbon tetrachloride on a cyclohexane 'probe' at various temperatures.

		274K	288K	306.6K	323K	343K
σ_w^{BZ}	ppm	- 0.1303	- 0.1265	- 0.1215	- 0.1170	- 0.1117
σ_w^{CT}	ppm	- 0.1389	- 0.1348	- 0.1295	- 0.1247	- 0.1192
$\Delta\sigma_w^{BZ-CT}$	ppm	+ 0.0086	+ 0.0083	+ 0.0080	+ 0.0077	+ 0.0075
	Hz	+ 0.52	+ 0.50	+ 0.48	+ 0.46	+ 0.45

Table 8.7

The contribution of $\Delta\sigma_w$ to the composite anisotropy screening of pure benzene as measured by a cyclohexane 'probe' at various temperatures.

		274K	288K	306.6K	323K	343K
δ_{obs}^{BZ-CT}	Hz	43.05	42.12	41.50	39.96	38.55
$\Delta\sigma_b$(calc)	Hz	9.42	9.25	9.04	8.85	8.64
$\Delta\sigma_w^{BZ-CT}$	Hz	0.52	0.50	0.48	0.46	0.45
σ_E^{BZ-CT}	Hz	0.00	0.00	0.00	0.00	0.00
σ_a^{BZ}	Hz	33.11	32.37	31.98	30,66	29.44

neo-pentane (these being the nearest approximations to cyclohexane). The suggestion that Raynes et. al.[100] have measured a composite $\sigma_a + \Delta\sigma_w$ screening is further confirmed by their results for benzene and carbon tetrachloride separately acting on the above solutes at 308K where a '$\Delta\sigma_w$' screening of $\sim$33Hz is indicated which is very much in line with the values given in table 8.1 for $\sigma_a + \Delta\sigma_w$ of benzene.

8.5 Further Comments on the Anisotropy Model for $\sigma_a + \Delta\sigma_w$

If the $\Delta\sigma_w$ portion of the composite anisotropy screening is as small as has been indicated, it follows (by reference to table 8.1) that it is necessary to attribute a σ_a screening of approximately 7Hz to TMS despite it supposedly being isotropic. This may not be unrealistic since the possibility that apparently isotropic molecules, having the facility of hindered rotation of substituents, may behave in a magnetically anisotropic manner e.g. the nitro groups of tetranitromethane, has already been referred to in chapter 5. On the basis of this explanation of the 'apparent' σ_a screening for TMS, it is clear that carbon tetrachloride should still be isotropic (since it is intrinsically spherically symmetrical); and the use of this compound as a reference for experimentally measuring $\sigma_a + \Delta\sigma_w$ screenings is vindicated.

8.6 The Variation of Mixture Composite Anisotropy Screenings ($\sigma_a + \Delta\sigma_w$) with Temperature

The results given in tables 8.1 and 8.2 indicate that the composite anisotropy screening in mixtures is temperature dependant. Assuming that the indications regarding the temperature variation of $\Delta\sigma_w$ for pure liquids (section 8.4) are valid in mixtures, it may be seen from figures 8.2 and 8.3 that variations in temperature do not affect the non-linearity of the pure σ_a screening with

composition. Becconsall[105,107] predicted a variation in σ_a with temperature such that an increase in temperature resulted in an increase in the screening, which is contrary to that generally found here. His suggestion was presumably based on the supposition that at any particular separation of solute and solvent a cone of permitted orientations of the solvent with respect to the solute may be defined. However, every orientation within this cone is not equally probable because intermolecular forces favour those orientations where the two molecules are in contact (i.e. on the surface of the permitted cone); and this acts so as to reduce the magnitude of σ_a. Therefore as the temperature increases, these intermolecular forces are reduced and the occupancy of the permitted cone becomes more random, hence there is an increase in the probability that the solvent molecule will occupy the central portion of the cone thus causing σ_a to increase. However, this would not appear to be completely correct; since as the temperature increases so does the thermal motion of the system. Hence the edges of the cone will in fact become even more favoured at higher temperatures thus leading to the observed reduction in σ_a. Furthermore, on increasing the temperature the average distance between the two molecules will increase and a larger permitted cone will be obtained; thus the average position of the solvent will be further away from the centre of the cone again leading to a reduction in σ_a.

Therefore the anisotropy screening of mixtures high in benzene content would be expected to become more positive with reduction in temperature, whereas those with a high proportion of carbon disulphide would be expected to become more negative. That this is indeed found may be seen from tables 8.1 and 8.2, where it may also be seen that cyclohexane acts in a similar manner to benzene, which is as expected.

8.7 Conclusions

It has been shown that the composite anisotropy screening is temperature dependant both for mixtures and for pure materials. Also, since the difference in the dispersion screenings of the solution and of the carbon tetrachloride reference on cyclohexane is small and almost temperature independant, it is believed that this conclusion may be reached for the separate magnetic anisotropy as well. It was considered that intermolecular forces governed not only the non-linear additivity of the composite anisotropy screening with mixture composition but also, to some extent, its temperature dependance.

Apart from the interest in their own right, the experimentally determined screenings given in table 8.1 (uncorrected for $\Delta\sigma_b$) provide the medium screening correction lines for the investigation of molecular complex formation at various temperatures by the new procedure (described in chapters 4 and 7) as discussed in the next chapter.

CHAPTER 9

The Use of the New Procedure to Investigate Molecular Interactions in Solution at Various Temperatures

9.1 Introduction

Since the new procedure described in chapter 4[59] gave reasonable values for the equilibrium quotient, K_x, and excess shielding, Δ_c, for complex formation its use was continued in the present investigation into molecular interactions in solution at various temperatures in order to obtain ΔH^o, $\Delta \varphi^o$ and ΔS^o for complex formation. The studies were made on systems previously examined in chapter 7, and the variations of the medium screening effects with temperature, which are required for this investigation, are obtained from chapter 8. These studies were as far as possible carried out by exactly the same procedure as that described in chapter 7.

The derivation of the thermodynamic parameters and the use to which they are put has already been discussed in general terms in sections 3.10 and 3.11; hence it is only necessary to summarize the method of determining ΔH^o, $\Delta \varphi^o$ and ΔS^o. It follows from the Gibbs-Helmholtz equation that

$$\frac{\partial \ln K_x}{\partial (1/T)} = -\Delta H^o / R \qquad 9,1$$

hence a plot of $\ln K_x$ against $1/T$ should have a slope, at 298K, of $-\Delta H^{o298}/R$, and the value of K_x at this temperature may be used to obtain $\Delta \varphi^{o298}$ from

$$\Delta \varphi^{o\,298} = -RT \ln K_x^{298} \qquad 9,2$$

ΔS^{o298} may then be obtained from ΔH^{o298} and $\Delta \varphi^{o298}$ by the use of equation 9,3

$$\Delta \varphi^{o\,298} = \Delta H^{o\,298} - T\Delta S^{o\,298} \qquad 9,3$$

9.2 The Procedure Adopted in the Variable Temperature Studies

The samples used in the variable temperature studies were generally those prepared for use at 306.6K, and details of their composition are recorded in table 7.4. However, the initial chloroform-benzene series

was unavailable and a new series was prepared, the composition of each sample being recorded in table 9.1.

Table 9.1

Composition of the new samples used in the variable temperature studies of complex formation.

Sample No.	n_B/n_A+n_B	$n_A(x10^2 mol)$	$n_B(x10^2 mol)$
a) Chloroform (A) - Benzene (B)			
18/0	0.0000	1.0000	0.0000
18/1	0.1178	2.8580	0.3816
18/2	0.2286	2.6696	0.8561
18/3	0.3927	1.4783	0.9559
18/4	0.4922	1.0179	0.9868
18/5	0.6060	0.8616	1.3251
18/6	0.6988	0.8575	1.9896
18/7	0.8012	0.5358	2.1518
18/8	0.8991	0.1742	1.5518
18/9	0.9493	0.1665	3.1168
18/10	0.9705	0.1132	3.7281
b) Vinylidene Chloride (A) - Benzene (B)			
14/11	0.1187	2.5232	0.3399
14/21	0.2618	2.3622	0.8377
c) TMS (A) - Benzene (B)			
33/101	0.9692	0.1593	5.0151

Additionally, two samples of the vinylidene chloride-benzene system (those of highest vinylidene chloride concentration) had deposited a white polymeric material on standing and one of the TMS-benzene samples had been broken. Replacements were prepared for these samples and details are again recorded in table 9.1. The temperatures at which the investigations were carried out were nominally 273K, 288K, (306.6K), 323K and 343K, except that, for the methyl iodide-benzene and vinylidene chloride-benzene systems, which froze at 273K, the lowest temperature used was 278K. The exact temperatures varied slightly from these but they were closely monitored, as described in section 2.9, for three

reasons: a) It was essential that the medium screening corrections should be measured at exactly the same temperature as that at which the measurement of the interaction chemical shift had been made. b) It was necessary for thermal equilibrium to have been reached before the measurements could be made, and this was assumed to have occured when the steady drift in the monitored temperature ceased. c) The exact temperature is required in the calculation of the thermodynamic parameters of complex formation. The measurement of the chemical shifts between the solute in the aromatic and inert solvents was exactly as described in section 7.2, the only additional precaution being the calibration of the chart paper at every temperature used in order to overcome the effects of the greater field drift obtained using the variable temperature probe.

9.3 The Experimental Results

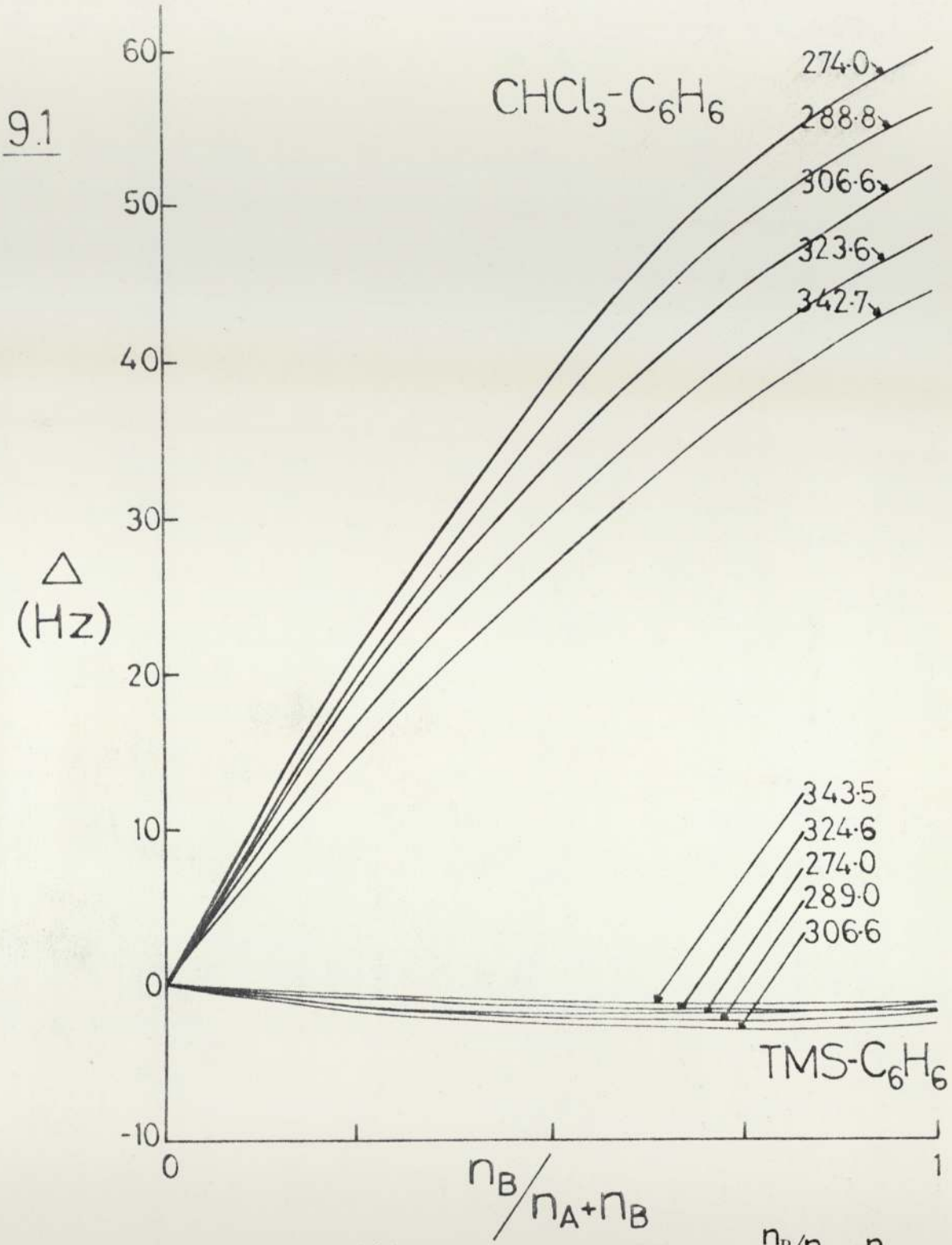
The experimental (interaction) chemical shifts, δ_{obs}, are recorded in table 9.2, with the exact temperatures at which they were measured. The δ_{obs}' corrections, corresponding to equation 4,12, were obtained from the relevant medium screening shifts at the same temperatures, these being recorded in table 8.1. The chemical shifts relating to complex formation, Δ(i.e. $\delta_{obs} - \delta_{obs}'$), are also recorded in table 9.2 but these in fact correspond to the 'best-line' values obtained from the difference between plots of δ_{obs} and δ_{obs}' against x_B, this procedure being adopted in order to rationalize the experimental error.

9.4 Data Evaluation

a) The Creswell and Allred Data Evaluation Procedure

Representative examples of the shifts due to complex formation, Δ, plotted against the aromatic mole fraction, x_B, are shown in figure 9.1. All the four systems considered in chapter 7 to form 1 : 1 molecular complexes (benzene with separately chloroform[31,70], ethylene chloride[60], methyl iodide[61] and vinylidene chloride[32,55]) show curves indicating a limiting shift at each temperature and this is shown for chloroform-

9.1



Shift variation (△) with solution composition ($n_B/n_A + n_B$) shown as a function of temperature for the representative systems indicated. The curves obtained at 306.6K are included from figure 7.5 for completeness.

Table 9.2

Shifts obtained in the two component interaction studies at the temperatures indicated.

Sample No.	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†
a) Chloroform (A) - Benzene (B)						
	274.0K			288.8K		
18/0	0.00	0.00	0.00	0.00	0.00	0.00
18/1	11.45	1.75	9.95	10.83	1.95	9.40
18/2	-	3.85	19.10	23.37	3.90	18.00
18/3	39.39	7.45	31.90	36.71	7.00	29.75
18/4	48.64	10.05	38.65	45.52	9.30	36.15
18/5	58.89	13.15	45.75	55.46	12.75	42.55
18/6	66.32	16.00	50.35	62.53	15.85	46.70
18/7	74.08	19.60	54.50	69.94	19.50	50.55
18/8	81.19	23.30	57.50	76.84	23.20	53.60
18/9	84.25	25.45	58.90	80.09	25.25	54.95
18/10	85.70	26.45	59.45	81.47	26.20	55.55
	323.6K			342.7K		
18/0	0.00	0.00	0.00	0.00	0.00	0.00
18/1	9.36	1.80	8.25	8.40	1.80	7.10
18/2	20.33	3.80	15.40	17.86	3.65	13.40
18/3	31.84	7.10	24.85	28.70	6.90	21.85
18/4	39.66	9.60	29.90	35.87	9.35	26.55
18/5	47.77	12.80	35.05	43.72	12.25	31.45
18/6	54.34	15.50	38.70	49.93	14.90	35.00
18/7	61.34	18.75	42.25	56.59	17.90	38.70
18/8	67.13	22.05	45.20	62.66	20.95	41.65
18/9	70.49	23.85	46.60	65.76	22.65	43.15
18/10	71.92	24.80	47.20	67.08	23.40	43.75

Table 9.2 (cont'd.)

Sample No.	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†
b) Ethylene Chloride (A) - Benzene (B)						
	274.0K			289.1K		
45/0	0.00	0.00	0.00	0.00	0.00	0.00
45/1	5.53	0.95	4.55	5.10	1.25	4.15
45/2	13.42	2.85	10.57	12.70	3.15	9.67
45/3	22.47	5.40	17.12	21.36	5.75	15.60
45/4	30.67	8.35	22.25	29.23	8.55	20.60
45/5	37.13	11.15	26.05	35.29	11.20	24.37
45/6	44.92	14.70	29.88	42.60	14.40	28.17
45/7	53.13	19.20	33.75	50.83	18.70	31.90
45/8	59.73	23.10	36.50	57.24	22.55	34.45
45/9	63.42	25.50	38.05	60,81	24.90	35.82
45/10	65.36	26.50	38.60	62.37	25.85	36.35
	323.7K			343.0K		
45/0	0.00	0.00	0.00	0.00	0.00	0.00
45/1	4.18	1.00	3.67	4.27	1.35	3.40
45/2	11.28	2.95	8.60	10.74	3.15	7.90
45/3	19.18	5.40	13.72	17.98	5.45	12.50
45/4	26.09	8.20	17.87	24.45	8.05	16.30
45/5	31.67	10.75	21.05	29.66	10.55	19.17
45/6	38.39	13.90	24.38	35.92	13.85	22.12
45/7	45.77	17.85	27.70	42.81	17.60	25.25
45/8	51.56	21.45	30.05	48.63	20.75	27.60
45/9	54.98	32.60	31.30	51.56	22.70	28.87
45/10	56.32	24.55	31.78	52.92	23.50	29.37

Table 9.2 (cont'd.)

Sample No.	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†
c) Methyl Iodide (A) - Benzene (B)						
	279.3K			288.9K		
15/0	0.00	0.00	0.00	0.00	0.00	0.00
15/1	6.54	1.70	5.35	5.83	1.70	4.55
15/2	15.01	3.75	11.80	14.56	4.15	10.45
15/3	24.90	7.55	17.45	23.74	7.70	16.00
15/4	30.27	10.65	20.65	29.16	11.00	19.15
15/5	‡	16.00	25.15	‡	16.10	23.80
15/6	44.04	17.80	26.60	42.95	17.70	25.25
15/7	50.31	21.10	29.25	48.59	21.00	28.00
15/8	56.34	24.50	31.95	55.01	24.20	30.70
15/9	59.59	26.20	33.25	57.82	25.70	32.05
15/10	-	26.85	33.80	-	26.30	32.60
	323.4K			342.2K		
15/0	0.00	0.00	0.00	0.00	0.00	0.00
15/1	5.28	1.40	3.45	4.97	1.40	3,50
15/2	13.14	4.90	8.30	12.12	3.75	8.30
15/3	21.71	8.70	13.25	20.51	7.50	12.85
15/4	26.70	11.20	16.35	25.13	10.00	15.60
15/5	35.90	15.35	20.85	33.79	14.10	19.60
15/6	39.33	16.80	22.35	‡	15.55	20.90
15/7	44.68	19.60	25.05	42.18	18.60	23.40
15/8	50.40	22.65	27.70	47.85	21.70	25.85
15/9	53.25	24.25	28.95	50.25	23.20	27.05
15/10	54.30	24.90	29.45	51.01	23.85	27.50

Table 9.2 (cont'd.)

Sample No.	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†
d) TMS (A) - Benzene (B)						
	274.0K			289.0K		
33/0	0.00	0.00	0.00	0.00	0.00	0.00
33/1	1.76	2.10	- 0.40	1.62	2.15	- 0.50
33/2	4.71	5.50	- 0.95	4.73	5.45	- 1.10
33/3	7.51	9.05	- 1.50	7.53	8.90	- 1.60
33/4	10.27	11.60	- 1.75	10.07	11.40	- 1.85
33/5	12.34	14.10	- 1.90	12.03	13.90	- 2.05
33/6	15.04	17.10	- 1.97	14.56	16.90	- 2.15
33/7	18.64	20.50	- 2.02	18.37	20.25	- 2.20
33/8	21.98	23.85	- 1.90	21.55	23.55	- 2.15
33/9	23.92	25.60	- 1.85	23.38	25.30	- 2.10
33/10	24.86	26.35	- 1.80	23.96	26.05	- 2.05
	324.6K			343.5K		
33/0	0.00	0.00	0.00	0.00	0.00	0.00
33/1	1.43	2.05	- 0.30	1.61	2.10	- 0.30
33/2	4.81	5.10	- 0.70	4.73	5.20	- 0.85
33/3	7.21	8.25	- 1.05	7.11	8.30	- 1.25
33/4	9.47	10.50	- 1.20	9.45	10.45	- 1.40
33/5	11.68	12.80	- 1.35	11.39	12.55	- 1.55
33/6	13.89	15.65	- 1.50	13.67	15.15	- 1.60
33/7	17.48	18.90	- 1.65	16.93	18.10	- 1.60
33/8	20.24	22.20	- 1.80	19.86	21.20	- 1.60
33/9	21.84	23.90	- 1.85	21.25	22.85	- 1.60
33/10	22.78	24.55	- 1.85	21.70	23.60	- 1.60

Table 9.2 (cont'd.)

Sample No.	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†	δ_{obs} (Hz)*	δ_{obs}' (Hz)*	Δ (Hz)†
e) Vinylidene Chloride (A) - Benzene (B)						
	278.9K			288.9K		
14/0	0.00	0.00	0.00	0.00	0.00	0.00
14/11	7.37	2.50	4.35	7.28	2.75	4.00
14/21	15.77	5.80	9.40	15.17	6.15	8.50
14/3	22.96	9.15	14.00	22.01	9.60	12.75
14/4	28.72	11.70	17.05	27.61	12.00	15.75
14/5	34.95	14.65	20.10	33.39	14.65	18.65
14/6	39.25	17.10	22.15	37.82	16.95	20.70
14/7	45.58	20.70	24.80	44.17	20.50	23.45
14/8	50.86	24.20	26.85	49.14	23.75	25.65
14/9	53.87	26.00	27.80	52.17	25.40	26.65
14/10	54.95	26.75	28.20	53.20	26.10	27.10
	322.9K			342.7K		
14/0	0.00	0.00	0.00	0.00	0.00	0.00
14/11	6.51	2.85	3.00	5.97	2.55	2.85
14/21	13.62	6.25	6.65	12.97	5.75	6.25
14/3	19.72	9.60	10.30	18.34	9.00	9.50
14/4	24.98	12.05	12.85	23.17	11.35	11.80
14/5	30.56	14.65	15.55	28.49	14.00	14.15
14/6	34.24	16.80	17.45	32.10	16.05	15.90
14/7	39.99	19.70	20.15	37.35	19.10	18.35
14/8	44.76	22.45	22.35	41.99	21.70	20.40
14/9	47.30	23.85	23.35	44.60	23.05	21.35
14/10	48.32	24.45	23.70	45.28	23.60	21.70

* these must be plotted to obtain the 'best-line' values.

† these values are obtained by subtracting δ_{obs}' from the 'best-line' values of δ_{obs}.

‡ main methyl iodide peak obscures methyl iodide peak from the capillary.

Table 9.3

Equilibrium quotients, K_x, and excess shieldings, Δ_c, obtained by the Creswell and Allred (CA)[62] and both Benesi-Hildebrand (BH)[44] procedures, at various temperatures. Data at 306.6K is included from tables 7.5 and 7.7.

Temperature (K)	K_x			Δ_c (ppm)		
	CA	BH(A)	BH(B)	CA	BH(A)	BH(B)
a) Chloroform (A)-Benzene (B)						
274.0	1.9_2	1.6_3	1.0_6	1.44_5	1.61_8	1.95_1
288.8	1.8_2	1.3_2	0.9_3	1.36_7	1.64_9	1.94_3
306.6	1.3_0	0.8_7	1.6_8	1.42_5	1.87_0	1.38_3
323.6	1.2_7	0.8_7	0.4_4	1.33_0	1.72_0	2.61_7
342.7	0.9_0	0.7_0	0.3_3	1.48_3	1.81_0	2.97_8
b) Ethylene Chloride (A) - Benzene (B)						
274.0	0.6_3	0.4_3		1.69_5	2.20_2	
289.1	0.5_7	0.5_3		1.71_1	1.78_7	
306.6	0.4_1	0.5_1		2.01_3	1.73_7	
323.7	0.4_7	0.4_4		1.67_8	1.78_1	
343.0	0.3_8	0.2_5		1.80_8	2.48_3	
c) Methyl Iodide (A) - Benzene (B)						
279.3	0.8_2	0.3_3		1.20_7	2.35_0	
288.9	0.5_9	0.2_7		1.44_0	2.58_7	
306.6	0.4_5	0.2_5		1.66_0	2.62_8	
323.4	0.3_1	0.2_5		2.07_9	2.54_7	
342.2	0.3_7	0.2_3		1.69_0	2.48_8	
d) TMS (A) - Benzene (B)						
274.0	31.7_1			-0.03_3		
288.9	17.5_2			-0.03_6		
306.6	14.5_7			-0.05_0		
323.4	2.9_2			-0.03_7		
342.2	23.1_1			-0.02_7		
e) Vinylidene Chloride (A) - Benzene (B)						
278.9	0.9_8	0.5_7		0.93_7	1.31_1	
288.9	0.6_2	0.3_6		1.17_6	1.74_0	
306.6	0.6_2	0.3_3		1.09_3	1.72_7	
322.9	0.2_5	0.2_7		2.00_1	1.89_7	
342.7	0.2_3	0.2_0		1.99_4	2.27_5	

Table 9.4

Thermodynamic parameters for complex formation calculated using the results obtained from both the Creswell and Allred (CA)[62] and Benesi-Hildebrand (BH)[44] data evaluation techniques together with some literature data for comparison.

System	ΔH^{o298} (kJ mol^{-1})			ΔG^{o298} (kJ mol^{-1})		
	CA	BH(A)	BH(B)	CA	BH(A)	BH(B)
Chloroform-Benzene	- 8.44	- 9.67	-13.86	- 1.01	- 0.28	- 2.50
" " [31]	- 9.03	*	*	- 0.63	*	*
Ethylene Chloride-Benzene	- 5.26	- 5.41	-	1.67	2.04	-
Methyl-Iodide-Benzene	-10.79	- 3.73	-	1.54	3.20	-
Vinylidene Chloride-Benzene	-18.51	-11.78	-	1.41	2.47	-
" " " [32]	- 6.06	*	*	1.58	*	*
	ΔS^{o298} (J mol^{-1}K^{-1})			K_x^{298}		
	CA	BH(A)	BH(B)	CA	BH(A)	BH(B)
Chloroform-Benzene	-24.92	-31.47	-38.09	1.50	1.12	0.70
" " [31]	-28.16	*	*	1.16	*	*
Ethylene Chloride-Benzene	-23.27	-24.97	-	0.51	0.44	-
Methyl Iodide-Benzene	-41.33	-23.23	-	0.54	0.28	-
Vinylidene Chloride-Benzene	-66.81	-47.80	-	0.57	0.37	-
" " " [32]	-25.67	*	*	0.71	*	*

* no data available

Table 9.6

The molar volume ratio for chloroform/benzene at various temperatures.

Temperature (K)	V_A ($\times 10^4 m^3 mol^{-1}$)	V_B ($\times 10^4 m^3 mol^{-1}$)	V_A/V_B
274.0	0.7829	0.8688	0.9011
288.8	0.7974	0.8844	0.9016
323.6	0.8338	0.9232	0.9031
342.7	0.8552	0.9462	0.9038

Table 9.5

Data used in the normal Benesi-Hildebrand[44] evaluation of K_x and Δ_c.

Sample No.	n_A+n_B/n_B	$1/\Delta^2_{273}$ ($\times 10^2$)	$1/\Delta^2_{288}$ ($\times 10^2$)	$1/\Delta^2_{323}$ ($\times 10^2$)	$1/\Delta^2_{343}$ ($\times 10^2$)	w*
a) Chloroform (A) - Benzene (B)						
18/6	1.4310	1.986	2.141	2.584	2.857	0.2
18/7	1.2481	1.835	1.978	2.367	2.584	0.5
18/8	1.1122	1.739	1.866	2.212	2.401	0.8
18/9	1.0534	1.698	1.820	2.146	2.317	1.0
18/10	1.0304	1.682	1.800	2.119	2.286	1.2
b) Ethylene Chloride (A) - Benzene (B)						
45/6	1.4355	3.347	3.550	4.102	4.521	0.2
45/7	1.2352	2.963	3.135	3.610	3.960	0.5
45/8	1.1143	2.740	2.903	3.328	3.623	0.8
45/9	1.0535	2.628	2.792	3.195	3.464	1.0
45/10	1.0317	2.591	2.751	3.147	3.405	1.2
c) Methyl Iodide (A) - Benzene (B)						
15/6	1.4201	3.759	3.960	4.474	4.785	0.4
15/7	1.2489	3.419	3.571	3.992	4.272	0.6
15/8	1.1110	3.130	3.257	3.610	3.868	0.8
15/9	1.0523	3.008	3.120	3.454	3.697	1.0
15/10	1.0308	2.959	3.067	3.396	3.636	1.2
d) Vinylidene Chloride (A) - Benzene (B)						
14/6	1.4588	4.515	4.831	5.731	6.289	0.2
14/7	1.2477	4.032	4.264	4.963	5.450	0.5
14/8	1.1103	3.724	3.899	4.474	4.902	0.8
14/9	1.0532	3.597	3.752	4.283	4.684	1.0
14/10	1.0306	3.546	3.690	4.219	4.608	1.2

* a weighting factor used, in the computer curve-fitting procedure, to place greatest emphasis on points of highest aromatic mole fraction.

benzene in the above figure. Values of K_x^{CA} and Δ_c, determined by the Creswell and Allred data evaluation method,[62] are given in table 9.3 for each system at each temperature studied, the values at 306.6K being obtained from table 7.5. Using these values of K_x^{CA}, the thermodynamic parameters $\Delta H^{o\ 298}$, $\Delta G^{o\ 298}$, $\Delta S^{o\ 298}$ and $K_x^{CA\ 298}$ are obtained from equations 9,1 to 9,3, and are recorded in table 9.4, where they are compared with literature values for the chloroform-benzene[31] and vinylidene chloride -benzene systems[32]. It may be seen that the agreement for the chloroform-benzene system is extremely good, but that for vinylidene chloride-benzene is much poorer. Nevertheless it appears that the new procedure can give comparable results to the well established data evaluation methods.

The values of K_x^{CA} and Δ_c^{CA} for the TMS-benzene interaction are also given in table 9.3. It may be seen that the results are not particularly systematic but they do suggest a) that a strong complex is formed with the possibility of multiple association (as discussed in section 7.7) and b) that an overall complex shift, Δ_c, of about - 3Hz is always obtained. These results serve to confirm that TMS is a very poor reference material for use with aromatic molecules.

b) The Normal Benesi-Hildebrand Data Evaluation Procedure

Using the experimental points with aromatic mole fraction ranging from 0.70 to 0.97 a normal Benesi-Hildebrand[44] type evaluation of K_x and Δ_c was made. The values of $^{n}A^{+n}B/n_B$ and $1/\Delta$ used (at each temperature) in this evaluation are recorded in table 9.5, and the values of K_x^{BH} and Δ_c obtained are given in table 9.3. These results were used in an alternative evaluation of the thermodynamic parameters of complex formation which are recorded in table 9.4. It is obvious from the discussion given in sections 3.3 - 3.7 that this evaluation is not carried out over a thermodynamically valid concentration range and some error must be expected, since it is necessary to get much closer to $^{n}B/n_{A+n_B} = 1.00$ than $^{n}B/n_{A+n_B} = 0.97$. However, the previously mentioned curve-fitting procedure was used in these evaluations and this should reduce the error.

It may be seen that the values ΔH^{o}_{298}, ΔG^{o}_{298} and ΔS^{o}_{298} obtained by the normal BH procedure[44] are, in many cases, very similar to those obtained by the more usual Creswell and Allred technique[62]. This tends to confirm the ideas expressed in section 3.9 that whilst K_x^{CA} may be in error, the thermodynamic data obtained from using it is reasonably reliable.

c) The Revised Benesi-Hildebrand Data Evaluation Procedure

It was shown, in section 3.8 c) that the amount of inert solvent present in a system must be corrected for the difference between its molecular dimensions and those of the interacting aromatic solvent. As originally conceived this applied to three component solutions but, as discussed in section 7.6, it may be extended to two component solutions by assuming a) that only 0.005 mf of the polar species A acts as solute and b) that the remainder of A acts as inert diluent. Adopting this procedure a repeat evaluation of the chloroform-benzene interaction data at various temperatures was made. This representative example was chosen because comparable data evaluated from three component studies is available (section 3.8 c). The values of n_S^{corr}, are obtained by multiplying the relevant values of n_A (obtained from table 9.1) by the molar volume ratio V_A/V_B at each temperature (obtained from table 9.6). $n_B+n_S^{corr}/n_B$ and $1/\Delta$ were then processed by the Benesi-Hildebrand method, the results being given in table 9.3. Thermodynamic data have been obtained from these results and are presented in table 9.4.

9.5 Accuracy of the Experimental Procedure

Consideration of the variable temperature results (table 9.3) indicates that the values for K_x and Δ_c are rather erratic (irrespective of the data evaluation technique) in that the reduction in K_x with increasing temperature is not so systematic as that reported by Huck[31] for chloroform-benzene and by Cooke[32] for vinylidene chloride-benzene; and Δ_c does not vary consistently. This behaviour is almost certainly due to the difficulty in accurately maintaining a particular temperature whilst three series of samples were measured, (one to obtain the interaction shifts and

two to provide the relevant medium screening corrections) hence the variable temperature studies have shown up a limitation of the procedure as originally conceived.

The difficulties encountered in this procedure may be grouped into two classes, a) experimental i.e. those associated with the temperature and b) data evaluational i.e. those associated with the graphical nature of the method. With regard to the first of these there are three important factors to be considered. Firstly, the difficulty in obtaining a given temperature (i.e. reproducibility); whilst a particular temperature may be accurately maintained for short periods of time, it was found to be difficult to return to exactly this temperature when measuring three series of samples. A further difficulty encountered was in reaching thermal equilibrium in each sample, particularly as each contained a reference capillary. The criterion adopted was that as soon as the temperature was constant it was assumed that thermal stability had been reached throughout the sample. Nevertheless it would, in fact,be possible for the temperature in the capillary to be up to 1K different from that being measured by the thermocouple, without there being a noticeable temperature variation with time. Ideally, each sample should have been left in the probe for about fifteen minutes in order to overcome this possibility. Secondly, there was considerable danger of the sample spinner becoming frozen and stopping when operating the variable temperature probe below 306.6K; and this danger would be magnified if samples remained in the probe for fifteen minutes before they were measured. Thirdly, it was found that there was a considerable drift in the applied field with time, when working with the variable temperature probe; as the rate of drift was to some extent dependant on the time a particular temperature had been maintained it was especially difficult to overcome this, even though the chart paper had been calibrated. The problems associated with the graphical nature of the determination are discussed in section 7.8 and they may be overcome, in future, by using the modified procedure discussed in that section.

9.6 Conclusions

It is clear, from the results given above, that the original version of the new procedure as described in section 7.2 is not completely satisfactory when used at various temperatures to obtain thermodynamic data regarding the interactions studied. Certainly the trends are reasonably accurately portrayed, but the variation of K_x and Δ_c with temperature is erratic and this results in the values of ΔH^{o298}, ΔG^{o298} and ΔS^{o298} obtained, being rather approximate. However, as these inaccuracies arise from a combination of errors involving both the graphical nature of the evaluation and also the difficulties in measuring three separate series all at exactly the same temperature, it is confidently predicted that use of the revised procedure, as described in section 7.8, should result in much greater accuracy in the parameters for complex formation and hence in the thermodynamic quantities.

In section 1.12 it was stated that a number of investigations were to be carried out and reported herein. These were a) to look at the thermodynamics of complex formation and of the data evaluation procedures available and to decide the proper way to evaluate the data, b) to determine which solvents, if any, could be considered to be inert (in particular towards aromatic molecules)and c) to investigate the effects on complex formation of substituents on the aromatic ring. The thermodynamics have been investigated in chapter 3, and a new procedure (chapter 4) has been devised to investigate the inertness of solvents (chapter 7) and also to look at interactions in general. Therefore, there only remains to investigate the effect of any substituents, present on the aromatic ring, on the parameters of complex formation and this is considered in the next chapter (chapter 10).

CHAPTER 10

Interactions Between the Haloforms and some Chlorobenzenes, and the Self-Association Complexes of these Chlorobenzenes

10.1 Introduction

In the summary of investigations to be carried out in this thesis (section 1.12) it was stated that the effect of aromatic substitution on the formation of intermolecular complexes required study. The formation of complexes between aromatics and simple solute molecules has received considerable attention[30], but in general, whenever these studies have been quantitative, benzene has been used. The methyl benzenes have however been used in one series of investigations[31,33] and in these it was found that no change in the concept or evaluation of the data was involved. In the present investigation, therefore, it was decided to consider the effect of a polar substituent, chlorine being chosen. In particular it was hoped to see if the types of complex and of structures were altered.

The Creswell and Allred (CA)[62] data evaluation procedure was used throughout this investigation instead of the thermodynamically correct Benesi-Hildebrand (BH)[44] method. The reasons for this were a) the basic overall experimental shifts measured were extremely small (around 4 Hz) in some cases and it would have been very difficult to obtain limiting tangents for such data by the BH procedure, b) in any case, because of the added complexity introduced by using polar substituents this work must be mainly comparative and nearly all the literature data has been evaluated by the CA method, and c) both p-dichlorobenzene and sym-trichlorobenzene (which have been used in this investigation together with chlorobenzene) have only a limited solubility in cyclohexane (the inert solvent) of 0.50 and 0.40 mf respectively hence the BH method cannot be used.

A further departure from the ideal, thermodynamically valid, procedure (see chapter 3), is occasioned by not correcting the values of n_S (number of moles of inert solvent) for the molar volume difference

between the inert and aromatic solvents (i.e. by the V_S/V_B ratio, discussed in section 3.8 c) and illustrated for the CA procedure in section 3.9). The approximation introduced by this departure may be justified because all the conclusions reached in chapter 10 are based on the consideration that the chloroform/bromoform-benzene interactions act as reference systems for the similar interactions with the chlorobenzenes. It may be seen from table 10.1A that a) the V_S/V_B ratio for each of the aromatic solvents is close to that for benzene and b) in all cases the V_S/V_B ratio is close to unity; where, of course, no correction to the basic Creswell and Allred results is necessary.

Table 10.1A

Molar volumes (V_B and V_S) and the ratio V_S/V_B for the aromatic solvents at 306.6K (*293K).

Solvent	V_B or V_S (x 10^5 m^3 mol^{-1})	V_S/V_B
Cyclohexane	10.9901	-
Benzene	9.0369	1.2162
Chlorobenzene	10.3160	1.0653
p-Dichlorobenzene	11.5504	0.9515
sym-Trichlorobenzene	12.4796*	0.8808*

Despite the criticisms levelled against the CA procedure in section 3.9, Cooke[32] has shown that the trends exhibited by the methyl benzene-chloroform complexes, wherein K_x and Δ_c increase with increasing methyl substitution of the aromatic[31,33], can be related to the nature of the interaction even using this procedure.

It is to be supposed that there will be a number of differences between complexes formed by the chlorobenzenes and those formed by benzene. The additional factors involved include a) a change in the π -and/or σ-electron density on the ring, b) an alteration in the electron distribution around the ring, c) an alteration in the bond anisotropy due to the change from C-H to C-Cl, d) a variation in the axial and planar polarizabilities of the aromatic molecule, e) the possibility of solvent self-association occurring and f) the possibility of other types of complex being formed. Because of these factors, which will be discussed in the succeeding sections, only approximate data, relating to any interaction, will be obtained.

10.2 The Experimental Procedure

Complex formation and solvent self-association were initially investigated without consideration of the other factors previously mentioned. Systems composed of the haloform (A) in the chlorobenzene (B) with cyclohexane as the non-interacting solvent and internal reference (S) were examined when considering complex formation, and systems composed just of the chlorobenzene (B) in cyclohexane (S) were investigated when considering solvent self-association. In each complexing system a constant, low mole fraction (0.01 or less) of A was used and the amounts of B and S were chosen to cover as large a solute proton shift range as possible; the amounts of B and S were similarly varied in the self-association studies. A limiting factor in the case of p-dichlorobenzene and sym-trichlorobenzene was that they did not dissolve in cyclohexane to give solutions of greater mole fraction than 0.50 and 0.40 respectively. However, it has been shown by Cooke[32] that, using the Creswell and Allred procedure[62], almost identical values of K_x and Δ_c are obtained when the evaluations are carried out a) over the aromatic concentration range 0.0 - 1.0 mf and b) over the range of 0.0 - 0.2 mf. Hence the inability to use the entire concentration range is of little consequence.

Another problem encountered was the close proximity of the chloroform resonance to that of the aromatic which precluded the use of certain aromatic concentration ranges and in fact meant that the chloroform-sym-trichlorobenzene series could not be measured at all, (an indication was however obtained that the chloroform proton was deshielded and this fact is used in the discussion sections). In every case the chemical shift between the solute proton and cyclohexane was measured by the sideband technique (section 2.8), and this was repeated six times to minimize random errors and to allow an accuracy of $\pm$ 0.002 ppm to be obtained.

10.3 The Investigation of the Basic Haloform - Chlorobenzene Complex

The parameters required for an investigation into the nature of the haloform-chlorobenzene interaction are the additional screening of the solute proton in the complex, relative to that in the non-complexed state, Δ_c, and the equilibrium quotient, K_x, for the formation of the complex. Previous investigations into the formation of haloform and pseudo-haloform complexes with benzene[31,33,55,61,70] have assumed that 1 : 1 complexes are formed; this assumption being based on the work of Reeves and Schneider[72] who cited cryoscopic data in favour of this type of complex, and also on the constancy of ΔH with temperature[66]. The formation of 1 : 1 complexes is still considered to be possible in the interactions studied herein but they may be of more than one type; the experimental results then being the time-average of all possible structures. Therefore, in order to highlight this possibility, the experimental results were initially processed assuming only the formation of 1 : 1 π -complexes.

The composition of the samples used and the appropriate observed haloform shifts, relative to cyclohexane, are recorded in table 10.18, and the values of K_x and Δ_c, obtained by the CA procedure[62], are given in table 10.2 together with the previously obtained results for the complexes formed between benzene and separately chloroform[31,70] and

Table 10.1B

The composition of the haloform-chlorobenzene systems studied, together with the shifts obtained measured relative to cyclohexane. The compositions given are uncorrected for solute or solvent self-association.

Sample No.	x_B	n_A ($\times 10^4$ mol)	n_B ($\times 10^3$ mol)	n_S ($\times 10^2$ mol)	δ^{S-A}_{obs} (Hz)
a) Bromoform (A) - Chlorobenzene (B)					
6/0	0.000	1.4493	0.0000	1.2112	315.56
6/1	0.030	1.4137	0.4182	1.3507	314.38
6/2	0.049	1.8675	0.6664	1.2950	313.72
6/3	0.083	1.9518	1.2439	1.3804	312.73
6/4	0.180	1.7816	2.8858	1.3142	309.86
6/5	0.282	2.5979	5.2416	1.3313	307.31
6/6	0.424	3.0137	9.5654	1.2970	304.48
6/7	0.501	2.1805	13.4840	1.3413	302.92
6/8	0.716	1.0489	8.9178	0.3536	299.72
6/9	0.789	1.1893	12.7980	0.3427	299.00
6/10	0.838	2.8103	13.7830	0.2675	298.56
b) Chloroform (A) - Chlorobenzene (B)					
7/0	0.000	1.1493	0.0000	1.2801	339.18
7/1	0.032	1.1225	0.4298	1.3214	338.26
7/2	0.056	1.0680	0.7907	1.3206	336.92
7/3	0.082	2.0339	1.1450	1.2893	*
7/4	0.219	1.9635	3.5317	1.2609	333.00
7/5	0.327	2.2542	5.9205	1.2202	330.97
7/6	0.403	3.0006	8.3593	1.2386	329.17
7/7	0.520	2.1972	13.6680	1.2628	327.37
7/8	0.683	1.4274	7.8523	0.3647	325.09
7/9	0.777	2.3380	12.6960	0.3638	324.11
7/10	0.863	2.8163	11.8330	0.1881	323.39

Table 10.1B (cont'd.)

Sample No.	x_B	n_{A_4} (x 10^4 mol)	n_{B_3} (x 10^3 mol)	n_{S_2} (x 10^2 mol)	δ^{S-A}_{obs} (Hz)
c) Bromoform (A)- p-Dichlorobenzene (B)					
5/0	0.000	1.4493	0.0000	1.2111	315.50
5/1	0.034	1.5806	0.4518	1.2841	315.18
5/2	0.054	1.9830	0.7444	1.2935	315.07
5/3	0.082	1.4857	1.1285	1.2675	314.96
5/4	0.105	1.6875	1.4849	1.2672	314.90
5/5	0.147	1.5549	2.2278	1.2889	314.57
5/6	0.197	2.0756	3.1176	1.2734	314.49
5/7	0.248	1.6926	4.2297	1.2854	314.35
5/8	0.292	1.8311	5.3319	1.2936	314.26
5/9	0.395	1.6976	8.3397	1.2770	314.04
5/10	0.491	2.5096	12.7190	1.3166	313.93
d) Chloroform (A) - p-Dichlorobenzene (B) ‡					
3/0	0.000	1.1493	0.0000	1.2801	339.17
3/1	0.040	0.9206	0.5256	1.2758	339.04
3/2	0.050	1.9476	0.6603	1.2500	339.06
3/3	0.083	1.1208	1.1475	1.2687	338.97
3/4	0.104	0.9999	1.4137	1.2166	338.81
3/5	0.139	1.8102	2.0907	1.2914	338.82
3/6	0.194	1.4919	3.1898	1.3242	338.72
e) Bromoform (A) - sym-Trichlorobenzene (B)					
4/0	0.000	1.1755	0.0000	1.2088	315.39
4/1	0.030	0.5583	0.4000	1.2776	315.45
4/2	0.052	0.8985	0.7240	1.3266	315.42
4/3	0.084	1.7872	1.1576	1.2675	315.62
4/4	0.099	1.8097	1.4321	1.3053	315.79
4/5	0.143	2.0004	2.1803	1.3053	315.81
4/6	0.206	1.2744	3.1375	1.2103	316.22
4/7	0.236	1.7251	3.8260	1.2307	316.37
f) Chloroform (A) - sym-Trichlorobenzene (B) - a deshielding of of the chloroform proton is indicated.					

* obscured by a peak of the complex chlorobenzene system, at approximately 335 Hz.

‡ samples from aromatic mf 0.2 have the chloroform proton obscured by the p-dichlorobenzene.

Table 10.2

The equilibrium quotients, K_x, and excess screenings, Δ_c, for the haloform-chlorobenzene complexes, before and after allowing for solvent self-association.

System	K_x		Δ_c (ppm)	
	Uncorrected	Corrected for solvent self-association	Uncorrected	Corrected for solvent self-association
Chloroform-Benzene	1.16[31,70]	1.16	1.620[31,70]	1,620
Chloroform-Chlorobenzene	1.03	0.89	0.572	0.764
Chloroform-pDichlorobenzene	2.88	1.00	0.023	0.073
Chloroform-sym-Trichlorobenzene	†	†	- ve †	- ve †
Bromoform-Benzene	1.08[31]	1.08	1.640[31]	1.640
Bromoform-Chlorobenzene	1.01	0.87	0.624	0.847
Bromoform-pDichlorobenzene	3.67	3.09	0.040	0.059
Bromoform-sym-Trichlorobenzene	0.00_4^*	0.00_2^*	- ve	- ve

† insufficient data to obtain a K_x value, but a proton deshielding is indicated.

* no limiting shift is apparent, thus the value of K_x is probably invalid.

Table 10.3

The separation of the haloform proton from the plane of the aromatic ring (R_1) in the haloform-chlorobenzene complexes, needed to explain the excess screenings given in table 10.2 (before and after allowing for self-association).

System	R_1 (pm) Uncorrected for solvent self-association	R_1 (pm) Corrected for solvent self-association
Chloroform-Benzene	311[31,70]	311
Chloroform-Chlorobenzene	452	423
Chloroform-pDichlorobenzene	> 600	> 600
Chloroform-symTrichlorobenzene	> 600	> 600
Bromoform-Benzene	309[31]	309[31]
Bromoform-Chlorobenzene	439	395
Bromoform-p Dichlorobenzene	> 600	> 600
Bromoform-symTrichlorobenzene	> 600	> 600

bromoform[31]. It may be seen that the experimental shift variations given in table 10.1B are in many cases small and may be considered to be little greater than experimental error. Also, in view of the fact that an internal reference has been used in the measurement of these shifts, it is possible that they may be due to the various medium screenings affecting the reference and solute differently. Whilst it is acknowledged that this could be a possible explanation, it must be stressed that a) the shifts obtained in the haloform-chlorobenzene complexes (systems 6 and 7) are larger than could reasonably be explained by medium screening variations and that b) a consistent explanation of the experimental results is given in the following sections which provides sensible geometries for the haloform-chlorobenzene complexes of the chlorobenzenes. It is

accepted, however, that variations in the medium screenings could affect the conclusions reached but, in view of the fact that these represent trends rather than exact statements,not to any significant extent.

Using Johnson and Bovey's tables[152] of screenings around the benzene molecule (contained in a recent publication[9]), it may be shown that the additional screening of the haloform proton, when fully complexed with benzene, can be explained by the proton being situated on the six-fold axis at a distance of 311pm from the plane of the aromatic ring in the case of chloroform and 309pm in the case of bromoform. It is known that in chlorobenzene the individual π-electron densities on specific carbon atoms are considerably modified[183] butthe overall π-electron density on the ring is little different from that on benzene, hence it is believed that these tables will still be valid for the chlorobenzenes. Spiesecke and Schneider[184] have investigated systems where the substituent interacts with the aromatic ring (such substituents as $-NO_2$, $-NH_2$, -CHO and $-OCH_3$) and they concluded that to then correctly interpret the shifts of the o-, m- and p-hydrogens they must invoke three effects, namely induction, resonance (implying interaction with π-electrons) and bond anisotropy. However, because of the small change in overall π-electron density on the ring in the chlorobenzene series the assumption may initially be made that the 'ring current' screenings are similar to those of benzene. Therefore the separations of the haloform proton from the plane of the aromatic ring in the chlorobenzene complexes may be calculated, and these distances (R_1) are recorded in table 10.3.

These results clearly indicate that simple π-complexes (i.e. those in which the haloform proton is situated on the aromatic six-fold axis) cannot possibly explain the nature of the haloform-chlorobenzene interaction since most improbable geometries are

proposed with an interaction distance greatly in excess of 350 pm (the maximum separation at which the concept of complex formation is considered valid on energy considerations[31-33]). It is necessary, therefore, to consider the effects which may be causing the more 'complex' results obtained. The following may be involved a) self-association of solute and/or aromatic solvent, b) the C-Cl bond anisotropy and its effect on the screening of the haloform proton, c) the effect of the substituent chlorines on the 'ring current' around the conjugated aromatic π-system and any consequent alteration in the screening and d) the possibility of other types of complex being formed, in particular a dipole-dipole interaction between the aromatic chlorine and the haloform proton. Point d) is most important since a dipole-dipole (n-type) interaction would deshield the haloform proton since it would then be situated in the plane of the aromatic ring, and would, therefore, provide an explanation for the very low screening obtained for the p-dichlorobenzene and sym-trichlorobenzene complexes. Complexes of this type have been reported previously[72], but no rigourous results have been presented for interactions with the chlorobenzenes. The above suggestions will be dealt with individually in order to attempt to obtain sensible geometries for these complexes.

10.4 The Effect of Solute and Solvent Self-Association on the Parameters for Complex Formation

Self-association effects may be divided into two types, those related a) to the solute and b) to the aromatic solvent. The equilibrium quotient for self-association, K_x^{SA}, for chloroform has been reported[185] as 0.16 on the mole fraction scale which although small is not negligible; however, it has been shown[32,55] that the effect this has on the amount of solute available for complex formation (assuming that self-associated solute is inert) has no noticeable effect on the equilibrium quotient for complex formation, K_x, even

when K_x^{SA} is several times larger. Indeed, it has been shown[31] that even by halving or doubling the concentration of solute (to 0.005 mf or 0.02 mf) K_x and Δ_c are only slightly affected. Because of the higher concentration of the aromatic solvent its self-association, especially if a large equilibrium quotient is obtained, will clearly be more important and may even be critical. Quantitative work on this type of effect is rather limited[49,52,84,186-187], and in fact no work on the chlorobenzenes has been reported. However, complexes of the chlorobenzenes with benzene are known[168] and both solvent shifts, (as 5 per cent solutions relative to a 5 per cent solution in carbon tetrachloride, and thus not to be confused with the excess shielding, Δ_c^{SA}, required for structural determinations) and possible structures have been reported; therefore it is quite reasonable to expect that the chlorobenzenes will also complex with themselves. The procedure adopted for determining the equilibrium quotients of these complexes is as follows: It is assumed that a 1 : 1 self-association complex can be obtained, its formation being represented as

$$2B \rightleftharpoons B\cdots\cdots B$$

with the equilibrium quotient, K_x^{SA}, expressed in mole fraction units, for this equilibrium being defined by

$$K_x^{SA} = \frac{n_{BBj}\,(n_{Bj} + n_{Sj} - n_{BBj})}{(n_{Bj} - 2n_{BBj})^2} \qquad 10,1$$

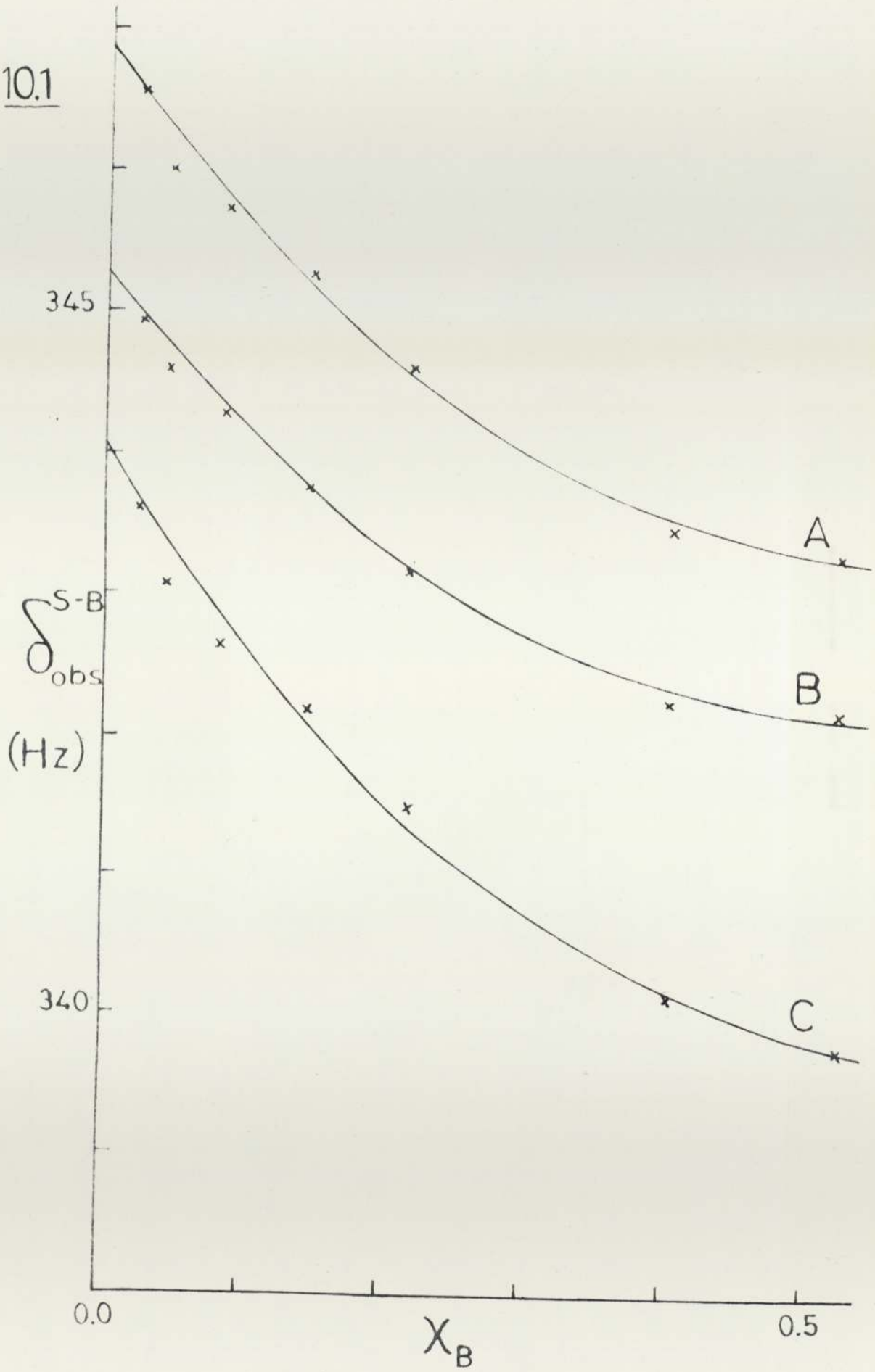
where n_{Bj} and n_{Sj} are the numbers of moles of the chlorobenzene and cyclohexane initially present and n_{BBj} the number of moles of self-associated complex at equilibrium; the subscript j referring to the jth sample.

In order to determine K_x^{SA}, a concentration series of each chlorobenzene in cyclohexane was prepared with mole fractions of the aromatic ranging from about 0.50 to 0.01, solubility considerations precluding the use of the whole concentration range. The observed shifts of the chlorobenzenes, measured relative to cyclohexane,

together with the numbers of moles of aromatic solvent and inert reference in each sample are recorded in table 10.4. These were evaluated using a modified form of the Creswell and Allred data evaluation procedure[62]. This has necessarily to be altered to include equation 10,1 and also to allow for the fact that both species in the complex areidentical; thus the regression, which is normally performed on δ_{obs} against C/A (i.e. $^{n}AB/n_{A}$), must in this particular example be on δ_{obs} against C/B (i.e. $^{n}BB/n_{B} = {}^{2n}B/n_{B}$). The equilibrium quotients and excess shieldings obtained are given in table 10.5.

It may be noted that three series of chemical shifts and hence three values of K_{x}^{SA} and Δ_{c}^{SA} are obtained for chlorobenzene. Strictly the spectrum of chlorobenzene is an AA'BB'C, but at the low concentrations used in some samples of this investigationthis could not be resolved completely and as an approximation the shifts of a number of the more prominant peaks were measured and a mean value for K_{x}^{SA} and Δ_{c}^{SA} obtained which could then be used in the usual way. This would appear to be reasonably valid because the relative separations of these peaks did not change markedly with concentration(figure 10.1) and none of the three values obtained deviates from the mean by more than 20 per cent. p-Dichlorobenzene and sym-trichlorobenzene are symmetrical and hence there is only one peak to be measured.

Knowing K_{x}^{SA}, and by assuming that self-association occurs independantly of complex formation and that a particular solvent molecule will not be both complexed and self-associated at one and the same time, it is possible to correct the quantities of active solvent for the effects of its self-association. This correction cannot be applied absolutely and it is therefore necessary to evaluate the maximum effect of solvent self-association and thus obtain the minimum amount of aromatic available for complexing with the haloform. This value is then used in a repeat evaluation of K_{x} and Δ_{c} for the



The observed shifts (δ_{obs}^{S-B}) measured relative to cyclohexane for the three chlorobenzene peaks (A, B, C) plotted against the mole fraction of aromatic (X_B), showing the similarity of their respective variations with mixture composition.

Table 10.4

The composition of the chlorobenzene systems used in the self-association studies of these molecules, together with their chemical shifts measured relative to cyclohexane.

Sample No.	x_B	n_B ($\times 10^3$ mol)	n_S ($\times 10^2$ mol)	δ_{obs}^{S-B} (Hz)		
a) Chlorobenzene (B) - Cyclohexane (S)				(A)	(B)	(C)
11/1	0.022	0.2801	1.2691	346.57	344.94	343.61
11/2	0.043	0.5697	1.2577	346.00	344.60	343.07
11/3	0.084	1.1508	1.2512	345.74	344.29	342.65
11/4	0.145	2.1668	1.2816	345.29	343.76	342.18
11/5	0.217	3.6196	1.3039	344.61	343.17	341.49
11/6	0.404	8.5604	1.2646	343.50	342.23	340.13
b) p-Dichlorobenzene (B) - Cyclohexane (S)						
12/1	0.050	0.6745	1.2841		342.08	
12/2	0.077	1.0600	1.2694		341.82	
12/3	0.149	2.2222	1.2729		341.01	
12/4	0.247	4.1749	1.2732		340.10	
12/5	0.407	8.5639	1.2491		339.43	
12/6	0.486	12.2700	1.2957		339.31	
c) sym-Trichlorobenzene (B) - Cyclohexane (S)						
13/1	0.018	0.2362	1.2971		343.76	
13/2	0.053	0.7346	1.3141		343.34	
13/3	0.074	1.0656	1.3252		342.91	
13/4	0.148	2.2053	1.2676		342.09	
13/5	0.289	5.6291	1.3861		340.67	

Table 10.5

The equilibrium quotients, K_x^{SA}, and excess screenings, Δ_c^{SA}, for the chlorobenzene self-association complexes.

Aromatic Solvent	K_x^{SA}	Δ_c^{SA} (ppm)
Chlorobenzene - peak A	0.52	0.213
- peak B	0.65	0.175
- peak C	0.45	0.265
Chlorobenzene (average)	0.54	0.218
p-Dichlorobenzene	2.13	0.131
sym-Trichlorobenzene	0.36	0.369

interactions between the haloforms and the chlorobenzenes. Obviously these are approximate and Lussan[187] has derived a method of correcting for solvent self-association which does not need a knowledge of K_x^{SA} and which is mathematically a more exact way of evaluating K_x and Δ_c in such cases. However, this procedure was not adopted in the present case because K_x^{SA} and Δ_c^{SA} were of interest in their own right, and also because Lussan's method required successive extrapolations to infinite dilution in a series of samples which would have resulted in considerable experimental error. Equally, Kuntz and Johnston[49] have analysed the self-association of solvents and have obtained K_c^{SA} and Δ_c^{SA} by the superposition of two log-log plots. Again the graphical nature of their work increases the possibility of error.

The corrected K_x and Δ_c values are given in table 10.2. As before, the use of Johnson and Bovey's screening values[152] enables the positions of the haloform proton in the complex to be evaluated, assuming a straightforward π-interaction, and the results are recorded in table 10.3. Again, these are not in accordance with sensible geometries and it is, therefore, clear that a simple π-complex cannot reasonably explain the experimental results obtained even after allowing for the self-association of the solute and active solvent.

10.5 The Effect of Possible Dipole-Dipole Interactions

No type of π-interaction other than that discussed above appears valid in the complexes considered. The haloform has only one proton to act as a π-electron acceptor and it would appear unlikely that the halogen atoms would behave in this way. With chlorobenzene there is a possibility of a general dipole-dipole interaction but not with p-dichlorobenzene and sym-trichlorobenzene (since these do not have an overall dipole moment). There remains, however, the possibility of a solute dipole-solvent substituent dipole interaction (i.e. between the aromatic chlorine atoms and the haloform proton) occurring in each case. Adopting the procedure used for π-complexes, the screening due to the

aromatic ring current can be calculated in such a n-type complex by assuming van der Waals contact between the chlorine and hydrogen. It is found that in this interaction the haloform proton is situated in the plane of the ring at a distance of 609.5 pm[163] from the aromatic six-fold axis and thus experiences an excess screening of - 0.1250 ppm[152]. Thus, complex formation entirely of this type, whilst offering a possible explanation of the experimental results obtained using sym-trichlorobenzene as the aromatic solvent, is clearly insufficient to predict the results obtained in the other solvents.

It appears, therefore, that a change in emphasis is required in this investigation and that it is necessary to consider that both types of complex may be formed, the relative proportions of each being variable depending on the aromatic solvent. The number of available sites and the relative life-times of the two different complexes were deemed to be the most important factors affecting the relative amounts formed. In order to obtain any information about these amounts it is necessary to make certain assumptions regarding the distances of the haloform proton from the centre of the aromatic system. It was decided that, irrespective of the aromatic solvent considered the separation of the haloform proton from the plane of the aromatic ring would be taken as 311 pm for a chloroform π-complex and 309 pm for a bromoform π-complex, and that for both haloforms the proton would be taken as 609.5 pm from the aromatic six-fold axis in an n-type complex. This clearly ignores the fact that as the strength of the complex alters so does the internuclear separation[31,33]; however, without this approximation it would not be possible to make proposals regarding the structures of the complexes considered.

Two possible sites are available for π-complexes (above and below the aromatic ring) and p sites for n-complexes (where p is the number of substituent chlorines on the aromatic). The n-type complexes are assumed to be arranged such that the molecular dipole

of the haloform is aligned parallel to the dipole of the carbon-chlorine bond; the π -complexes are formed such that the mean position of the proton is along the aromatic six-fold axis. For each complex the following screenings were calculated, bearing the above assumptions in mind: a) for the formation of π -complexes only, b) for the formation of both types of complex, when it is considered that the only governing factor is the number of interaction sites available (i.e. no account was taken of the strengths of the various interactions) hence σ_{TOT} is given by

$$\sigma_{TOT} = \frac{2 \times \sigma_{\pi} + p \times \sigma_{n}}{2 + p} \qquad 10,2$$

and c) for the formation of n-type complexes only. These results are given in table 10.6 together with the experimental excess screenings. Consideration of the results shown in this table indicates that, to a first approximation, there is a reasonably steady graduation from a simple π -complex formed in benzene to an n-type complex formed in sym-trichlorobenzene. That this is not unreasonable may be shown as follows: firstly, the number of sites of attack for n-type complexes increases whilst those for π -complexes remain constant, secondly, a solvent local dipole-solute dipole interaction may reasonably be expected to be much stronger than a dipole-induced dipole (π -complex) interaction and thirdly, the presence of chlorine atoms in the aromatic system would tend to reduce the π -donor capacity of the aromatic ring[72], thus again favouring the n-type complex on increasing the chlorine substiution. In order to clarify this point further calculations were made to determine the relative proportions of the two types of complex in a hypothetical, fully complexed system assuming the experimental screenings to be correct. These are recorded in table 10.7 and clearly show this graduation. It is clear from tables 10.6 and 10.7 that by using equation 10,2 a reasonable indication of the structures of the haloform-chlorobenzenes complexes is obtained.

Table 10.6

Experimental and calculated screenings assuming a) π -complex, b) π - and n-complexes both equally probable and c) n-complex. Also the effect of correcting for $\Delta\chi^{C-Cl}$ is shown.

Complex	Type of Complex	Excess screening (ppm)			
		Experimental (SA inc)	No $\Delta\chi$ corr	$\Delta\chi$ corr a)	$\Delta\chi$ corr b)
Chloroform-Benzene	π -	1.620	1.620	-	-
Chloroform-Chlorobenzene	π -	0.764	1,620	1.566	-
	π- and n-		1.038	1.016	-
	n-		- 0.125	- 0.042	-
Chloroform-pDichlorobenzene	π -	0.073	1.620	1.512	1.641
	π- and n-		0.748	0.745	0.748
	n-		- 0.125	- 0.021	- 0.145
Chloroform-sym·Trichlorobenzene †	π -	- ve	1.620	1.457	1.631
	π- and n-		0.573	0.562	0.580
	n-		- 0.125	- 0.035	- 0.120
Bromoform-Benzene	π -	1.640	1.640	-	-
Bromoform-Chlorobenzene	π -	0.847	1,640	1.585	-
	π- and n-		1.051	1.043	-
	n-		- 0.125	- 0.042	-
Bromoform-pDichlorobenzene	π -	0.059	1.640	1.531	1.660
	π- and n-		0.757	0.755	0.758
	n-		- 0.125	- 0.021	- 0.145
Bromoform-sym·Trichlorobenzene	π -	- ve	1.640	1.476	1.650
	π- and n-		0.581	0.569	0.588
	n-		- 0.125	- 0.035	- 0.120

† No data available for this series, only an indication of proton deshielding.

a) Calculated using $\Delta\chi^{C-Cl} = - 7.8 \times 10^{-12}$ m^3 mol^{-1}.

b) Calculated using values for $\Delta\chi^{C-Cl}$ as indicated in the text.

Table 10.7

Relative proportions of π - and n- type complexes in a hypothetical fully complexed situation.

Complexed species	π -			n-		
	No $\Delta\chi$ corr	$\Delta\chi$ corr a)	$\Delta\chi$ corr b)	No $\Delta\chi$ corr	$\Delta\chi$ corr a)	$\Delta\chi$ corr b)
Chloroform-Benzene	1.00	-	-	0.00	-	-
Chloroform-Chlorobenzene	0.51	0.50	-	0.49	0.50	-
Chloroform-p-Dichlorobenzene	0.11	0.05	0.12	0.89	0.95	0.88
Chloroform-sym-Trichlorobenzene	0.00	0.00	0.00	1.00	1.00	1.00
Bromoform-Benzene	1.00	-	-	0.00	-	-
Bromoform-Chlorobenzene	0.55	0.55	-	0.45	0.45	-
Bromoform-pDichlorobenzene	0.11	0.05	0.11	0.89	0.95	0.89
Bromoform-sym-Trichlorobenzene	0.00	0.00	0.00	1.00	1.00	1.00

In order to obtain a final structure the remaining factors mentioned in section 10.1 will be considered.

10.6 The Effect of Apparent Anisotropies and Ring Current Corrections

The results considered above are as yet uncorrected for any changes in screening due to the presence of chlorine in the aromatic system. Chlorine can have two major effects due firstly to the anisotropy in the magnetic susceptibility of the carbon-chlorine bond, and secondly to the variation in aromatic ring current caused by a modification in the π-electron density of the aromatic system. Since these two factors are effectively related to one another it is difficult to apply any rigourous correction for them; also any alteration in ring current requires the complete recalculation of Johnson and Bovey's elliptical integrals[152] in order to determine the revised screenings around the aromatic nucleus. It was, therefore, decided that any corrections made for these effects

would of necessity have to be approximate, in any case an order of magnitude correction will indicate the possible effect on the experimental results. From the work of Homer and Callaghan[189] a value for the 'apparent anisotropy' in the magnetic susceptibility of the carbon-chlorine bond (aliphatic) was available; this being $\Delta\chi^{C-Cl}_{app} = -7.8 \times 10^{-12}\ m^3\ mol^{-1}$, acting along the bond from a point of origin on the carbon atom. These authors stated that this value was not to be confused with an actual bond anisotropy since other effects were included; however, they found it to be very useful in predicting proton screenings at other points in aliphatic systems using the equation

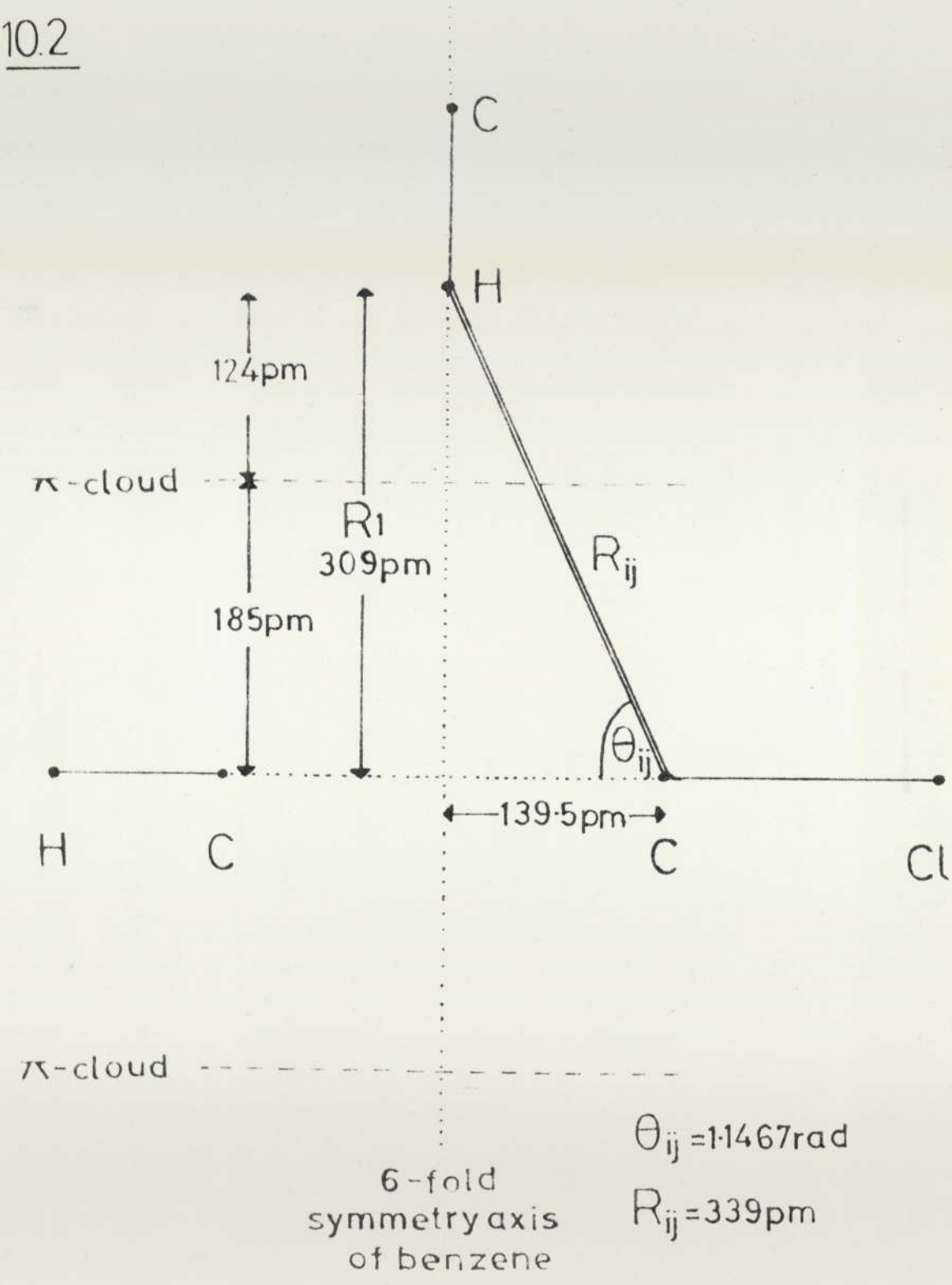
$$\sigma = \sum_i \frac{\Delta\chi^i(1 - 3\cos^2\theta_{ij})}{3R_{ij}^3} \qquad 10,3$$

where R_{ij} is the distance between the equivalent dipole in bond i, having an apparent anisotropy $\Delta\chi^i$, and the resonant proton (j) and θ_{ij} is the angle between this radius vector and the axis of bond i. As a first approximation it was decided to use this value (even though aromatic molecules were being considered) to determine the screening experienced by a haloform proton in a complex due to the carbon-chlorine bond anisotropy, and to correct the calculated results accordingly.

The approximate geometry of a typical complex is shown in figure 10.2, and the results obtained on the basis of this geometry are incorporated into tables 10.6 and 10.7 as correction a). These clearly show that the calculated corrections of $\sim$ - 0.054 ppm for each carbon-chlorine bond acting at the π -position and of $\sim$ + 0.083 ppm for an n-type complex have little effect on the theoretical amounts of π - and n-type complex formed. Since accurate proton screenings in chlorobenzene[188], and in p-dichlorobenzene and sym-trichlorobenzene (from extrapolation to infinite dilution of aromatic shifts in cyclohexane) were available these can be used to obtain a more realistic value of $\Delta\chi^{C-Cl}$ assuming no change in ring current between benzene and the three compounds. The relevant chemical shifts, at infinite dilution, with reference to TMS for benzene

$C_6H_5Cl - CHBr_3$

10.2



The geometry of a representative haloform-chlorobenzene complex, as used in the calculation of the screening effect of the C-Cl bond anistropy.

and the chlorobenzenes (since they are infinitely dilute they will not cause an interaction shift in TMS) are recorded in table 10.8, together with the additional screenings of the chlorobenzenes with reference to

Table 10.8

Values used to calculate apparent bond anisotropies needed to explain the additional screenings of the chlorobenzenes relative to benzene.

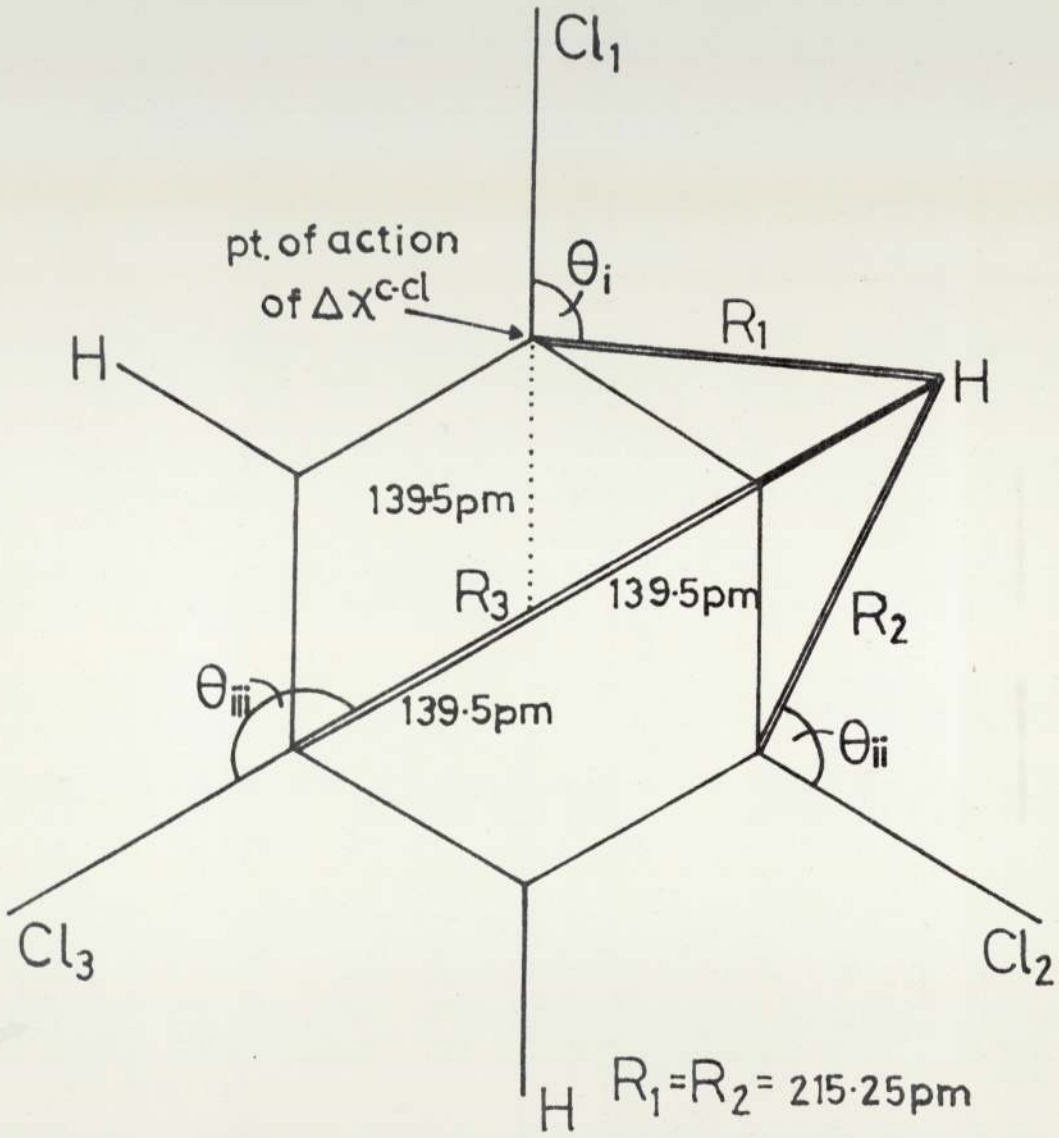
Compound (B)	δ^{TMS-B} (Hz)	$\delta^{CB-BENZENE}$ (ppm)	$\Delta\chi^{C-Cl}_{app}$ ($\times 10^{12}$ m^3 mol^{-1})
Benzene	432.79[188]	-	-
Chlorobenzene (o -	433.37[188]	- 0.0097	- 0.17
(m -	427.69[188]	+ 0.0851	- 7.52
(p -	424.65[188]	+ 0.1356	- 7.12
p - Dichlorobenzene	428.92	+ 0.0645	+ 1.48
sym-Trichlorobenzene	430.05	+ 0.0457	+ 0.51

benzene andthe apparent carbon-chlorine bond anisotropies necessary to explain these variations; a typical example of the geometries involved being shown in figure 10.3. It appears that these values will also include a contribution resulting from any ring current perturbations[183], since these would also affect the proton resonance position[190]. It must not, however, be supposed that the new apparent anisotropy values will indicate other than an order of magnitude for the ring current effect, they will certainly not provide an accurate correction. The new values obtained, $\Delta\chi^{C-Cl}_{app}$, are -7.1×10^{-12}, $+1.5 \times 10^{-12}$ and $+0.5 \times 10^{-12}$ m^3 mol^{-1} for chlorobenzene, p-dichlorobenzene and sym-trichlorobenzene respectively. As the new value for chlorobenzene is within the experimental limits of the previously reported value for $\Delta\chi^{C-Cl}_{app}$ [189], no new correction was attempted; new corrections were, however, calculated for the other two solvents and revised results are incorporated into tables 10.6 and 10.7. These results are clearly only slightly different from those uncorrected for apparent anisotropy and it is considered that, bearing

$p\text{-}C_6H_4Cl_2$

(Shielding w.r.t. benzene = +·0 457ppm)

10.3



$C - C = 139{\cdot}5pm$

$C - H = 108{\cdot}4pm$

$R_1 = R_2 = 215{\cdot}25pm$

$R_3 = 387{\cdot}40pm$

$\theta_i = \theta_{ii} = 1{\cdot}6431\ rad$

$\theta_{iii} = \pi\ rad$

The geometry of p-dichlorobenzene as used in the calculation of the apparent anistropy of the C-Cl bonds.

in mind the approximate nature of the corrections, these initial calculated values should be used for comparison with the experimental values.

For chlorobenzene it is possible to obtain an indication of the variation in screening due to any alteration in the aromatic ring current. The addition of the chlorine substituent alters the π-electron density on each carbon atom and hence the overall density on the ring; therefore the aromatic ring current is modified. Including both π- and σ-induction, the π-electron density on each carbon atom has been calculated[183] to be as follows (numbering from the carbon atom with the chlorine substituent): $C_1 = 0.9012$, $C_2 = C_6 = 1.0612$, $C_3 = C_5 = 0.9931$ and $C_4 = 1.0290$. Apart from the modification to the density on each carbon atom, the overall ring π-electron density has increased from 6.000 to 6.0388. It has been shown by Figeys et. al.[190] that the effective screening of the aromatic protons due to a variation in ring current may be given by

$$\Delta_{R.C.}(\text{ppm}) = 1.15 \times \left[\frac{J\mu(S)}{J\mu(B)} - 1\right] \qquad 10,4$$

where $\Delta_{R.C.}$ is the change in the ring current contribution in the substituted aromatic relative to benzene, and $J\mu(s)$ and $J\mu(B)$ are the calculated ring current intensities for the substituted aromatic and benzene respectively. Figeys et. al.[190] found that all the substituents that they studied lowered the ring current, resulting in an upfield shift of the aromatic protons. The ring current reduction was largest in cases where a 'quinonic' resonance form was important and this may be indirectly related to the Hammett σ constants for the substituents (since these are related to the electron donating/withdrawing power of the substituent, which is an important factor in obtaining the 'quinonic' forms). Comparison of the Hammett σ constant for -Cl[191] (+0.23) with those for substituents used by Figeys et. al.[190] in their calculations of $\Delta_{R.C.}$ ($-OCH_3$: $\sigma = -0.26$, $\Delta_{R.C.} = +0.082$ ppm; $-NH_2$: $\sigma = -0.65$, $\Delta_{R.C.}$

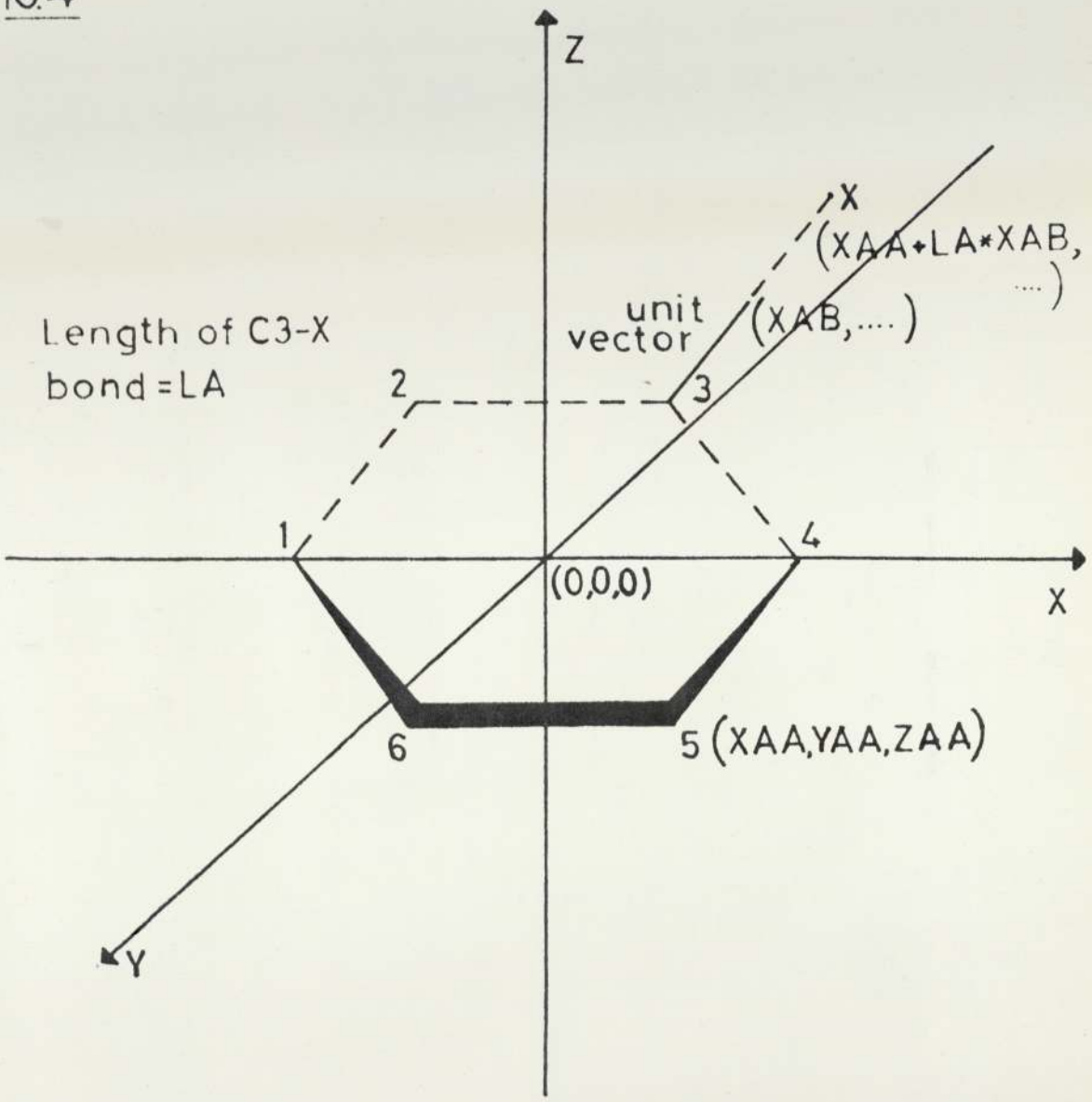
= + 0.146 ppm) leads to a value of $\Delta_{R.C.}$ for - Cl of about + 0.06 ppm. It seems reasonable to conclude, therefore, that the increased screening of the aromatic protons in chlorobenzene due to ring current perturbations is almost + 0.1 ppm which is sufficient, at least in the plane of the ring, to account for most of experimental screenings of these protons (see table 10.8). The calculated values of $\Delta\chi^{C-Cl}_{opp}$ would therefore appear to accommodate both the ring current and the bond anisotropy effects.

It would appear, from the results given in table 10.6 that both π- and n- type complexes are formed and that the formation of a n-type complexes becomes of increasing importance as the chlorine substitution on the aromatic ring increases (see tables 10.6 and 10.7). This may be justified by the fact that the dipole-dipole interaction of the n-type complex is stronger than the dipole-induced dipole interaction of the π-complex and because the π-donor capacity of the aromatic ring is reduced by chlorine substitution.

10.7 Structures of the Self-Association Complexes of the Chlorobenzenes

The equilibrium quotients for, and the additional screenings resulting from, the formation of self-association complexes by the chlorobenzenes have already been given in table 10.5. It is, therefore, of interest to attempt to determine the structures of these complexes. In order to do this it is necessary to devise a co-ordinate system for the aromatic rings so that the screenings and anisotropy corrections can be calculated for the complexes considered. The basis of the co-ordinate system is that the centre of ring A is taken as the origin of the system (0,0,0), as shown in figure 10.4. The co-ordinates of the carbon atoms of the ring are then as given in table 10.9; to obtain the co-ordinates of the substituents (X) it is necessary to consider unit vectors (1 pm in length) from each of the carbon atoms and evaluate the xyz co-ordinates, relative to that carbon atom, of the end of the unit vector. These co-ordinates are given in table 10.10, and they must be multiplied by the actual C - X bond lengths (C - H = 108.4 pm,

10.4



The co-ordinate system used in the calculation of the theoretical screening of the chlorobenzene self-association complexes.

Table 10.9

Co-ordinates of the carbon atoms in ring A (in pm).

Carbon Atom	x(XAA)	y(YAA)	z(ZAA)
C1	- 139.50	0.0	0.0
C2	- 69.75	120.81	0.0
C3	69.75	120.81	0.0
C4	139.50	0.0	0.0
C5	69.75	-120.81	0.0
C6	- 69.75	-120.81	0.0

Table 10.10

Co-ordinates of the terminal points of unit vectors from each carbon atom, relative to that carbon atom (in pm).

Substituent Atom	x (XAB)	y (YAB)	z (ZAB)
X1	- 1.00	0.0	0.0
X2	- 0.50	0.866	0.0
X3	0.50	0.866	0.0
X4	1.00	0.0	0.0
X5	0.50	- 0.866	0.0
X6	- 0.50	- 0.866	0.0

C - Cl = 170.0 pm) (LA) and added to the co-ordinates of the respective carbon atoms to give the actual co-ordinates of the substituent X(XA, YA, ZA). Thus

$$XA = XAA + (LA \times XAB) \qquad 10,5$$

and similarly for YA and ZA. Then to obtain the co-ordinates of the carbon and substituent atoms of ring B(referenced on the same system) it is necessary to add onto XAA···· and XA···· the co-ordinates of the centre of that aromatic ring with respect to ring A. Thus, in any given structure, as long as the co-ordinates of the atoms are known it is possible to calculate a) the ring current screening obtained as a

result of self-association, using the results of Johnson and Bovey[152] and b) screening corrections resulting from the anisotropy in the magnetic susceptibility of the carbon-chlorine bonds (using the values of $\Delta\chi^{C-Cl}_{app}$ obtained in section 10.6).

Theoretical values of Δ_c^{SA} have been calculated for a number of possible structures and compared with the experimental values; the structure giving the closest agreement being selected as the correct one. This requires the application of certain conditions, these being that a) the proposed structure must be justified on grounds other than the closeness of the experimental and calculated results, b) to allow for experimental error, any other structures giving fairly close agreement must be eliminated and c) the structure chosen must be of lower energy than any slightly perturbed state of this structure (i.e. it must be at a local energy minima). Examination of the results presented in table 10.5 indicates that, in all three complexes, the aromatic protons are shielded, hence all structures in which the two rings are in the same plane may be eliminated, as these would result in a deshielding of these protons. In addition, any structure which requires two chlorine atoms to be either touching or very close together is most unlikely since this could not be in a state of minimum energy. It should also be noted that no complexes were considered which contained more than two molecules, although these might be expected to occur in the more concentrated solutions; however, any bimolecular structures which allowed such a polymer to be built up in a symmetrical manner (or which could form both π - and n- type self-association complexes) were favourably considered. The remaining structures (which were assumed to involve van der Waals contact at at least one point) were assessed firstly by the construction of molecular models and secondly by the calculation of theoretical Δ_c^{SA} values.

Descriptions of the structures considered are given in table 10.11

Table 10.11

Descriptions of the structures considered in the examination of the self-association complexes of the chlorobenzenes (- ring faces parallel unless stated otherwise).

Designation	Atom lying on six-fold axis of		Separation of Ring Centres (pm)		Description
	Ring A	Ring B	Horizontal	Vertical	
A	Cl	Cl	309.5	365.0	Chlorines touching aromatic π-cloud.
B	H	H	247.9	370.0	aromatic ring systems in contact.
C	Cl *	* Cl	309.5	365.0	Screening of A by B is different from that of B by A, therefore average is required.
D	H †	† H	247.9	370.0	As for C.
E	other ring (B)	other ring (A)	0.0	370.0	Chlorine substituents are as far apart as possible, rings are vertically above each other and touching.
F	edge of ring (B)	edge of ring (A)	0.0	519.7	Chlorine substituents are as far apart as possible, rings are vertically above each other.
G	Cl	.	0.0	674.5	The second ring (B) is vertically above ring (A) and end on to it.
H	Cl	.	309.5	506.5	A chlorine atom of ring (B) lies on the six-fold axis of ring (A) and two protons of ring (B) sit on a chlorine atom of ring (A) - the two ring faces are perpendicular.

* a proton is situated very close to the six-fold axis.

† a chlorine atom is situated very close to the six-fold axis.

Table 10.12

Experimental and calculated screenings (in ppm) for the proposed self-association complexes of the chlorobenzenes, designated as in table 10.11. Values corrected and uncorrected for $\Delta\chi^{C-Cl}_{app}$ are included.

Structure Designation	Screenings (ppm)		
	Experimental†	Uncorrected for $\Delta\chi^{C-Cl}_{app}$	* corrected for $\Delta\chi^{C-Cl}_{app}$
a) Chlorobenzene			
A		0.103	0.084
B		0.358	0.351
C		0.202	0.188
D	0.218	0.256	0.241
E		0.340	0.304
F		0.323	0.288
b) p-Dichlorobenzene			
A		0.130	0.134
B		0.353	0.361
C		0.220	0.225
D		0.273	0.279
E	0.131	0.340	0.349
F		0.6	0.6
G		0.233	0.241
H		0.249	0.256
c) sym-Trichlorobenzene			
A		0.163	0.166
B		0.370	0.373
C	0.369	0.250	0.253
D		0.300	0.303
E		0.340	0.344

† from table 10.5.

* using the values of $\Delta\chi^{C-Cl}_{opp}$ obtained in section 10.6.

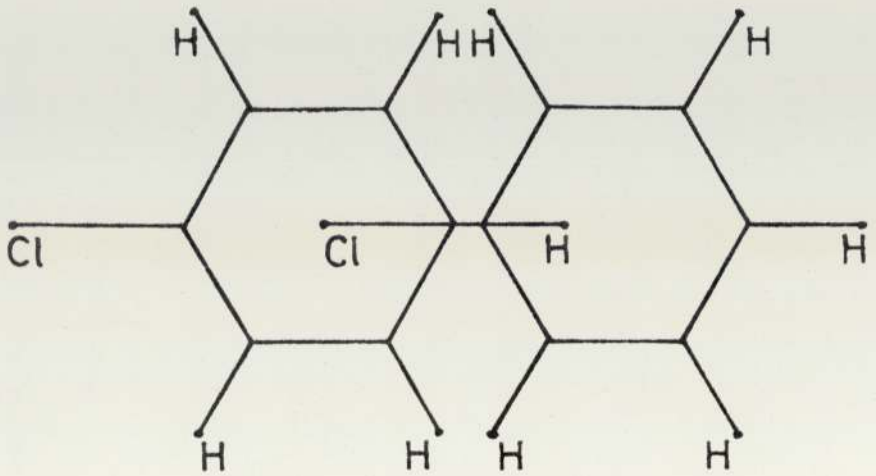
and the experimental and calculated Δ_c^{SA} values in table 10.12. It may be seen that only one possible structure is obtained for p-dichlorobenzene but that two rather similar structures appear possible for chlorobenzene and sym-trichlorobenzene - these various structures will now be considered in more detail. For chlorobenzene it might have been expected that a symmetrical structure would be obtained, with either chlorines (structure A) or protons (B) lying along the aromatic six-fold axis; however, neither of these correspond to the experimental value. This is in fact most closely approached by a structure in which the carbon-chlorine bonds are aligned, with one chlorine on the six-fold axis of the other molecule (C); this structure is shown in figures 10.5A and 10.5B. Another structure which is only slightly less favourable is that with a proton on the six-fold axis in place of chlorine (D), but this does suffer from the disadvantage that the two chlorine atoms are closer together. Structure C may be justified on the basis that as chlorobenzene is dipolar it would be expected to complex such that the maximum interaction could exist between the dipoles, and this occurs when they are aligned (i.e. with the carbon-chlorine bonds 2π rad apart).

For p-dichlorobenzene the only structure which appears to correlate with the experimental result is that in which the interaction occurs between chlorine atoms and the aromatic ring (A); this structure is shown in figures 10.6A and 10.6B. This would seem to be less favourable than a structure in which the interaction occurred between protons and the aromatic ring (B), but use of molecular models shows that structure A resulted in less interaction between the chlorine atoms and also allowed the two aromatic rings to align more closely. This is not the first occasion that interactions between atoms other than hydrogen and the aromatic ring have been proposed, since Ledaal[168] has suggested that the complexes formed between thiophene and benzene and between furan and benzene occur via sulphur and oxygen respectively;

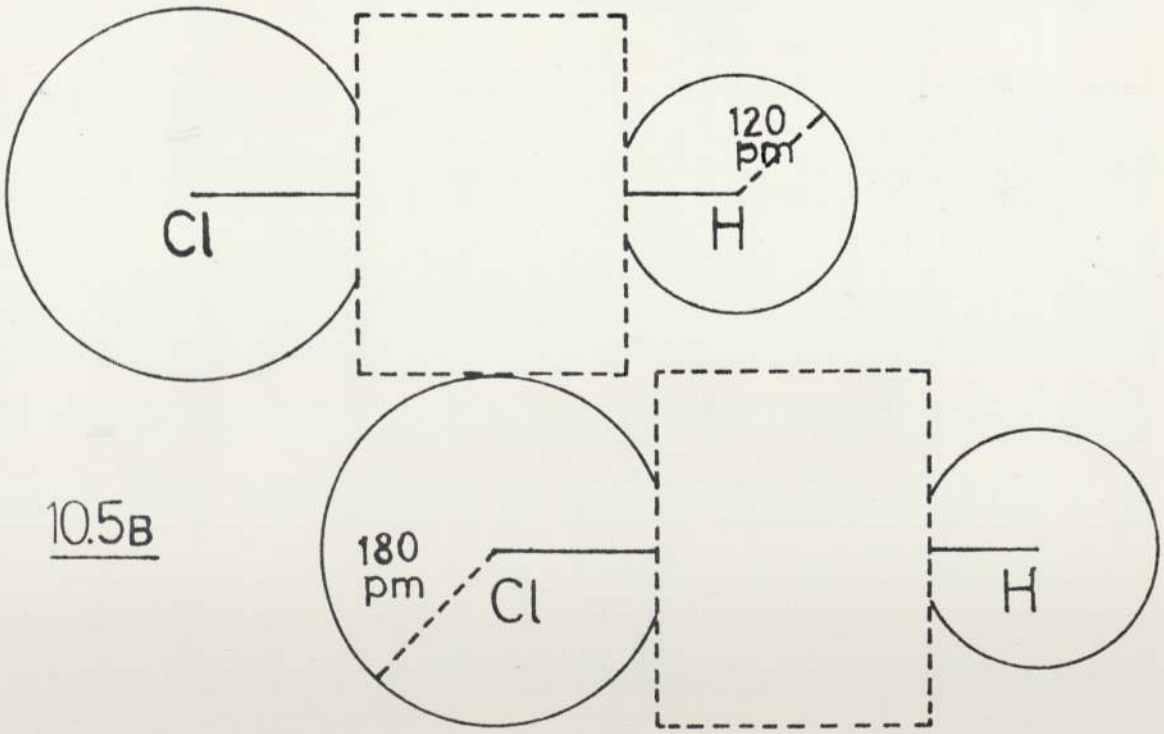
C_6H_5Cl

PLAN

10.5A



ELEVATION



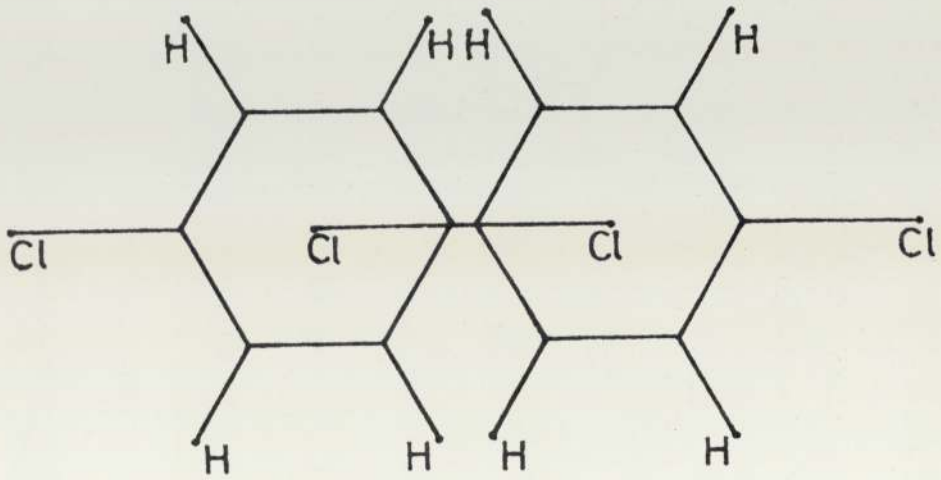
10.5B

The proposed structure (plan and elevation) of the self-association complex of chlorobenzene.

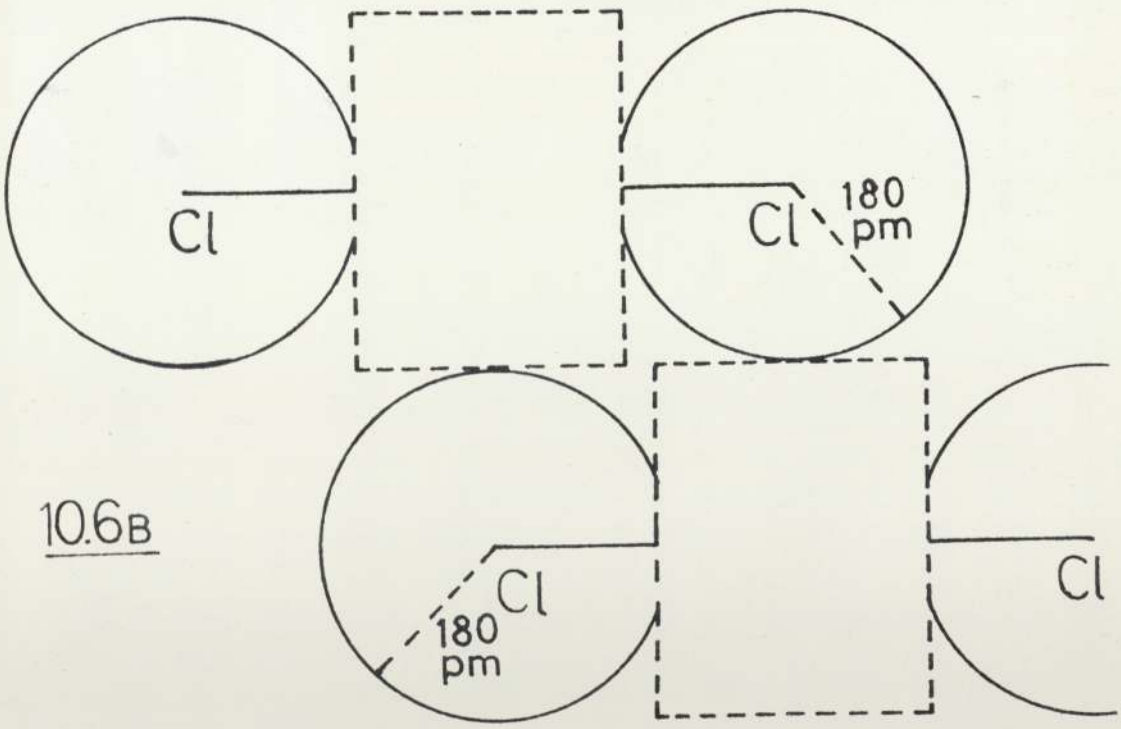
$C_6H_4Cl_2$

PLAN

10.6A



ELEVATION



10.6B

The proposed structure (plan and elevation) of the self-association complex of p-dichlorobenzene.

and it has been shown that the complex formed between hydrogen sulphide and benzene is also via sulphur[192].

Finally, for sym-trichlorobenzene two structures again appear possible, either with the two aromatic rings lying vertically above one another - the planes of the rings touching and the chlorine atoms aligned $\frac{\pi}{3}$ rad apart (E), or with the interaction occurring between protons and the aromatic ring(B). The use of molecular models appears to favour structure E because there is apparently a strong proton-chlorine interaction and very little chlorine-chlorine repulsion; the proposed structure is shown in figures 10.7A and 10.7B.

10.8 Conclusions

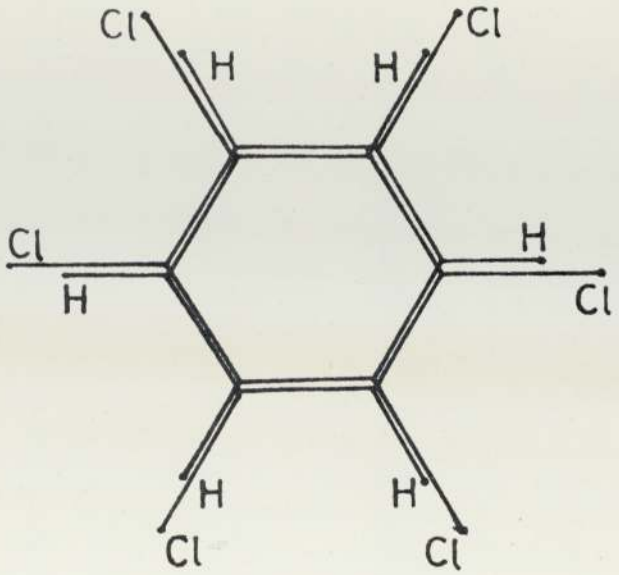
Assuming the validity of the experimental shifts measured it proved possible to obtain structures both for the complexes formed between the haloforms and some chlorobenzenes and also for the self-association complexes of these chlorobenzenes. A number of corrections were attempted - for the effect of the chlorine substituent on the aromatic altering both the ring current and the carbon-substituent bond anisotropy - but it would appear that, allowing for the approximate nature of these, they didnot affect the conclusions reached. Also it was only possible to evaluate approximately the effect of aromatic self-association on the amount of the chlorobenzene which was available for complex formation. Nevertheless, the structures proposed seemed to be reasonable, the only surprising suggestion being that of an interaction between an 'aromatic' chlorine and the aromatic π-system in the self-association complex of p-dichlorobenzene. However, it is known that halogen molecules interact with benzene in this way[193-194] and structures have also been proposed involving interactions between the aromatic π-system and 'aromatic' oxygen and sulphur atoms[168] and also with 'inorganic' sulphur[192].

It was unfortunate that, because of solubility limitations, use could not be made of either the new procedure for investigating molecular interactions in solution[59] or of a Benesi-Hildebrand type[44] evaluation

$C_6H_3Cl_3$

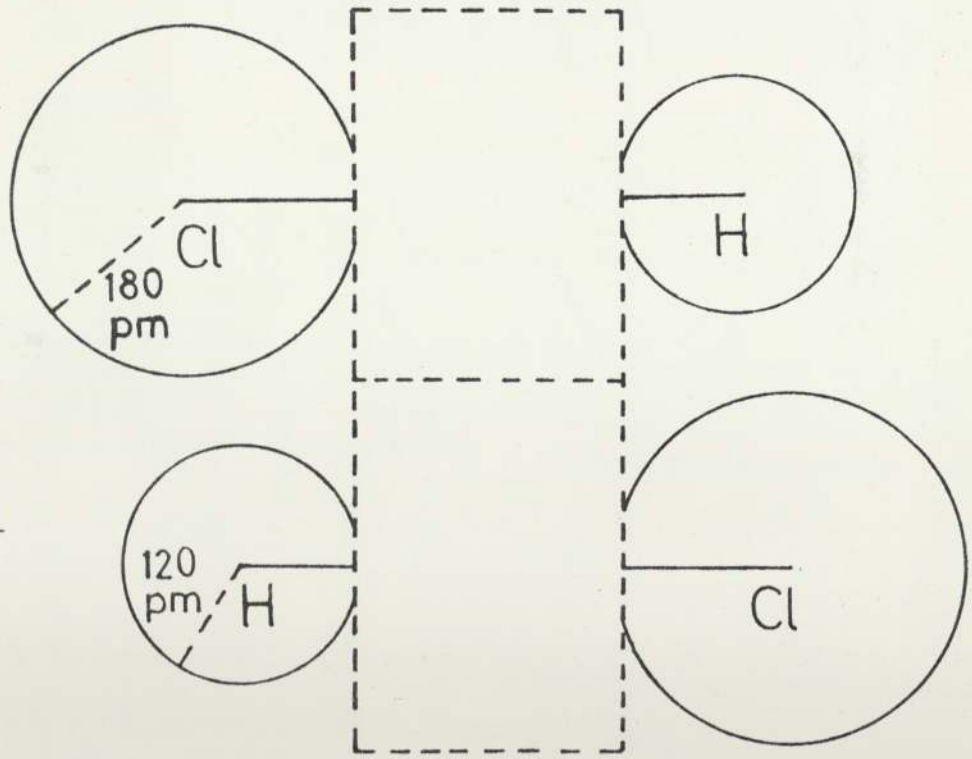
PLAN

10.7A



ELEVATION

10.7B



The proposed structure (plan and elevation) of the self-association complex of sym-trichlorobenzene.

of the resultant data. Nevertheless, the discussion in chapter 3 shows that the data recorded in this chapter should be self-consistent and hence the structural conclusions reached may be considered to be valid.

10.9 Final Conclusions

Because of the need to rationalize the study of molecular interactions in solution the work described in this thesis has been directed towards investigating a number of problems associated with such studies. In the past various concentration scales, inert solvents and references have been used almost indiscriminately with the result that much of the work described in the literature is not comparable. An attempt has been made therefore to use the thermodynamics of mixtures in order to determine the correct procedure for investigating complex formation. A consideration of two component systems appears to indicate that thermodynamic requirements are satisfied by the use of the Benesi-Hildebrand (BH) data evaluation procedure[44] and either the mole fraction or molarity concentration scales (in the latter case only if the limiting slope of the $^{1}/\Delta$ against $^{1}/$Concentration line is taken). Assuming that two component thermodynamics may be used to discuss three component solutions, similar conclusions apply to these with the proviso that on the mole fraction scale a correction must be made to the mole fractions to allow for the difference in the molar volumes of the inert and aromatic solvents. It was further shown that the Creswell and Allred (CA) procedure[62] was not thermodynamically valid but that it did, in fact, give equilibrium quotients which were linearly related to the true values. Furthermore ΔH for the formation of the complex, obtained from a plot of $\ln K$ against $^{1}/T$, would be exactly correct.

In order to investigate the inertness of solvents a new two component procedure, based on the use of the BH method, was devised. It was shown that cyclohexane could be considered to be inert but that TMS interacted strongly with benzene. As this procedure made use of an external reference it was necessary to undertake an investigation of medium screening

effects. In particular the anisotropy (σ_a) and dispersive (σ_w) screenings were found to require study and it proved possible to relate the variation, with mixture composition, of the combined $\sigma_a + \Delta\sigma_w$ screening of two component mixtures with the thermodynamics of perfect and imperfect mixtures. The new procedure has also been used to investigate some molecular interactions for which comparable data, obtained by the CA procedure, was available. In particular, thermodynamic parameters of complex formation were obtained and shown to be comparable to those obtained by the CA procedure.

Finally, the effects of aromatic substituents were considered, of necessity using the CA method, and it was concluded that, allowing for the reasonableness of the assumptions made, polar substituents had major effects on the type of molecular complexes formed. These effects are believed to be due to i/ ring current variations ii/ polar interactions of the substituent with the solute resulting in the formation of n-type complexes, and iii/ bond anisotropy effects.

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Molecular Complexes. Part VI.[1] A New Procedure for investigating Molecular Interactions in Solution By Nuclear Magnetic Resonance Spectroscopy

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Molecular Complexes. Part VI.[1] A New Procedure for investigating Molecular Interactions in Solution By Nuclear Magnetic Resonance Spectroscopy

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A new procedure, based on an external reference technique which largely accommodates screening effects of the media is proposed for the investigation of molecular interactions in two-component solution. Equilibrium quotients and aromatic-induced shift values obtained by this method for the interactions between benzene and, separately, chloroform, ethylene chloride, methyl iodide, and 1,1-dichloroethylene are compatible with results reported previously. It is shown that cyclohexane is inert to benzene whereas tetramethylsilane interacts strongly.

CONSIDERABLE attention has been devoted to the effects of molecular interactions in solution on n.m.r. chemical shifts.[2] In particular, extensive investigations have been carried out on molecular complexes formed by a variety of simple molecules (solute) with benzene and other simple aromatic molecules (solvent).[2-4] Several experimental procedures have been developed in order to study this type of interaction and obtain values for the equilibrium quotient (K) and aromatic-induced shift (Δ_{comp}) characteristic of complex formation. These studies have commonly been based on the investigations of two-,[5] three-,[6,7] or four-[8] component liquid mixtures. In each case the solute–solvent ratio has been varied and solute chemical shifts have been measured. Variations of the shifts with solvent concentration have been attributed to specific effects of the magnetic anisotropy of the aromatic molecule in the complex. These methods suffer from one or more of three main disadvantages, *viz.* (*a*) medium screening effects may not be adequately corrected for, (*b*) the reference and other solvents may not be inert, and (*c*) solution components may self-associate. In view of the suggestion that the binding in the complexes may be solute local dipole–aromatic induced dipole in nature,[9,10] point (*b*) is particularly

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important for internally referenced procedures, because even essentially nonpolar solvents or reference compounds possessing strong local dipoles may interact, specifically with benzene. Our procedure enables this point to be studied and largely accommodates the difficulties (*a*) and (*c*). For this we revert to the use of an external reference.

To study complex formation it is necessary to measure the difference between the chemical shifts of a particular solute nucleus in the free state and various complex equilibrium situations. This can be done by arranging that the solute (A) in a complexing aromatic solvent (B) is in the annulus (X) of a cylindrical sample tube, and that a coaxial capillary (Y) contains the solute in some non-interacting solvent (S). By neglect of all bonding interactions other than complex formation, the solute in the capillary will be entirely free, whereas the state of that in the annulus will be governed, for a sample j, by the mole-fraction equilibrium expression (neglecting activity coefficients):

$$K = \frac{[C]_j\,([A]_j + [B]_j - [C]_j)}{([A]_j - [C]_j)([B]_j - [C]_j)} \qquad (1)$$

if 1 : 1 molecular complex formation occurs according to

$$A + B \rightleftharpoons A \cdots B$$

$[A]_j$ and $[B]_j$ are the numbers of moles of A and B initially present and $[C]_j$ the number of moles of complex formed at equilibrium. Thus in the annulus and capillary the solute will be shielded differently due to the effects of complex formation and different medium screenings. The corresponding shift can be measured directly, but the specific shielding contribution due to the aromatic molecule in the complex must be abstracted from this.

If the absolute screening constant for a particular nucleus in the solute is σ, then the screening in the medium (σ_M) is defined by

$$\sigma_M = \sigma_a + \sigma_b + \sigma_E + \sigma_w + \sigma \qquad (2)$$

where σ_a, σ_b, σ_E, and σ_w have their usual significance.[11] When solute–aromatic interaction occurs an additional term σ_{comp}, representing the screening contribution of the aromatic species to the solute, must be included in equation (2). The dispersion (σ_w) and reaction field (σ_E) contributions are often considered to be less important than those due to bulk susceptibility (σ_b) and anisotropy (σ_a), particularly when differences in these terms which contribute to a chemical shift are considered.[12] Dispersion forces in liquid mixtures are thought to be additive,[13] and the contribution of these to the screening of the solute may be expected to be almost linearly additive and dependent on the mole fractions of the appropriate medium constituents. Corresponding conclusions may be drawn concerning reaction field contributions. Similarly, bulk susceptibility effects are known to be almost linearly additive as a function of the volume fraction of each of the components.[14] However, it has been shown that constituent screening contributions in mixtures that have been attributed to the anisotropy of the medium, which is considered to produce a composite $\sigma_a + \sigma_w$ contribution normally are not linearly additive mole or volume fraction functions of the pure constituent shieldings,[15] and hence should, in principle be individually determined. With the above comments in mind it is possible to devise expressions which represent the actual shielding of the nucleus in the solute, both in the annulus and capillary. This is most conveniently done by considering the effects on the solute of the appropriate contributions from the anisotropy, bulk susceptibility, and initially the composite-dispersion and reaction field screenings of each constituent in solution. The relevant values for the complex are, of course, inaccessible and it becomes necessary to assume that the bulk properties of the components in solution are independent of whether or not they are bound in a complex. The appropriate contributions of each component are then governed by the quantities of the materials initially present. The situation is considerably simplified if the mole fractions of solvents B and S, in the annulus and capillary, are equal. Then, if the configuration of the solute, and hence the absolute screening σ, is the same in both the free and complexed situations, the actual screenings in the annulus and capillary (assumed to be perfectly cylindrical) can be evaluated readily and the difference between these gives the measurable chemical shift $(\delta_{obs})_j$ as equation (3)

$$(\delta_{obs})_j = M_j(\sigma^B - \sigma^S) + (\sigma_{AX}{}^A)_j - (\sigma_{AY}{}^A)_j + \tfrac{2}{3}\pi \{[(V_S)_j - (V_B)_j]\chi_A + (V_B)_j\chi_B - (V_S)_j\chi_S\} + [C]_j/[A]_j\,\sigma_{comp} \qquad (3)$$

which, if no complex formation occurs, may be equated to $(\delta_{obs})'_j$ by omission of the last term. Equation (3) refers to a particular sample j having the same initial mole fractions of the two solvents (M_j) in the annulus and capillary, the corresponding (unequal) volume fractions being $(V_B)_j$ and $(V_S)_j$. χ_A, χ_B, and χ_S are the volume susceptibilities of the solute, aromatic, and inert solvent respectively, $(\sigma_{AX}{}^A)_j$ and $(\sigma_{AY}{}^A)_j$ are the magnetic anisotropy shieldings in the annulus and capillary, and σ^B and σ^S are individually the effective total shieldings afforded the solute by the reaction field and dispersion contributions of pure B and S (*e.g.* $\sigma^B = \sigma_E{}^B + \sigma_w{}^B$). Consequently, if for each one of a series of samples having different mole fractions, M_j, the chemical-shift difference between the solute in the annulus and capillary

[11] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.
[12] J. Homer, *Tetrahedron*, 1967, **23**, 4065.
[13] J. S. Rowlinson, 'Liquids and Liquid Mixtures,' Butterworths, London, 1959.
[14] (*a*) J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959. (*b*) W. R. Angus and D. V. Tilston, *Trans. Faraday Soc.*, 1947, **43**, 221. (*c*) S. Broersma, *J. Chem. Phys.*, 1949, **17**, 873.
[15] J. Homer, M. H. Everdell, E. J. Hartland, and C. J. Jackson, *J. Chem. Soc.* (*A*), 1970, in the press.

is plotted against M_j, the shift difference (Δ_j) between the resulting curve and the absolute reference line [from $(\delta_{obs})'_j$], may be represented by equation (4) where

$$\Delta_j = (\delta_{obs})_j - (\delta_{obs})'_j = \frac{[C]_j}{[A]_j} \Delta_{comp} \qquad (4)$$

σ_{comp} is equated with the aromatic-induced shift Δ_{comp}. If the line corresponding to the variation of $(\delta_{obs})'_j$ with M_j can be accurately determined the procedure described automatically corrects for any medium effects. Also, since the solute is contained at the same mole fraction in both the annulus and capillary, solute self-association ideally does not affect $(\delta_{obs})_j$ or $(\delta_{obs})'_j$ or, therefore, equation (4). However, since in the annulus complex formation occurs, the efficiency of the implicit procedure to correct for solute self-association may be reduced; self-association may also modify the operative value of $[A]_j$ in equation (1).

To test the procedure outlined above, we have investigated four solute–solvent systems for which evidence exists that 1 : 1 molecular complex formation occurs. These are those in which benzene complexes with chloroform,[7,16] ethylene chloride,[17] methyl iodide [4,18] and 1,1-dichloroethylene.[4] Similarly, we have investigated the interactions between cyclohexane and benzene and tetramethylsilane (TMS) and benzene, to establish if cyclohexane and/or TMS can be used as non-bonding solvents and references in future work. In view of the apparent success achieved with the assumption that cyclohexane is nonbonding with benzene, we have continued this in the early stages of our investigations. For each system, a series of 10 samples with different mole fractions of solvent was prepared in accordance with the above procedure. The purity of the materials was established by g.l.c. The capillaries (precison drawn, 2 mm. o.d.) were examined as described elsewhere [15] and only those considered to be perfectly cylindrical were used. Each sample of a particular series gave rise to two solute resonances which could be identified on relative intensity grounds. The chemical shifts between these were measured with a Perkin-Elmer R10 spectrometer, operating at 60·004 MHz and 33·4°. Each shift was measured six times to minimise random errors and the average shift value was taken as $(\delta_{obs})_j$.

Figure 1 shows a plot of $(\delta_{obs})_j$ against the mole fraction of benzene, M_j. To implement the proposed procedure the variation of $(\delta_{obs})'_j$ with M_j is nominally required. However, it is less involved and eventually more precise to correct the individually measured shifts corresponding to equation (3) for volume susceptibility, anisotropy, and dispersion screenings. To do this for each contributor individually would be difficult and prone to considerable error because of the temperature and concentration dependence of these parameters.[14,15] Nevertheless, the difficulties are easily overcome by use of the uncorrected ' anisotropy shift ' *versus* mole fraction curves reported elsewhere,[15] for the solvent mixtures studied here, at the relevant temperature. Bulk susceptibility, anisotropy, and in part dispersion screenings can then be allowed for in one step without incurring accumulative errors, as well as accommodating the effects of their dependence on temperature and mixture composition. This is achieved by measuring graphically, at the mole fractions for the shift measurements recorded in Figure 1, the difference in

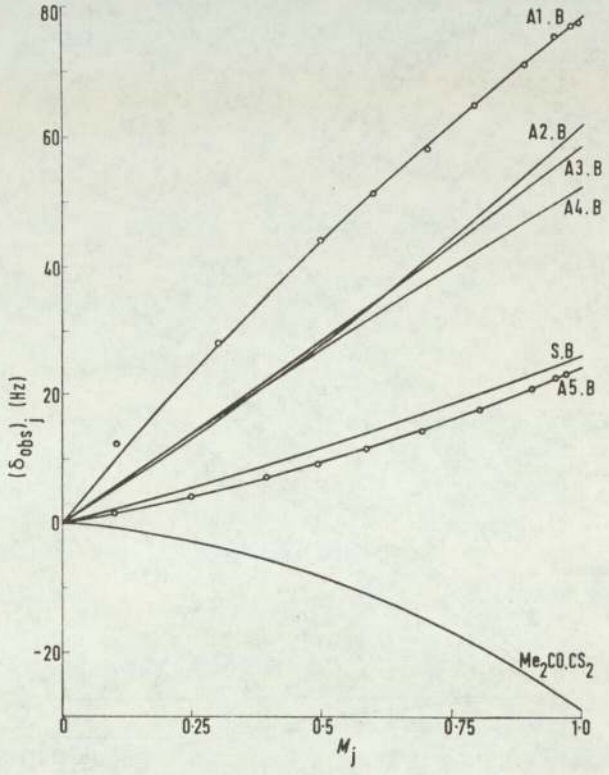

FIGURE 1 Shift $(\delta_{obs})_j$ variation with solution composition, corresponding to equation (3). In this and the following figure the curves can be identified by reference to the table and text. The curves are the best lines through the experimental points, which are included for the chloroform–benzene and tetramethylsilane–benzene systems as representative examples

chemical shifts between the appropriate two curves reported in ref. 15, and then subtracting these values from the $(\delta_{obs})_j$ values given in Figure 1. If this is done it follows that the operative form of equation (3) must become:

$$(\delta_{obs}{}^{corr})_j = \frac{[C]_j}{[A]_j} \Delta_{comp} + M_j[(\sigma_E{}^B + \sigma_w{}^{B'}) - (\sigma_E{}^S + \sigma_w{}^{S'})] \qquad (5)$$

where $\sigma_w{}^{B'}$ and $\sigma_w{}^{S'}$ are the residual dispersion screenings. If no complex formation occurs, only the composite second term is operative and this is assumed to be zero.[3,12] This assumption appears reasonable because the relevant

[16] P. J. Huck, Ph.D. Thesis, University of Aston, 1968.
[17] I. J. Smith, B.Sc. Project Report, University of Aston, 1969.
[18] B. Tempest, B.Sc., Project Report, University of Aston, 1968.

constituent interactions in these studies are less numerous than in the corresponding three-component studies where the same assumption is generally made. The result of the corrections is shown in Figure 2 for which Δ_j of equation (4) has been equated to $(\delta_{obs}{}^{corr})_j$; this is plotted against the mole fraction of benzene. Nonlinear deviations from the mole fraction axis (*i.e.* from $\Delta_j = 0$) are indicative of solute–aromatic interactions. If 1 : 1 molecular complex formation occurs, the curves of interest should be concave with respect to this axis in order that a limiting complex shift can be obtained, as

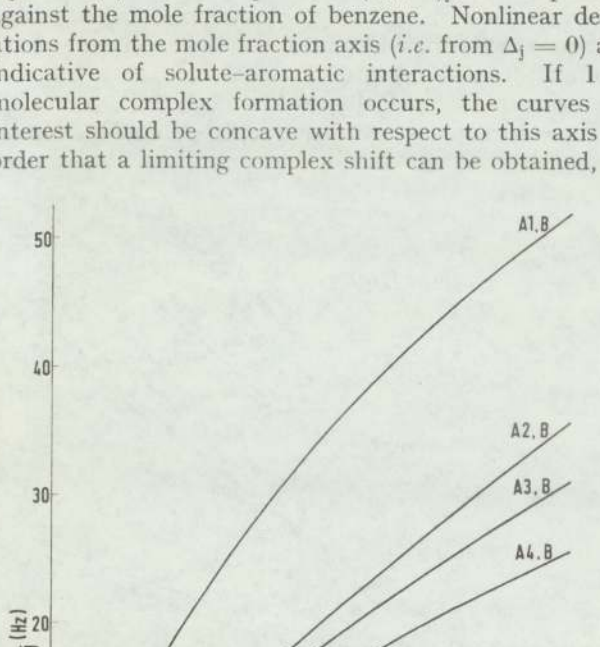

FIGURE 2 Shift variations with solution composition corresponding to equation (5)

would be the case for the formation of any A_nB_m complex. It can be seen that the cyclohexane–benzene line is linear with $\Delta_j = 0$. This is enforced by the choice of cyclohexane as the inert solvent and as the 'probe' for determining [15] $(\delta_{obs})'_j$, and so demonstrates the reliability of the procedure employed. The inertness of cyclohexane to benzene was however demonstrated by the procedure referred to above, using benzene as the 'probe' for determining $(\delta_{obs})'_j$ since this is most unlikely to experience significant shifts due to complex formation, even in extreme circumstances.[16] If the new $(\delta_{obs})'_j$ values are used to correct the appropriate plot in Figure 1, a line corresponding to that shown in Figure 2 for this system is obtained, which is linear and well within 1Hz of the mole fraction axis. This shows that cyclohexane is not involved in specific interactions with benzene and thus validates the results of other workers who have assumed cyclohexane to be inert. It can also be seen that the curves for the four systems which were expected to show solute–aromatic interactions are all concave with respect to the mole fraction axis; this indicates that a limiting complex shift can be achieved. Similar conclusions can be drawn from the TMS–benzene line. By use of an iterative procedure similar to that described elsewhere,[19] we have deduced values of the equilibrium quotients (K) and excess shieldings (Δ_{comp}) for the five systems and these are given in the Table.

TABLE

Equilibrium quotients (K) and excess shielding values (Δ_{comp}) for the formation of some solute–benzene complexes determined by the procedure described in the text and by a conventional three-component method

	K (mole fraction) at 33·4°		$\Delta_{comp.}$ (p.p.m.)	
Solute	This method	Three-component method	This method	Three-component method
(A1) Chloroform	$1{\cdot}1_5$	1·14 [a]	$1{\cdot}4_0$	1·62 [a]
(A2) Ethylene chloride	$0{\cdot}3_6$	0·96 [b]	$2{\cdot}1_9$	1·17 [b]
(A3) Methyl iodide	$0{\cdot}6_0$	0·70 [c]	$1{\cdot}3_5$	1·24 [c]
(A4) 1,1-Dichloroethylene	$0{\cdot}7_5$	0·50 [d]	$1{\cdot}0_0$	1·26 [d]
(A5) Tetramethylsilane	$9{\cdot}5_4$		$-0{\cdot}0_5$	

[a] Ref. 19. [b] Ref. 17. [c] Ref. 18. [d] Ref. 4.

The results are reasonably consistent with those available from three-component studies. Complete agreement is not expected because of the effect of the inert material in the three-component systems and because activity coefficients have been neglected. In fact the data presented were evaluated by assuming that K and Δ_{comp} were independent of solution composition. This is unlikely and so the values quoted are averages for the whole composition range. Therefore, whilst they do allow comparisons of the characteristics of molecular complexes on a consistent basis,[9,10] their precise meaning is uncertain. It is of interest therefore that equation (4) can be modified to the Benesi–Hildebrand form [20] and used to obtain values for K and Δ_{comp} when M_j approaches unity; this treatment would have greater thermodynamic validity.

For the TMS–benzene system the shifts curve back towards the mole fraction axis when a large excess of benzene is present. Since this does not appear to be due to experimental error, it indicates that the equilibrium is more involved than for simple 1 : 1 molecular-complex formation. Therefore, the K and Δ_{comp} values quoted were calculated using the shifts below 0·7 mole fraction of benzene, and should only be taken as an indication of the approximate values of the parameters pertaining to the interaction assumed. It is particularly interesting

[19] P. D. Groves, P. J. Huck, and J. Homer, *Chem. and Ind.*, 1967, 915.

[20] H. A. Benesi and H. J. Hildebrand, *J. Amer. Chem. Soc.*, 949, **71**, 2703.

at the TMS–benzene results confirm those of Laszlo *al.*[21] who found an aromatic-induced shift of *ca.* 0·03 p.p.m. (infinite dilution) which is compatible with ır value of *ca.* −0·05 p.p.m. The approximate value r the equilibrium quotient is surprisingly large and ggests that TMS is a poor reference material for romatic compounds. We have also studied (Figures 1 nd 2) the interaction between carbon disulphide, B, and etone. The shape of the curve corresponding to quation (5) is inconsistent with the formation of a ngle, specific complex species. We therefore conclude at this is due either to the occurrence of multiple quilibria or to accumulative solvation; furthermore, ther systems resulting in lines of this shape may be terpreted on the same basis.

The method outlined above for the study of 1 : 1 molecular complex formation clearly gives approximate equilibrium quotient and aromatic-induced shift data compatible with the results obtained from investigations of three-component systems. More important however, it provides a convenient method for studying the ' inertness ' of solvents and interactions in genuine two-component solutions generally. It may be applicable, in a suitably modified form, to the study of more complicated association phenomena.

We thank Professor W. G. S. Parker for the provision of facilities and the S.R.C. for a Research Studentship to one of us (C. J. J.).

[9/842 *Received, May 20th,* 1969]

[21] P. Laszlo, A. Speert, R. Ottinger, and J. Reisse, *J. Chem. Phys.*, 1968, **48**, 1732.

Proton Nuclear Magnetic Resonance Studies of the Variation of 'Neighbour Anisotropy' Screening with Composition of Mixtures, and some Comments on its Relationship to the Thermodynamics of Solutions

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Proton Nuclear Magnetic Resonance Studies of the Variation of 'Neighbour Anisotropy' Screening with Composition of Mixtures, and some Comments on its Relationship to the Thermodynamics of Solutions

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The screening attributed to neighbour anisotropy effects for a series of liquid mixtures was experimentally determined as a function of constituent concentration. It is shown that anisotropy screenings of mixtures are not normally linearly additive mole- or volume-fraction functions of the anisotropy screenings of the pure constituents. It is proposed that the variation of anisotropy is a function of the 'degree of perfection' of the mixture, and the thermodynamics of perfect and imperfect mixtures are considered in relation to the variations observed.

THE screening of nuclei in molecules in liquid media is affected, in the absence of specific intermolecular interactions, by four factors which constitute the medium screening and contribute to the overall shielding [see equation (1) where σ_a, σ_b, σ_E, and σ_w have their usual

$$\sigma_{TOTAL} = \sigma_a + \sigma_b + \sigma_E + \sigma_w + \sigma \qquad (1)$$

significance,[1] and σ is the absolute screening constant for a particular nucleus]. If any one or more of the contributory screening terms of the medium affects the screening of a solute and a reference nucleus differently a contribution is provided to the measured chemical shift. Generally, it has been considered that screening effects of the medium only provide significant contributions to chemical shifts when measured relative to an external reference. It is, therefore, desirable to evaluate these effects quantitatively in order that adequate account may be taken of them. Whilst the bulk susceptibility effect can be accounted for by the use of familiar expressions,[2] no rigorously applicable relationships are available for the other effects. In fact, it has often been accepted that differences in the volume bulk susceptibility term (σ_b) have been the major contributor to the effect of the medium on the total measured chemical shift, and hence only this term was considered. This appeared to be partially justified because procedures for estimating the electric field (σ_E) and dispersion force (σ_w) contributions have indicated that differences in these terms may have only a small effect on the overall chemical shift.[3,4] However, recent experimental investigations of dispersion [5] and magnetic anisotropy [3,6] screenings have indicated that both may be much larger than previously anticipated. Nevertheless, differences between the dispersion screenings of a particular solute in different solvents may be small,[5] so that the corresponding differences in magnetic anisotropy screenings determined by making this assumption [3,6] in fact may be often very much the larger of these two effects. However, they may be difficult to separate experimentally for anisotropic solvents and as yet cannot adequately be predicted theoretically. We are, therefore, forced to consider a joint $\sigma_a + \sigma_w$ shielding. This may reasonably be assumed to be influenced by steric and anisotropic effects [5,6] and therefore will be referred to hereafter simply as the anisotropy screening. The experimentally accessible composite term $\Delta\sigma_a + \Delta\sigma_w$ can then be used for correcting chemical shifts. It appears necessary therefore to consider both 'medium anisotropy' and bulk susceptibility effects, but to a first approximation not electric field (for nonpolar solutes) and separate dispersion force effects, when correcting externally referenced chemical shifts.

Generally, externally referenced chemical shifts are measured for a dilute solution of the solute in a pure solvent, with reference to a pure compound. However, we have found it necessary to make use of mixed solvents in order to investigate molecular interactions in solution [7] and hence have been forced to consider the variation of the major screening effects $\sigma_a + \sigma_w$ and σ_b as a function of mixture composition. If volume bulk susceptibility is assumed to be a linearly additive volume fraction function of the volume bulk susceptibilities of the pure constituents of the mixture [8-10] its effect should easily be accounted for. However, no evidence is at hand concerning the additivity or otherwise of constituent anisotropy contributions in mixtures. The work described herein is directed towards investigating experimentally the nature of the variation of medium anisotropy with composition of the mixture.

EXPERIMENTAL

As a result of our interest in the interaction between various solutes and benzene,[7] we have chosen to study initially the variation of medium anisotropy with solution composition in a series of two-component mixtures made up of benzene or cyclohexane with separately, chloroform, ethylene chloride, methyl iodide, and vinylidene chloride. Several other systems were subsequently studied and these will be referred to later. The method employed [3] requires

[1] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.
[2] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1965, vol. 1.
[3] J. Homer, *Tetrahedron*, 1967, **23**, 4065.
[4] J. Homer and P. J. Huck, *J. Chem. Soc.* (*A*), 1968, 277.
[5] W. T. Raynes and M. A. Raza, *Mol. Phys.*, 1969, **17**, 157.
[6] J. K. Becconsall, *Mol. Phys.*, 1968, **15**, 129.
[7] J. Homer, E. J. Hartland, and C. J. Jackson, *J. Chem. Soc.*, (*A*), 1970, 931.
[8] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.
[9] W. R. Angus and D. V. Tilston, *Trans. Faraday Soc.*, 1947, **43**, 221.
[10] S. Broersma, *J. Chem. Phys.*, 1949, **17**, 873.

that a solution containing a low concentration (*ca.* 0·5% w/w) of an isotropic solute, with no strong local dipoles, dissolved in the anisotropic mixture, be placed in the annulus surrounding a precision capillary containing the same concentration of the solute in carbon tetrachloride acting as isotropic reference. The solute chosen by Homer [3] was tetramethylsilane (TMS), but in view of the work of Laszlo *et al.*[11] who stated that TMS may interact with benzene, a highly anisotropic solvent in common use, cyclohexane was used as solute because evidence from our related work [7] shows that this is inert. Cyclohexane is anisotropic but because of its low concentration this is unlikely to affect the measurements made. This solute reference was added in the same concentration to each of a series of samples of different composition for each solvent system; the purity of all materials used was established by g.l.c. Each sample of a particular series gave rise to two solute resonance lines which could be identified by relative intensities. The corresponding chemical-shift differences were measured with a Perkin-Elmer R10 spectrometer operating at 60·004 MHz and 33·4°. Each shift was determined six times to minimise random errors.

The chemical shift between the two solute resonances has separate contributions due to the volume bulk susceptibility, dispersion force, and magnetic anisotropy effects; the electric field term is zero. Whilst it is convenient to assume that any differences in the dispersion force contributions to the measured chemical shift will be negligible, we should attribute this, after correction for volume bulk susceptibility (assuming no volume change on mixing), to the composite anisotropy term for the mixture. To make use of the familiar equation for bulk susceptibility corrections it is necessary to use perfectly cylindrical reference vessels.[2,12] The precision capillaries (2 mm. o.d.) were tested to ensure they could be considered perfectly cylindrical by observation of the spectrum of a sample of TMS in the annulus of a sample tube surrounding a capillary which also contained TMS; deviations from perfect cylindrical uniformity of the capillary would result in the observation of two discrete TMS signals.

RESULTS

The measured shifts (Δ) are shown as a function of mole fraction of one component in Figure 1. The corresponding curves corrected for susceptibility on a simple additivity basis are shown in Figure 2, and, with the assumption of the linearity of this correction, indicate the variation of medium anisotropy (σ_a) (more exactly $\sigma_a + \Delta\sigma_w$ the combined real anisotropy and differences in dispersion screenings) with solution composition. The latter curves then indicate that mixed medium anisotropy screenings are not linearly additive mole fraction functions of the anisotropy screenings of the pure constituents; moreover they would not be linearly additive volume fraction functions. The significance of the apparent deviations from linearity of the curves shown in Figure 2 depends upon the validity of the assumption that the volume susceptibility corrections to the screening can be made in a linearly additive manner, and upon the relationship between the experimental error and the magnitude of the deviation. It is realised that the deviations from linearity in terms of the anisotropy shift are relatively small, and that the apparent nonlinearity of the lines could arise from extremely fortuitous accumulation of experimental errors. The reproducibility of the ethylene chloride–benzene curve has been investigated, therefore, to eliminate this possibility. The absolute position and reproducibility of such a curve could be considerably influenced by not achieving thermal equilibrium for each sample, by variable contributions to the measured shifts caused by different non-co-axial arrangements of the capillaries, and by differences in solute concentration between the samples. The first of these was minimised by

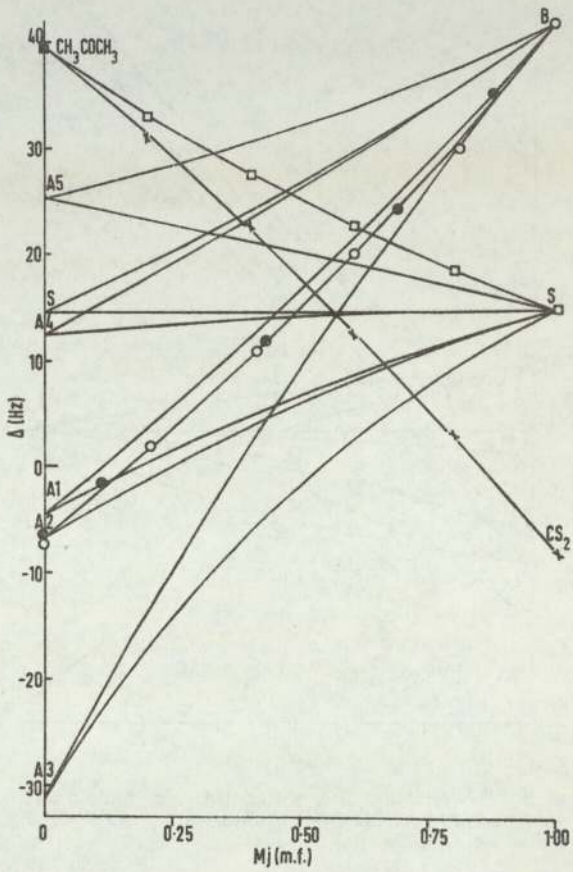

FIGURE 1 The variation of Δ (the shift difference between cyclohexane in the anisotropic solvents and in carbon tetrachloride) with constituent mole fraction in several mixtures. The curves are the best lines through the experimental points of which representative examples are given for the ethylene chloride–benzene (○), acetone–carbon disulphide (×) and acetone–cyclohexane (□) systems. The reproducibility of the curves is demonstrated by the ethylene chloride–benzene system (○ and ●). A1, $CHCl_3$; A2, $CH_2Cl{\cdot}CH_2Cl$; A3, MeI; A4, $CH_2{:}CCl_2$; A5, $SiMe_4$; S, C_6H_{12}; B, C_6H_6

ensuring that the samples were at thermal equilibrium before the shift measurements were made. The effect on the measured shifts of tilting a capillary was investigated and found to be negligible. The variation of solute concentration was investigated by determining the anisotropy shielding of an ethylene chloride–benzene mixed solvent system at the fixed mole ratio of 0·7195 : 1 of benzene to ethylene chloride with different solute concentrations. With the weight percentages of 0·61, 1·01, 2·10, and 2·51 of cyclohexane the anisotropy shieldings obtained were 11·15,

[11] P. Laszlo, A. Speert, R. Ottinger, and J. Reisse, *J. Chem. Phys.*, 1968, **48**, 1732.
[12] D. J. Frost and G. E. Hall, *Mol. Phys.*, 1966, **10**, 191.

11·19, 11·18, and 11·00 Hz respectively. It is evident from these results that small variations in the cyclohexane concentration around the value used (0·5%) have little effect on the shieldings obtained; nevertheless, the concentration used should be as low as possible. With this order of

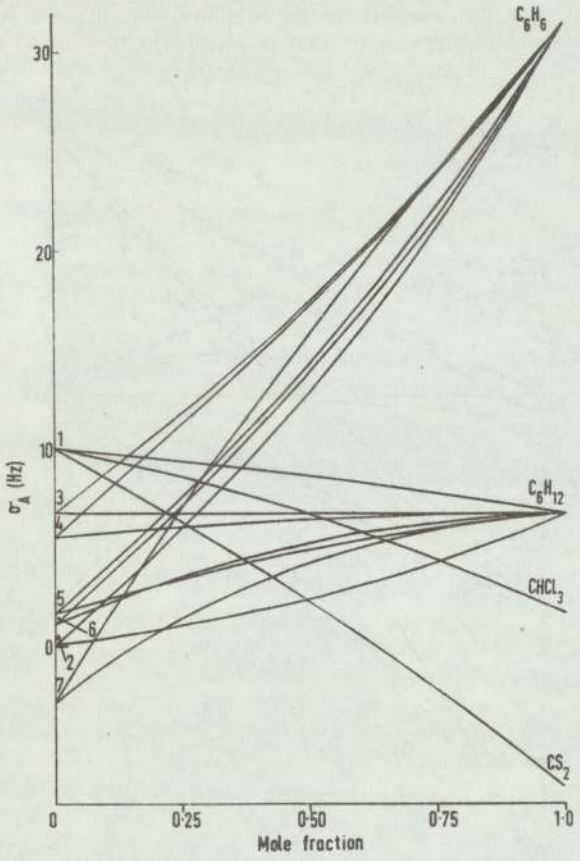

FIGURE 2 The variation of σ_A with constituent mole fraction in several mixtures. 1, Me_2CO; 2, $SiMe_4$; 3, C_6H_{12}; 4, $CH_2{:}CCl_2$; 5, $CHCl_3$; 6, $CH_2Cl{\cdot}CH_2Cl$; 7, MeI

cyclohexane concentration we have remeasured the variation in anisotropy shielding of the ethylene chloride–benzene system with concentration to test the general reproducibility of the procedure, and, despite use of different capillaries we obtained a second curve completely consistent with the first shown in Figure 1.

DISCUSSION

Deviations from the Assumed Additivity of Volume Susceptibility.—Whilst the curves given in Figure 2 illustrate experimentally genuine nonlinearity, the volume susceptibility corrections could give rise to this because volume changes may occur on mixing. This could cause the effective volume susceptibility screening by the components to be a nonlinearly additive function of the volume fraction of the pure bulk screening effects, and result in the curvature shown.

From the work of Angus *et. al.*,[9] the susceptibilities of mixtures appear to be linearly additive functions of composition within experimental error. However, Broersma [10] investigated both the volume and mass susceptibilities of mixtures and, despite the relative insensitivity of the inductance technique used in part,[13] found that for some mixtures nonlinear variations of volume susceptibility with component volume fraction were obtained and that in general materials having no volume change on mixing showed linear variations of volume susceptibility with composition, whereas those for which a volume change was obtained could give nonlinear variations. In the latter case he suggested that, in general, the deviation from linearity of the volume susceptibility should not exceed 5×10^{-3} of the susceptibility effect. Exceptionally he found variations of the order of 40×10^{-3} for both water–ethanol and water–acetic acid, for which large volume changes on mixing are known to occur. For the systems which we have studied the volume changes on mixing are quite small (see Table where the reduced excess

System	V^{excess} (cm.^{3} mol.$^{-1}$)	ρ ($\times 10^2$)
Ethanol–water	−1·4 [a]	−3·66
Acetone–chloroform	−0·19 [b]	−0·25
Benzene–cyclohexane		+0·66 [c]
Benzene–ethylene chloride	+0·24 [d]	+0·29
Benzene–bromobenzene	Negligible [e]	Negligible
Chloroform-methyl iodide	Negligible [f]	Negligible
n-Heptane-n-hexane	Negligible [g]	Negligible

[a] A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, 1953, **15**, 161. [b] L. A. K. Staveley, W. I. Tupman, and K. R. Hart, *Trans. Faraday Soc.*, 1955, **51**, 323. [c] S. E. Wood and A. E. Austin, *J. Amer. Chem. Soc.*, 1945, **67**, 480. [d] Ref. 23. [e] Ref. 20. [f] Ref. 19. [g] Ref. 17.

volume of mixing (ρ) of ethanol–water may be compared with the values for several of the systems studied here). We define the reduced excess volume change on mixing by equation (2) where V^{excess} is the volume change on mixing equimolar quantities of the components to form one mole of the mixture and V_1^0 and V_2^0 are the molar volumes of components 1 and 2.

$$\rho = \frac{V^{excess}}{\frac{1}{2}(V_1^0 + V_2^0)} \qquad (2)$$

It is probable, therefore, that for the systems studied the deviation from linearity of the volume susceptibility as a function of mixture composition may not be more than *ca.* 5×10^{-3} of the susceptibility effect, which implies a maximum deviation of *ca.* $0{\cdot}003 \times 10^{-6}$ c.g.s. units or 0·36 Hz at 60 MHz. This is much smaller than many of the deviations from linearity shown in Figure 2. That the anisotropy screening of mixtures need not be either a linear mole- or volume-fraction function of the anisotropy of the solution constituents can be demonstrated unambiguously by reference to the ethanol–benzene and carbon tetrachloride–nitrobenzene systems, which Broersma [10] found to show insignificant deviations from linear variation of volume susceptibility with volume fraction. We have studied these two systems; the anisotropy screenings (with the assumption of a linear volume susceptibility correction) plotted as

[13] B. N. Figgis and J. Lewis, ' Technique of Inorganic Chemistry,' eds. H. B. Jonassan and A. Weissberger, Interscience, 1963, vol. 4.

functions of mole- and volume-fraction of one of the constituents are shown in Figure 3. For the ethanol–benzene system the work of Broersma allows a simple linear volume susceptibility correction to be made, and, therefore, since the corrected lines which result are curved, it appears that anisotropy screenings of mixtures are nonlinear functions of solution composition. For the carbon tetrachloride–nitrobenzene system the relatively small deviation from linearity of the volume susceptibility versus volume fraction plot [10] could result in a

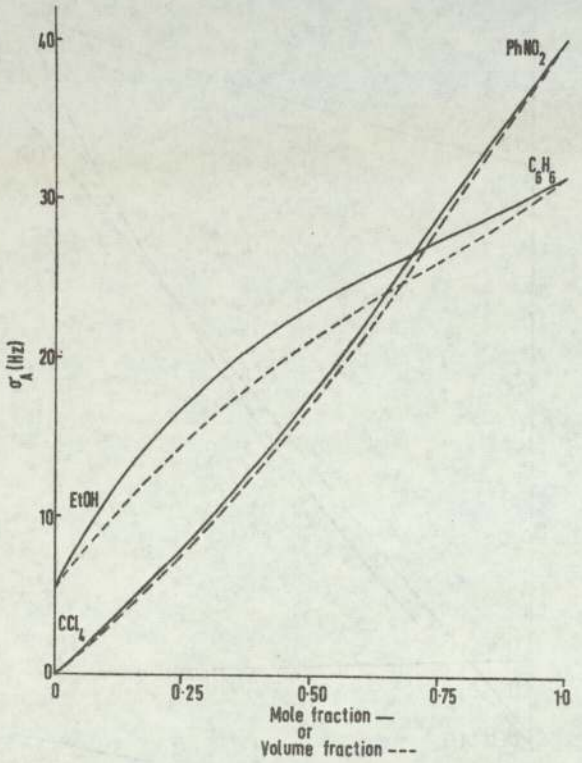

FIGURE 3 Variation of σ_A with mole- and volume-fraction of one of the constituents for the systems ethanol–benzene and carbon tetrachloride–nitrobenzene

maximum deviation of 0·2 Hz from linearity in the corresponding anisotropy plot, which is much smaller than that found. This provides further confirmation that medium anisotropy screenings need not be linear functions of mole- or volume-fraction of one of the constituents in a mixture.

The anisotropy plots shown in Figures 2 and 3 (and subsequently 4) may be in error because the values used for the simple linear volume susceptibility corrections have been taken directly from ref. 2. These values are valid at a temperature other than that at which our measurements were made and so, because of the temperature dependence of volume susceptibility *via* density, the absolute position and shape of our lines may be modified to a small extent. It is fruitless to attempt any adjustments to our anisotropy plots because of this, since the small contributions to them afforded by the possible nonlinearity of volume susceptibility are unknown (for this reason alone the determination of real magnetic anisotropy screenings would be uncertain). This can make separate corrections for medium anisotropy to externally referenced chemical shifts uncertain, and, because of their nonlinearity, tedious. In any event these will necessarily be accompanied by the variable susceptibility and screening corrections. However, for practical purposes appropriate differences between uncorrected ' anisotropy shifts ', such as those shown in Figure 1, can be used to correct directly for both anisotropy and bulk susceptibility. The effects of the carbon tetrachloride reference solution cancel out; the effects on volume susceptibility of temperature, and of volume changes on mixing, are included.

The Variation of the Anisotropy of Mixtures with Composition.—Becconsall [6] predicted the separate magnetic anisotropy screening effect of benzene on a number of approximately spherical solute molecules with different molecular radii and compared these with the experimental values. The predictions were qualitatively sound but the solvent effects were almost twice those observed. His calculations were based on a model in which only those solvent molecules within a spherical shell effectively contacting the solute contribute to the solvent anisotropy; the remainder of the solvent molecules in the bulk sample are ineffective, provided bulk susceptibility corrections are made. Each solvent molecule in the effective shell is permitted all orientations such that the symmetry axis of the solvent molecule occupies a cone, the axis of symmetry of which lies along a radius vector from the solute. He suggested that the main source of error in his calculations could be due to the neglect of weak attractive dispersion forces across the small gaps between the solute and solvent molecules which would favour those orientations of the solvent molecular axis that are furthest from the radial orientation, *i.e.* that the assumption of a uniform distribution of the solvent orientations in the permitted cone is invalid. On the basis of this work, when mixed solvent systems are considered, the effects of dispersion forces between unlike solvent molecules in the effective anisotropy shell must be recognised. These could impose further restrictions on the permitted orientations of one or both of the solvent molecular types relative to those in their pure states. These restrictions will depend on the magnitudes of the various interactions, the composition of the effective shell, the molecular arrangement within it, and also on the shape of the solvent molecules in the mixture. Therefore, the magnetic anisotropy screenings (and dispersion screenings which are included in the values we have determined) of mixed solvents need not change in a simple linear fashion, particularly if specific interactions between the solvents occur. If this explanation is correct, then the solvent anisotropy effect should be temperature dependent (σ_w is accepted to be [1]); preliminary investigations show that this may be so, but in the opposite manner to that predicted by Becconsall [6] for the magnetic anisotropy.

A Possible Correlation Between the Thermodynamics of Solutions and their Anisotropy Screenings.—Linear variations in the anisotropy screening of mixed solvents as a function of composition can, on the basis of our explanation, only be expected when all the interactions between an effective anisotropic solvent molecule and all of its neighbours are the same and allow a uniform distribution of its orientations in the permitted cone. For this to be possible it is expected that there must be no specific interactions between solvent molecules (as they would tend to prevent random distribution), that the dispersion interactions between them must be the same whether the interacting species are alike or unlike, and that they must have similar shape. These resemble the requirements for the formation of a perfect mixture [14,15] for which the molar quantities of mixing, at constant temperature and pressure, are given by equations (3)—(7) where x_1 and x_2 are the mole fractions of the two

$$\Delta_m G^P = x_1 RT \ln x_1 + x_2 RT \ln x_2 \quad (3)$$

$$\Delta_m S^P = -x_1 R \ln x_1 - x_2 R \ln x_2 \quad (4)$$

$$\Delta_m H^P = \Delta_m U^P = 0 \quad (5)$$

$$\Delta_m V^P = 0 \quad (6)$$

$$\Delta_m A^P = \Delta_m G^P \quad (7)$$

components. The superscript P describes the perfect mixture. Equation (3) means that both components of the mixture obey Raoult's Law and that their chemical potentials may be described by equation (8) where

$$\mu_i = \mu_i^0 + RT \ln x_1 \quad (8)$$

μ_i^0 is for the pure liquid at the same temperature and pressure. Equation (6) means that the mixing process may be described also as one at constant temperature and constant volume.

It is well known that these equations may be given a theoretical foundation by use of the methods of statistical thermodynamics with the assumptions that [14] (i) the size and shape of the molecules of the two species are similar, (ii) the molecular distribution in the mixture is completely random, and (iii) the intermolecular forces between a pair of unlike molecules is the same as the arithmetic mean of the forces between the two pairs of like molecules. Condition (iii) is usually expressed by equation (9) (ref. 16) where ε_{11} is the free energy required

$$w' = \varepsilon_{12} - \tfrac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) = 0 \quad (9)$$

to bring together two molecules of component 1, each originally isolated in space, to the position they would occupy as ' nearest neighbours ' in the pure liquid, ε_{22} is the corresponding quantity for component 2 and ε_{12} that corresponding to the formation of an unlike pair 1, 2 so that when two liquids are mixed the quantity w' is proportional to the free energy required to separate the 1,1 pairs in one liquid and the 2,2 pairs in the second and to form 1,2 pairs in the mixture. The requirements (i)—(iii) are essentially equivalent to those suggested earlier for mixed solvents likely to show linear variations in the anisotropy screenings as a function of solvent composition. It might be expected, therefore, that this feature should be exhibited by solvent systems which are perfect mixtures.

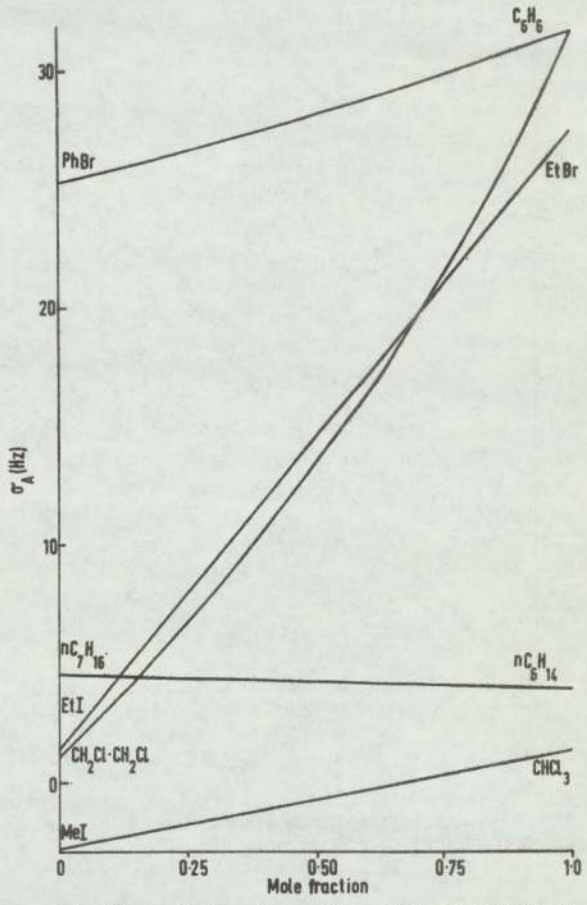

FIGURE 4 The variation of σ_a with constituent mole fraction in perfect and imperfect mixtures which obey Raoult's Law

No known mixture is perfect except that in which the molecules differ only by isotopic substitution but some mixtures are known which approach perfect behaviour very closely *e.g.* n-hexane–n-heptane,[17] ethyl bromide–ethyl iodide,[18] methyl iodide–chloroform [19] (all perfect *ca.* 30°), and bromobenzene–benzene [20] (perfect at 80°). We have studied the anisotropy screening variations of these systems and the resulting data (Figure 4) show that the lines are very close to the expected linearity.

[14] G. N. Lewis and M. Randall, ' Thermodynamics,' revised by K. S. Pitzer and L. Brewer, 2nd edn., McGraw-Hill, New York, 1961.

[15] J. H. Hildebrand and R. L. Scott, ' The Solubility of Non-electrolytes,' 3rd edn., Reinhold, New York, 1950.

[16] See, *e.g.*, E. A. Guggenheim, ' Mixtures, the Theory of the Equilibrium Properties of some Simple Classes of Mixtures, Solutions and Alloys,' Clarendon Press, Oxford, 1952.

[17] H. A. Beatty and G. Calingaert, *Ind. and Eng. Chem.*, 1934, **26**, 504.

[18] S. Glasstone, ' Thermodynamics for Chemists,' Van Nostrand, New York, 1947.

[19] N. D. Litvinov, *J. Phys. Chem.* (*U.S.S.R.*), 1940, **14**, 782.

[20] M. L. McGlashan and R. J. Wingrove, *Trans. Faraday Soc.*, 1956, **52**, 470.

For these systems the simple linearly varying correction employed for the volume susceptibility screening is valid and therefore the lines shown are meaningful. Within experimental error all of the systems, except bromobenzene–benzene, provide straight lines. In the latter case it is not surprising that a shallow curve is obtained since the temperature at which the anisotropy measurements were made was considerably different from that at which the system was reported to be perfect.

Under our experimental conditions the addition of cyclohexane may cause deviations of the main solvent system from perfect behaviour. However, its concentration is so low that the effect should be negligible. The observation of straight lines (Figure 4) suggests that the short range solute–solvent interactions are less important in causing deviations from linearity of the other mixtures (Figure 2) than the similar solvent–solvent effects in the anisotropically effective solvent shell. This indicates that neglect of the solute–solvent dispersion interactions does not provide a full explanation of the discrepancy between the predicted and measured solvent magnetic anisotropy screening.[6]

The curves shown in Figure 2 arise from mixtures which we believe to be imperfect. Imperfect mixtures are those, some or all of whose molar quantities of mixing differ from those given in equations (3)—(7).[15] They are usually classified in terms of their excess quantities of mixing. The excess free energy of mixing G^E is defined by equation (10) and the excess entropy of mixing by equation (11) and so on. It is possible that the values

$$G^E = \Delta_m G - \Delta_m G^P \qquad (10)$$

$$S^E = \Delta_m S - \Delta_m S^P \qquad (11)$$

of some of the excess functions may be zero. The most important classes of imperfect mixtures are (i) those for which G^E and H^E are finite but S^E is zero or very close to zero, (ii) those for which G^E and S^E are finite but H^E is zero or close to zero, and (iii) those for which G^E is zero or close to zero, but S^E and H^E are finite. Those of class (i) are sometimes called simple mixtures or regular mixtures.[15] They may be accounted for by a statistical model in which the distribution of the molecules is almost completely random, but in which the quantity $w' = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})$ is other than zero, *i.e.*, the departure from the equations of the perfect mixture is due almost entirely to a finite energy of interaction between the molecules of the different species. Those of class (ii) are sometimes called athermal mixtures,[15] in which the interaction energies are negligibly small and the departure from perfect behaviour is due almost completely to the nonrandom arrangements in the mixture. The solvent mixtures giving rise to all of the curves shown in Figure 2 (except the ethylene chloride–benzene system), belong to one of these two classes of mixtures; the acetone–chloroform system has also been studied and the results included here since this is particularly representative of systems showing negative deviations from Raoult's Law. That they are imperfect can be shown by classical thermodynamic experimental procedures.[14,15] It is more difficult to demonstrate that the mixtures belonging to class (iii) are imperfect. These mixtures appear to obey Raoult's Law so that G^E is zero but both H^E and S^E are finite. Since equation (12) holds, it follows that in such mixtures H^E and

$$G^E = H^E - TS^E \qquad (12)$$

TS^E must be of the same sign and of almost the same value. Ethylene chloride–benzene mixtures fall into this class. Such mixtures were thought, for many years, to be perfect since they appear to obey Raoult's Law [21] although Baud [22] had shown H^E to be finite. These results were confirmed by Coulson *et al.*[23] and discussed further by Herington.[24] It is of interest that although Raoult's Law is obeyed the lines in Figures 2 and 4, for this system, show considerable curvature, suggesting, as for the other solvent systems referred to in Figure 2, that this is indeed imperfect. In view of the apparent success of the explanations concerning the linearity or otherwise of the mixed solvent anisotropy screening variations with composition, it would be reasonable to suppose that the differences in the behaviour of the various binary mixtures described above would be paralleled by differences in their behaviour found by the traditional methods of thermodynamics. Since, for the perfect mixtures studied, the second differential of σ_a with respect to mole fraction proves to be zero, it was hoped to establish a correlation between the sign of the corresponding second differential for imperfect mixtures and the sign of one (or more) of the excess thermodynamic quantities of mixing (in particular, perhaps with the excess entropy of mixing at constant volume). Unfortunately no such correlation is evident, despite the apparent correlation with the signs of the reduced excess volume changes on mixing, given in the Table, since this in fact breaks down for the acetone–carbon disulphide system.

It is possible, therefore, that this method of measuring anisotropies of mixtures may afford a simple means of determining whether a mixture is perfect, with perfect mixtures giving straight lines and imperfect mixtures curves for plots of anisotropy against mole fraction of one of the constituents, (rather than volume fraction plots which are not so specifically applicable).

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