N.M.R. STUDIES OF THE FORMATION OF MOLECULAR COMPLEXES IN THE LIQUID PHASE.

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by

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SUMMARY

This thesis concerns the investigation by nuclear magnetic resonance spectroscopy of complexes formed transiently between polar aliphatic molecules (solutes) and aromatic solvents. The complexes are studied by the use of ^{1}H chemical shifts and spin-lattice relaxation times. The purpose of the work is to confirm the validity of procedures which have been developed previously to obtain more meaningful parameters than hitherto describing the formation of such complexes, and to investigate the mechanism of their formation.

The methods proposed for the evaluation of equilibrium quotients and the screening induced in the solute proton in the complex relative to that in the free state rely on measurements of its ^{1}H shift variation with the composition of mixtures of the solute, the aromatic and an inert solvent. Chemical shift data for the interaction between chloroform and $[^{2}H_{6}]$benzene occurring in several inert solvents have been measured to a higher accuracy than previously achieved, are analysed using the procedures referred to, and confirm the validity of these. Some observations are made concerning the effect of inert solvents and references used in these investigations.

The mechanism of formation of transient complexes is studied by analysing the variations in the magnitude of equilibrium quotients with the composition of three-component mixtures. The interactions occurring between several solutes separately with benzene, in cyclohexane, are investigated. A model for complex formation is proposed, which is quantitatively explained in terms of molecular ordering in the liquid medium.

Measurements of spin-lattice relaxation times in $[^{2}H]$

chloroform-benzene-cyclohexane mixtures of varying composition are analysed, and are shown to substantiate the model for complex formation deduced from the chemical shift analysis.

The conventional procedures used for the deoxygenation of samples used for spin-lattice relaxation time measurements are shown to be unsatisfactory, and a versatile chemical alternative is described.

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CHAPTER 1.

SOME THEORETICAL CONSIDERATIONS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY.

1.1. Introduction.

The hyperfine structure observed in the electronic spectra of certain atoms when using optical spectographs of high resolving power[1] led Pauli to suggest[2] that certain nuclei may possess angular momentum, and also a magnetic moment which could interact with electrons. Stern and Gerlach[3,4] subsequently showed that the measurable values of an atomic magnetic moment are discrete in nature, and, when an atom is placed in an inhomogeneous magnetic field, correspond to a space quantisation of the atom. The magnetic moment of the hydrogen nucleus was determined[5] by directing a beam of hydrogen molecules through a static magnetic field, which deflected the beam to an extent determined by the magnetic moment. The method was afterwards extended by using two oppositely inclined magnetic fields of similar gradients, the molecular beam being diffused by the first magnetic field, and focussed by the second on to a detector. The introduction of a radiofrequency signal between the two original fields, such that the oscillating magnetic component of the r.f. signal was perpendicular to the main field, showed that the density of molecules reaching the detector was reduced if the energy of the radiofrequency signal was equal to that required to induce transitions between the nuclear energy levels corresponding to the quantisation of nuclear magnetic moments[6].

In 1945 two independent groups of workers: Purcell,

Torrey and Pound[7], and Bloch, Hansen and Packard[8], both detected nuclear magnetic resonance signals from bulk samples of paraffin and water respectively. Using static magnetic fields of about 1 tesla, it is found that the corresponding oscillating field frequencies are in the range 0.1 - 100 MHz for different nuclei. Wide use has since been made of the fact that nuclear energy levels are dependent on the environment of the nucleus, enabling the determination of both nuclear properties and molecular structure[9-11].

It is convenient when discussing the theory of nuclear magnetic resonance spectroscopy to first consider an isolated nucleus in a magnetic field in order to deduce equations for the resonance condition, and associated resonance criteria, and then to investigate the properties of bulk samples including such important aspects as the nuclear energy level distribution, relaxation and saturation. Finally it is necessary to investigate the very important factors of the chemical shift, spin-spin coupling and exchange phenomena with respect to the nuclear environment.

1.2. Magnetic Properties Of Nuclei.

Certain nuclei may be considered to behave in a similar fashion to spinning bodies of a spherical or ellipsoidal shape, which possess angular momentum. Since an electric charge is associated with an atomic nucleus, a magnetic field is produced, the direction of which is coincident with the axis of spin. These magnetic properties may be conveniently represented by equation 1.1.

$$\vec{\mu} = \gamma \vec{I}\hbar \qquad 1.1.$$

where the vectorial parameters $\vec{\mu}$ and $\overrightarrow{I\hbar}$, the magnetic moment and angular momentum respectively, are related by the constant γ, the magnetogyric ratio, which is found to be characteristic of each nuclear species; $\hbar$ is the reduced Plank's constant ($h/2\pi$). The angular momentum of each nucleus is quantized, since the presence of a magnetic field gives rise to non-degenerate energy levels for the nucleus, corresponding to the values of the angular momentum which are given by half integral multiples of $\hbar$, and governed by the spin quantum number I.

The number of energy states is limited by the spin quantum number to $2I + 1$, with spin values from $- I$ to $+ I$. I may be equal to zero, in which case the nucleus has no magnetic moment, and does not give rise to magnetic resonance, but if it has a finite value (i.e. a multiple of ½), μ is also finite, and it is parallel to $I\hbar$. For this reason, μ must also be quantized, the different states corresponding to different orientations of μ within the reference coordinates pertaining to the nucleus.

1.3. Nuclei In A Magnetic Field.

When nuclei are placed in a magnetic field the allowed values of $I\hbar$ and μ correspond to different nuclear spin orientations relative to a reference axis, which is usually taken to be the same as the direction of the applied static magnetic field, and is conventionally designated as the z axis. When the magnetic moment of a nucleus, μ, is inclined at an angle θ to the static field, B_o, (Figure 1.1.) the energy of the nucleus is given by:

$$E = E_o + E_z \qquad 1.2.$$

where E_o is the energy of the nucleus in the absence of a magnetic field, and $E_z = - \vec{\mu}_z B_o$. The total energy is therefore:

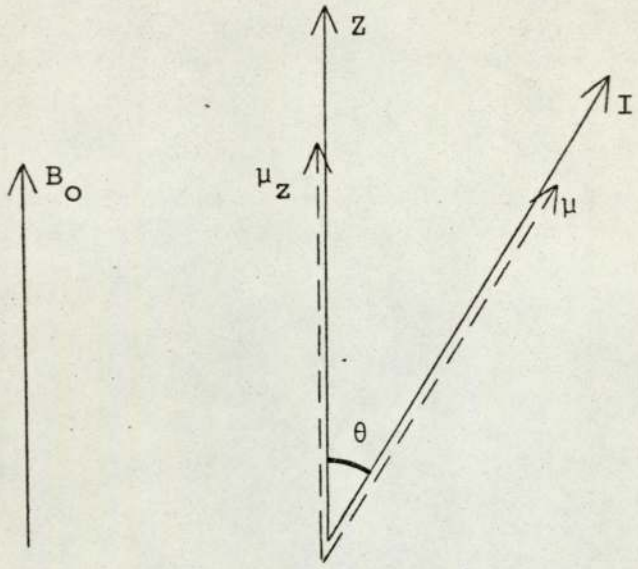


FIGURE 1.1. The vectorial relationship between the magnetic moment, μ, and the spin angular momentum, I.

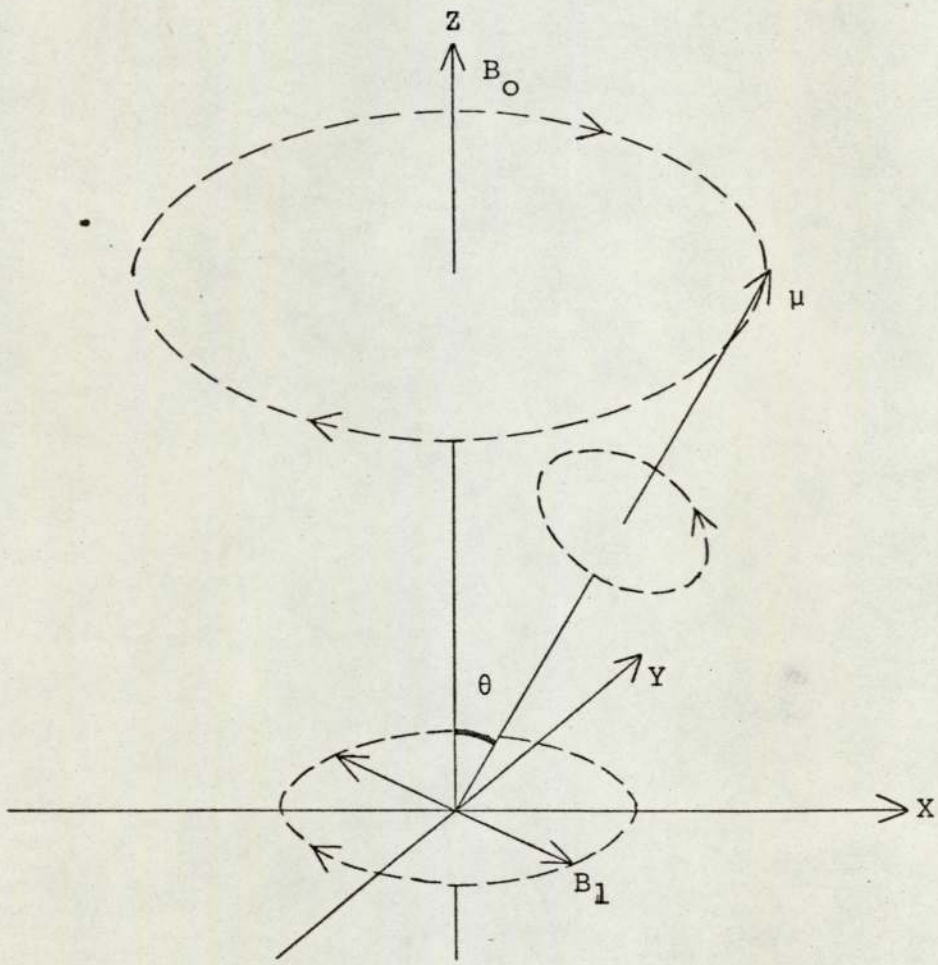


FIGURE 1.2. A representation of Larmor precession.

$$E = E_o - \vec{\mu} \cos \theta \, B_o \qquad 1.3.$$

and the quantised values of μ_z are governed by the allowed values of I, which can be represented by the nuclear magnetic quantum number, m, which is allowed the values I, (I - 1), (I - 2) ------ (-I + 2), (-I + 1), -I. It is evident that the angle of orientation of μ to the z axis, θ, is given by $\cos \theta = m/I$ and therefore the magnitude of the magnetic moment in the z direction is given by equation 1.4.

$$\vec{\mu}_z = m\vec{\mu}/I \qquad 1.4.$$

and also:

$$E_z = - m\vec{\mu}B_o/I \qquad 1.5.$$

The allowed energies of the magnetic moment are thus characterised by m, and differ from E_o by:

$$- \vec{\mu}B_o, - \frac{(I - 1)}{I}\vec{\mu}B_o \text{ ------ } \frac{(I - 1)}{I}\vec{\mu}B_o, \vec{\mu}B_o,$$

the energy between two adjacent levels being given by equation 1.6.

$$\Delta E = \frac{\vec{\mu}B_o}{I} \qquad 1.6.$$

Since it is only possible to induce a transition between adjacent nuclear energy levels[12], i.e. $\Delta m = \pm 1$, a particular nucleus may have only one characteristic value for ΔE for a given value of B_o. It is possible to induce transitions between the energy levels by subjecting nuclei in a magnetic field to a signal, the frequency of which corresponds to the energy difference, determined by the condition $\Delta E = h\nu$. The detection of changes in energy which result from inducing such transitions is the basis of the n.m.r. technique. From equation 1.6. it is evident that, in order to induce a nuclear absorption of energy, the frequency must be given by:

$$\nu = \frac{\vec{\mu}B_o}{\vec{I}\hbar} = \frac{\gamma B_o}{2\pi} \qquad 1.7.$$

This is the condition, therefore, for nuclear magnetic resonance to occur, and an absorption of energy will be detected by suitable equipment if the condition is satisfied.

1.4. Conditions For Nuclear Magnetic Resonance.

1.4.1. The Classical Description Of Nuclear Resonance.

The absorption of energy by nuclei in a magnetic field may most readily be understood by a classical consideration of a rotating charged particle which is subjected to a magnetic field, B_o. The magnetic moment, μ, of the nuclear dipole, when oriented at an angle θ to the axis of the applied field will experience a torque, L, which acts in order to align the moment with B_o. The value of L is given by equation 1.8:[12]

$$\vec{L} = d\vec{p}/dt = \vec{\mu}B_o = \gamma\vec{p}B_o \qquad 1.8.$$

where dp/dt is the rate of change of angular momentum. If the angular momentum vector is rotated at an angular velocity ω_o, then the rate of change of p is given by:

$$d\vec{p}/dt = \vec{p}\omega_o \qquad 1.9.$$

and, therefore, ω_o is given by the equation:

$$\omega_o = \gamma B_o \qquad 1.10.$$

The rate of change of the angular velocity, the Larmor precessional frequency, is thus determined by the value of the applied static field, B_o. Equation 1.10. may be re-written in terms of the frequency of precession, ν_o.

$$\nu_o = \gamma B_o/2\pi \qquad 1.11.$$

which shows that there is no dependence of ν_o on the direction of the reference axis, and the direction of the magnetic moment, μ, is fixed relative to coordinates

rotating at a frequency ν_o.

When a small rotating magnetic field, B_1, is applied perpendicularly to the static field, (Figure 1.2.), the direction of the rotation being about the direction of B_o, a torque equal in value to μB_1, will act upon the nuclear magnetic moment tending to align it with B_1. If B_1 is applied at a frequency not equal to ν_o, the direction of the torque will vary according to the difference between the two frequencies, but if B_1 rotates at a frequency equal to ν_o the torque will be constant, and the orientation of μ will be altered. The resonance condition may therefore be observed by varying the frequency of B_1 through the Larmor frequency, the oscillations of the magnetic moment being largest as the two frequencies correspond.

Normally, the frequency of B_1 is in the radiofrequency range. The signal is applied to a coil surrounding the sample under investigation, the coil being wound such that a field is produced at right angles to B_o which has two contra-rotating components. Only the field which rotates in the correct sense will induce transitions between the orientations of the magnetic moment, the other having no effect, and energy will be absorbed.

1.4.2. A Simplified Quantum Mechanical Treatment.

The equation defining the influence of a magnetic field on a magnetic moment, μ, is

$$\mathcal{H} = - \vec{\mu} B_o \qquad 1.12.$$

or, considering equation 1.1.,

$$\mathcal{H} = - \gamma \hbar B_o \vec{I} \qquad 1.13.$$

Where I is the operator in the Hamiltonian equation, and has values determined by the nuclear magnetic quantum

number, m. The values for the energy levels in the system are therefore given by:

$$E = -\gamma\hbar B_o m \qquad 1.14.$$

and transitions induced between the energy states allowed by this condition, may be considered to arise as a result of a perturbation of the system. The required properties of the oscillating field which permits this are determined by the effect of the spin operator, I, and its related eigenfunctions.

In a three-coordinate system, the operators I_x, I_y and I_z may be defined, together with a fourth, I^2, which relates to a probability function. Taking the simplest case of nuclei with spin, I, = ½, for example the proton, there are only two possible energy states, which are given by $\pm\gamma\hbar B_o$, and the eigenfunctions relating to these are usually denoted by α and β. If the oscillating field is applied in the same direction as the static field, i.e. the z direction, the probability of a transition occuring between the two states is:

$$P_z \propto (\alpha|\vec{I}_z|\beta)^2 = 0 \qquad 1.15.$$

and no transition can occur. However, the application of the oscillating field in either the x or y directions gives rise to finite transition probabilities given by equations 1.16. and 1.17. respectively.

$$P_x \propto (\alpha|\vec{I}_x|\beta)^2 = \tfrac{1}{2}\hbar \qquad 1.16.$$

$$P_y \propto (\alpha|\vec{I}_y|\beta)^2 = \tfrac{1}{2}\hbar \qquad 1.17.$$

The resulting change in energy is given by equation 1.14., where m can only be unity, and the frequency of the oscillating field must be:

$$\nu = \frac{\Delta E}{h} = \frac{\gamma B_o}{2\pi} \qquad 1.18.$$

In the general case of a nucleus of spin I, the transition probability between the energy levels m and $m^{\perp}$ is given by[14]:

$$P_x^{\perp} \propto (\Psi_m | I_x | \Psi_{m^{\perp}})^2 \qquad 1.19.$$

where Ψ_m and $\Psi_{m^{\perp}}$ are the eigenfunctions corresponding to the two energy states. The probability function is found to be non-zero only when $m = m^{\perp} \pm 1$, or $\Delta m = \pm 1$, thus determining the selection rule for nuclear transitions.

Whilst the classical concept of n.m.r. only predicts absorption of energy, the quantum mechanical picture also predicts an emission process, since $P_x^{\perp}$ is non-zero for $\Delta m = -1$ as well as $\Delta m = +1$.

1.5. The Distribution Of Nuclei Between Energy Levels.

The equations and selection rules represented above show that a system of identical nuclei at resonance exhibits equal probabilities of absorption, or stimulated emission of energy, although the probability of spontaneous emission is negligible[14]. However, in order to observe a nett change in absorbed energy, i.e. an n.m.r. signal, it is apparent that there must be a change in the distribution of nuclei between the energy levels. The observation of such an absorption of energy is permissable by virtue of the thermal Boltzmann distribution between the energy levels, which favours the lower state. Therefore, in the absence of a secondary field, B_1, for a system of N nuclei at a temperature T, the number of nuclei n_i, which occupy a level of energy, E_i is given by equation 1.20.

$$n_i/N = e^{-E_i/kT} / \sum_i e^{-E_i/kT} \qquad 1.20.$$

Since there are 2I + 1 possible states, the probability of a given nucleus occupying a particular energy level, m, is given by:

$$P^i = \frac{1}{2I + 1}(e^{+m\vec{\mu}B_o/IkT}) \qquad 1.21.$$

which, since $\mu B_o/IkT$ is small under normal conditions, approximates to:

$$P^i = (1 + m\vec{\mu}B_o/IkT)/(2I + 1) \qquad 1.22.$$

Therefore there is an excess of nuclei in the lower state. If I = ½, the probabilities of a nucleus being in the upper and lower states are given by equations 1.23. and 1.24. respectively.

$$P^{upper} = \tfrac{1}{2}(1 - \mu B_o/kT) \qquad 1.23.$$

$$P^{lower} = \tfrac{1}{2}(1 + \mu B_o/kT) \qquad 1.24.$$

These relationships show that the excess population in the lower state is increased with the magnitude B_o, and the sensitivity of the technique may be similarly increased by increasing B_o.

However, it is apparent that in order to maintain an excess of nuclei in the lower state some mechanism must exist by which nuclei may return from the higher to lower energy states after resonance. In the presence of a large secondary field (B_1), n.m.r. signals may disappear as the excess number of nuclei in the lower state tends to zero, the phenomenon being known as saturation, and is exhibited when nuclei return only slowly from the upper energy levels. In optical spectroscopy[15,16] no such effect is noticed since the return is usually rapid, and spontaneous. The mechanism of the return of nuclei from the upper to the lower states is known as relaxation, and will be discussed

further in Section 1.7.

1.6. Saturation Effects.

The phenomenon of saturation, described briefly above, is generally exhibited as a reduction in signal intensity and a broadening of the resonance line. In a spectrum consisting of several absorptions, each may be affected differently. Another possible effect of saturation is the stimulation of multi-quantum transitions[17], for which the selection rule $\Delta m = \pm 1$ does not apply[12].

For an assembly of similar nuclei of spin $I = \frac{1}{2}$, which are not subject to an oscillating field, B_1, the rate of change of the excess population, n, is determined by equation 1.25.

$$dn/dt = (n_{eq} - n)/T_1 \qquad 1.25.$$

where n_{eq} is the value of n at thermal equilibrium, and T_1 is a relaxation time, determining the rate at which nuclei return from the upper to lower energy levels. Upon the application of a secondary field of a frequency suitable for resonance to occur, the change in the excess population will be 2nP, where P is the probability per unit time for a transition to occur. Therefore, equation 1.25 becomes:

$$\frac{dn}{dt} = \frac{n_{eq} - n}{T_1} - 2nP \qquad 1.26.$$

If the steady state value for the excess number of nuclei in the lower energy state is defined as n_s then its magnitude will be determined by equation 1.27.

$$\frac{n_s}{n_{eq}} = (1 + 2PT_1)^{-1} \qquad 1.27.$$

The parameter P may be defined for a transition between the states m and m', as[18]:

$$P_{m\to m'} = \tfrac{1}{2}\gamma^2 B_1^2 |(m|I|m')|^2 \delta(\nu_{mm'} - \nu) \qquad 1.28.$$

$(m|I|m')$ is the relevant element of the nuclear spin operator matrix, and $\delta(\nu_{mm'} - \nu)$ is the Dirac delta function, which is always zero unless $\nu_{mm'} = \nu$. Unfortunately, the use of this latter function predicts an infinitely narrow absorption, which is never observed, and must be replaced by a function $g(\nu)$ which predicts an absorption of finite width, and is given by:

$$\int_0^\infty g(\nu)d\nu = 1 \qquad 1.29.$$

For $I = \frac{1}{2}$, equation 1.28. may be reduced to:

$$P_{m\to m'} = \tfrac{1}{4}\gamma^2 B_1^2 g(\nu) \qquad 1.30$$

and hence:

$$\frac{n_s}{n_{eq}} = (1 + \tfrac{1}{2}\gamma^2 B_1^2 T_1 g(\nu))^{-1} \qquad 1.31.$$

The ratio n_s/n_{eq} is known as the saturation factor, Z, and its value is at a minimum, Z_o, i.e. maximum saturation, when the function $g(\nu)$ is maximum. Defining a second relaxation time T_2 as:

$$T_2 = \tfrac{1}{2}g(\nu) \qquad 1.32.$$

then

$$Z_o = (1 + \gamma^2 B_1^2 T_1 T_2)^{-1} \qquad 1.33.$$

Z_o will therefore be determined by the magnetogyric ratio, the strength of the oscillating field, and two relaxation times, one of which is related to the line shape; Z_o can never be zero.

1.7. General Comments On Relaxation Processes.

When the oscillating field, B_1, is of the correct frequency to induce nuclear transitions, the excess population of nuclei in the lower energy state decreases, and the rate

of absorption of energy is correspondingly decreased. However, there are processes which tend to restore the thermal distribution of energy levels, and combat the saturation effect. These processes are known as relaxation, and their nett effect is to remove excess energy from an excited spin state. There are two major types of relaxation process, spin-lattice relaxation and spin-spin relaxation, which are related to the parameters T_1 and T_2 respectively in equation 1.33.

1.7.1. Spin-Lattice Relaxation.

The distribution of nuclei between energy levels is determined by equation 1.20., and this is still applicable in the presence of an oscillating field because a rise in temperature occurs. The so-called spin temperature, T_s, is distinguishable from the temperature of the bulk medium (the lattice) because of the generally small interaction between nuclear spins and their environment. However, this small interaction does facilitate the equilibration of energy levels, because heat flow from nuclei to the lattice opposes the reduction of the excess population of the lower energy state.

The nature of the interaction between nuclei and the adjacent lattice is best understood in terms of the mechanical motions of molecules. Because all molecules have magnetic properties, the effect of molecular rotation, vibration and translation is to produce randomly fluctuating magnetic fields which will be experienced by other nuclei. Since these fluctuating fields are random a situation may arise in which the resultant frequency of fluctuation at an adjacent nucleus in any energy state is the same as the precessional frequency of that nucleus. Should such a situation arise a transition

may be induced, which in this case will cause a stimulated emission or absorption of energy, which is transferred to or from the surrounding lattice (in the form of heat). Obviously from a thermodynamic standpoint the probability of absorption is less than that for emission. This spin-lattice relaxation mechanism is also responsible for the initial process of equilibration of nuclei between energy states when a static magnetic field is applied to the system, and will be investigated in more detail in Section 2.B.

1.7.2. Spin-Spin Relaxation.

The relaxation processes which occur via the interaction of two adjacent precessing nuclei are effected by the mutual exchange of spins, rather than exchange of energy between the nucleus and the lattice. Each nucleus possessing a magnetic moment produces both static and oscillating fields, and if the latter is of such a frequency to induce a transition in a neighbouring nucleus, an exchange of spins may occur. Although the general environment of the nucleus in unimportant, only identical nuclei can exchange spins in this manner, and consequently the total spin energy remains constant. The time spent by individual nuclei in the upper or lower energy states is reduced by this mechanism, which obviously does not contribute to the excess number of nuclei in the lower state. The phase coherence between nuclei which are exchanging spins is characteristically lost in a time T_2, known as the spin-spin relaxation time.

The effects of spin-lattice and spin-spin relaxation mechanisms on resonance line widths are marked, and will be discussed further in Section 1.9., but it is important to note that in systems where molecular motion is considerably restricted, e.g. solids and viscous liquids, the time T_1

is usually much larger than T_2, and since line widths are proportional to the inverse of the time spent in the available states, these systems usually exhibit broad resonance lines, although other factors also contribute in these cases.

1.8. The N.M.R. Behaviour Of Macroscopic Samples.

The experimental observation of the n.m.r. phenomenon depends on the use of large assemblies of nuclei, in order to observe, with adequate sensitivity, the absorptions which occur. If a magnetic field is applied to such a macroscopic sample, the resultant of the nuclear magnetic moments will appear as a nuclear magnetisation, $\vec{M}_o$, described by equation 1.34.

$$\vec{M}_o = \chi_o B_o \qquad 1.34.$$

where χ_o is defined as the static magnetic susceptibility of the sample, and B_o is the strength of the static field. Obviously the preceding arguments concerning isolated nuclei cannot be applied in this case, and it is convenient to adopt the quantitative approach of Bloch[19-21] when considering the effect of an oscillating field on the nuclear magnetisation vector.

The important difference between $\vec{M}_o$ and $\vec{\mu}$ is that whilst the latter has components in all directions, when not undergoing resonance, $\vec{M}_o$ only possesses a component in the z direction, due to cancellation of the x and y components.

For a single nuclear magnetic moment:

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu}B_o \qquad 1.35.$$

and for an assembly of moments:

$$\frac{d\vec{M}}{dt} = \gamma\vec{M}B_o \qquad 1.36$$

In the resonance experiment, the oscillating field is applied at right angles to B_o, and the three components of the magnetic field are given in the x, y and z directions by (Figure 1.3.):

$$B_x = B_1 \cos\omega t$$

$$B_y = -B_1 \sin\omega t$$

$$B_z = B_o$$

Hence equation 1.36. may be resolved into three components when B_1 is applied:

$$\frac{d\vec{M}_x}{dt} = \gamma(\vec{M}_y B_o - \vec{M}_z B_y) = \gamma(\vec{M}_y B_o + \vec{M}_z B_1 \sin\omega t) \qquad 1.37.$$

$$\frac{d\vec{M}_y}{dt} = \gamma(-\vec{M}_x B_o + \vec{M}_z B_x) = \gamma(-\vec{M}_x B_o + \vec{M}_z B_1 \cos\omega t) \qquad 1.38.$$

$$\frac{d\vec{M}_z}{dt} = \gamma(\vec{M}_x B_y - \vec{M}_y B_x) = \gamma(-\vec{M}_x B_1 \sin\omega t - \vec{M}_y B_1 \cos\omega t) \qquad 1.39.$$

The result of the random phase distribution of the individual nuclear magnetic moments is to average M_x and M_y to zero if there is no oscillating field present, and $M_z = M_o$, the static magnetisation, because the system is in equilibrium.

However, if equilibrium or steady state conditions do not exist, for example after a resonance condition has been passed, then M_z approaches M_o exponentially according to equation 1.40.

$$\frac{d\vec{M}_z}{dt} = \frac{\vec{M}_o - \vec{M}_z}{T_1} \qquad 1.40.$$

Where T_1 is the longitudinal, or spin-lattice, relaxation time.

It is possible for M_x and M_y to differ from zero if a group of nuclear moments are precessing in phase, but if

the phase coherence is lost in a time T_2, the transverse, or spin-spin, relaxation time, the rates of approach of M_x and M_y to their equilibrium values may be assumed to be also exponential, and are given by:

$$d\vec{M}_x/dt = - \vec{M}_x/T_2 \qquad 1.41.$$

$$d\vec{M}_y/dt = - \vec{M}_y/T_2 \qquad 1.42.$$

These three equations describing relaxation processes are therefore effectual in modifying the basic rates of change of magnetisation in each of the three directions, and combination of equations 1.37. - 1.42. gives:

$$\frac{d\vec{M}_x}{dt} = \gamma(\vec{M}_y B_o + \vec{M}_z B_1 \sin\omega t) - \frac{\vec{M}_x}{T_2} \qquad 1.43.$$

$$\frac{d\vec{M}_y}{dt} = \gamma(\vec{M}_z B_1 \cos\omega t - \vec{M}_x B_o) - \frac{\vec{M}_y}{T_2} \qquad 1.44.$$

$$\frac{d\vec{M}_z}{dt} = \gamma(-\vec{M}_x B_1 \sin\omega t - \vec{M}_y B_1 \cos\omega t) + \frac{\vec{M}_o - \vec{M}_z}{T_1} \qquad 1.45.$$

which are the equations derived by Bloch, and describe the behaviour of a macroscopic sample during a magnetic resonance experiment (Figure 1.3.).

In order to simplify the solution of these equations they are referred to a set of axes which rotates about the z axis with the frequency of the field B_1, thereby fixing the values and direction of both B_o and B_1. The rotational frequency of the frame of reference is ω, and is varied such that resonance occurs when $\omega = \omega_o$. The component of M along the direction of B_1 is known as in-phase, and that perpendicular to B_1, is out-of-phase, and are denoted by the components u and v respectively (Figure 1.4.). The relationship between them is given by:

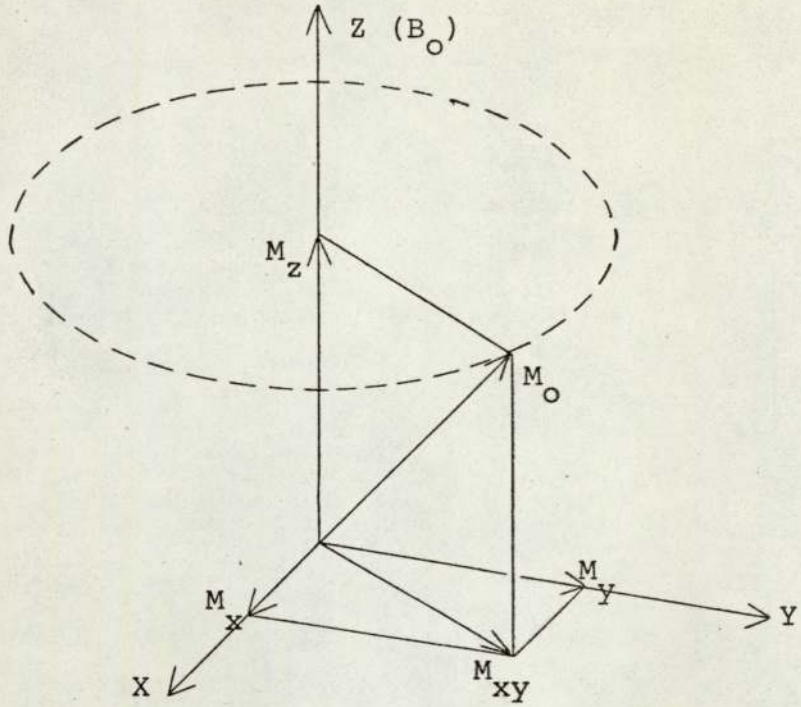


FIGURE 1.3. Resolved components of the magnetization vector.

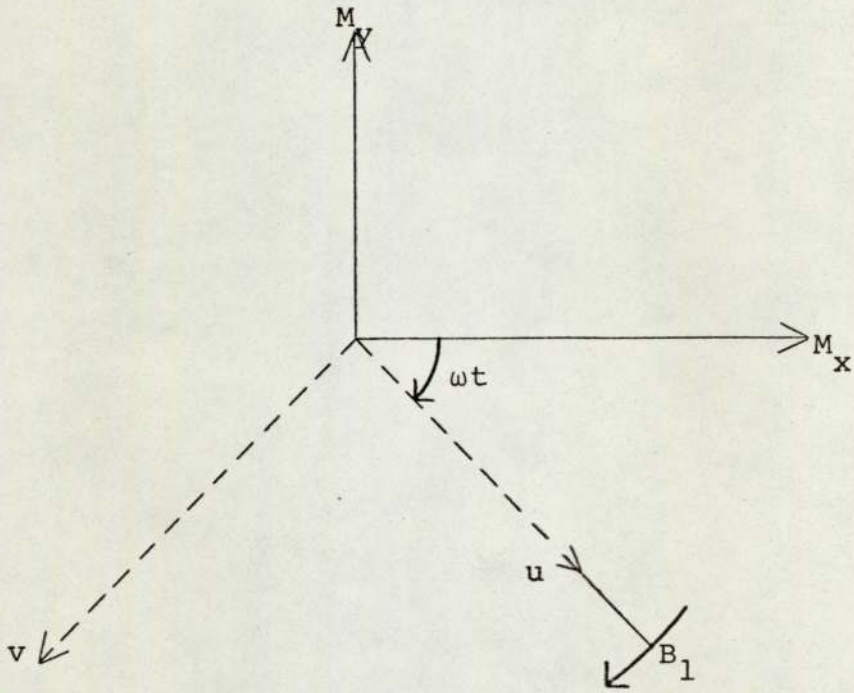


FIGURE 1.4. The transverse components of the magnetization vector with respect to fixed and rotating axes.

$$\vec{M}_x = u \cos \omega t - v \sin \omega t \qquad 1.46.$$

$$\vec{M}_y = - u \sin \omega t - v \cos \omega t \qquad 1.47.$$

These equations may be substituted into equations 1.43. - 1.45., and by consideration of equation 1.8:

$$\frac{du}{dt} + \frac{u}{T_2} + (\omega_o - \omega)v = 0 \qquad 1.48.$$

$$\frac{dv}{dt} + \frac{v}{T_2} - (\omega_o - \omega)u + \gamma B_1 \vec{M}_z = 0 \qquad 1.49.$$

$$\frac{d\vec{M}_z}{dt} + \frac{(\vec{M}_z - \vec{M}_o)}{T_1} - \gamma B_1 v = 0 \qquad 1.50.$$

Assuming a steady state condition at resonance, for which the rate of change of M_z must be zero, so that the absorption of radiofrequency energy is exactly balanced by the energy lost from the nuclei and transferred to the lattice, it is possible to solve equations 1.48. - 1.50. for u, v and M_z:

$$u = \vec{M}_o \gamma B_1 T_2^2 (\omega_o - \omega)/D \qquad 1.51.$$

$$v = \vec{M}_o \gamma B_1 T_2 / D \qquad 1.52.$$

$$\vec{M}_z = \vec{M}_o (1 - T_2^2 (\omega_o - \omega)^2)/D \qquad 1.53.$$

where $D = 1 + T_2^2(\omega_o - \omega)^2 + \gamma^2 B_1^2 T_1 T_2$

From these equations it may be shown that, if B_1 is of the order of 10^{-7} tesla, and T_1 and T_2 no greater than a few seconds, the v-mode (absorption) signal should be proportional to $\gamma B_1 T_2/(1 + T_2^2(\omega_o - \omega)^2)$, and describes a Lorentzian line shape[19,22] (Figure 1.5.). When $\omega = \omega_o$ the signal is at its maximum, and proportional to $\gamma B_1 T_2$. The u-mode, or dispersion signal (Figure 1.5.) is only used infrequently, although it is especially useful in certain circumstances.

The absorption line spectrum may be integrated over all

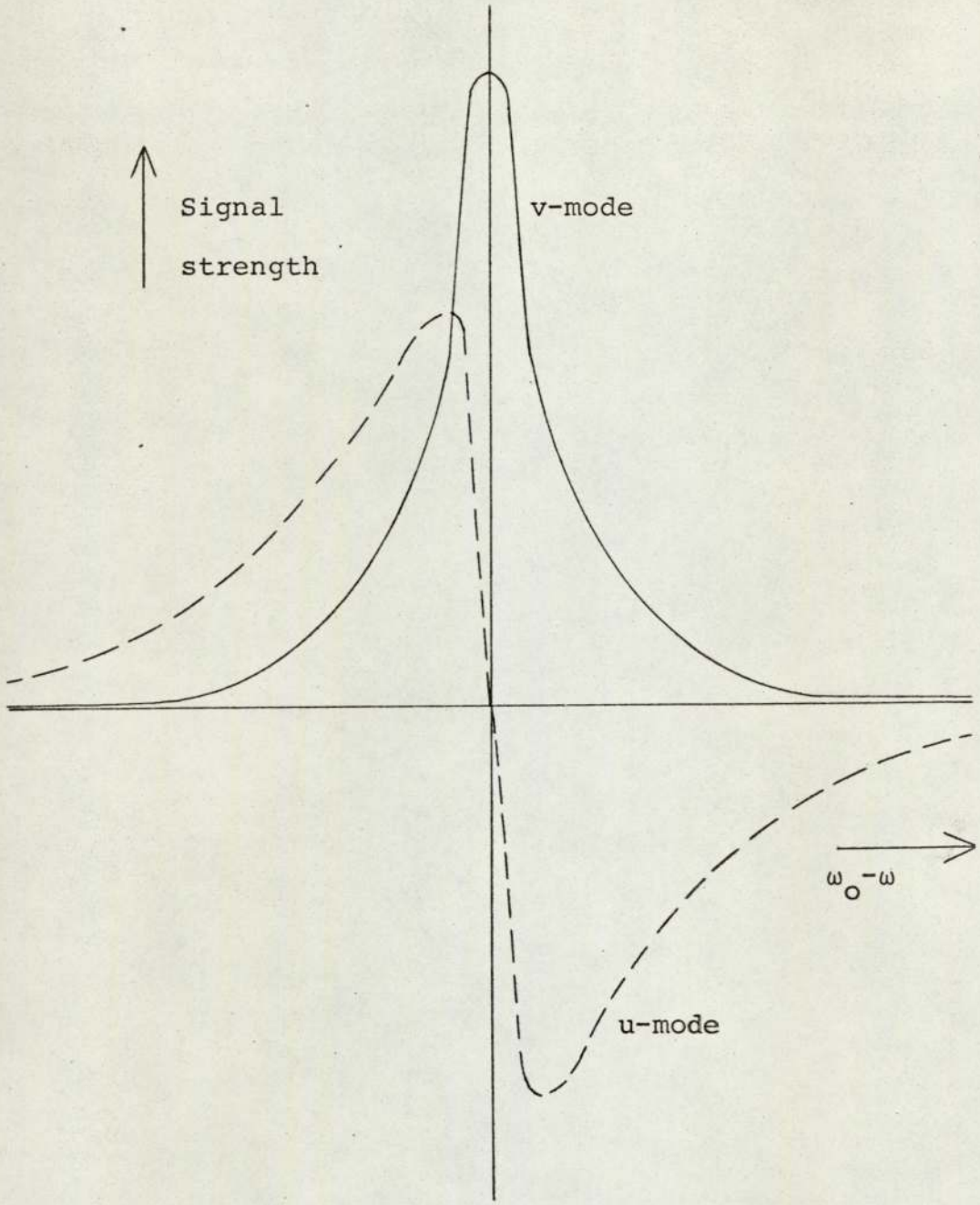


FIGURE 1.5. The absorption (v-mode) and dispersion (u-mode) line shapes for nuclear magnetic resonance absorptions.

values of $(\omega_o - \omega)$, resulting in signals proportional to χ_o, which, described by equation 1.34., is a function of the number of nuclei per unit volume. The area under each absorption line is, therefore, proportional to the number of nuclei of each type undergoing resonance; the n.m.r. technique is therefore quantitative.

1.9. The Factors Affecting Line Widths.

An absorption line exhibited by nuclei undergoing resonance may be represented approximately by a Lorentzian curve[19,22], and the simple quantum mechanical approach shows that this line should be infinitely narrow. However, as indicated by the inclusion of $g(\nu)$ the line does have a finite width due to several effects. The width of an absorption line is defined as its width at half height expressed in terms of either the applied field or frequency. The two main factors determining the line width are the relaxation times T_1 and T_2, and these will now be discussed, along with the other major contributing effects.

1.9.1. Spin-Lattice Relaxation.

The mechanism of spin-lattice relaxation places a restriction on the life-time of a nucleus in a given spin state, and hence there is some degree of uncertainty in the time which lapses before the nucleus changes its energy state. Heisenberg's Uncertainty Principle requires that

$$\Delta E \, \Delta t = \hbar \qquad 1.54.$$

and since

$$\Delta E = h\Delta\nu \qquad 1.55.$$

it is evident that

$$\Delta\nu = 1/2\pi\Delta T \qquad 1.56.$$

From the theory of spin-lattice relaxation $\Delta T = 2T_1$ (Section 2.B), and thus

$$\Delta\nu = 1/4\pi T_1 \qquad 1.57.$$

which defines the uncertainty in the frequency of a given absorption line, and shows that small values for T_1 will give rise to broad lines.

1.9.2. Spin-Spin Relaxation.

The effect of spin-spin relaxation on line widths is analagous to the effects described in the preceding section, since its mechanism places some uncertainty on the lifetime of a particular nuclear spin state, and a corresponding uncertainty in the frequency at which resonance will occur.

1.9.3. The Effects Of Paramagnetic Species.

The effects of electronic paramagnetism, occurring in some compounds of transition metals, but also simpler molecules such as oxygen are often very large compared with the magnitude of those of nuclear magnetic moments and magnetic resonance is often undetectable in these samples. Unpaired electrons may give rise to large magnetic fields at the nucleus, which modulate the static field, B_o, to varying extents depending on the rotational, vibrational and translational position of the molecule. The main effect is the provision of more efficient spin-lattice relaxation mechanisms, and consequent reduction of the magnitude of T_1. The result is a very large broadening of the line, which may therefore be of a sufficiently low level to remain undetected, although it is possible to observe the spectra of very dilute solutions of paramagnetic species[23].

1.9.4. Magnetic Dipole Interaction.

The effect of a magnetic dipole on the width of an absorption line is analagous to the magnetic effect produced by unpaired electrons, but is much smaller. Magnetic moments

of neighbouring nuclei may modify the magnetic fields at a particular nucleus, the rotating components resulting in spin-spin relaxation broadening, and the static component in the B_o direction in magnetic dipole broadening.

The latter component, resulting from the effect of a nucleus a distance r from the nucleus under consideration, and lying on a line inclined at an angle θ to the axis of the magnetic field B_o, is given by:

$$B_{static} = -\mu(1 - 3\cos^2\theta)/r^3 \qquad 1.58.$$

Where random motion is possible, $3\cos^2\theta = 1$, and no nett field is produced; thus for gases and liquids the effect is negligible. In a solid sample, however, the local field may have a value ranging between $+ 2\mu/r^3$ and $- \mu/r^3$, and results in resonance occuring over a range of field values, so hν will not be well defined.

Experiments have been performed on solid samples under conditions where the term $3\cos^2\theta$ is artificially averaged to unity by either spinning the sample rapidly at an angle of $54^o\ 44'$[24], or pulsing B_1, in three perpendicular directions in turn such that the average magnetisation vector is at the same angle[25]. A combination of these two procedures may result in high resolution spectra being obtained from a solid material.

1.9.5. Quadrupole Effects.

Some nuclei may possess quadrupole moments arising from a non-spherical distribution of nuclear charge, and the phenomenon is evident in all nuclei of spin greater than ½. Quadrupoles may precess in the presence of an electric field gradient, and the nuclear energy levels are displaced. The effect of this interaction is to provide an additional spin-

lattice relaxation mechanism, which, as described previously, affects the line width by virtue of the reduction of T_1.

1.9.6. Magnetic Field Inhomogeneity.

If the strength of the static magnetic field is not constant over the whole volume of the sample, it is evident that resonance may occur over a range of frequencies, corresponding to the variation in B_o. The problem may be partially resolved by spinning the sample rapidly enough to average out the field inhomogeneity experienced by the nuclei.

1.9.7. Other Factors Affecting Line Shapes.

The other major reasons for deformation of an absorption line are saturation, which has been described previously, and a relaxation phenomenon resulting in 'ringing'. The effect of saturation is to decrease the excess number of nuclei in the lower energy state, which is characterised by the saturation factor Z_o described by equation 1.30.,but this applies specifically to the band centre, but saturation may also occur at the band edges where the effect will be less, and line broadening may occur.

The 'ringing' effects arise from sweeping quickly through a resonance line[26], and arise from the inability of the nuclear magnetisation to follow variations in the frequency of the applied oscillating field. After the resonance line has been passed there may be a difference between the frequencies of precession and B_1, which therefore gives rise to low frequency intermodulation signals[27] whose amplitude decays at a rate proportional to T_2 enabling measurement of T_2. The presence of extensive ringing is usually indicative of good magnetic field homogeneity and long spin-spin relaxation times in liquids.

It has been shown[15] that the effect of spontaneous emmission on the life-time of higher energy levels, and consequently line-widths, is negligible.

1.10. Some General Comments On Chemical Shifts.

The actual value of the magnetic field experienced by nuclei is not always equal to B_o because of the small fields originating from inter - and intramolecular interactions, which affect the magnetic characteristics of electrons or groups of electrons in the molecule. If the static field is altered by a factor σ, the screening constant, the actual field which a nucleus experiences will be:

$$B_{local} = B_o(1 - \sigma) \qquad 1.59.$$

Since σ is usually positive, B_o is effectively reduced, and the splitting of nuclear energy levels is less. A higher static field must therefore be applied to cause resonance at a given frequency. Differences in values of σ for different nuclei of the same isotope will result in the observation of more than one resonance line for that isotope. The difference in the resonance condition for the two lines is characterised by the chemical environments of the nuclei, and is hence designated the chemical shift, δ[28]. Consequently, for two isotopically identical nuclei in environments i and j, having screening constants σ_i and σ_j respectively, the chemical shift is given by:

$$\delta_{ij} = \sigma_i - \sigma_j \qquad 1.60.$$

It is difficult to measure field strength accurately, and since it is virtually impossible to measure the resonance line for a nucleus devoid of all electrons, the absolute value of chemical shifts may not be obtained. Therefore chemical shifts are measured in frequency terms relative to

a reference compound which has a sharp, well defined absorption line. The reference compound used most commonly for proton spectra is tetramethyl silane (T.M.S.), although any resonance which can be measured accurately is usable.

The dimensionless quantity δ may then be defined for practical purposes as:

$$\delta = \frac{B - B_r}{B_r} \times 10^6 \text{ p.p.m.} \qquad 1.61.$$

where B is the field at resonance for the nucleus under investigation and B_r is that for the reference. Since B is proportional to frequency, there is a corresponding equation:

$$\delta = \frac{-(\nu - \nu_r) \times 10^6}{\text{Oscillator frequency}} \text{ p.p.m.} \qquad 1.62.$$

where ν and ν_r are analagous to B and B_r in equation 1.61.

When T.M.S. is employed as a reference compound negative values for δ usually result, since its resonance occurs at higher field strength than most other proton absorptions because the nuclei are more shielded. δ values are therefore more often quoted on the τ scale[29] which is defined as:

$$\tau = 10 + \delta \qquad 1.63.$$

On this scale most proton resonances have positive τ values, and the scale is defined by designating a value of $\tau = 10$ to the resonance of T.M.S., infinitely dilute in carbon tetrachloride.

Many of the investigations reported in this thesis depend on the measurement and analysis of chemical shifts, and a further discussion of the origin of screening constants, and their importance, is given in Chapter 2.

1.11. Spin-Spin Coupling.

The use of modern high resolution n.m.r. spectrometers makes it relatively easy to produce very sharp absorption lines, and under these conditions it is found frequently that chemically shifted absorptions are themselves composed of several lines, generally known as multiplets[30], and that such splitting arises when a molecule contains two or more nuclei in chemically different environments[12,31]. The magnitude of the splitting is found to be independent of the static field applied[32], and is quoted in Hz. The characteristic parameter of this splitting is the coupling constant, J, and is usually only a few Hz in magnitude for protons.

The origin of spin-spin coupling is attributable to interaction between the nuclear moments within a molecule, and it has been proposed[33,34] that the multiplets arise from interaction between closely associated nuclear spins. If I_1 and I_2 are nuclear spin vectors then the interaction between them is proportional to their scalar product, and does not average to zero. Ramsey and Purcell[35] suggested that the interaction may occur indirectly through the electrons of the molecule, since a nuclear spin will tend to orient adjacent electrons, the orientation being transferred via other electrons to another nuclear spin, and although their mathematical approach is almost insoluble, it shows that this mechanism is important, but does not rule out other types of magnetic interaction[36]. These other types of magnetic interaction include; electron-orbital, orbital-spin, spin-spin and spin-external field interactions which may become more important in certain circumstances. If δ is of the same order as J, spectra are designated as second

order, whilst, if $\delta >> J$, first order spectra are found. The difference between first and second order spectra will be discussed below.

First order spectra are characterised by equal line spacings and regular line intensities, whilst second order spectra are characterised by irregular line spacings and intensities.

It is convenient for the purpose of spectral analysis to identify individual types of nuclei by letters i.e. A,B,C....L,M,N....X,Y,Z. Nuclei with the same chemical shifts, and which are coupled equally to other resonant nuclei in the molecule, are deemed magnetically equivalent and denoted by the same letter, but nuclei which are only chemically equivalent and have unequal couplings are differentiated by primes. If $\delta \sim J$ non-equivalent nuclei are given adjacent letters, but if $\delta >> J$ the nuclei are denoted by letters which are far apart alphabetically. For example, resonance lines for acetaldehyde are subject to the condition $\delta >> J$, and is designated an AX_3 system, whilst a para-substituted benzene, including two different substituents, is labelled AA'BB', and gives rise to a symmetrical but second order spectrum.

If an absorption line A is due to n_A equivalent nuclei (in one molecule), and a line X due to n_X equivalent nuclei, a first order coupling treatment states that A is split into $(2n_X I_X + 1)$ equally spaced lines and X is split into $(2n_A I_A + 1)$ lines. This mutual effect requires that the splitting of both absorptions is equal in magnitude although the number of lines in each multiplet may be different, depending on the number of nuclei to which the resonant nucleus or group of nuclei is coupled. The intensities of

the peaks of the multiplet are given by the coefficients of a polynomial of degree depending upon I, and for $I = \frac{1}{2}$ are given by 1, n, n(n - 1)/2!, n(n - 1)(n - 2)/3! etc., where n is the number of nuclei causing the splitting.

The relative intensities of the peaks within a multiplet are more easily explained by a consideration of a nucleus of spin ½, with spin states $m = \pm\frac{1}{2}$, or α and β. If this nucleus is in a chemical group containing three of its type, such as a methyl group, the following total spin states are possible:

	ααα	ααβ	αββ	βββ
		αβα	βαβ	
		βαα	ββα	
Total spin	$+ 3/_2$	$+ \frac{1}{2}$	$- \frac{1}{2}$	$- 3/_2$

A neighbouring nucleus will 'see' four different total spin states, corresponding to four different intramolecular magnetic interactions, and its resonance line will split accordingly into four. However, since the probabilities of the $\pm\frac{1}{2}$ states occuring are three times those of the $\pm\ 3/_2$ states the relative intensities of the appropriate line will be 1:3:3:1.

Second order spectra generally exhibit irregular line spacings and intensities, and are generally more complex due to changes in nuclear energy levels, and often cannot be analysed unambiguously without the aid of a computer program.

1.12. Chemical Exchange Phenomena.

Chemical exchange processes affect n.m.r. spectra, and these have been studied widely in recent years in order to investigate molecular interactions. The types of inter-

actions studied have included charge-transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole; the latter type, occurring between polar solutes and aromatic solvents, form the major point of interest in this thesis.

If a resonant nucleus is able to exist in two distinct environments, and can exchange readily between the two, (e.g. the acidic protons of an organic acid may exchange with those of a solvent containing hydrogen atoms), then the lifetimes of the states I and II, τ_I and τ_{II} respectively, will dictate the appearance of the spectrum. If δ_I and δ_{II} are the shifts (in H_z) of the resonant nucleus in each of the two states, then if τ_I and τ_{II} are long compared with $2\pi(\delta_I-\delta_{II})$ two lines will be observed. Alternatively if τ_I and τ_{II} are short compared with $2\pi(\delta_I-\delta_{II})$ a single absorption will be seen. Intermediate times will give rise to broad or slightly split absorptions, and in some cases changing the temperature of the sample can change a single line into a well-resolved doublet.

When τ_I and τ_{II} are both short the time averaged shift (δ_{obs}) may be exactly defined by equation 1.64.[37]

$$\delta_{obs} = P_I\delta_I + P_{II}\delta_{II} \qquad 1.64.$$

where P_I and P_{II} are described by equations 1.65. and 1.66. respectively,

$$P_I = \tau_I/(\tau_I + \tau_{II}) \qquad 1.65.$$

$$P_{II} = \tau_{II}/(\tau_I + \tau_{II}) \qquad 1.66.$$

and are the fractions of time spent by the resonant nucleus in the states I and II. Equation 1.64 may also be used in this general form to describe relaxation processes occurring at sites I and II under conditions of chemical exchange. Homer and Cooke[38,39] have shown that equation 1.64. must be

modified in circumstances where magnetically and chemically equivalent sites are involved.

The principal concern in this thesis is the investigation of 1:1 molecular complexes of the type

$$A + B \rightleftharpoons A \ldots\ldots B \qquad 1.67.$$

occurring in a solvent, S, which is supposedly inert. It is necessary in these studies to measure the chemical shift of the species A, δ_A, which is a bulk magnetic parameter. A is regarded as a solute, against thermodynamic convention, whilst the species B and S are both regarded as solvents. The solute A, is present in mixtures of A, B and S in two distinct states, namely an uncomplexed or 'free' state, and a complexed state with the aromatic, B. τ_I and τ_{II} are very much shorter than $2\pi(\delta_I - \delta_{II})$ for this type of reaction, and therefore a single absorption line is seen. The reaction is studied by measuring the change in the shift associated with small fixed quantities of A, when the concentrations of B and S are varied. Equation 1.64. is usually interpreted such that the time fractions P are represented by population functions, and thus the equivalent of equation 1.64. in terms of A, B and AB is:

$$\delta_{obs} = \frac{n_{AB}}{n_A}.\delta_c + \frac{n_A - n_{AB}}{n_A}.\delta_{free} \qquad 1.68.$$

or

$$\Delta_{obs} = \frac{n_{AB}}{n_A}.\Delta_c \qquad 1.69.$$

where δ_{free} is the shift of uncomplexed A, δ_c is the theoretical shift of A in the complex, n_A is the total number of moles of A and n_{AB}, the total number of moles of complex, AB, formed at equilibrium. Δ_c and Δ_{obs} are defined as:

$$\Delta_c = \delta_c - \delta_{free} \qquad 1.70.$$

$$\Delta_{obs} = \delta_{obs} - \delta_{free} \qquad 1.71.$$

For the well documented reaction between chloroform, A, and benzene, B, in cyclohexane, S,[40-44] the upfield shift of the chloroform proton, measured relative to cyclohexane, decreases as the ratio of the concentrations of B to S decrease. Although the variation is not linear it is possible to calculate parameters describing the equilibrium from this variation. The reasons for the chemical shift variation of the solute, A, will be described in Chapter 2, the increased screening resulting from the formation of a π - complex via a dipole-induced dipole mechanism.

Δ_c, which describes the shielding of the solute proton(s) in the complex, has been supposed to be characteristic of the complex formed, and may be determined if the ratio n_{AB}/n_A is known, and can then be used, as described in section 4.1.1., to calculate the geometry of the complex. Since the parameter n_{AB}/n_A is not measurable, because of the transient nature of the complex, except by using a different approach[38,39] to the problem, Δ_c and the equilibrium quotient (i.e. the expression for the equilibrium constant for the reaction devoid of activity coefficients which is given by $K = [A]\ [B]/[AB]$ on the mole fraction, molar and molal concentration scales) are determined by a number of different processes,[45-48] of which only two are of interest here, since it has been shown[49] that others give either inferior results to, or are no more accurate than these two. These two methods are due to Creswell and Allred,[46] and Benesi and Hildebrand[45] which utilise iterative and extrapolation data processing

procedures respectively. The use of these two procedures should give rise to the values for Δ_c and the equilibrium quotients which are independent of the concentration scale, but this is found not to be so[47,50-52]. A further apparent anomaly is that Δ_c and the equilibrium quotients appear to vary for the same reaction occurring in different solvents.

The two methods will first be proposed in their basic commonly used, forms, and subsequently, by reference to thermodynamic conditions, it will be shown how they may be modified to enable parameters devoid of the above anomalies to be obtained. Moreover, it will be shown how they may be used to obtain meaningful values for Δ_c and the equilibrium quotients.

1.13. The Creswell-Allred Procedure.

The data processing method, due originally to Creswell and Allred[46], depends on the ability to construct an expression for the ratio n_{AB}/n_A, and for the equilibrium quotients, in which all terms are known. It must not, therefore, contain activity coefficients. The equilibrium quotients on the mole fraction, molarity and molality concentration scales are given by equations 1.72., 1.73. and 1.74. respectively:

$$K_x = \frac{x_{AB_{eq}}}{x_{A_{eq}} x_{B_{eq}}}$$

$$= n_{AB} \frac{(n_A + n_B + n_s - n_{AB})}{(n_A - n_{AB})(n_B - n_{AB})} \qquad 1.72.$$

where n_i is the number of moles of species i,

$$K_c = \frac{c_{AB_{eq}}}{c_{A_{eq}} c_{B_{eq}}}$$

$$= n_{AB} \frac{(n_A - n_{AB})V_A + (n_B - n_{AB})V_B + n_S V_S + n_{AB} V_{AB}}{(n_A - n_{AB})(n_B - n_{AB})} \qquad 1.73$$

where V_j is the partial molar volume of species j,

$$K_m = \frac{m_{AB_{eq}}}{m_{A_{eq}} m_{B_{eq}}}$$

$$= n_{AB} \frac{W_S}{(n_A - n_{AB})(n_B - n_{AB})} \qquad 1.74.$$

where W_S is the mass of the solvent in kg.

These expressions for the equilibrium quotients applicable to reactions of the type described by equation 1.67., are substituted into the equation describing the fast exchange processes (1.68.), a combination of equations 1.68. and 1.72. giving:

$$\delta_{obs} = \Delta_c \left[\frac{K_x n_B + K_x n_A + n_S \pm \sqrt{((K_x n_B + K_x n_A + n_S)^2 - 4K_x n_A n_B)}}{2K_x n_A} \right] + \delta_{free} \qquad 1.75.$$

Similar equations may be derived in terms of K_c and K_m. Equation 1.68. shows that a plot of δ_{obs} against n_{AB}/n_A should be a straight line, and thus if values for n_{AB}/n_A are calculated for selected values of K_x it has been assumed that a reasonable value of K_x is obtained when the plot is linear. A computer program is used, which has been devised in this laboratory, to facilitate the calculations[53].

1.14. The Benesi-Hildebrand Procedure.

The Benesi-Hildebrand[45] method was originally conceived for processing data obtained from ultra-violet spectroscopic studies, but it may readily be extended for use with other techniques, including n.m.r. Its use depends, as does also the Creswell-Allred procedure, on the ability to deduce expressions for K_x, K_c and K_m, which are independent of the concentration of B over an experimentally viable range of composition, which means that the initial concentration of A must be very much smaller than that of B. Under this latter condition, equations 1.72., 1.73. and 1.74. become:

$$K_x \simeq \frac{n_{AB}\ (n_B + n_S)}{(n_A - n_{AB})n_B} \qquad 1.76.$$

$$K_c \simeq \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB})n_B} = \frac{n_{AB}\ V}{(n_A - n_{AB})n_B} \qquad 1.77.$$

$$= \frac{n_{AB}}{(n_A - n_{AB})c_B}$$

where V is the mean molar volume of the solution.

and $$K_m \simeq \frac{n_{AB}W_S}{(n_A - n_{AB})n_B} = \frac{n_{AB}}{(n_A - n_{AB})m_B} \qquad 1.78.$$

It follows from equations 1.76., 1.77. and 1.78 that the equalities

$$K_x = \frac{K_c}{V} = \frac{K_m}{W_S} \qquad 1.79.$$

should apply.

The use of the method depends on equation 1.69., so that a knowledge of δ_{free} is required, unlike in the case of the Creswell-Allred procedure. It follows from this equation that:

$$\frac{1}{\Delta_{obs}} = \frac{(n_B + n_S)}{n_B K_x \Delta_c} + \frac{1}{\Delta_c} \qquad 1.80.$$

$$\frac{1}{\Delta_{obs}} = \frac{V}{n_B K_c \Delta_c} + \frac{1}{\Delta_c} \qquad 1.81.$$

and

$$\frac{1}{\Delta_{obs}} = \frac{W_S}{n_B K_m \Delta_c} + \frac{1}{\Delta_c} \qquad 1.82.$$

which are the n.m.r. analogues of the original Benesi-Hildebrand equation. If the equilibrium quotients are independent of the concentration of B on any of the three scales then a plot of $1/\Delta_{obs}$ against $1/x_B$, $1/c_B$ or $1/m_B$ should be a straight line from which values for Δ_c and K_x, K_c or K_m can be obtained.

1.15. Investigations To Be Carried Out In This Thesis.

The chemical exchange processes described in the previous sections may be used to investigate many facets of molecular interactions in liquids by employing analytical methods such as the Creswell-Allred and Benesi-Hildebrand procedures. Of particular interest in this thesis are the dipole-induced dipole reactions which result in the formation of transient molecular complexes between polar solutes and aromatic molecules. The nature and mechanism of their formation is of specific interest. Recent work[40,41,49], on reactions of this type, using the model system of chloroform + benzene, dissolved in several supposedly inert solvents, has indicated how parameters accurately describing the interaction may be obtained. The initial investigations here will be directed towards the validation of these suggestions. Attempts will be made to resolve difficulties concerning the effects of solvents (S) and internal references in this type of approach.

The mechanism of formation of the type of complex mentioned above is a subject of special interest, and the considerable amount of chemical shift data which has been accumulated in this laboratory will be used to develop a theory for complex formation in terms of a short-range, ordered, cage model. The results of the investigation have suggested that more precise information concerning this mechanism may be obtained by the study of spin-lattice relaxation times, and the use of these will be investigated. Special attention will be paid to the initial problems of sample preparation and evaluation of the data obtained in terms of complex formation, in order to enable more elegant experiments to be carried out in the future.

CHAPTER 2.

SOME COMMENTS ON THE ORIGIN OF CHEMICAL SHIFTS AND SPIN-LATTICE RELAXATION PROCESSESS.

In the previous chapter some general comments were made concerning the chemical shifts, and screening constants, and also spin-lattice relaxation times, and the mechanisms by which relaxation could occur. Since the investigations reported in this thesis are based on the measurement of chemical shifts and spin-lattice relaxation times, the purpose of this chapter is to attempt to define clearly the origins of and contributions to both parameters.

2.A. The Chemical Shift.

2.A.1. Introduction.

Since the chemical shift, δ, of a particular group of resonant nuclei is determined by the chemical environment of the group, it is evident that the screening (or shielding) constant is also determined by the chemical environment. Screening contributions can conveniently be subdivided into individual contributions due to the different effects experienced at the resonant nuclei.

The chemical shift, like some other physical parameters, may be expressed in the form of a virial expansion. It is readily shown that, in the gas phase, the chemical shift is proportional to the density of the sample, a plot of shift against density being linear in nature. It is thus apparent that only two terms of the virial expansion are of importance, and that equation 2.1. applies:

$$\delta = (\sigma_o - \sigma_R) + \sigma_1/V_m \qquad 2.1.$$

where σ_o and σ_1 are the first and second virial screening

coefficients, σ_R the screening constant of the reference, and V_m the molar volume of the sample. The two important terms in the virial expression are due to intra - and intermolecular effects respectively. Thus the total screening of a nucleus A, σ^A, is given by equation 2.2.

$$\sigma^A = \sigma^A_{intra} + \sigma^A_{inter} \qquad 2.2.$$

It is found that equations 2.1. and 2.2. may also be extended to the liquid phase, and, therefore, any difference or change in the values of the contributions will effectively change the chemical shift of a nucleus with respect to a given reference. The contributions due to intermolecular effects are the most important in the context of this thesis, and these will be treated in greater detail than the intramolecular effects. It should be noted, however, that the calculation of all screening contributions is difficult at present.

2.A.2. Intramolecular Effects.

Several attempts have been made to calculate the screening constant of a nucleus in a molecule.[54-56] The approach of Ramsey[55,56] has been most useful, for whilst the calculation of σ is not practicable, generally because a knowledge of the wavefunctions of excited states are required, it has been possible to interpret the contributions to intramolecular screening in classical terms. Ramsey's theory requires that a positive contribution to the screening arises from a diamagnetic term, and a negative contribution from a paramagnetic term. Saika and Slichter[57], however, proposed that the total intramolecular screening should be divided into three parts, due to the paramagnetic and

diamagnetic contributions proposed by Ramsey, and also a contribution arising from the effects of electrons in other atoms. It is more convenient, however, to propose four contributions; described for a nucleus A by:

$$\sigma^{A}_{intra} = \sigma^{AA}_{dia} + \sigma^{AA}_{para} + \sum_{A \neq B} \sigma_{AB} + \sigma_{deloc} \qquad 2.3.$$

The terms in equation 2.3. will now be discussed.

2.A.2.1. The Diamagnetic Term.

When an atom having a spherically symmetric electron distribution is placed in a magnetic field, currents of electrons are induced which are diamagnetic in nature. The screening term σ^{AA}_{dia} is therefore proportional to the strength of the applied field, and is produced at the nucleus by the moment induced by electron motion. The value of σ^{AA}_{dia} will depend on the electron density around the nucleus, and hence upon the electronegativity of atom A, and other groups attached to it.

2.A.2.2. The Paramagnetic Term.

Paramagnetic screening contributions, σ^{AA}_{para}, arise when the electron distribution around the nucleus is not spherically symmetric, and will be non-zero if electrons are not confined around the nucleus in a pure s - orbital[58]. If it is non-zero σ^{AA}_{para} may be considered to arise from an induced mixing of ground and excited electronic states by the applied field[59,60], but since the energies and wave-functions of these states are not generally known, the term proves difficult to calculate.

In physical terms σ^{AA}_{para} may be thought of as an anisotropic modulation of the static magnetic field, B_o, whilst the hindrance characterised by σ^{AA}_{dia} is isotropic.

2.A.2.3. Interatomic Shielding.

The interatomic shielding term $\Sigma_{A\neq B}\sigma_{AB}$ may be thought to arise from the neighbour anisotropy effect[61]. The effect of a static magnetic field on a molecule containing two groups with effectively different magnetic susceptibilities is to induce a magnetic dipole along their principal axis, which produces secondary magnetic fields at neighbouring nuclei. This secondary field is the origin of the interatomic term. The magnitude of the effect is only dependent on the nature of the atom or group causing the secondary field, and the distance between the point dipole and the nucleus, r, allowances being made for the angle, θ, between the directions of r and the magnetic dipole. Using the McConnell equation[61], which applies to axially symmetric groups only, calculations can readily be made:

$$\sigma_{AB} = (\chi_{11} - \chi_{1})(1 - 3\cos^2\theta)/3r^3 \qquad 2.4.$$

where χ_{11} and χ_{1} are the parallel and perpendicular components respectively of the magnetic susceptibility of the bond between the two atoms or groups defining the magnetic dipole.

2.A.2.4. Delocalised Electron Shielding.

The screening term σ_{deloc} arises from the contribution due to the movement of electrons in a conjugated molecule. Secondary fields are induced by these which may add or subtract from the applied magnetic field effective at a nucleus. A closed loop of delocalised electrons, for example, as in aromatic molecules, will be induced to circulate, giving rise to a current and hence to a magnetic field. Nuclei lying in the plane of the circulating electrons will be deshielded relative to those lying on its symmetry axis.

The effect of these intramolecular contributions to nuclear screening is to produce spectra which contain information concerning the nature of the environment of a particular resonant nucleus in a molecule. The importance of the terms varies between molecules, and also between different types of nuclei. For ^{19}F chemical shifts the most significant contribution is thought to be due to the electric fields produced by the highly polar bonds,[62] which contribute to σ_{dia}^{AA} and σ_{para}^{AA}, whilst ^{1}H chemical shifts are thought to be influenced largely by differences in bond anisotropy, and its effect on the term $\Sigma_{A\neq B}\sigma_{AB}$.

Variations in intramolecular contribution to the screening constant are dependent on changes in both electric and magnetic fields, and the intermolecular, or solvent, effects may be considered as perturbations on these fields. These effects will now be considered in detail.

2.A.3. Intermolecular Effects.

The screening term σ_{inter} arises from the direct or indirect effects of solvents or other molecules on the molecule containing the nucleus being studied. In a similar fashion to the σ_{intra} term, σ_{inter}, the total screening of a solute nucleus due to surrounding molecules, may be considered to arise from several different intermolecular effects[63], and may be written:

$$\sigma_{inter} = \sigma_b + \sigma_a + \sigma_w + \sigma_E + \sigma_S \qquad 2.5.$$

In equation 2.5. σ_b is a contribution which is proportional to the volume magnetic susceptibility of the bulk medium, σ_a is due to anisotropic effects occurring in the susceptibility of solvent molecules, σ_w takes in to account van der Waals interactions between solute and solvent

molecules, whilst σ_E allows for the effect of a reaction field of the solvent which is induced by polar solutes. σ_S refers to the screening contribution arising from specific interactions occurring in the sample, between the solute and the solvent, or other solute molecules.

Because the purpose of the investigations reported in this thesis is to examine this last type of contribution, the effect of the term σ_S will be examined in greater depth in Chapter 4.

There are two widely used methods for providing reference nuclei, firstly by dissolving the reference material in the liquid or solution under investigation (internal reference), or by inserting a sealed capillary tube containing the reference compound into the main sample tube (external reference). Differences in the terms of equation 2.5. may be significant for nuclei in different environments, and the external reference procedure must consequently be used with care. The use of referencing techniques will be further discussed in Chapter 6 with respect to the elimination of solvent effects.

The importance of intermolecular contributions to the screening of a nucleus is underlined when considering the chemical shift of a nucleus relative to a convenient reference. Medium effects can affect both solute and reference equally if they are in dilute solution, but if they are affected differently a correction is necessary in order to provide solvent independent values for shifts.

Some of the investigations reported here concern the measurement of changes in the chemical shift of the solute, A, which is equivalent to measuring differences in

intermolecular screening constants (i.e. $\Delta\sigma^{A}_{inter}$).

Whilst numerous theories have been proposed by other workers to enable the evaluation of the individual contributions to intermolecular screening, the separation of these contributions poses some problems. σ_b[64,65] may be evaluated reasonably accurately, but σ_w may only be obtained from the use of isotropic solvents. For anisotropic polar and non-polar solvents the contributions $\sigma_a + \sigma_w + \sigma_E$ and $\sigma_a + \sigma_w$ respectively may be obtained. Although numerical expressions have been derived to enable separation of these terms, the inclusion in them of shape and scaling factors must cast some suspicion on their accuracy, but these are necessary in order to account for molecular motion. It is unfortunate, therefore, that some directional molecular interactions have the effect of reducing the randomness of the system, and invalidate these expressions. Some doubt is therefore thrown upon the validity of equation 2.5.

Recently, however, a procedure has been developed by Weiner and Malinowski[66-69] which shows that equation 2.5. is correct, and also enables accurate separation of these contributions. Their method is based on a factor analysis of chemical shifts, in which the gas phase shift of a solute, $\delta_g(i)$, is a factor and permits isolation of σ_w from σ_a. For a solute, i, and solvent, α, the chemical shift, $\delta(i,\alpha)$, is given by:

$$\delta(i,\alpha) = \delta_g(i) + \sigma_b(\alpha) + \sigma_a(\alpha) + \sigma_w(i,\alpha) + \sigma_E(i,\alpha) + \sigma_S(i,\alpha) \qquad 2.6.$$

where the terms have their previously defined significance. The equation is similar to that proposed by Buckingham et al[63], except that here allowance is made for specific

interactions, and analysis of the shifts enables each term to be evaluated. For polar solutes the σ_E contribution is treated as an effective dielectric term, σ_{E1}, which disappears if the solvent is non polar. The results are in general accord with a previous theory due to Linder[70] and explain the origin of the empirical additivity rules of Raynes[71].

The individual contributions of intermolecular screening can now be discussed with confidence in their real meaning.

2.A.3.1. Bulk Magnetic Susceptibility.

The presence of an applied static field, B_o, will have the effect of polarising a bulk medium, which may be regarded as a continuum of solvent molecules, interspersed with solute molecules, and which has macroscopic properties very close to those of the pure solvent. The polarisation of the bulk medium gives rise to a modified field strength at a molecule in a medium of volume susceptibility χ_v, which is given by:

$$B_{eff} = B_o[1 + (4\pi/3 - \alpha)\chi_v] \qquad 2.7.$$

where α is a shape factor introduced to allow for the vessel containing the sample, and is equal to $4\pi/3$ for a sphere, and 2π for a cylinder whose length is large compared with its radius. Since cylindrical tubes are normally used to contain samples under investigation the contribution to the intermolecular screening is $(2\pi/3)\chi_v$. Thus the observed shift must be corrected for the difference in susceptibility at the sample and reference nuclei by the use of equation 2.8.

$$\delta^{R-S}_{corr} = \delta^{R-S}_{obs} - 2\pi(\chi_{vR} - \chi_{vS})/3 \qquad 2.8.$$

where δ^{R-S}_{obs} and δ^{R-S}_{corr} are the observed and corrected chemical

shifts respectively, and χ_{vR} and χ_{vS} are the total volume susceptibilities of the materials containing the reference (R) and sample (S) nuclei respectively. The use of the internal reference technique obviates the need for correction since χ_{vR} and χ_{vS} are equal, but the use of external reference capillaries requires the correction of chemical shifts unless χ_{vR} and χ_{vS} can otherwise be made equal.

2.A.3.2. Solvent Anisotropy.

Some solvent molecules may show an anisotropy in their magnetic susceptibility, which may influence the local static field experienced by a particular nucleus, and contribute significantly to the total intermolecular screening constant, especially when the solute and solvent molecules interact sterically so that effective relative random motion is restricted. Calculations of the magnitude of σ_a are possible for simple solute molecules, including spherical solutes of varying molar volume. Of the many attempts to calculate σ_a[72-77], those due to Becconsall[76] and Homer and Redhead[77] are probably the most accurate, although the approaches of Bothner-By and Glick[72], Abraham[73] and Rummens[75] are useful qualitatively.

Becconsall[76] has obtained values due to the screening effect of pure benzene, the assumption of his model being that only solvent molecules within a sphere of influence around the solute effectively contribute to σ_a, whilst all those solvent molecules which are outside the sphere have no contact with the solute, and therefore provide no contribution. The benzene molecule may be considered to exhibit a cone of movement on the surface of a spherical solute, and since this implies that isotropic motion is not

possible, different susceptibilities and screenings must exist parallel (σ_{11}) and perpendicular ($\sigma_{\perp}$) to the plane of the benzene ring. The difference in susceptibilities in these two directions is given as:

$$\Delta\chi = (1 - 3\cos^2\theta)/r^3 \qquad 2.9.$$

where θ is the angle between the benzene C_6 axis and the line of length r joining the centres of the solute and benzene molecules. σ_{11} and $\sigma_{\perp}$ are then given by:

$$\sigma_{11} = \Delta\chi/r^3 \qquad 2.10.$$

$$\sigma_{\perp} = -2\Delta\chi/r^3 \qquad 2.11.$$

The simple cage model proposed by Homer and Redhead[77] enables the calculation of values of σ_a for non-polar solutes which provide good agreement with experimentally determined values. The method is based on the cage model proposed by Rummens[75], but instead of imposing the condition that extreme solute-solvent orientations are the sole contributing factors, they used Abrahams equation[73] (2.12.) to obtain $(\sigma_{pair})_a^{average}$ in equation 2.13.[75]

$$\sigma_a = -\frac{2}{3}10^{30}\Delta\chi \frac{r - h}{(r + 2h)(r^2 + h^2)^{3/2}} \qquad 2.12.$$

$$\sigma_a = (Z\sigma_{pair})_a^{average} \qquad 2.13.$$

In equations 2.12. amd 2.13. r and h are the radius and half height respectively of a cylindrical solvent molecule, Z is the number of solvent molecules in contact with the solute, and $(\sigma_{pair})_a^{average}$ is the total anisotropic screening of a solute by one solvent molecule.

Equation 2.12. requires that the solute is considered to move over the entire cylindrical surface of the cylinder,

and thus the solute nucleus under investigation must adopt all possible positions relative to the solvent. Hence, in order to obtain $(\sigma_{pair})_a^{average}$ from equation 2.12., h and r must be replaced by h_{av} and r_{av} given by equations 2.14. and 2.15. respectively for the outer nuclei of the solute:[77]

$$h_{av} = (a^2(a + 2s)^2/(a + s))^{1/3} \qquad 2.14.$$

$$r_{av} = (b^2(b + 2s)^2/(b + s))^{1/3} \qquad 2.15.$$

where a is the sum of h and the van der Waals radius of the outer resonant nucleus, W, b = r + W, and s is the outer radius of the solute. For the inner solute nucleus h_{av} and r_{av} are recalculated by substituting $w = w + s - s^1$, where s^1 is the inner solute radius.

The factor Z is simply given by:

$$Z = \pi(r_A + r_S)^2/r_S^2 \qquad 2.16.$$

where the subscripts A and S refer to the solute and solvent respectively, and r is the assumed radius of A or S. σ_a can now be calculated from equation 2.13.

Homer and Redhead[77] critically compared the results they obtained with the experimentally determined values obtained by Rummens[75]. The calculated and experimental results are in good agreement, and enabled them to show that the change in σ_a when changing the solvent from pure benzene to pure cyclohexane was less than 0.03p.p.m. It is apparent, therefore, that it is not possible to disregard changes in the σ_a contribution due to altering the composition of the benzene/cyclohexane solvent mixtures such as are used in the studies reported here. However, it is to be expected that σ_a will vary little over the small range of compositions

used, and shift corrections will not be made, since it is possible that such corrections may give rise to even greater errors.

2.A.3.3. Van der Waals Screening.

Van der Waals, or dispersion screening, σ_w, arises from molecular interactions which result in mutual distortion of molecular electronic structures, giving rise to a contribution which is solvent dependent. The basic mechanism of these interactions may be thought of in terms of the time-variant dipoles in molecules which polarise each other, resulting in changes in the original electron distributions, which are effectively paramagnetic in nature[78]. This mechanism may be treated similarly to the electrical approach to coupled oscillators. The method proposed by Howard, Linder and Emerson[79] was used by Homer and Huck[80] to determine changes in σ_w contributions in the three-component nitroform-aromatic-cyclohexane systems. The method is based on the fact that whilst the average value of the effective electric field in non-polar molecules is zero, the mean square value, $\langle F^2 \rangle$, is non-zero, and may be calculated via the free energy, G, arising from the interactions described above:

$$G = - \langle m^2 \rangle g/8 \qquad 2.17.$$

where $\langle m^2 \rangle$ is the average square of the oscillating dipole moment of the free molecule, and

$$g = (2n_S^2 - 1)/(2n_S^2 + 2)a^3 \qquad 2.18.$$

where n_S is the refractive index of the medium, and a the radius of the molecule under investigation. It may be shown that

$$\langle F^2 \rangle = \frac{3}{4} hg \left[\frac{\nu_A \nu_S}{\nu_A + \nu_S} \right] \qquad 2.19.$$

where the subscripts A and S refer to the solute and solvent respectively, and ν is a mean absorption frequency calculable from the ionisation potential of A or S. Equation 2.20. may be shown to apply:

$$\sigma_W = -B\langle F^2\rangle \qquad 2.20.$$

where B is a function of the solute polarisability, perpendicular to the bond containing the nucleus being studied.

Homer and Huck's calculations[80] showed that σ_W did not exceed 0.002p.p.m. when changing the solvent from pure cyclohexane to pure benzene, and at the time was considered to contribute negligibly to the observed shift variation. However, since their results were not determined experimentally (there is considerable doubt as to the correct value of B), and because the data here are of a significantly higher accuracy, it is not justifiable to ignore this very important effect. Additionally, these equations have been criticised[81] and it has been shown that equation 2.21., deduced by de Montgolfier[82], is more satisfactory.

$$\sigma_W = -6 \left[\frac{(n_S^2 - 1)^4}{(2n_S^2 + 1)(n_S^2 + 2)^2} \right]_S \left[\frac{K_A B.\Delta E_A}{\alpha_A} \right]_A \qquad 2.21.$$

where K_A is a site factor, ΔE_A approximates to the solute ionisation potential, and α_A is the solute polarisability. It is obvious from equation 2.21. that, as long as the solute is the same, changes in σ_W which arise from changing solvents are totally dependent on the refractive index of the solvent. Changes in σ_W in the systems studied in this thesis are directly attributable to changes in the refractive index of the aromatic-solvent mixture, since chloroform is used

throughout as the solute. Equation 2.21. shows that, in cases such as this, where one solute is being studied in different solvents, the knowledge of ionisation potentials and other parameters is not required to predict the changes in σ_W.

In studies of the formation of molecular complexes the diluent used should be identical to the aromatic molecule in all respects except in the ability to form complexes. Any variation in properties between the two molecules, especially in refractive index and dielectric constant, which are proportional to dispersion and electric field effects(Section 2.A.3.4.) respectively will be reflected in the values of parameters pertaining to complex formation, and cannot be considered to be negligible. These aspects of intermolecular screening will be discussed in Chapters 5 and 6.

2.A.3.4. Electric Field Effects.

The screening term σ_E is effectively a reaction field term arising from the polarisation by the solute of a significant volume around the solute, an estimation of this volume being deduced in Chapter 7. The polarisation of a solvent by a polar solute containing the nucleus under investigation causes an electric field, E, to arise acting along the axis of the dipole which caused it, thus decreasing the screening constant via a reaction field. The magnitude of σ_E is given generally as:[10]

$$\sigma_E = (2 \times 10^{-5}) - (2 \times 10^{-2})E - (10^{-18})E^2 \quad 2.22.$$

If E arises from an external field the average value of σ_E in a mobile liquid or gas is zero, but will not be so if E arises from a polar molecule, when it is independent of random motion. For spherical molecules a model has been

proposed by Buckingham[83,84] which enables calculation of σ_E. The solute is considered to be a sphere of radius r with a point dipole μ_A at the centre, and the solvent is considered as a continuous medium of dielectric constant ε_S. The reaction field, R, may then be deduced from equation 2.23.

$$R = \frac{2(\varepsilon_S - 1)(n_A^2 - 1)}{3(2\varepsilon_S + n_A^2)\alpha_A} \mu_A \qquad 2.23.$$

where n_A is the refractive index of pure solute, and α_A is the polarisability of the sphere given by $\alpha_A = r^3(n_A^2 - 1)/(n_A^2+2)$ For non-spherical molecules the method of Diehl and Freeman[85] may be employed in which the dipole is considered to be at the centre of a non-spherical cavity. The reaction field equation so obtained is also dependent on the dielectric constant of the solvent.

The major point which arises from this brief discussion of σ_E contributions concerns the range of concentration employed in these studies. It is apparent that if the reaction field in mixtures of aromatic and solvent does not change with the ratio of the concentration of the components, σ_E will be constant, and therefore unimportant. If this is not so, and the range of composition is small, σ_E may probably be neglected with some confidence. In the present investigations, however, since there is some difference in the dielectric constants of the aromatic and solvent components, it is not to be expected that σ_E will remain constant over the chosen ranges of composition.

The arguments proposed in the previous section concerning the use of different solvents, each with the same solute, also apply to equation 2.23., and since $\varepsilon_S \simeq n_S^2$ for

the materials employed here, variations in σ_W and σ_E may be allowed for simultaneously, as shown in Chapter 5.

2.A.3.5. Some General Comments On The Effects Of Specific Association.

The screening term σ_S is introduced to allow for specific molecular interactions which may occur between solute and solvent such as H-bonding, charge transfer, dipole-dipole and dipole-induced dipole effects, of which the latter type are of particular interest in this thesis. It is usually assumed that the interaction between polar solutes and aromatic molecules, in the presence of an inert solvent, may be interpreted as the formation of a transient collision complex[85-89], which implies a short lived[90-94] orientation of the aromatic molecule with respect to the polar solute, that is brought about by a dipole-induced dipole interaction.

As mentioned previously the purpose of the investigations reported in this thesis is to study similar complexes between polar solutes, A, and benzene, B, in the presence of a supposedly inert solvent, S, according to the equilibrium:

$$A + B \rightleftharpoons A \ldots B \qquad 2.24.$$

The characteristic properties of the complex will be discussed further in Chapter 4, but it is important to discuss here the effects σ_S on the appearance of an n.m.r. spectrum.

The formation of bimolecular AB complexes may be considered to be a chemical exchange process in which the solute A has complexed and uncomplexed environments, the exchange being of such a rate that only an averaged resonance is observed (Section 1.12.). The spectrum for the widely used model system of chloroform, A, benzene, B and

cyclohexane, S, is represented schematically in Figure 2.1. The observed chemical shift, δ_{obs}, depends on the relative times spent by the chloroform molecule in the free and complexed states, and its variation with concentration enables the calculation of equilibrium parameters describing the reaction. The methods available for treating this data have been discussed in Chapter 1.

2.B. Spin-Lattice Relaxation Processes.

2.B.1. Introduction.

The n.m.r. spin-lattice relaxation time, T_1, is a parameter which reflects indirectly the basic molecular interactions which are the subject of investigation within this thesis. The results of both previous and present research into the nature of bimolecular complexes using chemical shifts have shown that it is necessary to gain further information, in absolute terms, regarding the mechanism of their formation. The spin-lattice relaxation time is a parameter which enables this information to be obtained, and has been used in the investigations reported here in order to substantiate some of the indications provided by the analysis of chemical shifts. A detailed discussion of the nature of spin-lattice relaxation processes is given in this section in order that the implications of the experimental results obtained may be fully understood. Some general comments were made in Section1.9.1., and these will be elaborated upon in terms of the relevant theoretical approaches, and contributions to the relaxation process for systems containing one and two distinct types (i.e. chemically non-equivalent)of nuclei.

2.B.2. One Spin Systems.

The initial equilibration of nuclear energy levels

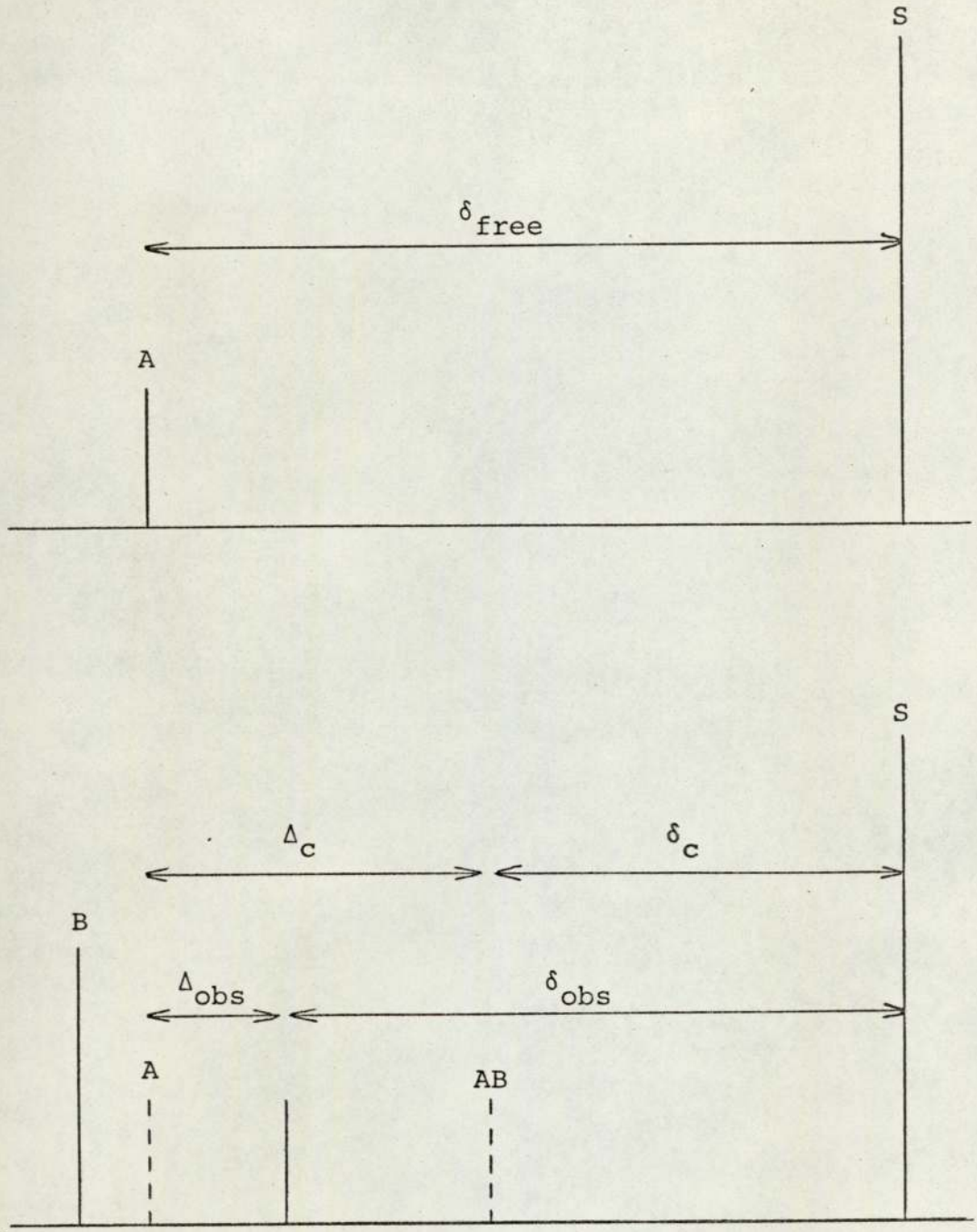


FIGURE 2.1. The effect of the shielding term σ_s on the chemical shift of chloroform, A, reacting specifically with benzene, B, in an inert solvent, S, according to the equation $A+B \rightleftarrows A\cdots B$. The diluting solvent S is also used as an internal reference.

upon the application of a static magnetic field is determined by a spin-lattice relaxation process of the general type described in Section 1.9.1., and characterized by the spin-lattice relaxation time, T_1. Defining n_1 and n_2 as the number of nuclei in the upper and lower energy states of a nuclear system of spin, $I = \frac{1}{2}$, the rate of change of the excess number of nuclei per unit volume, n, may be evaluated as a function time. At equilibrium it is apparent that:

$$n_1 P_1 = n_2 P_2 \qquad 2.25.$$

where P_1 and P_2 are the upward and downward transition probabilities, relating to relaxation, respectively. Using equation 1.20., equation 2.25. may be rearranged to give:

$$\frac{P_2}{P_1} = \frac{n_1}{n_2} = e^{-2\mu B_o/KT} \simeq 1-2\mu B_o/KT \qquad 2.26.$$

Providing the energy associated with the relaxation process is small compared with the total energy of the system then P_2/P_1 is independent of n_1/n_2. If P is the mean of P_1 and P_2:

$$P_1 = P(1 - \mu B_o/KT) \qquad 2.27.$$

$$P_2 = P(1 + \mu B_o/KT) \qquad 2.28.$$

and the rate of change of population is:

$$\frac{dn_1}{dt} = \frac{-dn_2}{dt} = n_2 P_2 - n_1 P_1 \qquad 2.29.$$

Therefore the rate of change of the excess number of nuclei in the lower state is given by:

$$\frac{dn}{dt} = 2(n_2 P_2 - n_1 P_1) \qquad 2.30.$$

since transitions alter the value of n by 2. Substituting

equation 2.27. and 2.28. into 2.30 gives:

$$\frac{dn}{dt} = -2P((n_1 - n_2) - (n_1 + n_2)\mu B_o/kT)$$

$$= -2P(n - n_{eq}) \qquad 2.31.$$

where n_{eq} is the excess number of nuclei in the lower state at equilibrium. Integration of 2.31. gives

$$n - n_{eq} = (n_o - n_{eq}) \exp(-2Pt) \qquad 2.32.$$

where n_o is the initial value of n. T_1 is defined as the characteristic half life time for the relaxation of a nucleus from the upper to the lower state, and is therefore given by equation 2.33.

$$T_1 = 1/2P \qquad 2.33.$$

and equation 2.32. becomes:

$$n - n_{eq} = (n_o - n_{eq}) \exp(-t/T_1) \qquad 2.34.$$

which demands that for a single spin system the rate at which equilibrium is reached is governed exponentially by T_1.

This approach is easily extrapolated to the equation for macroscopic samples. The equations derived by Bloch[19,20,21] which were discussed in Chapter 1, show that:

$$d\vec{M}_z/dt = (\vec{M}_o - \vec{M}_z)/T_1 \qquad 2.35.$$

which is analagous to equation 2.31., and integration of it gives:

$$\vec{M}_o - \vec{M}_z = \vec{M}_o e^{-t/T_1} \qquad 2.36.$$

which is analagous to equation 2.34. M_z and M_o are equivalent to $(n_o - n)$ and $(n_o - n_{eq})$ respectively.

It is important to note that, unless certain equilibrium conditions are applicable to the system, the parameter M_o is not equal to the equilibrium value for the magnetisation, but may be represented more accurately as $M_{z(eq)}$. Hence $M_o = M_{z(eq)}$

only when the secondary field, B_1, is of an intensity which results in the maximum v-mode signal. However, it is usual to represent $M_{z(eq)}$ by M_o, even if this condition is not fulfilled, and thus M_o will be used in this conventional way in this thesis.

Equation 1.53. is applicable under any steady state condition, but it is apparent that the interpretation of peak height as a measure of M_z is only valid if B_1 is very small (i.e. $\gamma^2 B_1^2 T_1 T_2 << 1$). It is recognised that this condition must be fulfilled in order to measure values for T_1 without prior knowledge of T_2 and B_1, and that in these circumstances M_o is more realistically represented as $M_{z(eq)}$.

2.B.3. Two Spin Systems.

The equations for spin-lattice relaxation for systems containing a pair of interacting non-equivalent spins were originally derived by Solomon[95], using modified Bloch equations. Close analogies exist between these equations and those derived by McConnell[96] for systems undergoing chemical exchange. Both sets of equations are in fact coupled differential equations in which the coupling arises from the existence of a probability per unit time for magnetisation at one site to be transferred to a second site. In either approach the probability is proportional to the increase in magnetisation at the first site over the equilibrium value. The equations derived by Solomon[95] may be rewritten[97]:

$$\frac{d\vec{M}_z^A}{dt} = -\frac{\vec{M}_z^A - \vec{M}_o^A}{T_{AA}} - \frac{\vec{M}_z^B - \vec{M}_o^B}{T_{BA}} \qquad 2.37.$$

$$\frac{d\vec{M}_z^B}{dt} = -\frac{\vec{M}_z^A - \vec{M}_o^A}{T_{AB}} - \frac{\vec{M}_z^B - \vec{M}_o^B}{T_{BB}} \qquad 2.38$$

where the superscripts A and B refer to the magnetisations of spins A and B respectively, and the subscripts A and B

refer to the types of interaction which contribute to the relaxation times, and will be discussed further in the following sections.

McConnell's equations[96] for systems of two interacting spins in which chemical exchange is occurring are:

$$\frac{dM_z^A}{dt} = \frac{M_o^A - M_z^A}{T_{1A}} - \frac{M_z^A}{\tau_A} + \frac{M_z^B}{\tau_B} \qquad 2.39$$

$$\frac{dM_z^B}{dt} = \frac{M_o^B - M_z^B}{T_{1B}} - \frac{M_z^B}{\tau_B} + \frac{M_z^A}{\tau_A} \qquad 2.40.$$

where M_o^A and M_o^B are the equilibrium z magnetisations at sites A and B, τ_A and τ_B are the residence times at A and B, and T_{1A} and T_{1B} are the spin-lattice relaxation times at A and B respectively. McConnell assumed that the relaxation processes at the two sites A and B were independent, and was able to derive an expression for the effective lifetimes of the spin states at the two sites. Whilst the approach of McConnell is certainly well suited to the study of the type of molecular interactions which are the subject of the investigations in this thesis, it was felt that more relevent information could be obtained initially by the use of Solomon's equations, and derivatives of them.

Although much qualitative work has been carried out using two-spin systems it has been a problem to measure accurately the values for the spin-lattice relaxation times because of theoretical difficulties, namely that in the two equations 2.37. and 2.38. there are four variables. The attempted solutions to this difficulty will be discussed in Chapter 4.

2.B.4. Contributions To The Relaxation Process.

2.B.4.1. Systems Of One Spin.

In a similar fashion to screening constants, spin-lattice relaxation times may be divided into individual contributions, which are additive in the form of time constants. Therefore, even for a system containing only a single type of resonant nucleus there are more contributions than the number of equations describing them. Single spin systems obey equation 2.36., and T_1 may be subdivided into intramolecular and intermolecular contributions:[18]

$$\frac{1}{T_1} = \frac{1}{T_{1(intra)}} + \frac{1}{T_{1(inter)}} \qquad 2.41.$$

where $T_{1(intra)}$ and $T_{1(inter)}$ may be expanded further in terms of basic molecular interactions. It is more important to know the extent of relaxation processes inside and outside the molecule in question rather than attempt to divide these contributions further, and this has been attempted in several ways. The simplest of these methods is to dilute a protonated molecule with its deuterated analogue. The contributions can then be deduced by consideration of the relative intermolecular effects of the two analagous molecules. Bonera and Rigamonti[98-100] have carried out extensive studies in this way for the benzene and acetone molecules. The reorientational correlation time, τ_d, which is the typical time for molecular reorientation, was found to be responsible for the intramolecular contribution, and can therefore be equated with a rotational contribution if other factors are negligible. The intermolecular contribution arises from local field fluctuation caused by the motion of neighbouring molecules, and in the case of deuterated

analogues Bonera and Rigamonti showed that allowances could be made for $T_{1(inter)D}$ by modifying equation 2.41. to:

$$\frac{1}{T_1} = \frac{1}{T_{1(intra)}} + \frac{1}{T_{1(inter)}}(\alpha-(1-\alpha)F) \qquad 2.42.$$

where α is the fraction of protonated liquid and $F = \frac{16}{9}(\gamma_D/\gamma_H)^2$. Gaisin[101], and Reeves and Yue[102] have arrived at similar conclusions for the acetone system, although in both cases the magnitudes of the contributions are different to those obtained by Bonera and Rigamonti. Powles and Figgins[103] have obtained similar results for the benzene system, but have shown that since:

$$(1/T_{1(inter\ C_6H_6)})/(1/T_{1(inter\ C_6D_6)})$$

$$= {}^3/_2(\gamma_H/\gamma_D)^2[I_H(I_H + 1)]/[I_D(I_D + 1)] = 24 \qquad 2.43.$$

equation 2.42. can be expressed as:

$$\frac{1}{T_1} = \frac{1}{T_{1(intra)}} + \frac{1}{24}(1 + 23\alpha)\frac{1}{T_{1(inter\ C_6H_6)}} \qquad 2.44.$$

Plots of $1/T_1$ against α are then linear at all temperatures.

Giulotto et al[104] have studied the hydrogen-bonded molecular clusters of phenol by observing T_1 values in carbon tetrachloride solution. They showed that T_1 is sensitive to molecular clustering, and restriction of random motion, whilst no such effect was noticed in a similar system of chlorobenzene diluted in carbon tetrachloride. Their conclusions suggest that the intramolecular and intermolecular contributions are probably more readily appreciated by their representation as $T_{1(rotational)}$ and $T_{1(translational)}$ respectively.

Since the intermolecular, or translational, contribution

to T_1 depends on molecular motion it is apparent that the viscosity of the medium must play some part in the overall process, and this has been shown to be true for a wide variety of systems[103,105-113]. Powles and Figgins[103] have shown that the variation of the value of T_1 with temperature correlates well with translational motion, and dependent properties such as self-diffusion and viscosity. They have used the equation derived by Hubbard[114] for comparison of experimental and theoretical values of $T_{1(inter)}$. Hubbard's expression is:

$$\frac{1}{T_{1(inter)}} = \frac{12}{5}\pi h^2\gamma^4\frac{N}{dD}\left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 --- \right] \qquad 2.45$$

where N is the number of molecules per unit volume, d is the distance of closest approach for spherical molecules of radius a, b is the distance of each proton from the centre of the molecule, and D is the self-diffusion constant given by equation 2.46.

$$D = kT/3\pi\eta d \qquad 2.46.$$

where η is the viscosity of the medium. For the benzene - $[^2H_6]$benzene system this equation requires modification in view of the far from spherical shape of the benzene molecule and the consequent doubt as to the appropriate value for d, although other workers[91] have used it satisfactorily for other molecules. The appropriate formula for the benzene molecule is:[97]

$$\frac{1}{T_{1(inter)}} = \frac{2}{5}\pi h^2\gamma^4\frac{N_s}{dD} \qquad 2.47.$$

where N_s is the number of protons per unit volume, and its use provides good correlation between calculated and experimental values for $T_{1(inter)}$ Equations 2.45. - 2.47

are sometimes expressed in terms of a translational correlation time, τ_T, given by $d^2/2D$, so that the equation applicable to spherical molecules becomes:

$$\frac{1}{T_{1(inter)}} = \frac{24}{5}\pi h^2\gamma^4 N d^{-3}\left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 ----\right]\tau_T \quad 2.48.$$

τ_T may be calculated to give an indication of the nature of the molecular motion in any liquid, and variations in its magnitude (usually of the order of 10^{-11} - 10^{-12} seconds) are indicative of the nature of molecular shapes and interactions.

Equations 2.45 and 2.47. show that $T_{1(inter)}N/D$ should be temperature independent[109]. Powles[103,108] has shown that a plot of $T_{1(inter)}(N\eta/T)/(N\eta/T)_{298K}$ falls slightly with temperature, although the value of $T_{1(inter)}$ $(N\eta)/(N\eta)_{298K}$ is almost invariant.

Hubbard[114] has also derived an expression for $T_{1(intra)}$, given by equation 2.49.

$$\frac{1}{T_{1(intra)}} = \frac{3}{2}h^2\gamma^4\sum_{i>j}(r_{ij}^{-6})\tau_d \quad 2.49.$$

where r_{ij} is the distance between protons i and j in benzene, and τ_d is the reorientational correlation time, analagous to τ_T. The value of τ_d calculated by Powles[103] does not agree well with the theoretical value given by the Debye formula $4\pi\eta a^3/3kT$[109,115], or that obtained by Raman scattering[115], but correlates well with that obtained by the Rayleigh scattering of light[116].

Plots of log $T_{1(inter)}$ and log $T_{1(intra)}$ seperately are usually linear with reciprocal temperature[103,108,109], and the activation energies for the relaxation process are of about 1 - 2 kJ.mol^{-1}. Non linearity in the log $T_{1(intra)}$

plot is usually attributed to spin-rotation contributions[115,117] which are given[114] in terms of τ_{sr}, the spin-rotation correlation time, and the corresponding relaxation time T_{1sr}.

The spin-rotation mechanism may be thought to arise from an interaction between the nuclear spin and molecular rotation. The relaxation due to nuclear spin interaction usually contributes to the parameter T_2, but when molecular motion (total or internal) modifies this interaction the resultant oscillating fields are attributable to a spin-lattice type mechanism. An additional relaxation process is introduced in this way, and supplements the normal dipolar effects. In this case $T_{1(intra)}$ is given by equation 2.50.

$$\frac{1}{T_{1(intra)}} = \frac{1}{T_{1(intra-dipolar)}} + \frac{1}{T_{1sr}} \qquad 2.50.$$

2.B.4.2. Systems Of Two Spins.

The contributions to the relaxation processes in a system of two spins are similar to those in one spin systems, but the coupling of magnetisation vectors makes their analysis a considerably more difficult procedure. In this thesis, the discussion of the results obtained from the measurement of spin-lattice relaxation times for two spin systems does not warrant such detailed analysis, a general qualitative consideration will be proposed.

Solomon[95,118], and Mackor and Maclean[119] have proposed that spin-lattice relaxation in a system of molecules with two unlike spins may originate from intra - or intermolecular interactions between like and unlike spins, and that the values of the relaxation times are related to the nature of the interaction. Mackor and Maclean showed that, generally,

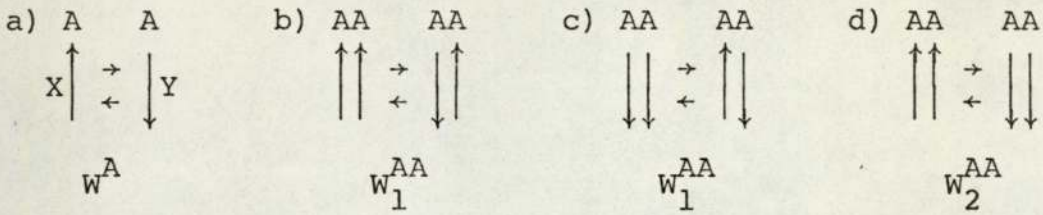
hydrogen spins are relaxed predominantly by intermolecular dipole interactions whilst fluorine nuclei are relaxed mainly by intramolecular spin-rotation interactions, and their method, in combination with measurements of the nuclear Overhauser effect, allows the determination of the contributions from the various types of interaction, which have been described in the previous section.

The equations derived by Solomon[95] for a system of two spins were given in section 2.B.3., and of specific interest here are the interactions and contributions to the relaxation processes, which are represented by T_{AA}, T_{BB}, T_{AB} and T_{BA}. Assuming that the state of a spin system may be described in terms of population levels, it is possible to derive expressions[95,119] for 1/T in terms of transition probabilities (W), which are pictorially represented in Figure 2.2.

These contributions may occur intra - or intermolecularly, but, for simplicity, it is necessary to assume that all interactions are of a magnetic type, e.g. dipole-dipole, although relaxation effects induced by quadrupole moments may be included in the W^A and W^B terms, which inherently include effects due to unobserved spins, e.g. deuterium or chlorine, and dissolved paramagnetic impurities such as oxygen. W^A and W^B may, on the other hand, originate from spin-rotation or fluctuating stationary field effects. In Figure 2.2. X and Y represent two different lattice states, including unobserved spins.

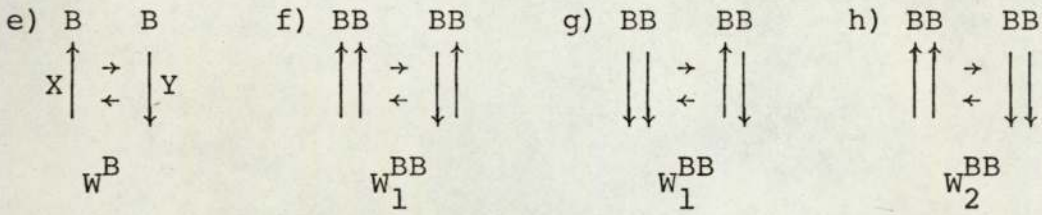
In the expression for $1/T_{AA}$ the process leading to the probability W_2^{AA} involves the simultaneous flip of two spins, whilst W_1^{AA} involves change in only one spin, but will

A+A INTERACTIONS:



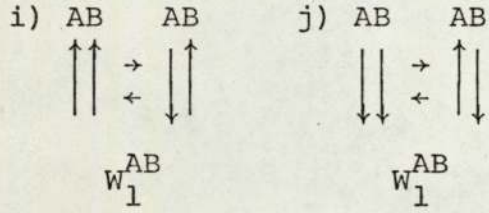
W^{A} W_1^{AA} W_1^{AA} W_2^{AA}

B+B INTERACTIONS:



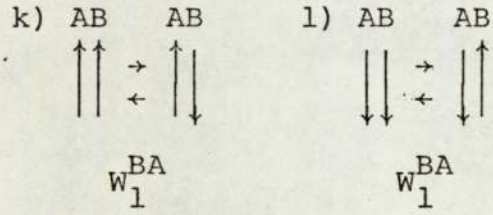
W^{B} W_1^{BB} W_1^{BB} W_2^{BB}

A+B INTERACTIONS, A SPINS RELAXING:



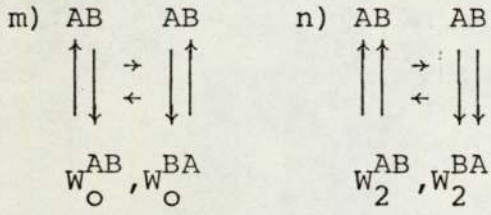
W_1^{AB} W_1^{AB}

A+B INTERACTIONS, B SPINS RELAXING:



W_1^{BA} W_1^{BA}

A+B INTERACTIONS, A AND B SPINS RELAXING:



W_o^{AB}, W_o^{BA} W_2^{AB}, W_2^{BA}

FIGURE 2.2. A pictorial representation of the relaxation processes in a two spin system (A and B, I=½). The interactions a) and e) are caused by magnetic interactions between one spin and extraneous fields due, for example, to anisotropic shielding, whilst the others are considered to be caused by interactions between pairs of spins. X and Y represent two different lattice states.

occur twice as often. Hence both these terms have a coefficient of 2. The relative weights of the W^{AB} processes may be analysed in a similar way. The terms W_o^{BA} and W_2^{BA} may be understood by a consideration of M_z^B as it approaches M_o^B after perturbation. By the W_2^{BA} process M_z^B will tend to drag M_z^A, but will have the opposite effect by the process W_o^{BA}, both interactions involving the simultaneous flip of one A and one B spin. Thus $1/T_{AA}$ may be expressed as a sum of these transition probabilities, and is given by equation 2.51.

$$1/T_{AA} = 2(W_2^{AA} + W_1^{AA}) + (W_2^{AB} + 2W_1^{AB} + W_o^{AB}) + W^A \qquad 2.51.$$

The other relaxation times may be deduced in a similar fashion and are given by:

$$1/T_{BA} = W_2^{BA} - W_o^{BA} \qquad 2.52.$$

$$1/T_{AB} = W_2^{AB} - W_o^{AB} \qquad 2.53.$$

$$1/T_{BB} = 2(W_2^{BB} + W_1^{BB}) + (W_2^{BA} + 2W_1^{BA} + W_o^{BA}) + W^B \qquad 2.54.$$

It should be noted that unless the W^{AB} and W^{BA} contributions are entirely intramolecular they will not be equal but will be weighted according to the number of A and B spins respectively. This may be represented by the equations 2.55. and 2.56. respectively:

$$(W^{AB})_{intra} = (W^{BA})_{intra} \qquad 2.55.$$

$$M_o^A\,(W^{AB})_{inter} = M_o^B\,(W^{BA})_{inter} \qquad 2.56.$$

Hoffman and Forsen[120-123] have conducted a series of experiments using spin-lattice relaxation times to study chemical exchange, and have developed an accurate method for measuring the relaxation times in a system of two spins,

which will be discussed in Chapter 4. The similarity between McConnell's[96] equations for chemical exchange and Solomon's[95] equations for relaxation in two spin systems is evident from the forms of equations 2.37.-2.40., and from equations 2.52. and 2.53. it follows that the coupling between the magnetisations of A and B will be in the same direction if $W_o^{BA} > W_2^{BA}$ and $W_o^{AB} > W_2^{AB}$, which will be true if scalar magnetic interactions dominate the mutual relaxation[77].

The system of chloroform-benzene-cyclohexane (inert solvent) will be used as a model to carry out investigations into the use of spin-lattice relaxation times as a method for gaining information about the molecular interactions in the three-component liquid. It is evident from the foregoing discourse that such a three spin system would be extremely complicated to analyse, and has only been investigated fully in solid samples[124],(although a partial analysis has been carried out for 2,6-dibromoaniline[125]). However, from the conclusions reached in Chapter 7 of this thesis it will be apparent that the problem of studying the mechanism of complex formation may be approached just as readily by making the three-component mixture an effective two spin system. This may be done by the use of $CDCl_3$ rather than $CHCl_3$, when contributions due to the spins of deuterium and chlorine may be included in the terms W^A and W^B, as described previously, although the magnitude of the equilibrium quotient will be altered (Chapter 5). An analysis of the relaxation times of the benzene and cyclohexane will enable information to be gained concerning the modification of the liquid structure due to the introduction of chloroform.

2.B.4.3. Unwanted Contributions.

It is evident from the preceding discussion that any contribution to the relaxation process which cannot be quantified may give rise to extraneous results, even though the effect may be included in the terms W^A and W^B. The major origin of unwanted contributions is through dissolved paramagnetic impurities, which, although they may be in very low concentration, may have a significant effect on the efficiency of relaxation processes, and as described in Section 1.9.3., influence line widths. Whilst the presence of such impurities has little effect on the appearance of a normal n.m.r. spectrum, if in low concentration, their influence on the values obtained for spin-lattice relaxation times is often remarkable in its effect.

The most important impurity commonly found in n.m.r. samples, and the only one of any significance in the context of this thesis, is molecular oxygen. The oxygen molecule is paramagnetic and, if dissolved in the sample under investigation, will contribute to an unknown extent to the spin-lattice relaxation times of the nuclei in the sample, rendering any analysis of them meaningless. Muller-Warmuth[126] has studied the effects of oxygen on the relaxation times of electron spin resonance spectra, and found that the paramagnetic contribution may alter the relaxation process by up to two orders of magnitude. Most of the authors previously mentioned have noted the necessity of the efficient removal of oxygen from samples, and others have made specific reference to the effects of dissolved oxygen on n.m.r. relaxation times[127-129]. Nederbragt and Reilly[129] noted the variation in T_1 due to differences in $T_{1(intra)}$ and $T_{1(inter)}$

which were deduced by the basic theory due to Bloembergen, Purcell and Pound[18]. These variations were attributed to the presence of oxygen.

However, despite the apparent awareness of the problem it is noticeable from the literature that values for T_1 obtained for the same compounds by different workers are not reproducible. Typical examples are the values obtained for benzene[105,106,108,127,129-133] which range between 18.0 and 22.0 seconds at very similar temperatures, and for the ring protons of toluene(12.5 to 16.0 seconds)[127,129,132,134].

It is apparent, therefore, that in order to obtain meaningful results pertaining to molecular interactions it is necessary to remove all traces of oxygen from the sample under investigation, and also that a simple technique for the preparation of such samples must be developed. Investigations into the ways in which this may be done are reported in Chapter 8.

2.B.5. The Mechanism Of Spin-Lattice Relaxation.

The discussion in the previous sections has been directed mainly towards an explanation of the origins of the contributions to the relaxation process, but little has been said concerning the structure of liquids and the nature of molecular movements which give rise to these contributions. Within this section, therefore, the various models which have been proposed will be discussed. Whilst there are several current theories describing mixtures of simple liquids[135,136], only those which have been used extensively for the explanation of interactions leading to relaxation processes will be compared.

The basis for nearly all the investigations which have been reported in the jump-diffusion model in which

it is proposed that during diffusion through the medium a molecule reorients from time to time in large-angle jumps rather than by slower general rotation and translation. Powles[108,137-140] has made several studies of this method of the analysis of relaxation processes, and has shown how molecular motions, both reorientational and translational, in liquids may be treated from a theoretical standpoint in order to provide a basis for the study of dipolar interactions and reorientation. The reorientational correlation frequency, ν_c (i.e. the jump frequency), may be shown to be related to temperature for low viscosity liquids[138], and that for molecules such as water the translational and reorientational motions are closely related, whilst for benzene the motions are distinctly independent. Powles and Green[139] have analysed relaxation times in terms of dipole-dipole and spin-rotation magnetic interactions, and have obtained some reliable correlation times for the molecular motion of many benzene derivatives. They have also deeply investigated the physical processes involved in the spin-rotation contribution (T_{1Sr}), and found it to be largely independent of the details of molecular reorientation and is due mainly to intramolecular rotation rather than rotation of the whole molecule. Sharma and Gupta[141,142] have found it necessary to modify the basic jump-diffusion model in order to account for the continuous diffusion of the centre of vibrations in a quasi-crystalline vibrational state. The molecule is thus considered to undergo continuous diffusion between fast jumps. Muller[143] has calculated the r.m.s. jump distance in liquids from $T_{1(inter)}$, and has found that for simple molecules the distance is of the order of the

molecular diameter.

The general application of this model to real systems is sometimes misleading, especially when molecular aggregates exist in the liquid. Several authors have found that experimental values are below theoretical ones, using both the jump-diffusion and other more complicated models[144-146] and they have attempted to resolve the problem by considering the inadequacies of the model, although it is likely that their experimental samples contain impurities in the form of molecular oxygen. In this latter respect it is noticeable that other workers who have obtained higher T_1 values (i.e. less dissolved oxygen) at the same temperatures have found the model remarkably accurate in its predictions, and that T_1 is quite insensitive to the finer details of the model[147], although Resing et al[148] have pointed out that the formulation of a distribution of correlation times (τ_T and τ_d) is necessary for accurate quantitative interpretation of molecular motional relaxation.

Anderson[92-94] has presented a theoretical and experimental examination of the effect of molecular association, of the type described in this thesis, on the rotational motions of molecules, and concluded that a molecular association which moves as a unit and whose lifetime is longer than the rotational correlation time should considerably affect T_1. Other workers[90,91] have shown this to be a correct assumption using model systems of chloroform and benzene. Hindman and Svirmickas[149] have interpreted the large activation energy and entropy for low temperature relaxation processes in water as being due to a mechanism involving the synchronous motion of several water molecules, and consequently did not need to change the basic model to

account for these quantifiable differences.

2.B.6. Relaxation Processes For Different Nuclei.

Whilst the majority of reported investigations into relaxation processes have used the ^{1}H nucleus[150], there are few instances, apart from ^{13}C, of the use of other nuclei. The investigations in this thesis are to be carried out with the aid of the measurement of ^{1}H spin-lattice relaxation times, but, as has been proposed previously, it has been necessary to incorporate into the system molecules containing deuterium (i.e. $CDCl_3$) The relaxation processes of other nuclei will therefore be discussed briefly.

Mantsch et al[151] have shown in an elegant study of the stereochemical dependence of ^{2}H relaxation times that the relaxation of the deuterium nucleus is induced entirely by an intramolecular quadrupole mechanism. Consequently this nucleus is of little use in the investigations of molecular interactions, although it is ideal for studies of intra-molecular stereochemistry, rotation and anisotropic motion. Dietrich and Kosfeld[152] have shown that in protonated chloroform there is no spin-rotation exchange at normal temperatures, but Huntress[90] has shown that deuterium in $CDCl_3$ relaxes extremely quickly (1.8s) compared with hydrogen in $CHCl_3$ (80s)[91]. It appears therefore that the relaxation process of both ^{2}H and ^{35}Cl are not dependent on their intermolecular environment, although they may influence relaxation processes in other molecules. Indeed, Sato and Nishioka[91] have shown that ^{2}H and ^{35}Cl will contribute negligibly to the relaxation of chloroform provided that ^{2}H is not contained in the chloroform molecule, but is in some other molecule. Analogy between their results and the proposed system for investigation would seem to suggest

that $CDCl_3$ acts only as a diluent as far as the proton relaxation times of benzene and cyclohexane are concerned, but that its effect on the chemical environment will enable differences to be seen in the relaxation times of benzene and cyclohexane. These workers also consider that the proportionality between $1/T_1$ and viscosity is doubtful, as illustrated by Bull and Jonas[106], and concluded that variations in viscosity of their systems due to changes in concentration were negligible. This assumption is also valid in this context, although it is still important that all measurements are made at the same temperature, since there is an undoubted relationship between this and $1/T_1$.

The relaxation processes of the ^{13}C nucleus are of little consequence in the context of this thesis, mainly because of its low natural abundance, but Spiess et al[153] have assumed that the intermolecular dipole-dipole interaction may be safely neglected for carbon atoms bound directly to a hydrogen atom[154], although the spin-rotation mechanism is important[155]. Its effect on the present investigations may therefore be ignored.

CHAPTER 3.

PRACTICAL REQUIREMENTS FOR THE OBSERVATION OF HIGH RESOLUTION N.M.R. SPECTRA.

3.1. Introduction.

In Chapter 1 the general considerations applicable to a system containing resonant nuclei were discussed, and it is evident from a combination of equations 1.1., 1.6. and 1.59. that, for a nucleus i in a particular chemical environment to undergo resonance:

$$\nu_i = \gamma B_o(1 - \sigma_i)/2\pi \qquad 3.1.$$

It is easily seen from equation 3.1. that either the static field, B_o, or the frequency, ν, of the applied oscillating field may be varied in order that the resonance can be observed; spectrometer systems employing both operational modes are currently available.

All spectrometers are comprised of the following basic components: a permanent or electromagnet of high stability and homogeneity to provide the static field, B_o, a high stability r.f. source which is conveniently applied to a coil surrounding the sample, a detection system based on a single coil[156] or crossed coils[157], the signal from which is fed to an r.f. receiver and amplification/demodulation system, and, finally facilities for presentation of the signal via a cathode ray tube or recorder. The basic requirements of each of these components of a high resolution spectrometer will now be discussed in turn, and subsequently, specific reference will be made to the instrument used for these investigations, and its use in obtaining accurate values for chemical shifts and

spin-lattice relaxation times.

3.1.1. The Magnet.

The permanent or electromagnets which are commonly used in n.m.r. spectrometers normally have a field strength of between 1 and 2.5 tesla. Whilst a permanent magnet has the advantages of reliability, stability and negligible running costs, an electromagnet system is very versatile because the field may be varied extensively, enabling the observation of different isotopes at the same frequency, or observation of the same nuclear type at varying field strengths and corresponding frequencies, which is often advantageous in the analysis of complex spectra. On the other hand a permanent magnet system requires a different radiofrequency source for each nuclear type. A third type of magnet which is becoming more popular is the superconducting magnet which is capable of producing fields of up to 8 tesla, but due to its high cost and the necessity of using liquid helium to maintain the conducting wire at about 10K, they are not common. Some of the data reported in Chapter 7 of this thesis were obtained using an instrument employing the latter type of magnet system, but the details of its operation will not be discussed further.

In order to observe the absorptions due to nuclei in different chemical environments, and spin-spin coupling effects, it is necessary to use a magnet possessing a high field homogeneity. The normal pole gap is between 10 and 20 mm, which is wide enough to contain the probe, which in turn holds the sample and radiofrequency transmitter and detection coils. To obtain the necessary field homogeneity in this gap, the pole pieces of the magnet, normally 130 -

150 mm in diameter, are ground optically flat[158], accurately aligned, and must be of a high quality metal alloy. The inherent homogeneity of an electromagnet or permanent magnet commonly in use is only about 1 part in 10^6, but may be improved in two ways.

Firstly, Golay or shim coils are used, which are situated in pairs adjacent to each pole piece of the magnet. Direct currents of variable values are passed through the coils in order to produce field gradients in the pole gap. The direction of the field gradients so produced can be optimised to counteract much of the inherent inhomogeneity in the basic field of the magnet, and the resolution may be improved to about 1 part in 10^8. This, however, still corresponds to a line width of 1 Hz at 100 MHz, which is not always sufficient to resolve finely coupled spectra, and a second improvement must be sought.

The inhomogeneity in the static field subjects any sample placed in the probe (perpendicular to the field, except for superconducting magnets when the sample tube axis is parallel to the field) to a field gradient, which causes the field to differ by an amount ΔB_o over the volume occupied by the sample. The sample may be spun rapidly to average out this deficiency, because it then behaves as though it were experiencing the time averaged field $(B_o \pm \frac{1}{2}\Delta B_o)$. The rate of spinning required to achieve this effect is given by $(\gamma\Delta B_o/2\pi)$, and is usually about 40 - 50Hz. When the frequency of sample rotation reaches this value the inhomogeneities in the field are effectively reduced by an order of magnitude, and line widths of 0.05Hz or less, at 100MHz, may be obtained. This corresponds to a resolving

power of 5 parts in 10^{10}, and is comparable to naturally occurring line widths.

In order that accurate chemical shift measurements may be made the field strength must be stable to a high degree, short term drift being more important in this respect than long term drift. To overcome this problem permanent magnets are usually enclosed in draught-free thermostatted enclosures, whilst electromagnets are normally used in conjunction with a field frequency lock system, which keeps the ratio of field and frequency constant, facilities being provided, however, for sweeping the spectrum. This type of system will be discussed further in Section3.2.4. Both types of magnet are also provided with a field compensator, which is a device employed to minimise external field variations. Whilst most magnets are designed so that the effect of external fields is almost negligible, minor, but important, fluctuations may still occur, and are detected in coils situated near the polepieces or in a field node. The voltage induced by extraneous fields is amplified and used to apply the necessary correction through an additional set of field coils wound on to the pole pieces.

3.1.2. The Magnet Field Sweep.

According to equation 3.1. either the frequency of the oscillating field or the intensity of the static magnetic field may be varied, whilst the other remains constant, in order to sweep through a range of possible resonance conditions. However, since the equipment required for frequency sweep is more complex, it has been more convenient in the past to employ the field sweep mode, and keep the frequency constant. However most modern spectrometers now

include facilities for both sweep modes. To provide the modulating field, a variable current is fed to two Helmholtz coils mounted accurately close to the sample and may be derived from a simple sawtooth generator. Using this method the spectrum can be swept repeatedly, and control is easily provided for sweep rate and amplitude (sweep width). The use of such a linear sweep unit facilitates the optimisation of spectral conditions for a particular sample because an oscilloscope may be readily connected and the spectrum observed before a permanent record is made. This facility also permits adiabatic fast passage experiments to be performed (Section 3.4.1.).

The spectrum is usually recorded at a slow sweep rate, typically 0.04p.p.m./second, and this may be provided by use of the sawtooth generator described above, by the application of a slowly varying voltage to the field compensator, which will linearly correct the field, or from a voltage derived from a motor driven potentiometer linked to a recorder. When permanent record of a spectrum is made, the field (or frequency) sweep corresponds to the x-axis, and the detector output to the y-axis, the signal normally being presented in the absorption, or v- mode.

3.1.3. The Radiofrequency Oscillator.

Since the strength of the magnetic field of a permanent or electromagnet is limited commonly to about 2.5 tesla, the maximum frequency which may be used is also limited, by equation 3.1. for a particular type of nucleus. For ^{1}H and ^{19}F spectra this frequency is about 100 MHz, although the use of a superconducting magnet can increase this limit to as much as 330 MHz. Radiofrequency oscillators must be of comparable

stability to magnetic fields, because of the fixed proportionality between them, and this is usually effected by obtaining the required frequency by multiplication of selected harmonics of a thermostatted, oscillating crystal. The strength of the oscillating field should also be stable, and automatic gain controls are usually built in to the output r.f. amplifiers. This constant output may then be attenuated as required before the signal is fed into the probe. It is possible to use one crystal for several different output frequencies, but most commonly,seperate crystals for each required frequency are employed since this simplifies the complexity of the mixer and multiplier amplification stages in the r.f. unit.

The technique of frequency sweeping will be described later in this chapter in terms of the spectrometer used in this study, since each of the several systems commercially available is quite complex.

3.1.4. The Probe And Detection System.

The probe, which is manufactured from a non-magnetic material, usually aluminium, and is placed between the pole pieces of the magnet, contains the r.f. transmitter/receiver coils, field sweep coils, provision for spinning the sample (usually by means of an air turbine), and often a receiver preamplifier and auxiliary modulation coils. There is usually some provision to enable fine positioning of the probe assembly, because it is sometimes found that absorption signals shift when shim coils are operated unless the probe position and hence the sample position is optimised relative to magnetic centre.

The single coil detection system, first used by Purcell,

Torrey and Pound[7], is a twin-T bridge circuit, and has been used in many spectrometers because of its good stability (essential if a mixture of u- and v- mode signals is to be avoided) and sensitivity. It consists of two coils in parallel, one surrounding the sample, and the other a dummy. The small absorption or dispersion signal may be detected at resonance as an out-of-balance e.m.f. across the prebalanced bridge. The absorption mode may be selected by introducing a leakage of the transmitter signal out of phase with the dispersion signal, which effectively increases the detected magnetisation in the z direction.

The cross coil system will be discussed in Section 3.2.2. in the context of the spectrometer used in these investigations.

3.2. The Varian HA100D Spectrometer.

This spectrometer is designed around an electromagnet of high field homogeneity, which is optimum at 2.349 tesla. The corresponding nominal frequency for proton resonance is 100 MHz, but signals are detected at 99.9975 MHz and 100.0025 MHz in the field and frequency sweep modes respectively. The magnet current is continuously variable, and a fine field trimmer is provided to compensate for day to day changes in the field strength. Current is supplied to the magnet via a comprehensive solid state power supply unit fed from a three-phase mains supply, and contains regulator and passgate circuits to protect against ±10% variations in line voltage.

The magnet itself is mounted in a trunnion support yoke, and the main coils are cooled with thermostatted water, resulting in a fairly steady temperature within the pole pieces of about 306K. The pole pieces of the magnet are protected with covers containing the Golay coils, and the

whole assembly is contained in an insulation jacket to minimise the effects of ambient temperature changes on the field intensity and sample temperature. A sensitive field compensator corrects for any magnetic field drifts automatically, and may be used as a sweep unit by providing a false error signal. This latter facility is built into the unit to enable different ranges of field sweep to be studied.

3.2.1. The Probe.

The probe assembly used in the spectrometer is precision milled from a single aluminium forging in order to produce maximum stability, and contains field sweep coils for modulation of the static field, a transmitter coil for producing the r.f. field, and a receiver coil for detecting the n.m.r. signal. These coils are in the crossed-coil formation and their operation will be discussed in the following section. Two adjusting knobs are situated on both sides of the probe in order to optimise, via paddles, the leakage between the two coils. A detector preamplifier is placed in a housing away from the pole pieces.

The receiver coil is wound on a former which is aligned close to the sample with its magnetic axis parallel to the axis of the sample tube. The transmitter coils are wound in two sections either side of the receiver coil so that their axes are perpendicular. A Faraday shield is placed between the transmitter and the receiver coils to minimise electrostatic induction. The sweep coils and receiver coils are located in slots in the side of the probe at some distance from the transmitter with their magnetic axes parallel to the main field. Provision is made for sample spinning by a milled P.T.F.E. turbine which is fitted round the sample. The

spectrometer is optimised for use with 5mm outside diameter tubes although it is possible to use 4.65mm tubes using a specially made turbine. The use of the latter has been necessary for some of the investigations reported here.

3.2.2. The Detection System.

The crossed coil detection system used in the HA100D spectrometer is similar to that employed by Bloch, Hansen and Packard[8] in one of the first n.m.r. experiments. The coils are positioned in the probe so that their magnetic axes are at right angles, although the receiver coil is mounted such that coupling between the coils may introduce a leakage between transmitter and receiver coils. This voltage leakage is controlled by a paddle, a semi-circular metal sheet, which is positioned in the r.f. field such that its rotation provides a means for adjustment of the r.f. flux, and hence the leakage. The introduction of the paddle into the r.f. field allows the required signal mode to be readily selected, in a similar fashion to the single coil detection system. A controlled leakage introduced in phase with the absorption signal effectively suppresses the dispersion mode, the amount of leakage being dictated by the signal strength, although fine adjustment of this parameter is not as important experimentally as some others, for example, the r.f. field strength.

3.2.3. The Sweep Unit.

The linear sweep unit employed in this instrument is similar in operation to the general type described previously in that variable sweep times and continuously variable sweep widths, due to the sawtooth waveform, are available. Provision is also made for reversing the direction of sweep. However, the electronics of the unit are designed to ensure maximum stability

and are more complex than in some field sweep systems. The saw-tooth voltage is derived from a phantastron oscillator and is used to modulate a 50 KHz signal which is applied from a seperate oscillator circuit. This modulated 50 KHz signal is amplified in two stages and fed from the output of a push-pull amplifier 180° out of phase with an unmodulated 50 KHz signal. The mixing of the two signals provides a stable linear d.c. sweep which is connected to the d.c. modulation coils on the probe in order to modulate the static field, B_o.

The Varian HA100D spectrometer may be employed in two distinct modes: the HA mode, which uses the field frequency lock system, and the HR mode, which only provides a field sweep facility, but may be used over very wide sweep widths, and at fast sweep times, enabling the monitoring of particular resonances with time. Both operational modes have been used in this study, and will now be discussed.

3.2.4. The HR Mode.

In the HR mode the field-frequency lock system is not used, and the system is simplified to the r.f. unit and detector, an integrator/decoupler unit and presentation facilities. The system is based on phase-sensitive detection circuits and field modulation which enable the stability of the spectrum base line to be improved. The detailed operation of the HR mode is shown in schematic form in Figure 3.1. The radiofrequency unit consists of a stable, crystal driven oscillator which supplies a fixed frequency transmitter and a high gain superheterodyne receiver, the latter being isolated from subsequent circuitry by a buffer amplifier which prevents frequency variation with impedance changes. The r.f. power is stabilised by an a.g.c. circuit to 0.5 watt and is attenuated by a means of a comprehensive array of push button switches.

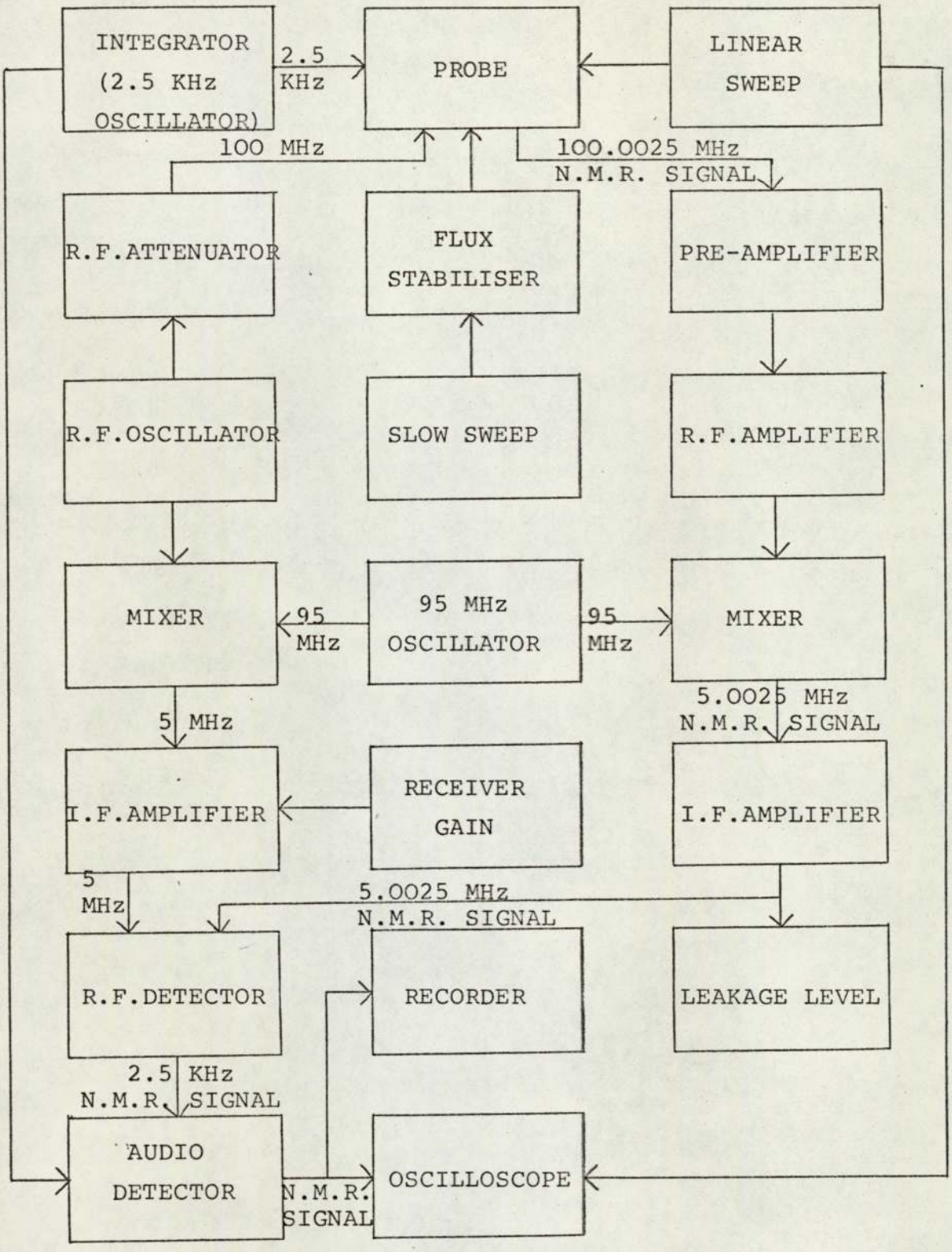


FIGURE 3.1. A schematic representation of the Varian HA-100D spectrometer operating in the HR mode.

A 2.5 KHz signal of variable phase and amplitude derived from the integrator/decoupler unit is applied to the a.c. modulation coils in the probe and modulates the 100 MHz signal, such that the resonance is detected as an amplitude modulated signal at 99.9975 or 100.0025 MHz. The field sweep is nominally applied from a slow sweep unit which drives the flux stabiliser, but in practise may be supplied just as easily from the linear sweep unit which drives the d.c. coils in the probe, although fine adjustment of the sweep rate is not possible by this method. The n.m.r. signal detected at the receiver is returned via the detector preamplifier in the probe to the r.f. unit, where it is amplified in two stages, the gain adjustment being provided by bias variation rather than direct impedance loading via a potentiometer. The r.f. signal is reduced to a nominal 5 MHz intermediate frequency by mixing with a local oscillator output of 95 MHz, and receives further amplification prior to r.f. detection via a reference 5 MHz signal derived from the control section I.F. amplifier of the unit. The n.m.r. signal is applied to the r.f. detector to produce an a.f. signal at 2.5 KHz, and subsequently to an a.f. detector, the reference phase being adjustable so that the required mode, absorption or dispersion, may be selected. The resulting d.c. voltage corresponding to the n.m.r. signal is further amplified and applied to the y-axis of an oscilloscope or recorder, or may be integrated before final presentation. High frequency noise components in the signal may be filtered out by a switchable R.C. circuit before final display. Using this modulation sideband technique it is possible to discriminate against changes in r.f. levels due to variations in probe balance, radiofrequency changes and r.f. leakage, since all variations are effectively cancelled and not detected.

3.2.5. The HA Mode.

3.2.5.1. The Field Frequency Lock System.

The mode of operation of an internal or external lock system is essentially simple, but requires twice as much circuitry as an instrument without this facility. The system is used in order to compensate for short-or long-term instability in the r.f. oscillators or magnetic field strength, and operates, as described previously, in order to hold the field strength and radiofrequency in constant proportion. The HA100D employs an internal lock system, for which a reference material is added to the sample under investigation and is consequently subject to the same conditions as the sample. The n.m.r. signal from the reference is detected in the control channel at the centre of the dispersion mode so that any movement of the signal gives rise to a finite voltage in the detector. The signal is amplified, applied to the field compensator, and the instability is corrected. The other signals are processed seperately in an analytical channel and ultimately are passed to the recorder. Figure 32. is a schematic representation of the internal field-frequency lock system, the detailed operation of which will now be discussed.

The radiofrequency field applied to the sample in the spectrometer is at 100 MHz and acts as a carrier for modulation signals, at audiofrequencies of ±2.5 KHz. N.M.R. signals are detected at fields corresponding to these upper and lower sideband frequencies as well as the 100 MHz centreband signal. The resulting signals are seperated by phase-sensitive detectors corresponding to each frequency, thus enabling the mode of detection, absorption or dispersion, to be selected by adjusting the audiofrequency reference phase applied to the synchronous detector. The reference phase of the control

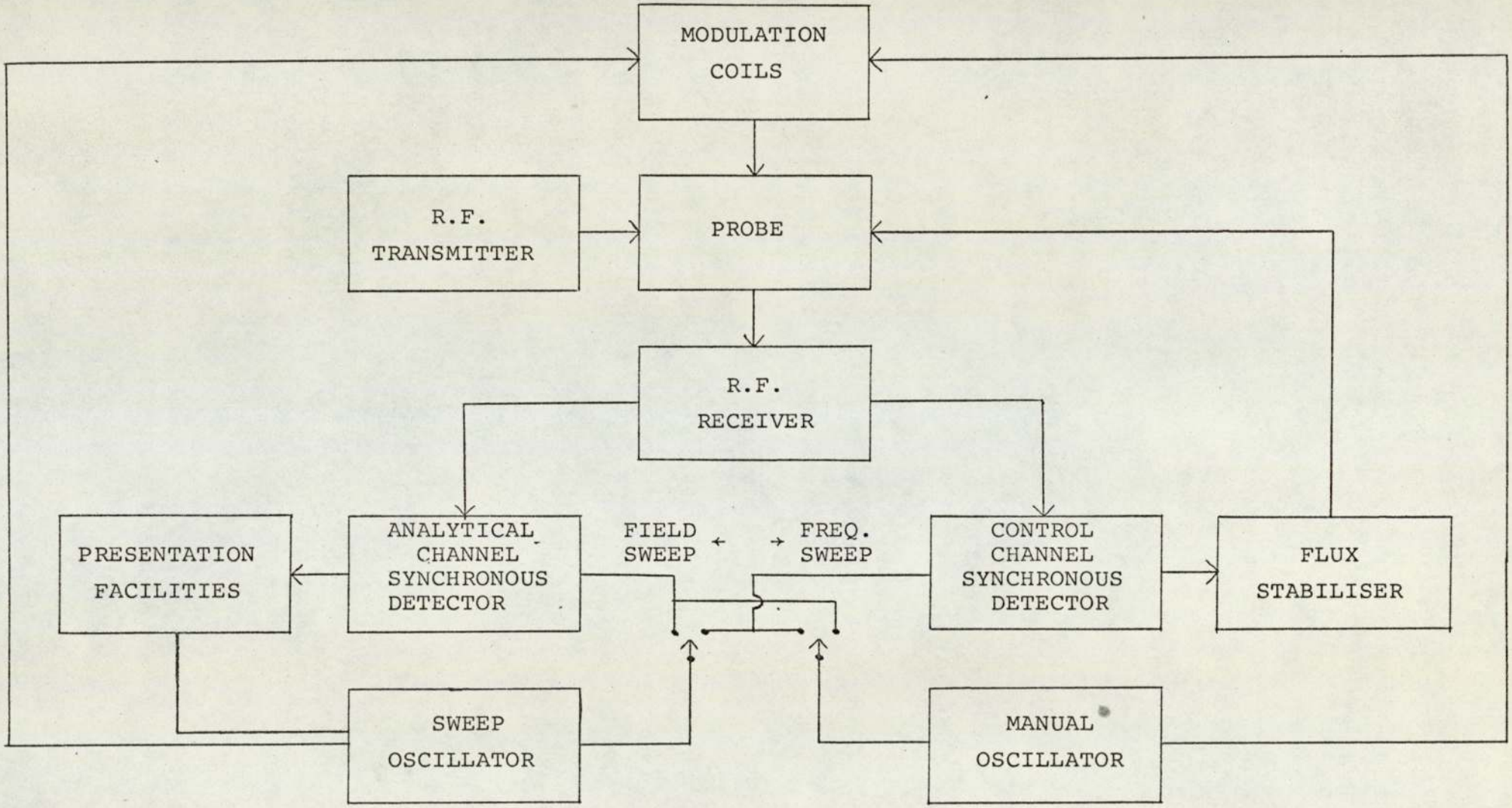


FIGURE 3.2. A schematic representation of the internal field-frequency lock system of the Varian HA-100D nuclear magnetic resonance spectrometer.

(lock) channel detector is adjusted so that a dispersion signal is presented. In frequency sweep mode the reference frequency of the lock signal is derived from a variable frequency manual oscillator, which may be adjusted in order to position the rest of the spectrum at a convenient point for observation. The shape of the dispersion mode signal is ideally suited for use as an error detector because while the frequency at which it is detected is identical to the manual oscillator frequency no signal is presented to the flux stabiliser. However, any small discrepancy will generate a positive or negative relative voltage from the dispersion signal which may be used to correct for field or frequency drift by the application of a d.c. voltage of the relevant sign to the flux stabiliser and thence through correction coils to the magnet. The detected lock signal may be readily monitored on an oscilloscope and may be adjusted for maximum unsaturated amplitude, before the control circuitry is locked, by varying the modulating field applied by the flux stabiliser. When the lock signal is maximised (i.e. the dispersion signal is zero) the error signal may be switched into circuit, thus neutralising any further drift.

For many of the samples used in the investigations reported here the intensity of the signal used as lock reference was not sufficient to enable easy adjustment of the position of the signal, relative to the reference oscillator, because it was below the general level of noise. This was remedied by connecting the lock signal output to an audio amplifier and speaker so that it could be aurally distinguished from background noise. In order to ensure that the correct signal was being monitored, provision was made for comparison with the reference frequency, and an a.c. voltmeter

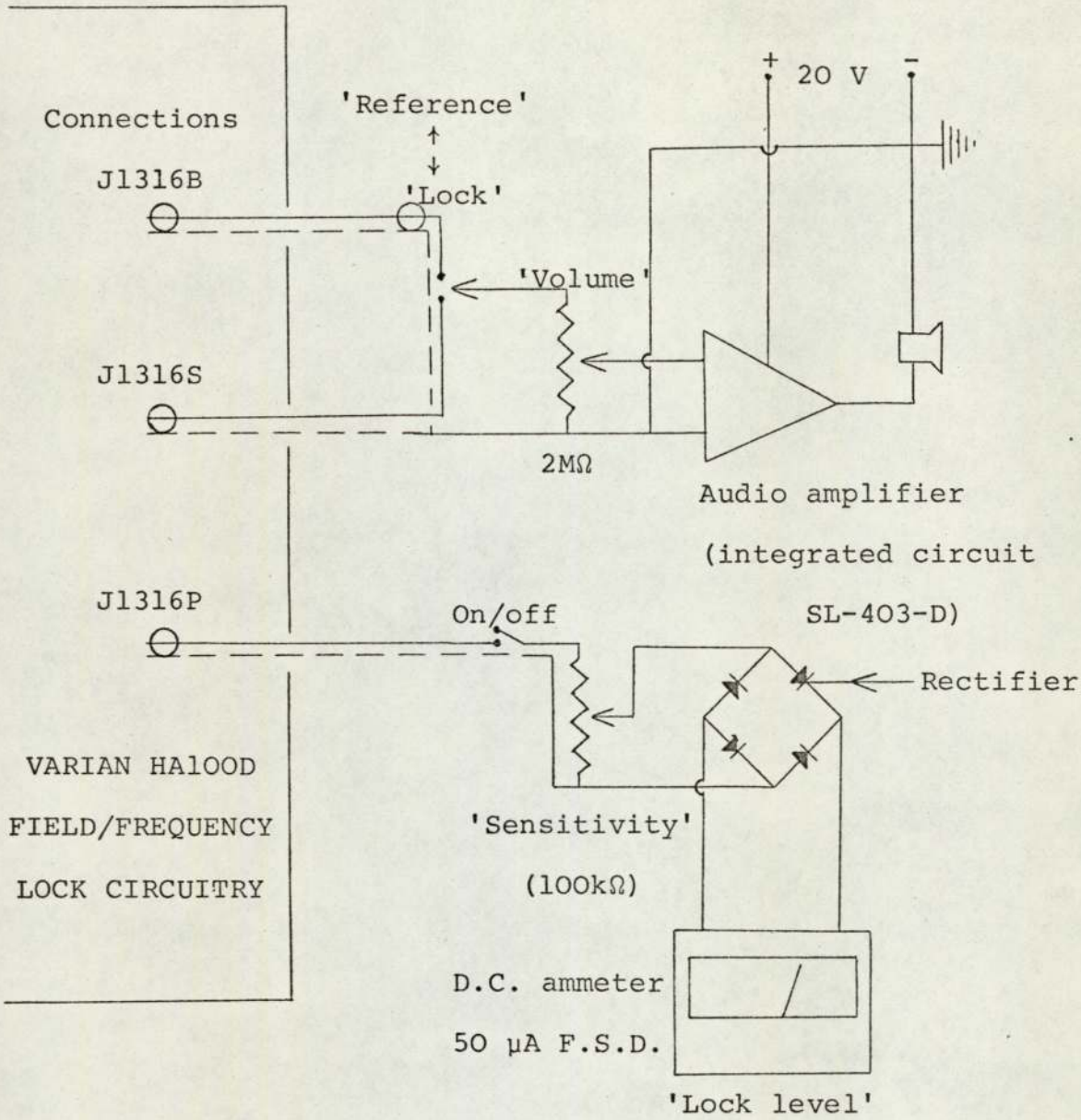


FIGURE 3.3. The connection of the Varian HA1OOD to the audio amplifier circuitry used to detect weak lock signals.

connected to detect changes in level (Figure 3.3). Whilst an oscilloscope or meter does not discriminate between different frequencies, and only detects total voltage, the ear can discriminate between quite small energy differences of different frequencies, and enables a low level, but constant signal to be picked out quite clearly amongst random noise for which each frequency has a relatively low acoustic energy.

Reference to Figure 3.2. shows how either field or frequency sweep modes may easily be accomodated within this system of field-frequency lock. In the field sweep mode the analytical detection channel operates at constant frequency, the reference being provided by the manual oscillator, whilst the sweep oscillator is connected to the control (lock) channel using the low frequency modulation side bands. The variable frequency provided by the sweep oscillator is used as the control channel reference and results in the lock signal generating a linearly varying d.c. error signal, which is applied to the field compensator unit. A linearly varying field is thus generated in order to hold the lock signal at the correct position. Hence the whole spectrum is swept by observation at constant frequency in the analytical channel. The advantage of this system of field sweep is that detected differences in phase are negligible over wide sweep ranges.

The frequency sweep mode requires that the magnetic field is kept constant, and thus the control channel reference is provided by the manual oscillator, which may be set to any frequency conducive to providing the optimum conditions for observation for the rest of the spectrum; the lock system only operates in the presence of field or frequency drift. The sweep oscillator provides the analytical channel reference,

and the frequency is swept by a potentiometer mechanically linked to the x-axis of the recorder. The high frequency modulation side bands are used to detect resonances, and lines appear in the same order as for field sweep since movement of the recorder arm from left to right corresponds to decreasing modulation frequency. It should be noted that the phase of the lock signal is inverted when changing between sweep modes so that it is in the correct sense for regulation.

The use of the frequency sweep mode permits the application of external oscillators to perform spin-decoupling and nuclear Overhauser effect experiments, using the available double or even triple resonance facility. It is possible however to apply external oscillators in order to perform this type of experiment in the field sweep (HR) mode also, and this will be described is a subsequent section.

Five possible sweep widths are available using the field-frequency lock system, varying from 50 to 1000 Hz. The sweep oscillator is designed so that the sweep terminates at 2500 Hz (i.e. the extreme right of the recorder) whatever the sweep width. If the manual oscillator is also set to 2500 Hz, then the lock signal is present, usually being evident as a beat signal, at this position on the recorder. However, it is often required to observe a portion of the expanded spectrum which is outside this predesignated range, and this may be effected by off-setting the manual oscillator above or below this frequency. This adjustment displaces the lock signal in either direction, depending on the sweep mode, and brings a different section of the spectrum within the range of the recorder.

3.2.5.2. The Detailed Operation of the HA Mode.

The HA mode of operation is controlled, apart from

display facilities, by the r.f. unit, which is common to the HR mode, and the Internal Reference Stabilization Unit. The latter, as described previously, adjusts the main field to allow for minor variations in field or frequency and keeps these two parameters in constant proportion. The unit houses the audiofrequency and phase detection circuitry for both signal and control channels, and is interconnected with the r.f. unit, field compensator and presentation facilities. Its mode of operation can be appreciated by reference to Figures 3.2. and 3.4.

The transmitter section comprises two audiofrequency oscillators: the sweep oscillator, variable from 3500 Hz to 2500 Hz, and a manual oscillator, variable from 1500 to 3500 Hz. The frequency of the former is controlled by the movement of the recorder along its x-axis, and the latter by panel controls which are used to vary the position on the recorder of the lock signal. The oscillator circuits are identical modified Wien bridge sine wave generators, and are tuned for 50, 100, 250, 500 and 1000 Hz and 1500 - 2500 and 2500 - 3500 Hz sweep ranges. The voltage gain for these oscillator circuits is supplied by a conventional amplifier of variable gain with a thermistor controlled output. A switch on the front panel of the unit enables the selection of the lock signal, sweep or manual oscillators, an external signal, or the difference (detected by a frequency difference phase detector) of the two oscillator frequencies to be presented to the oscilloscope or the Varian 4315A frequency counter.

As described previously, either oscillator may be used as the reference signal, depending on the sweep mode (Figure 3.4.). The two frequencies are applied to the a.c. coils on the probe after suitable amplification and filtering, and

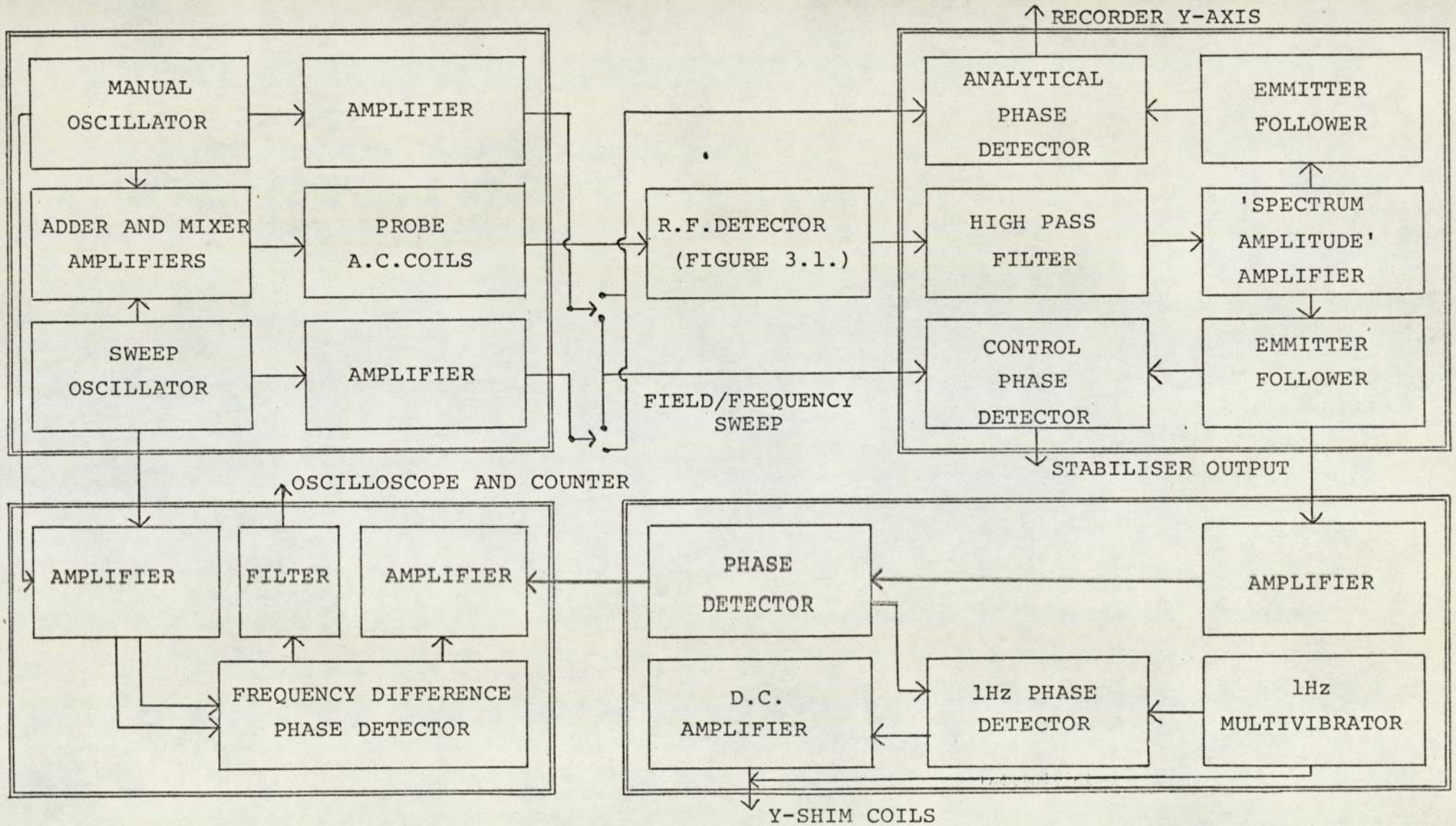


FIGURE 3.4. A schematic representation of the Varian HA-100D spectrometer operating in the HA mode.

independently modulate the 100 MHz r.f. carrier. Intermodulation products must necessarily be minimised in order that spurious signals do not result. The detected n.m.r. signals are processed by the receiver in the r.f. unit in a similar fashion to the HR mode process, and are reduced to audiofrequency signals modulated with the n.m.r. information. The signals are amplified in a circuit of variable gain controlled by the 'Spectrum Amplitude' potentiometer, and containing filters to eliminate spinner noise, and are then split into the respective control and analytical channel constituents. The control channel resonance is amplified, phase-sensitively detected, and filtered, whilst other resonances are similarly processed in the analytical channel. Impedance matching for the respective signals is provided by two separate emitter-follower circuits. The demodulation frequencies of the respective signals are introduced, according to the mode of sweep, via the 'Sweep Field/Frequency' switch.

The control signal is applied through the 'Lock On' switch to the Stabilisation Filter which removes extraneous noise, and passes the d.c. signal to the flux stabiliser to complete the loop. The d.c. n.m.r. signal is similarly detected and passed to the Integrator/Decoupler where it is amplified, filtered and, if required, integrated, prior to being applied to the recorder y-axis circuits.

An additional facility availiable in the HA mode of operation is the Autoshim, which enables the magnetic field homogeneity to be optimised automatically. The control adjusts the shim current to the y-axis coils in response to amplitude changes in the lock signal (Figure 3.4.). Initial homogeneity adjustments must be accurate for effective autoshim control

and it does not work well on very small lock signals such as those used in these investigations. Hence, it has not been used extensively, although, where appropriate, it has been employed with little difficulty.

Changes in signal amplitude are usually caused by external effects, and may be corrected with the y-axis homogeneity control. Very small changes may be detected more readily by modulating the signal at a rate of about 1 Hz and use is made of this fact in the autoshim unit. The y-axis current is modulated by a 1 Hz square wave multivibrator and in turn modulates the intensity of the n.m.r. signal. Shim currents of other than optimum value will cause the 1 Hz modulation to be detected as the optimum value is passed, and error signals may be produced by a phase-sensitive detector, and fed to the shim coils in order to maintain the current at optimum value.

3.2.5.3. Probe Temperature.

The variable temperature accessory used to control the sample temperature has not been used in this study, and will consequently not be discussed further. The temperature within the probe was, however, measured frequently and was calculated in the conventional manner by observing the chemical shift between the methyl and hydroxyl protons of methanol. The variation of this shift with temperature is depicted in Figure 3.5.

3.3. The Accurate Measurement Of Chemical Shifts.

For normal n.m.r. spectra, absorptions are recorded on calibrated chart paper, and approximate values for chemical shifts may be deduced from measurement of the separation between recorded lines. The investigations reported here, however, require shifts to be measured to an accuracy of 0.1 Hz

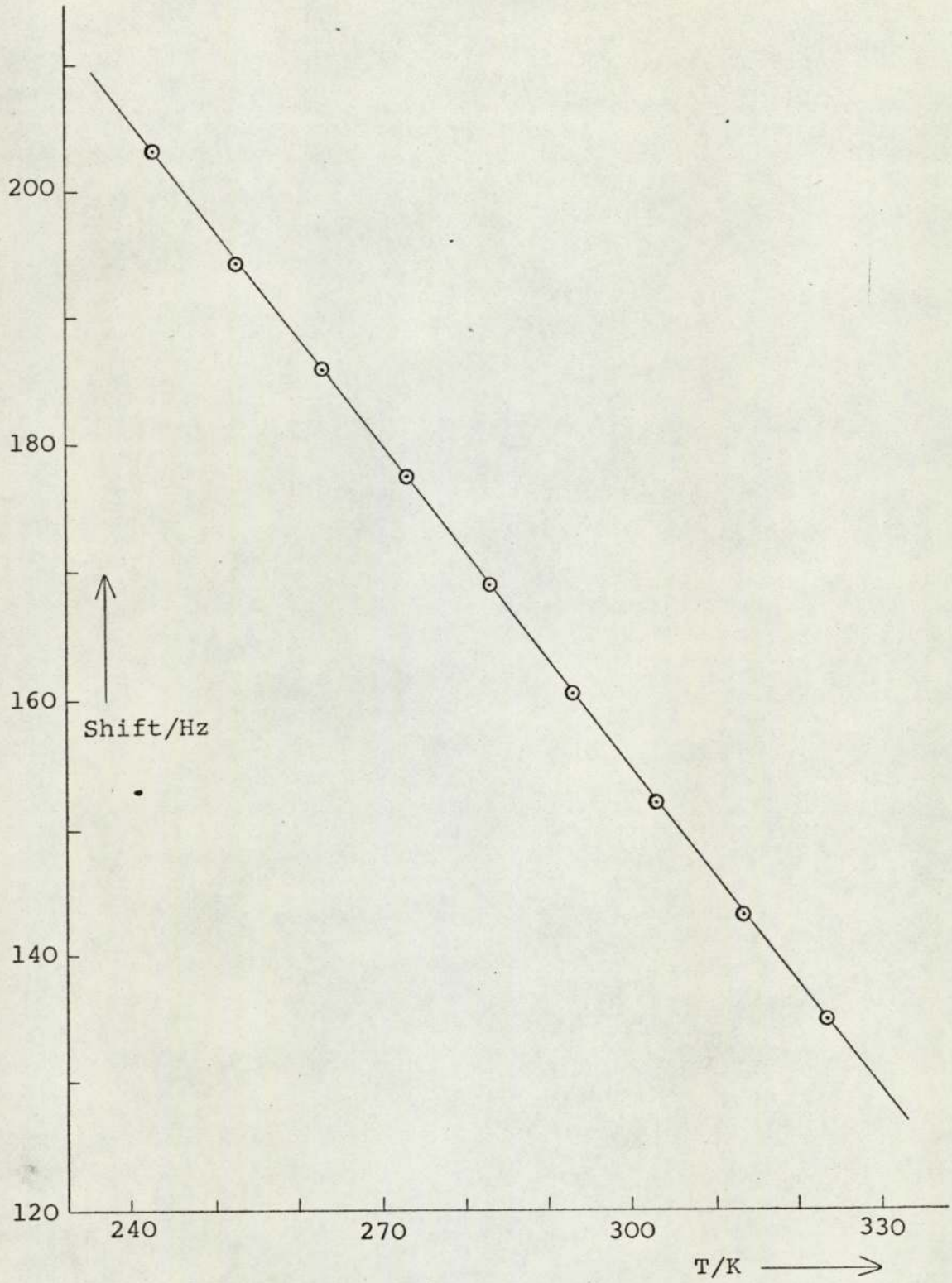


FIGURE 3.5. The variation of the chemical shift between the methyl and hydroxyl protons of methanol with respect to temperature.

or better, and this may readily be effected as follows. The flat-bed recorder of the Varian instrument provides a choice of nine possible sweep times, but it is necessary to record all absorption lines at the same speed, and filter conditions to avoid inaccuracies due to response deficiences. The field sweep lock mode was used in order to minimise phase differences between absorption peaks.. The spectra were drawn out in an expanded form (100 Hz sweep width) several times, and the position of each peak was measured by placing the pen at a stationary position corresponding to the peak maxima and counting the sweep and manual oscillator frequencies on the Varian frequency counter. Subtraction gives the chemical shifts of the peaks relative to the lock signal. The chemical shifts between other absorptions were calculated by measuring each absorption relative to the lock signal and subtracting the two values. This is necessary because the manual oscillator frequency may be varied when the spectrum is expanded. Shifts were found to be reproducible to within ±0.1 Hz, even for very small lock signals. The averaging of several values reduces this error further.

3.4. The Measurement Of Spin-Lattice Relaxation Times.

It is apparent from the simple equation (3.2) applicable to single spin systems that in order to measure values for T_1, the equilibrium value of the magnetisation, M_o, must be perturbed to give a magnetisation, M_z, which will approach M_o exponentially with time, t, according to

$$M_o - M_z = M_o e^{-t/T_1} \qquad 3.2.$$

There are several methods for perturbing the magnetisation, or realistically, changing the angle of the magnetisation vector. The methods which are available will be discussed in turn; those of specific interest in the context of this thesis will

be considered in greater depth.

3.4.1. Adiabatic Fast Passage Techniques.

The adiabatic fast passage (A.F.P.) technique is based on Bloch's nuclear induction experiment[19] which differs from most other nuclear magnetic resonance experiments in that a comparatively large radiofrequency field, B_1, is applied. This field is sufficient to cause a considerable change in nuclear magnetisation in one passage through a resonance. Bloch showed that if the radiofrequency field is large enough the magnetisation may be reversed by passing the main field across the resonance value. For this to happen Bloch's adiabatic condition must be satisfied:

$$|dB_o/dt| << |\gamma| B_1^2 \qquad 3.3.$$

where $2B_1$ is the amplitude of the r.f. field and dB/dt is the rate of change in the main field. Equation 3.3. ensures that the magnetisation nutates many times during the passage through resonance. It is also apparent that resonance must be passed in a time less than T_2 otherwise transverse magnetisation components will decay, (since $T_1 > T_2$, T_1 may be ignored). Therefore a sweep through resonance must take less time than T_2 so that the time spent at or near resonance is $B_1/(dB_o/dt)$; the second condition described by equation 3.4. is therefore also necessary.

$$B_1/(dB_o/dt) << T_2 \qquad 3.4.$$

The conditions necessary for adiabatic fast passage are therefore given by:

$$\frac{1}{T_2} << \frac{1}{B_1}\left|\frac{dB_o}{dt}\right| << \gamma B_1 \qquad 3.5.$$

and may always be satisfied by making the rate of field sweep and B_1 sufficiently large.

The method was first developed by Drain[159], who used

it for measuring the relatively short spin-lattice relaxation times of paraffin wax, glycerine, liquid hydrogen and water, and also by Conger and Selwood[23] for measuring even shorter times in paramagnetic solutions. However, the method is more suited to the measurement of relaxation times of about five seconds, and has been used thus by the great majority of workers for proton resonance work.

The simplest method of employing the technique is to modulate the main field with a triangular[129,160,161], trapezoidal[108,162], or more unusually a sine wave[159], the varying voltage being conveniently applied to the field compensator to drive the field in a sweeping fashion. The resonance is swept through and monitored on the return of the sweep, the rate of which is then adjusted so that no absorption is observed on the return, the magnetisation then being zero. Assuming 100% inversion of the magnetisation, T_1 may be computed from[23,107]

$$T_1 = \Delta t/\ln 2 \qquad 3.6.$$

where Δt is sweep period between the A.F.P. and monitoring the signal. However, it is often questionable whether 100% inversion occurs in all A.F.P. experiments, and hence there may be unknown errors in this method. A far more accurate technique has been introduced by Anderson, Steele and Warwick[163] and is known as the adiabatic fast passage with sampling method, (AFPS). This technique involves the use of a repetitive field sweep and increasing the r.f. field on one sweep only(i.e. to give a 180° pulse) for which the conditions dictated by equation 3.5. must still be satisfied. The 180° pulse inverts the magnetisation which may then be monitored during its decay to M_o by a low level r.f. field.

For a single spin, equation 3.2. is applicable, and may be modified to:

$$\ln(M_o - M_z) = \ln M_o - t/T_1 \qquad 3.7.$$

A plot of $\ln(M_o - M_z)$ against t yields T_1 from the slope of the line. M_o is the final resonance intensity after equilibration or initial intensity before the A.F.P. experiment and M_z is the intensity at time t. As shown previously, if B_1 is very small, M_z is directly proportional to peak height, thus enabling the simple evaluation of T_1. A typical example of an AFPS experiment is shown schematically in Figure 3.6.

The different methods of measuring relaxation times by A.F.P. methods have been discussed by many workers. Janzen et al[164] have pointed out that only the plot method described above gives a relaxation time independent of the degree of inversion of M_z during the adiabatic passage, and represents a major advantage over null[159] and symmetric modulation[97,128] methods which may be used more conveniently for shorter relaxation times. Parker and Jonas[162] have carried out extensive calculations of the v-mode line shape, and the dependence of M_z on the conditional equation 3.5., with special reference to the A.F.P. technique. They concluded that even under seemingly ideal conditions the degree of inversion was only 0.98 - 0.99, and resulted in errors of 2 - 3% in values for T_1 obtained by the null and symmetric modulation methods.

Powles[165] has extensively reviewed the theory of the A.F.P. method, and obtained equations for systems of two spins[108], which will be discussed further in a subsequent chapter. Heatley[166,167] has analysed the behaviour of a

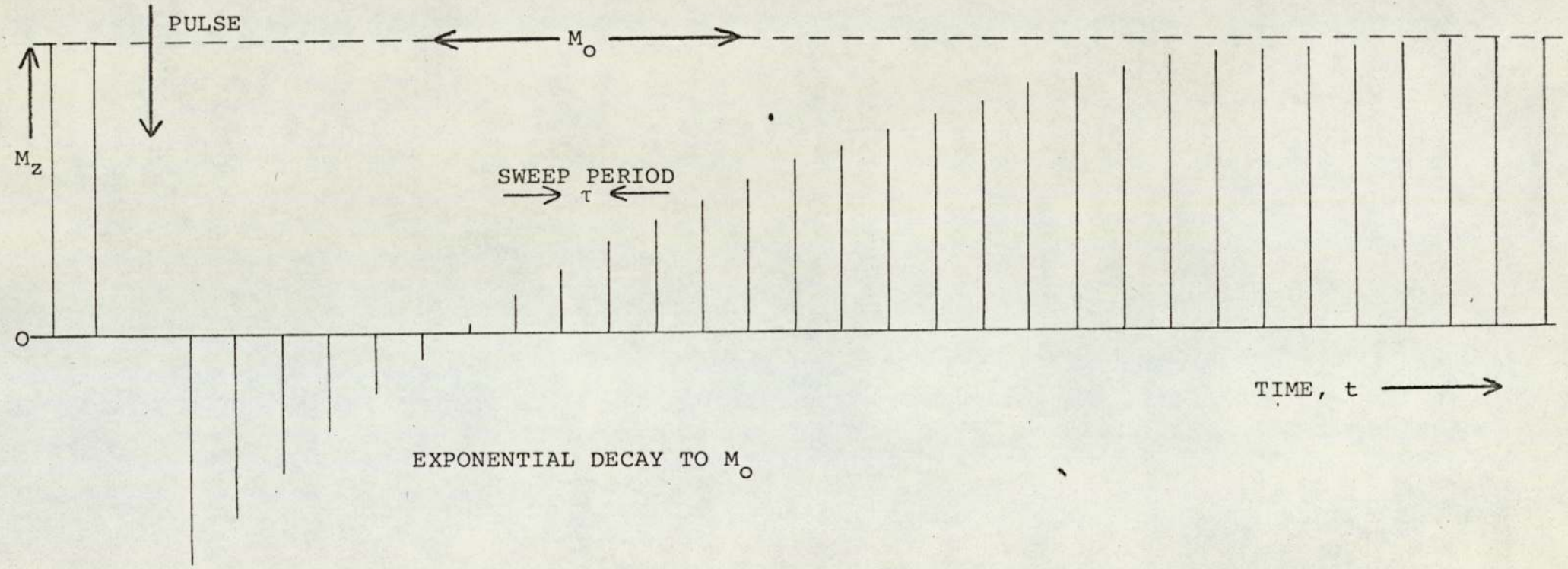


FIGURE 3.6. A schematic example of an A.F.P.S. experiment on a single spin system. The sweep period, τ, is usually about 1 second, the sweep being used to monitor the exponential decay of M_z to its equilibrium value M_o.

spin-system under A.F.P. conditions and has shown how a factor may be introduced into the decay equations, which allows for incomplete inversion of the magnetisation if the conditions dictated by equation 3.5. are not fulfilled. When the factor equals -1 the general A.F.P. equation results, but its introduction for other values of inversion enables one to carry out other methods of measurement, such as progressive saturation, which will be discussed in the subsequent section.

3.4.2. Saturation Techniques.

There are several methods for measuring T_1 values which depend on the saturation of the resonance. One of these is to measure signal height as a function of time after the sample has been placed in a strong magnetic field, B_o. At the beginning of the experiment all nuclear levels are equally populated and take a finite time to reach equilibrium, this time being dictated, as described previously, by T_1. However, this method is not practicable for obvious reasons, although a similar result may be achieved by saturating the line and then observing the recovery time[18]. Whilst both these procedures can be used to calculate T_1 by equation 3.7. the latter is preferable. In this case the measurement is made after saturation by field sweeping, in a similar fashion to the AFPS monitoring procedure, with a sufficiently small r.f. field so that the polarization is not appreciably perturbed. The time spent in resonance must be small compared with the sweep period so that the effects of T_2 are small, and that spin-lattice relaxation during resonance is negligible. Under these conditions the height of the absorption signal will be proportional to M_z.

These methods offer little advantage over the AFPS

method except that the value of M_z at t = 0 is known. This factor is of little importance here and hence these possibly less accurate procedures will not be further investigated.

The method developed by Heatley[166,167] known as the 'repetitive sweep progressive saturation technique', is exceptionally useful for the measurement of very weak absorptions. For example, Heatley has measured the relaxation times of ^{13}C sidebands by this method. The magnetisation is initially at thermal equilibrium and then subjected to a moderately high r.f. field which induces a progressive saturation until a partially saturated, constant, magnetisation is observed. The high r.f. field used means that small signals are significantly increased in intensity, and resolution is better than for some other methods. Heatley has shown that T_1 may be deduced from equations 3.8. and 3.9.

$$M_z(n) - M_z(\infty) = (ae^{-\tau/T_1})^{n-1}\left[M_z(1) - \frac{M_o(1 - e^{-\tau/T_1})}{(1 - e^{-\tau/T_1})}\right] \qquad 3.8.$$

$$\frac{d(\ln|M_z(n) - M_z(\infty)|)}{dt} = \ln(|a|e^{-\tau/T_1}) \qquad 3.9.$$

where $M_z(n)$ and $M_z(\infty)$ are the values of M_z after n sweeps and at equilibrium respectively, a is the inversion factor and τ is the sweep period. The relaxation time calculated from this decay is only an effective T_1 given by:

$$1/T_1^* = 1/T_1 - \ln(|a|/\tau) \qquad 3.10.$$

Therefore a knowledge of a is required in order to calculate T_1 from equation 3.8. or 3.10. It is generally difficult to find a except for AFP sweeps and when monitoring signals with low r.f., when it is assumed that a = - 1 and a = + 1 respectively. The inversion factor may, however, be determined

from equation 3.9.,in terms of $e^{-\tau/T_1}$. A measurement of the ratio $M_z(\infty)/M_o$ enables T_1 to be calculated using equation 3.8.

The use of this method in the context of the current work has been precluded by lack of time, but its use holds promise for future work, since it provides all the assets of an AFPS experiment as well as being more sensitive.

3.4.3. Other Methods.

Many other methods are available for the measurement of spin-lattice relaxation times, but are mostly difficult to implement or are inaccurate.

Bloembergen et al[18] derived T_1 from the measurement of the field strength B_1 which produces the maximum value of the v-mode signal at resonance. At this point equation 3.11. applies.

$$\gamma^2 (B_1)^2 T_1 T_2 = 1 \qquad 3.11.$$

and knowledge of T_2 and B_1 enables calculation of T_1. The calculation of T_2 is more difficult, and may not be to the required accuracy.

Other methods, which are generally modifications of the AFP method, have been described by many workers[168-170], but these generally involve extensive equipment modification and are potentially no more accurate. However the present trend towards the use of Fourier Transform spectrometers has enabled the development of many new techniques which are applicable to ^1H and ^{13}C resonances. These are mainly pulse techniques, the AFP method being suitably modified, or different pulse sequences being used. It is necessary to decouple proton nuclei from ^{13}C spectra in order to obtain pure exponential decays of the magnetisation[171,172] and it

is found that pulse techniques often give rise to higher T_1 values than A.F.P. methods.

The pulse techniques are normally of a repetitive nature, except for a ^1H A.F.P. where 180°-t-90° pulses are used[173]. The sequence for ^{13}C is usually $(-T-180^o-t-90^o-)_x$ where T is long compared with T_1[174], but has been modified by Freeman and Hill[175] so that spectral data present all signals in the same sense. This pulse sequence is $(-T-90^o_\infty-T-180^o-t-90^o-)_x$ where 90^o_∞ is an isolated pulse during the long waiting period.

Since it has not been possible to study relaxation processes by employing such pulse techniques they will not be discussed further.

3.4.4. Practical Considerations.

From the foregoing discussion of the most common methods employed for the measurement of spin lattice relaxation it is apparent that the most suitable techniques for the present investigations are the A.F.P.S. and saturation-recovery methods. These two techniques are extremely similar, differing only in the angle of the initial pulse, the former using a 180° pulse, whilst the latter uses a 90° pulse. Of these two methods the A.F.P.S. technique is inherently more accurate because it provides more data for a given sweep rate, and it will therefore be used in all investigations reported in this thesis.

It is necessary to discuss how the equipment used in the present work may be employed for the measurement of T_1 values by A.F.P.S. methods. Sykes and Wright[176] have shown how a Varian HA100 spectrometer may be modified so that spin-lattice relaxation times may be measured in samples containing a reference material to provide a lock signal.

Rather than sweeping the field rapidly, a condition which the lock circuitry cannot keep up with, they employed a fast frequency sweep using a voltage controlled generator and pulsing circuit. The system is suitable for use with a time-averaging computer to increase signal strength, but it was found necessary to use an external fast response recorder. Owing to time limitations it was not possible to employ this procedure, and the simpler procedure which will now be described makes use of suggestions made by Heatley[166] and Hoffman and Forsen[123].

Hoffman and Forsen showed that the use of the HA mode was precluded unless the extensive modifications proposed above were employed, and concluded that intensity measurements performed in the HA mode, even with these modifications, may not be any more reliable than those obtained in the HR mode.

Their experimental method, which will be used in the investigations reported in Chapter 8, involves recording signals obtained by phase-sensitive detection in the integrator/decoupler unit which is operated in the side-band mode, rather than centreband mode. In the centreband mode the modulation index is such that the r.f. level is similar at sideband and centreband resonances, and adjustment of phase permits the suppression of the first sidebands. In the sideband mode, however, the modulation index is decreased and the audio modulation is phase-shifted by 90°. Since the effective r.f. level at the sideband is a function of the modulation level, it is necessary to increase the r.f. power by about 40dB to obtain a usable sideband signal. The r.f. phase may then be adjusted for absorption mode at the sideband, and the audio phase to suppress the centreband. Adiabatic

fast passage pulse conditions may therefore be obtained by switching from sideband to centreband mode over the appropriate portion of the sweep period, which increases the r.f. power at the sideband by approximately 40dB. Whilst it is not possible to obtain perfect inversion by this method, this is of no consequence for the AFPS method.

Both Heatley, and Hoffman and Forsen used the phantastron linear sweep unit of the Varian instrument, rather than applying an external modulation to the field compensator, as this reduces the complexity of the system.

The response of the Varian flat-bed recorder is not sufficient to deal with continuous monitoring of a signal at intervals of one second or less, primarily because of its built-in filter characteristics, and also because of its transport mechanism. Substantial chopping was found to occur on some high intensity peaks. Heatley used a fast response Hellige galvanometer recorder, and the availability of such an instrument in the author's laboratory enabled accurate signal intensity measurements to be made. This recorder has a response from d.c. up to at least 150Hz, and ample control over speed and signal levels. It was checked for response linearity at 10Hz, a frequency close to the input signal response, at levels from zero to full scale deflection. The response graph of deflection against input voltage is linear, as illustrated by Figure 3.7.

The investigations to be carried out in Chapter 8 will be directed towards the measurement of the effect of [^{2}H]chloroform on the relaxation times of benzene and cyclohexane, the three component mixture being effectively reduced to two spins, as described previously, by the use of deuterated chloroform. In order to study such a two spin

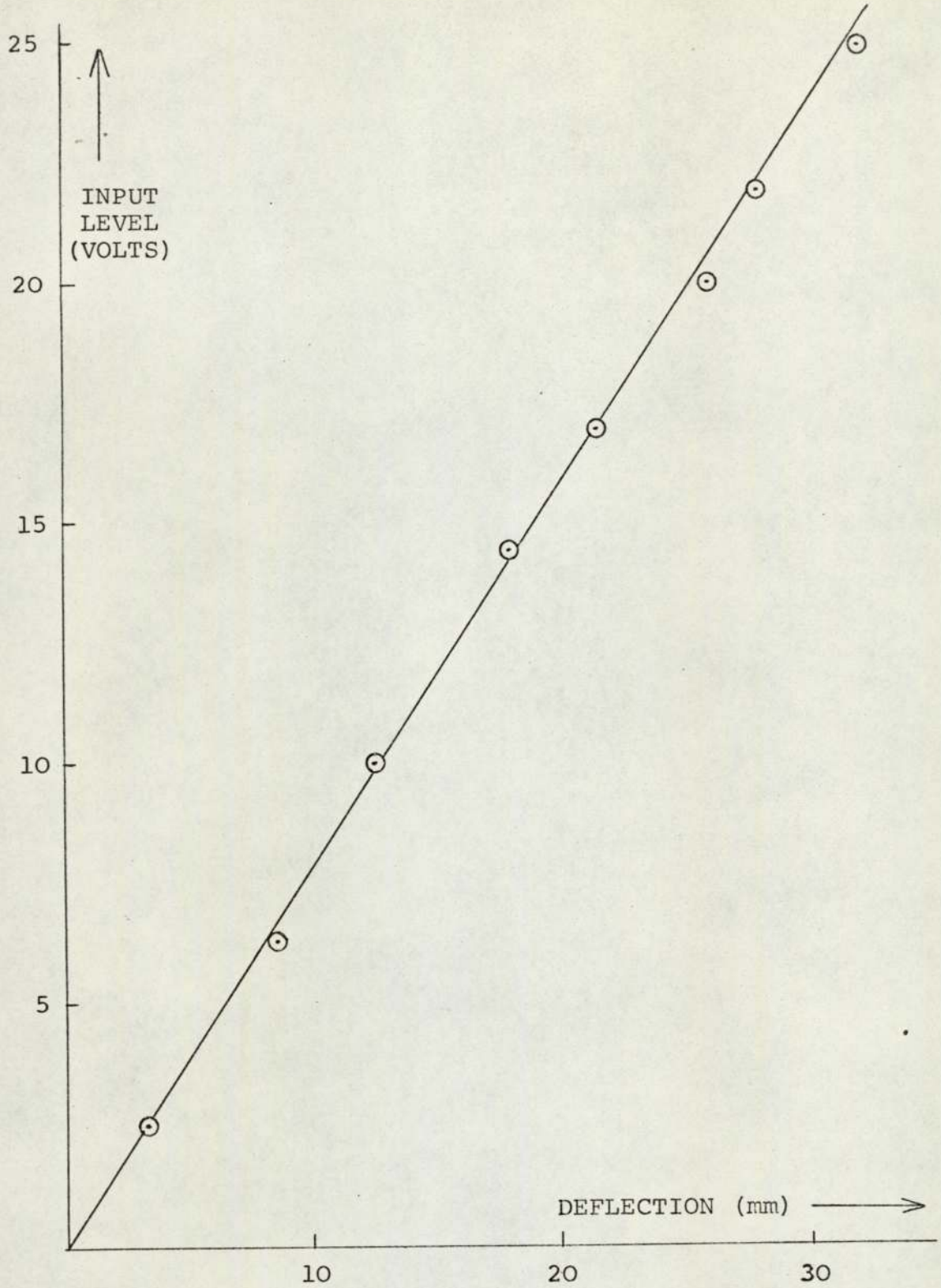


FIGURE 3.7. The response of the Hellige galvanometer recorder used to record signal intensities for A.F.P.S. experiments.

system it is necessary to introduce an external modulation frequency to saturate out one resonance in order that values for T_{AA}, T_{BB} etc. (equations 2.37. and 2.38.) may be obtained (i.e. a double resonance experiment). Hoffman and Forsen have shown that modulation frequencies can be applied in the HR mode by directly modulating the signal from the r.f. unit to the probe. The frequency settings are not critical, however, due to the large sweep width employed (up to 15 p.p.m.). The oscillators used were a Muirhead-Wigan D-890-A Decade Oscillator and an Airmec Type 422 signal generator, and frequencies of these were counted on the Varian, a Venner 3336 and an Airmec 422 counters.

A further critical appraisal of the AFPS method for measuring spin-lattice relaxation times will be given in the context of the proposed investigations later in this thesis.

3.4.5. Practical Difficulties.

The important practical difficulties which must be overcome before attempting to measure relaxation times are primarily the removal of oxygen from samples, and the determination of the optimum size of the sample. The previously discussed factor of the effect of oxygen on relaxation times and its exclusion from samples will be investigated in Chapter 8, and a simple method will be described that has been devised to exclude oxygen. T_1 results obtained for samples so degassed will be compared with previously reported T_1 values, and with those obtained in this laboratory by other degassing techniques. The extension of the method to prepare samples with a high quantitative accuracy will be described.

Van Geet and Hume[177] have reported that it is essential that the magnetic field be relatively inhomogeneous in order that pure exponential recovery of the magnetisation is to be observed. To ensure that the decay was exponential these workers did not spin the sample. Hoffman and Forsen[123] have also purposely offset the shim current controls to achieve the best conditions. It is reasonable to suppose that samples used for relaxation time studies should not be spun anyway because of the unnatural molecular motion which could possibly result, and consequently affect the self-diffusion constants.

Powles[108] has shown that it is necessary to ensure that all the sample should be well inside the transmitter coil. There are then no nuclei which have not been subjected to the A.F.P. which can diffuse or convect into the receiver coil.

These procedures have been adopted in these investigations. The position of the coils on the Varian HA100D instrument used was ascertained by the vertical adjustment of a very small sample in the probe and noting the size of the resulting peak. The maximum sample length was found to be about 10mm, and its position marked on the sample depth gauge for subsequent reference.

CHAPTER 4.

SOME COMMENTS ON THE NATURE OF AND REFINEMENTS TO METHODS OF STUDYING TRANSIENTLY FORMED MOLECULAR COMPLEXES.

4.1. Introduction.

In Chapter 2 of this thesis some general comments were made concerning the factors contributing to the chemical shift and relaxation processes, including those due to specific association. In this chapter some observations and comments will be made concerning the nature of specific interactions and transiently formed molecular complexes in solution, and the rationalisation of nuclear magnetic resonance spectroscopic methods to investigate these phenomena. Particular reference will be made to the processing of data which are obtained from such studies, and to the methods by which it is possible to obtain parameters describing the interactions.

The basic chemical equation describing the type of interaction studied here is

$$A + B \rightleftharpoons A \ldots B \qquad 4.1.$$

where A is a polar solute and B is an aromatic molecule. The formation of an AB complex implies that there is a short lived orientation of the aromatic molecule with respect to the solute molecule, which has arisen by such interactions as dipole-induced dipole, or dipole-quadrupole. The investigation of the nature and mechanism of formation of some of these complexes is the subject of subsequent chapters.

The large upfield shift of the chloroform proton resonance which is observed when it is dissolved in benzene was reported some years ago,[42,178-179] and is interpreted as being due to the effects of specific association between the

chloroform and benzene molecules[42-44,85-94]. It is apparent from the magnitude of the shift that the hydrogen atom of the chloroform molecule must be closely involved with this interaction; this has been further substantiated by infrared studies[42,180-184]. The increased screening arises from the secondary field produced by the circulation of electrons in the conjugated π-orbitals of the benzene molecules which is induced by the magnetic field, B_o. It is the change in screening which permits the evaluation of the equilibrium quotients and Δ_c by the methods outlined in Chapter 1. However, the uncritical use of these methods has led to many conclusions which are of questionable significance. Therefore, in the following discourse, the observations of other workers must be treated with reservation.

N.m.r. can be used successfully to study the nature of the interaction because changes in the environment of A will result in changes in the effective aromatic induced shift. Any mechanism which is proposed to account for this must take into account the nature, stereochemistry, stoichiometry and strength of the complex formed, and these important factors will be considered seperately with a view to forming an overall representation of molecular complexes. An understanding of these factors will form a basis for the development and confirmation of methods for processing n.m.r. data which result in the calculation of meaningful equilibrium parameters.

The information which is potentially available from n.m.r. studies of molecular complexes may only be retrieved by careful consideration of the validity of these studies and the current understanding of the nature of liquids, liquid mixtures and the molecular interactions which are

relevant to these. Since relatively little is known about the liquid phase in comparison with solids and gases, it is, perhaps, not surprising that many investigations have given rise to descriptions of molecular complexes which are, at best, of questionable significance. This is additionally true because it is only recently that those studies using n.m.r. chemical shifts in attempts to elucidate the problems have been put on a sound foundation[40,41].

It is, therefore, the purpose of this chapter, firstly, to describe in detail the nature and theoretical background of these recently revised n.m.r. procedures in order that investigations may be carried out to confirm the validity of the modifications under conditions of high experimental accuracy. Secondly, the use of another important n.m.r. parameter, the spin-lattice relaxation time, to obtain information concerning molecular interactions in solution, particularly interactions of the molecular complex type, will be discussed. The spin-lattice relaxation time, T_1, is a macroscopic parameter which may be reduced to a molecular level, whilst the chemical shift has a molecular basis, but may be extrapolated to the bulk medium. It is anticipated, therefore, that the use of spin-lattice relaxation times may enable information to be forthcoming which it is difficult to obtain by chemical shift measurements, (i.e. accurate representations of the mechanism of complex formation). Measurement of T_1 and its related parameter η, which is due to the nuclear Overhauser effect,[185] have been used very little for investigations of this type, although their importance in the investigation of biological systems and stereochemical effects is well known.

4.1.1. The Origin Of Aromatic Induced Shifts Which Permit Studies Of Complex Formation.

The effects of specific association and exchange processes in liquids and liquid mixtures on the appearance of n.m.r. spectra have been discussed in Chapters 1 and 2, and it is evident that the chemical shift induced in the solute on complex formation is dependent on the screening effects produced by the aromatic molecule.

It is important to note that for the type of interaction investigated here there is no evidence for actual charge transfer between the two molecules. Absorption bands in the U.V. spectra of the weakly bound systems studied by Abraham[186] were not typical of this type of mechanism, and Homer and Huck[80] found that whilst the complexes formed between nitroform and some methylbenzenes (strongly bound) do have U.V. absorptions which could be associated with charge transfer, the extinction coefficient of these was only about 50, whilst a true charge transfer band usually has an extinction coefficient of about 10,000.[187]

The characterisation of the screening which results from ring current effects in aromatic molecules has been the subject of considerable effort and the models which have been proposed may be used quantitatively in explaining aromatic induced shifts in solute molecules, as long as it is assumed that no distortion of the π- electron cloud occurs.

In one of the earliest attempts the π- electrons were considered to move in the plane of the aromatic ring[188], giving rise to a current, I, described by equation 4.2.

$$I = \frac{ne^2 B_o \cos\theta}{4\pi mc} \qquad 4.2.$$

where n is the number of circulating electrons, m is the

mass of the electron and cos θ a term which allows for the time-averaged orientation of the ring with respect to the direction of the magnetic field B_o. The current may be considered to be analagous to a point dipole acting along the C_6 axis of the aromatic, its magnitude being given by equation 4.3.

$$\bar{m} = ne^2a^2B_o\cos\theta/(4mc^2) \qquad 4.3.$$

where a is the radius of the aromatic ring. Equation 4.4., therefore, gives the screening contribution of the ring current to an aromatic proton which is a distance R from the ring centre.

$$\sigma_{hor} = \frac{ne^2a^2\cos^2\theta}{4mc^2R^3} \qquad 4.4.$$

The comparison of the calculated value of - 1.83 p.p.m. with the experimentally deduced value of - 1.48 p.p.m.[189], the chemical shift difference between benzene and the unconjugated 1,3-cyclohexadiene, is favourable. However, the validity of this comparison is subject to some doubt because it has been shown[190] that the experimentally determined value includes a significant $\Delta\sigma_{AA}^{dia}$ contribution.

This treatment may be extended[80] to resolve the screening into vertical and horizontal components, by considering the π- cloud as two point dipoles situated on the C_6 axis, a distance 2d apart. The horizontal and vertical screenings are then given by equations 4.5. and 4.6. respectively.

$$\sigma_{hor} = \frac{ne^2a^2\cos^2\theta}{4mc^2(R^2+d^2)}\left[\frac{3d^2}{R^2+d^2} - 1\right] \qquad 4.5.$$

$$\sigma_{vert} = \frac{ne^2a^2\cos\theta}{4mc^2}\left[\frac{1}{((R_1-d)^2+a^2)^{3/2}} + \frac{1}{((R_1+d^2)^2+a^2)^{3/2}}\right] \quad 4.6.$$

where R_1 is the distance of a point on the six-fold axis from the plane of the ring. For a value of d = 0.064 nm, a value of σ_{hor} = - 1.35p.p.m. may be deduced, which agrees well with the experimental figure.

Johnson and Bovey[189] have extended the treatment due to Waugh and Fessenden[191], which involves the use of elliptic integrals because of the horizontal and vertical contributions, and have shown that if 2d is taken as 0.918 of the aromatic ring radius, then the calculated results are in excellent agreement with the experimental observations for a wide range of aromatic molecules. Published tables, based on their calculations, may be used to deduce the screening values at various coordinates around the aromatic nucleus.

4.1.2. The Nature Of The Interaction.

Whitney[49] has attempted the correlation of the screening values with the chemical shifts induced in the solute in order to deduce structures for the complexes formed between chloroform and several alkylbenzenes, but found that in some cases steric factors were important, and although his results substantiate the findings of previous workers[192-194], only qualitative inferences were justified because of these factors.

Klink and Stothers[195-197] have found strong evidence that the polar solute molecule induces a transient dipole in the aromatic, and suggested that the interaction may be considered to be of a dipole-induced dipole nature,

a conclusion which has been reaffirmed by Homer and Cooke[198], and Schneider[199]. It has been proposed[192] that the transient dipole originates from the promotion of an aromatic π electron to a π^*_p anti-bonding orbital.

Schneider[199] proposed that the benzene ring lies as far as possible from the negatively charged region of the solute, and supported his dipole model by plotting the observed chemical shifts for a series of polar substituted methanes against the ratio of their dipole moment, μ, and molar volume, V. The latter parameter defines the mean distance of closest approach to the benzene molecule. A linear relationship was found to exist between the chemical shift and μ/V.

The evidence of Klink and Stothers[195-197], and also that reported by Ronayne and Williams[200], suggests that the benzene molecule acts as an electron donor to sites in solutes which are electron deficient, and that the orientation of the benzene molecule to these sites is dictated by local dipole-induced dipole interactions. However, as stated previously, there is no evidence for actual electron transfer between aromatic and solute.

Homer and Cooke[198] have shown that the simple dipole model may be extended to one in which complex formation is considered to arise through the local bond dipoles of the solute inducing an electric moment in the polarisable aromatic molecule. For interaction to occur in this way it is not necessary for the solute to possess a permanent molecular dipole, but only highly polar bonds. This explains why molecules with no permanent dipole, for example carbon tetrachloride, interact specifically with aromatic molecules. However, where a molecular dipole exists they suggest that

this governs the mutual orientation of the interacting species.

The explanation of the interactions between polar solutes and aromatic molecules in the above manner provides a means for estimating the strength of them, and will be dealt with in more detail in Section 4.1.4.

The evidence which has been put forward shows that the formation of complexes in liquid mixtures between polar solutes, or solutes with highly polar bonds, and non-polar aromatic molecules is an attractive interaction of a dipole-induced dipole nature. N.M.R. spectroscopy is a very convenient means of investigating the phenomenon because electron currents induced in the π electron cloud of the aromatic molecules give rise to large screening contributions at the solute molecule, which vary according to its position, orientation, and general environment in the liquid mixture. It is immediately obvious, therefore, that dilution of the aromatic component of the mixture with a suitable solvent enables the evaluation of equilibrium parameters for the interaction.

4.1.3. The Stereochemistry And Stoichiometry Of The Complex.

Whilst the stereochemical and stoichiometric aspects of any chemical reaction are essentially separate, in the case of molecular interactions it is difficult to judge their importance independently of each other, since, although specific interaction between a solute and an aromatic molecule may be the most important factor in terms of the data which are obtained, there must also be influences from other molecules in the liquid mixture. The other molecules which influence the interaction could be those of either the solute, aromatic or solvent used as a diluent; further comment will

be made on the nature of these other effects during the subsequent chapters. However, it is not difficult to imagine that the stoichiometry of a complex will influence the stereochemistry to a marked extent. A typical example of this type of effect is the complex formed between dimethyl-formamide and benzene[201], the chemical shifts being thought to be consistent with a co-planar configuration. Homer and Cooke[38], however, have shown the similar interaction between acetone and benzene to be a pseudo 1:2 (solute/aromatic ratio) complex, where the benzene molecule is exchanging between the two methyl groups, and the equation for the fast exchange process is modified.

In this work, however, it is not necessary to consider these interdependent aspects in depth, since for the majority of the investigations, the general assumption that many complexes have 1:1 stoichiometry is justified. Evidence for this assumption comes mainly from cryoscopic studies which show that the chloroform-toluene[186] and chloroform-mesitylene[202] complexes are 1:1 in nature, and it is reasonable to assume that these molecules associate in a 1:1 ratio in solution. Further evidence for the stoichiometries of molecular complexes has been based on the Benesi-Hildebrand[45] equation, which is of the form,

$$\frac{1}{\Delta_{obs}} = \frac{1}{K[B]_o\Delta_c} + \frac{1}{\Delta_c} \qquad 4.7.$$

and was discussed in section 1.14. The linearity of a plot of $1/\Delta_{obs}$ against $1/[B]_o$ has been quoted as evidence for 1:1 stoichiometry, but Johnson and Bowen[203] have shown that this is not substantial evidence. Similarly, Baker and Wilson[88] have proposed that a modified form of equation 4.7. should enable stoichiometries to be deduced. However, Whitney[49]

has shown their approach to be invalid, primarily because of the large concentration range used (the importance of restricting the range is shown later in this chapter), but also because they fail to allow for the fact that if a 1:n complex is formed there must also be 1:(n-1), 1:(n-2) etc. complexes in solution, and since no complex of a greater than 1:1 stoichiometry has at present been reported their proposals cannot be proved.

An alternative method which has been used extensively in this laboratory is that due to Orgel and Mulliken[204] who proposed that the heat of formation of a complex, ΔH, should be independent of temperature if a simple 1:1 complex is formed. ΔH is deduced from equation 4.8.

$$\left[\frac{\delta(\Delta G/T)}{\delta(1/T)}\right]_p = \Delta H \qquad 4.8.$$

and combining this with equation 4.9.,

$$\Delta G = - RT\ln K_x \qquad 4.9.$$

equation 4.10 is obtained, which shows that a plot of $\ln K_x$ against 1/T should be a straight line of slope $-\Delta H/R$.

$$-R\left[\frac{\delta(\ln K_x)}{\delta(1/T)}\right]_p = \Delta H \qquad 4.10.$$

If complexes are present which have other stoichiometric ratios than 1:1 they would be expected to form by consecutive interactions, and the above plot would not be linear. However, the results which have been obtained in the past are now subject to some doubt because of the use of the Benesi-Hildebrand[45] and Creswell and Allred[46] procedures in their basic forms for data processing, which are not valid in all circumstances. Their limitations were discussed in sections 1.13. and 1.14. It should be noted that whilst heats of formation of complexes are generally independent of

temperature, interaction energies are temperature dependent.

The stoichiometries of the complexes to be studied in subsequent chapters have been assumed to be of the 1:1 type, and the data obtained has been processed accordingly. No abnormal effects have been investigated which are attributable to the effects of varying stoichiometric ratios, and the above assumption can, therefore, be considered justified. Nevertheless, it should be noted that the steric factors of complex formation must be dependent upon stoichiometry.

No mention has been made of the possibilities of two solute molecules complexing with one of the aromatic type, because in all of the investigations carried out in this thesis the concentration of solute is so low that this type of interaction is statistically highly improbable.

Two extremes of configuration are apparent for 1:1 complexes formed between benzene and polar solute molecules these being (A) a planar model in which the solute dipole is parallel to the plane of the aromatic ring, and (B) a model in which the dipole of the solute is coincident, or nearly so, with the six fold axis of the benzene ring. There is much evidence to support the validity of model B although this may not always be the case. It has been found that the solvent shifts of 5-substituted 1,3-dioxans[205] and adamantyl halides[206] are best understood in terms of a non-planar model. Hassel[193] has demonstrated that the crystalline benzene-bromine complex is similar in nature to model B. However, by far the most important evidence with respect to the interactions studied here is that given by Homer and Cooke[198,207], who carried out rigorous calculations for models of simple complexes, their approach

also having a strong significance in the investigation of the strengths of molecular complexes.

Since benzene is twice as polarisable in the plane of the ring than along the six-fold axis, it would be reasonable to suppose that a planar orientation is more favourable. However, the interaction energy of a benzene molecule with a dipole is greater along the six fold axis, and signifies that model B would be preferred, as long as no other factors such as the stereochemistries of either molecule are important (Figure 4.1.). The six-fold axis model may be considered not as a static model, but such that the solute molecule adopts a series of orientations in successive collisions at an angle α to the six-fold axis, the time average of which is the static model. A dynamic model of this nature is necessary in order to explain the observed variations in interaction energies with temperature[192], since changes will be apparent in the angle α, depicted in Figure 4.2.

Huntress[90] has shown by correlation time studies of the systems $CDCl_3 + C_6H_6$ and $CHCl_3 + C_6D_6$ that chloroform rotates four times slower in benzene than in its pure form, and attributed the anisotropic molecular orientation to be due to association, on the C_3 axis of chloroform, with benzene molecules. The errors which are inherent in this type of investigation are rather high, and while some authors have interpreted their results as being due to the formation of molecular complexes[90,91], others have drawn the conclusion that the lifetime of the complex is so short that it cannot be considered as a discrete entity[92-94,208]. The most convincing results[91] show that the translational correlation time of chloroform is increased by an order of magnitude

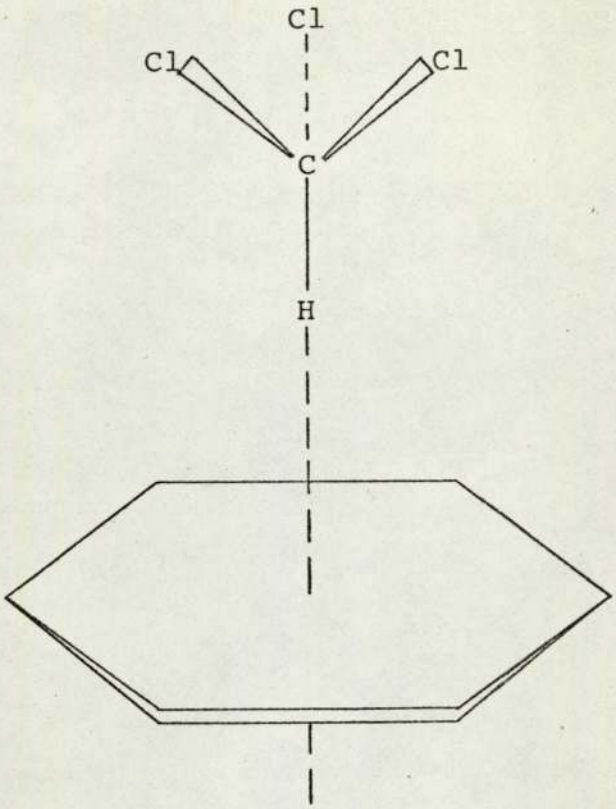


FIGURE 4.1. A schematic representation of the 1:1 chloroform-benzene six-fold axis complex.

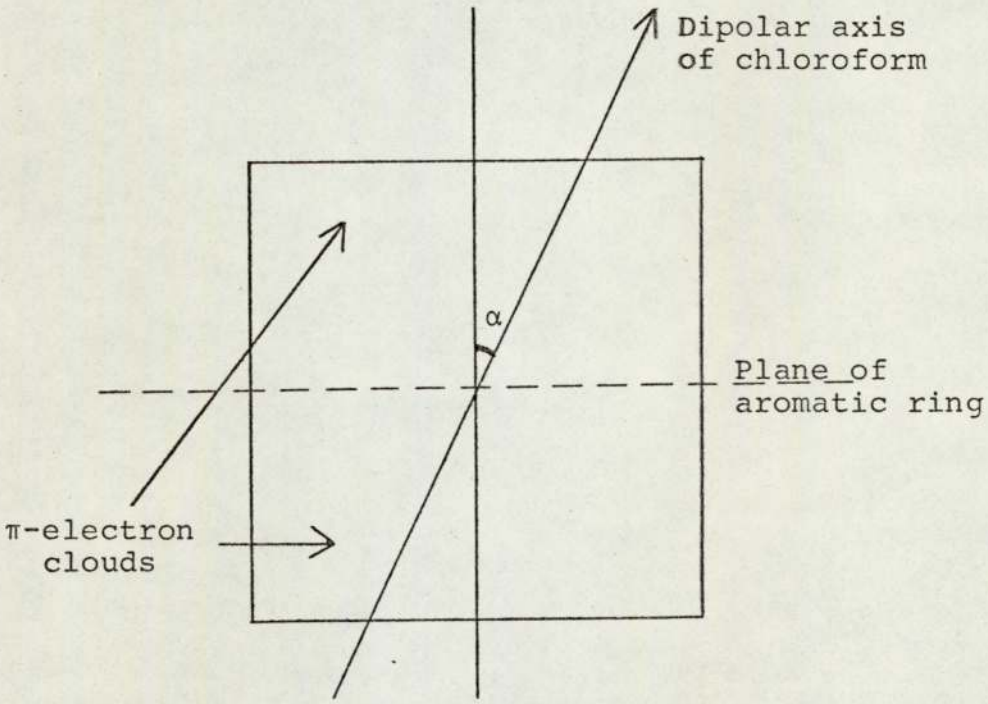


FIGURE 4.2. The suggested orientational variation of chloroform in the chloroform-benzene complex.

when it is mixed with benzene, and is in this case about 3×10^{-10} sec. The failure of some workers to detect a discrete complex does not mean that interaction of the nature described does not occur at all.

The conclusions of the correlation time studies, notwithstanding the accuracy of the results obtained, indicate that the model B proposed above must be further modified, and the effects of fast exchange processes on n.m.r. spectra further substantiate this need. The indications are that the complex must be only transiently formed, the solute molecules exchanging rapidly in jump-like steps between aromatic molecules, and that when complexes are formed the solute molecules will adopt configurations, which on time average, are described by the static model shown in Figure 4.1., which is stereo-specific in nature[209]. This fast exchange mechanism is similar to the jump-diffusion model sometimes used as the basis for relaxation processes. The n.m.r. technique, however, has a response time which only enables the observation of time averaged environments, and the parameters which are obtained by its use must relate to an average of the dynamic model proposed.

4.1.4. The Strength Of The Interaction.

The postulated existence of an equilibrium interaction between solute and aromatic molecules provides a working basis for the measurement of the strength of the interaction in thermodynamic terms. Indeed, the fact that induced chemical shifts are variable with temperature has been proved for a wide variety of solutes[195-197,201,208,210,211], and the thermodynamic parameters ΔS, ΔH and ΔG can be obtained from plots of $\ln K_x$ (where K_x is the equilibrium

quotient which may be obtained for the reaction) against 1/T and equations 4.9., 4.10., and 4.11.

$$\Delta G = \Delta H - T\Delta S \qquad 4.11.$$

ΔH is usually found to be of the order of 4KJ mol^{-1}, and is constant with temperature, which demonstrates that the interaction is weak, and that ΔH is not a realistic measure of the strength and stability of the complex, which would be expected to vary with temperature. ΔS is similarly almost temperature independent, but ΔG, which varies noticeably with temperature offers a realistic measure of the probability of a complex being formed. This is consistent with the variation of translational correlation times with temperature.

The shift induced in the solute in the complex, Δ_c, has been suggested to be a measure of the strength of the bimolecular interaction[212], but its variation with temperature is not significant, and while this does not support the concept of being associated with reaction strength, it is still a good measure of the distance of closest approach of the two interacting molecules, which would be expected to be fairly constant with temperature. A knowledge of the distance of closest approach enables the interaction energy to be calculated by the method of Homer and Cooke[198], and, therefore, may indirectly be a measure of the reaction strength.

It is apparent that Δ_c reflects the configuration of the time averaged complex, and that K_x is an excellent measure of the strength of the interaction. Homer and Cooke have shown that a good correlation exists between the interaction energies calculated by them and the equilibrium quotients obtained for a variety of reactions, and while

the quantitative use of their method is not applicable to the present investigations, it is important to note that K_x reflects the stability of the complex, a higher value for K_x representing an increase in the lifetime of the interaction if Δ_c remains approximately constant. It will be shown in the following chapter that increased values for K_x may be due to steric or other less apparent effects which stabilise the complex formed. Whitney[49] has shown this to be true by investigations of the interactions of chloroform with a variety of substituted benzenes. He found that the expected correlation existed between ΔG and K_x, but could not correlate interaction energies, calculated by consideration of the aromatic polarisabilities in a similar fashion to Homer and Cooke[198], unless allowances were made for the steric effects of the alkyl substituents of the aromatic molecule.

4.2. The Use Of N.M.R. Chemical Shifts.

4.2.1. Modifications To The Benesi-Hildebrand Procedure.

It is apparent from the results[47,50-52] which have been obtained from both the procedures mentioned earlier that certain anomalies exist in the comparison of these results. These anomalies are, firstly, that the chemical shift, Δ_c, induced in the solute in a bimolecular complex appears to depend on the concentration scale used to define and process the data, and, secondly, that K, the equilibrium quotient, and Δ_c depend on the 'inert' solvents used for studying the reaction. In order to resolve these difficulties it is necessary to consider the thermodynamic properties of liquid mixtures so that a data processing method may be forthcoming which, when used under the correct conditions is independent of concentration scale and inert solvent.

Recent work[40,41,49] in this laboratory has shown that these difficulties may be resolved in this way, and the salient points of the argument are considered below.

There are three major points which need to be investigated, these being (a) the conditions under which the previously mentioned data processing procedures are valid, (b) the effect of the inert solvent, and (c) a rationalisation of concentration scales, particularly the molal scale, which in the form of equation 1.78. is rather ambiguous, because at infinite molality the Benesi-Hildebrand plot still has a finite slope.

4.2.1.1. The Thermodynamics Of The System.

In order to resolve the anomalies described above, the thermodynamics of the system, at both low and high concentration of the component B, will be considered in order that the range of concentration which provides the most meaningful results can be chosen for subsequent investigations.

At a low concentration of A and B in S the solution will be ideal and the values for γ^H, the Henry activity coefficient, for all active species will approach unity. The chemical potentials of each species at equilibrium are, therefore, represented on the mole fraction, molar and molal scales by equations 4.12., 4.13. and 4.14. respectively.

$$\mu_i = \mu_i^\theta + RT\ln x_i \qquad 4.12.$$

where $\mu_i^\theta = \lim_{x_i \to o}(\mu_i - RT\ln x_i)$

$$\mu_i = \mu_i^c + RT\ln c_i \qquad 4.13.$$

where $\mu_i^c = \mu_i^\theta + RT\ln V_m$

$$\mu_i = \mu_i^m + RT\ln m_i \qquad 4.14.$$

where $$\mu_i^m = \mu_i^\theta + RT\ \ln M_S$$

where V_m is the molar volume and other terms have their previously defined significance. For these equations to be valid each species must be entirely surrounded by molecules of the solvent, S, and the equilibrium quotients are given by:

$$RT\ln K_x' = RT\ln \frac{x_{AB_{eq}}}{x_{A_{eq}}\ x_{B_{eq}}} = \mu_A^\theta + \mu_B^\theta - \mu_{AB}^\theta = -\Delta G^\theta \qquad 4.15.$$

$$RT\ln K_c' = RT\ln \frac{c_{AB_{eq}}}{c_{A_{eq}}\ c_{B_{eq}}} = \mu_A^\theta + \mu_B^\theta - \mu_{AB}^\theta + RT\ln V_m$$

$$= -\Delta G^\theta + RT\ln V_m \qquad 4.16.$$

$$RT\ln K_m' = RT\ln \frac{m_{AB_{eq}}}{m_{A_{eq}}\ m_{B_{eq}}} = \mu_A^\theta + \mu_B^\theta - \mu_{AB}^\theta + RT\ln M_S$$

$$= -\Delta G^\theta + RT\ln M_S \qquad 4.17.$$

on the mole fraction, molar and molal scales respectively, where ΔG^Θ is the standard free energy change for the reaction at infinite dilution.

However, the use of the n.m.r. technique at such low concentrations is not experimentally feasible because of problems of sensitivity of detection and chemical shift changes. Also, one of the conditions applicable to the Benesi-Hildebrand procedure is invalid, (i.e. the initial concentration of B, $[B]_o$, is much greater than that of A, $[A]_o$). The effect of a larger concentration of B must

therefore be discussed. The immediate effect of this is that γ_B^H is no longer unity, and the chemical potentials of B on the respective scales will be:

$$\mu_B^{x'} = \mu_B^{\theta} + RT\ln\gamma_B^H + RT\ln x_B \qquad 4.18.$$

$$\mu_B^{c'} = \mu_B^{c} + RT\ln\gamma_B^H + RT\ln c_B \qquad 4.19.$$

$$\mu_B^{m'} = \mu_B^{m} + RT\ln\frac{M_S}{1+m_B M_S} + RT\ln m_B \qquad 4.20.$$

and the respective equilibrium quotients will be given by:

$$RT\ln K_x = \mu_A^{\theta'} + \mu_B^{\theta} - \mu_{AB}^{\theta'} + RT\ln\gamma_B^H \qquad 4.21.$$

$$RT\ln K_c = \mu_A^{\theta'} + \mu_B^{\theta} - \mu_{AB}^{\theta'} + RT\ln\gamma_B^H + RT\ln V_m' \qquad 4.22.$$

where V_m' is the new value of V_m , which will differ for each value of C_B,

$$RT\ln K_m = \mu_A^{\theta'} + \mu_B^{\theta} - \mu_{AB}^{\theta'} + RT\ln\gamma_B^H + RT\ln\frac{M_S}{1+m_B M_S} \qquad 4.23.$$

It is evident from equations 4.21.,4.22. and 4.23. that the concentration of B has an effect on equilibrium quotients obtained from studies within this concentration range and therefore it is not possible to use the Benesi-Hildebrand, or the Creswell-Allred procedures because both require that equilibrium quotients are independent of the concentration of B over the range under investigation.

It is, therefore, necessary to consider the range in which B is at a high concentration with respect to both A and S, where its fugacity will only slightly be affected by A and AB. The chemical potential of B can be described over the whole concentration range on the mole fraction

scale as:

$$\mu_B = \mu_B^o + RT\ln\gamma_B^R + RT\ln x_B \qquad 4.24.$$

where μ_B^o is the chemical potential of pure B at the same temperature, and γ_B^R is the Raoult activity coefficient of B. The variation of the fugacity of B with x_B is represented by the alternatives shown in Figures 4.3. and 4.4., γ_B^R being given by the ratio ac/bc, which show that as $x_B \rightarrow 1$ the shape of the curve is not important, and equation 4.24. therefore reduces to:

$$\mu_B = \mu_B^o + RT\ln x_B \qquad 4.25.$$

Since $x_B = V_{BS}C_B$, where V_{BS} is the molar volume of the mixture, the chemical potential of B at high concentration on the molar scale is given by equation 4.26.

$$\mu_B = \mu_B^o + RT\ln V_{BS} + RT\ln C_B \qquad 4.26.$$

The chemical potential of B referred to the molal scale is similarly given by equation 4.27.[38]

$$\mu_B = \mu_B^o + RT\ln x_S M_S + RT\ln m_B \qquad 4.27.$$

It has been shown[40,49] that since, at this concentration, A and AB are surrounded almost entirely by B, rather than S, μ_A and μ_{AB}, expressed in terms of the molar and molal scales, are only independent of n_B/n_S if the molar volumes and molar masses respectively of B and S are equal.

Therefore, if the mole fraction of B is close to unity, the equilibrium quotients derived from equations 4.25., 4.26. and 4.27. are given by:

$$RT\ln K_x'' = \mu_A^{\theta''} + \mu_B^o - \mu_{AB}^{\theta''} = -\Delta G^o \qquad 4.28.$$

$$RT\ln K_c'' = RT\ln K_x'' + RT\ln V_{BS} \qquad 4.29.$$

$$RT\ln K_m'' = RT\ln K_x'' + RT\ln x_S M_S \qquad 4.30.$$

where $\mu_i^{\theta''}$ is the modified chemical potential of species i

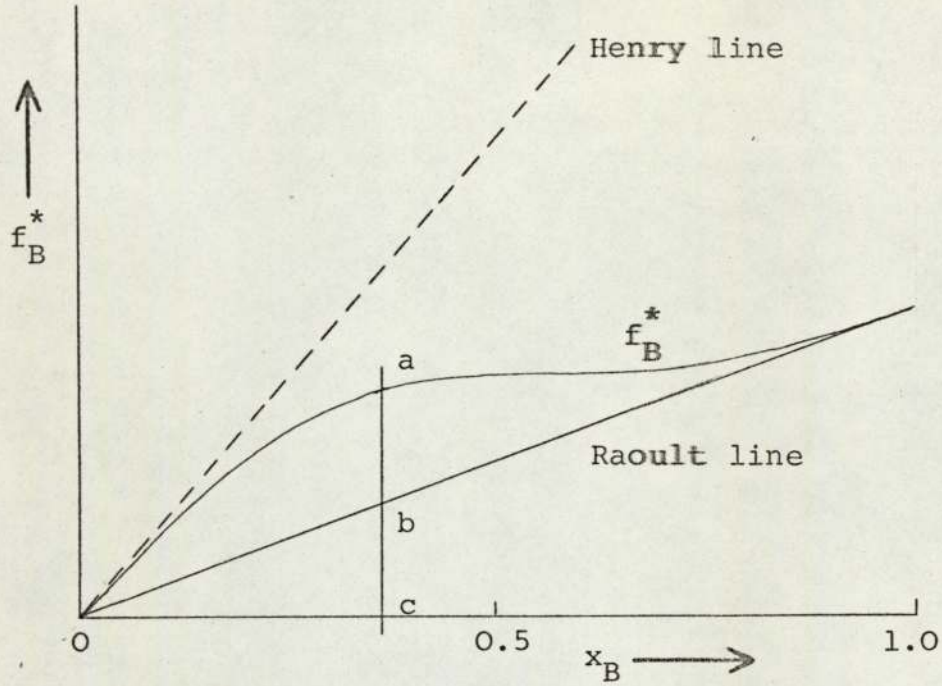


FIGURE 4.3. A typical plot of the fugacity of B, f_B^*, against the mole fraction of B, x_B, where the Raoult activity coefficient, γ_B^R, is greater than unity.

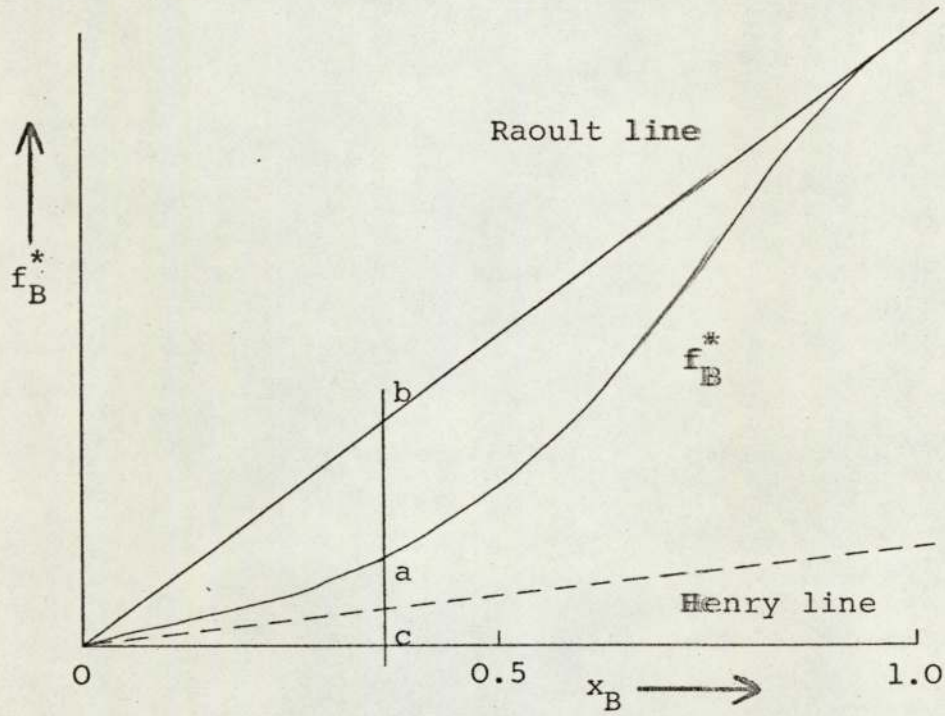


FIGURE 4.4. A typical plot of the fugacity of B, f_B^*, against the mole fraction of B, x_B, where the Raoult activity coefficient, γ_B^R, is less than unity.

at high concentrations of B, but ignoring departures from ideal behaviour, and x_S is the mole fraction of the solvent .

As with the thermodynamic parameters defined for conditions of low concentration of B, equations 4.29. and 4.30. show that K_c'' and K_m'' respectively are dependent on a molar volume and a molar mass term respectively. It is apparent that K' and K'' are not the same because of the modified values for μ_A^θ and μ_{AB}^θ, and the inclusion of the term μ_B^o in equations 4.28., 4.29. and 4.30. The quantities ΔG^θ and ΔG^o are not the same as the free energy change resulting from the formation of one mole of the complex from isolated A and B.

The preceding arguments show that in order to obtain meaningful values for the equilibrium quotients, and therefore Δ_c, it is only realistic in experimental terms to evaluate data when both A and S are present in low concentration in B. Any investigations over wide concentration ranges will result in some average of K' and K'' being evaluated. It is apparent from the literature that when using different solvents, consistent results can only be obtained if the molar scale is used,[52] whilst both the other scales give rise to anomalous results.

The relationship between the equilibrium quotients is given by equation 1.79., and K_c will be independent of composition only if the molar volume of the mixture is similarly independent. K_x may be independent of x_B over a similar concentration range, but, even then, the equilibrium quotient will only be constant if variable factors fortuitously cancel. Thus the condition is imposed that the partial molar volumes of B and S in the mixture should be identical. Similarly, K_m can only be independent of

composition if the molecular weights of B and S are the same. If, however, a Benesi-Hildebrand, or Creswell-Allred, plot is made over a range for which K_x is not independent of x_B, a straight line may result for molar scale data if the variation in V_{BS} is opposite to that in K_x, and therefore K_c will appear to be less dependent on the concentration scale used for its evaluation than will K_x. It is to be expected that K_x will depend on the nature of S because μ_A^θ and μ_{AB}^θ are so dependent.

Using the chloroform (A) - benzene (B) - cyclohexane (S) system as a model it was indicated by Homer et al[40] that if the concentration of A is below 0.005 mole fraction then Henry's Law is obeyed, and that the effect of the changing environment on the chemical potentials of A and AB when x_B is varied from 0.9 to 1.0 is negligible. Over this range γ_B^R is very close to unity[213-215] and may be ignored.

It appears that, subject to these conditions, an equilibrium quotient can be evaluated which is independent of composition, and is free of activity coefficients. The definition of K_x by equation 4.28. indicates an independence of x_B and therefore meaningful values for K_x and Δ_c should result from the use of the Benesi-Hildebrand method if these parameters are evaluated at $x_B = 1$. The use of the Creswell-Allred method, however, will result in an average value for K_x over the range of concentration studied, but its magnitude will be similar to that obtained by the Benesi-Hildebrand procedure if a plot of $1/\Delta_{obs}$ against $1/x_B$ is linear.

4.2.1.2. The Nature Of The Solvent.

In order to correct for the apparent anomalies

concerning the use of the mole fraction scale two modifications have been proposed:[40] firstly, to allow for variations in δ_{free} with the composition of the three-component mixture and, secondly, to allow for the nature of the so-called 'inert' solvent. The former modification was shown to be of little consequence, the ultimate results obtained being only slightly altered, and hence will be ignored. It seems, however, that $\mu_A^{\theta''}$, $\mu_{AB}^{\theta''}$ and γ_B^R are not completely constant in the range 0.9 to 1.0, but depend on the nature of S, and its concentration.

The solvents required in investigations of this nature to change δ_{obs} should be identical to B in all properties except in the ability to form a complex. Whilst there are subtle differences between each solvent, which will be discussed further in Chapter 5, the most important difference between molecules of B and S is in their relative sizes. Ideally, S should be a molecule such as that depicted in Figure 4.5., and should replace one molecule of B. In a real system, however, (Figure 4.6.) one molecule of solvent may displace more or less than one molecule of B, and δ_{obs} will consequently appear to change more or less than is to be expected. As a reasonable approximation it was shown[40] that if one molecule of S behaves as V_S/V_B (i.e. the ratio of the molar volumes of B and S) molecules of inert B, the expression for x_B becomes:

$$x_B^{corr} = n_B V_B/(n_B V_B + n_S V_S) \qquad 4.31.$$

ignoring the negligible contribution due to the very small concentration of A. The expression for the molarity of B is not altered by this modification. The Benesi-Hildebrand equation (1.64.) pertaining to the mole fraction scale

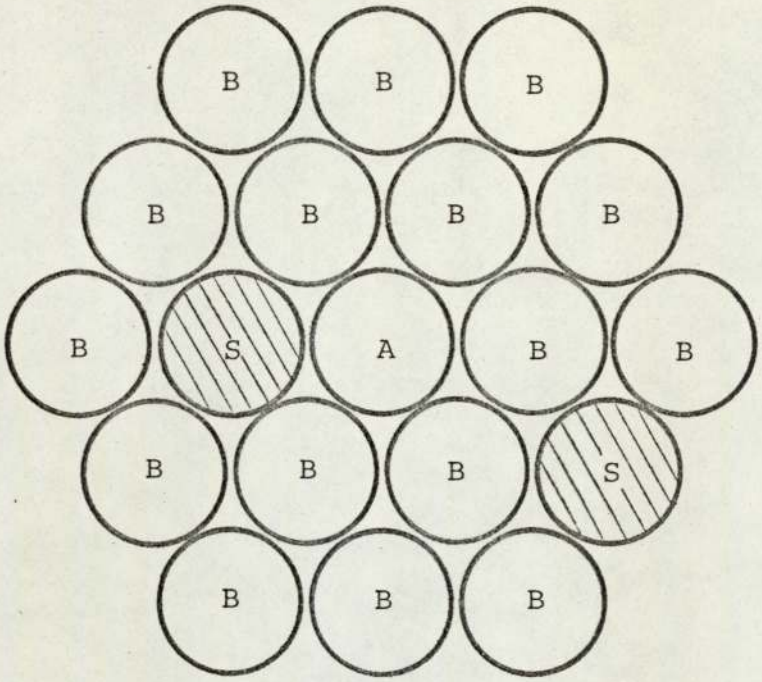


FIGURE 4.5. A schematic representation of the environment of the solute, A, where S is an ideal solvent molecule.

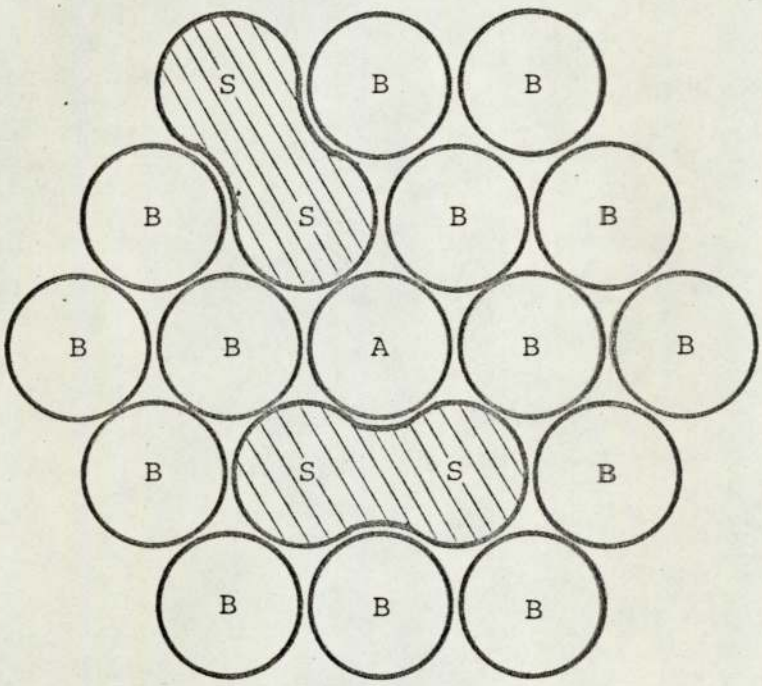


FIGURE 4.6. A schematic representation of the environment of the solute, A, where S is a real solvent molecule.

therefore becomes equation 4.32.

$$\frac{1}{\Delta_{obs}} = \frac{n_B + n_S V_S/V_B}{n_B K_x \Delta_c} + \frac{1}{\Delta_c} \qquad 4.32.$$

These equations were used by Homer et al[40] to obtain consistent values of K_x for the chloroform + benzene reaction occurring in a variety of solvents, and values for Δ_c compared well with those obtained from evaluation on the molar scale. The number of moles of inert solvent is always weighted by its molar volume on the molar concentration scale and does not require modification, and thus comparisons between K_x and K_c showed remarkably good agreement with equation 1.79., i.e. at $x_B = 1$, $V_{BS} = V_B = K_c/K_x$. The inclusion of the amount of A present in the liquid mixture in the concentration expressions was shown to be unimportant, unless K_x is less than unity.[40]

4.2.1.3. The Molal Scale.

The use of the molal concentration scale in the Benesi-Hildebrand equation has not so far been mentioned because it presents rather different problems to those encountered with the rationalisation of the mole fraction and molar scales. It may be expected that when x_B tends to unity, a value of K_m compatible (via equation 1.79.) with K_x and K_c should be obtained, and that the values of Δ_c deduced on all the three scales should be identical, because the contribution to equation 4.30. involving the mass of the solvent should be negligible. However, this is not so, the fact having been admirably demonstrated by Homer and Whitney[41] using the chloroform-benzene system, for which they analysed the data by plotting $1/\Delta_{obs}$ against $1/m_B$, ($m_B = n_B/n_S V_S \rho_S$ where ρ_S represents the density of S) and deducing K_m and Δ_c at zero solvent concentration, which in molality terms is $m_B = \infty$.

If K_m is represented by equation 4.30., which does not include terms due to the variation of the activity coefficients of A, B, and AB, and shows a dependence on the solvent, K_m is also represented by equation 1.78., which requires K_m to be zero at $m_B = \infty$. However, it is an experimental fact that a plot of $1/\Delta_{obs}$ against $1/m_B$ has a finite slope.

To rationalize this anomaly it was suggested that K_m is expressed in terms of K_c, defined by equation 1.77., using the equation:

$$K_m = \frac{K_c \rho_S}{V_B m_B \rho_S + 1} \qquad 4.33.$$

The equation for the Benesi-Hildebrand plot (equation 1.82.) therefore becomes:

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_c \rho_S m_B \Delta_c} + \frac{1}{\Delta_c}\left(1 + \frac{V_B}{K_c}\right) \qquad 4.34.$$

Equation 4.33. shows that even if K_c is independent of composition, K_m cannot be because of variations in m_B. Thus the normal form of the Benesi-Hildebrand equation in terms of the molal scale (equation 1.82.) is meaningless, but from equation 4.34. it is apparent that a plot of $1/\Delta_{obs}$ against $1/m_B$ should have a slope (S) and intercept (I) represented by equation 4.35. and 4.36. which have been used previously by Kuntz et al[52].

$$1/I = K_c \Delta_c / (K_c + V_B) = \text{"}1/\Delta_c^m\text{"} \qquad 4.35.$$

$$I/S = \rho_S (K_c + V_B) = \text{"}1/K_m\text{"} \qquad 4.36.$$

Calculations of 1/I and I/S showed that there was an excellent agreement with experimental values for these parameters. The explanation of the paradox is, therefore,

based upon the interrelated factors of the definition of the molal scale and the incompatibility of a macroscopic thermodynamic analysis of shifts and their molecular basis, i.e. the same type of problem encountered in the rationalization of the mole fraction and molar concentration scales.

The full form of equation 4.30. is:

$$RT\ln K_m = \mu_A^{\theta''} + \mu_B^{o} - \mu_{AB}^{\theta''} + RT\ln x_S M_S + RT\ln \frac{\gamma_A^H \gamma_B^R}{\gamma_{AB}^H} \qquad 4.37.$$

Neither γ_A^H nor γ_{AB}^H can be considered to tend to unity under the normal definition of molality since the concentration of S is also very low. However, if, firstly, molality is defined relative to a mixed solvent system[216], such that the single solvent molecular weight is replaced by the weighted average of the molecular weights of the two solvents, and, secondly, S is considered as 'inert' B, the problem can be resolved.

The concept of a mixed solvent system in this case is valid because uncomplexed benzene is also, in effect, a solvent, although it does not appear to be so with respect to the n.m.r. technique. Under these conditions the chemical potentials of A and AB are given by equation 4.38.

$$\mu_i = \mu_i^{\theta''} + RT\ln \frac{M_B M_S}{W_B M_S + W_S M_B} + RT\ln m_i \qquad 4.38.$$

where M_B and M_S, and W_B and W_S are now defined as the molecular weights and masses of the components B and S respectively, and $W_B + W_S = 1kg$. In these circumstances both A and AB may be considered to obey Henry's Law, and their activity coefficients will be equal to unity.

In order to be consistent with the rationalization of the mole fraction and molar scales, it is necessary to

regard S as 'inert' B, so that the molality of 'active' B is given by equation 4.39.

$$m_B' = n_B/(n_S V_S \rho_B + n_B V_B \rho_B) \qquad 4.39.$$

Therefore, equation 4.37. may be rederived from the chemical potentials of μ_B, μ_A and μ_{AB} to give equation 4.40.

$$RT\ln K_m' = \mu_A^{\theta''} + \mu_B^{o} + \mu_{AB}^{\theta''} + RT\ln\rho_B V_B + RT\ln \frac{\gamma_A^H \gamma_B^H}{\gamma_{AB}^H} \qquad 4.40.$$

Subject to the above conditions the three activity coefficients will tend to unity as the concentration of S tends to zero, and K_m will be independent of both the concentration of B and the nature of S. The Benesi-Hildebrand equation of the molal scale therefore becomes:

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_m' \; m_B' \Delta_c} + \frac{1}{\Delta_c} \qquad 4.41.$$

which provides values for K_m and Δ_c which have been shown to be compatible with the results obtained for these parameters on the mole fraction and molar scales[41].

4.2.2. The Correct Use Of The Benesi-Hildebrand and Creswell Allred Procedures.

The above arguments have shown how the anomalies concerning the results reported by previous workers may be resolved, and it is necessary here to show how both the Benesi-Hildebrand and the Creswell-Allred procedures can be used under the correct experimental conditions to obtain values for K_x, K_c, K_m and Δ_c which are of significance.

The modified Benesi-Hildebrand procedure provides the means for obtaining the most meaningful results from experimental data because the form of the equation allows extrapolation to zero solvent concentration, i.e. $x_B^{corr} = 1$, $C_B = 1/V_B$ and $m_B' = 1/M_B$, at which point Δ_c and

K_x, K_c, or K_m, depending on the concentration scale used, can be deduced, and compared in the light of equation 1.79. Also, at $x_B^{corr} = 1$, activity coefficients tend to unity, and while they cannot be discounted altogether, values for the equilibrium quotients will be more comparable at zero concentration of the solvent. The Benesi-Hildebrand procedure allows a curve to be fitted to a plot of $1/\Delta_{obs}$ against the reciprocal of the concentration of B if this is necessary, and the slope and intercept of the curve to be evaluated at zero solvent concentration by taking a tangent at this point. This is particularly important for the equilibrium quotients deduced on the molar and molal scales which show a solvent dependence. The concentration range should be restricted to $x_B = 0.9$ to 1.0, and $x_A =$ 0.005 or less.

The latter conditions are also applicable to the Creswell-Allred procedure, although equilibrium parameters of a similar value to those obtained from the Benesi-Hildebrand procedure have been obtained over a wider concentration range, probably due to the fortuitous cancellation of activity coefficient terms. The proposed modifications to the definition of the mole fraction and molal concentration scales apply equally to this procedure, although it is apparent that, unless the slope of a plot of $1/\Delta_{obs}$ against $1/x_B$ is the same at $x_B = 1$ as the average of the slopes over the whole plot, only average values for Δ_c or the equilibrium quotients can be obtained.

Whitney[49] has shown, however, that the parameters may be meaningful because of the previously proposed reason that activity coefficients cancel over the whole experimental range, and that consistent values could be obtained from

investigations over wide ranges of concentration. The Creswell-Allred method has been used for the investigations described in Chapter 7 of this thesis, and its validity will be further discussed with respect to the nature of the investigations to be carried out.

4.2.3. Data Processing Procedures.

Within this section the procedures will be described which have been used to deduce values for Δ_c and the equilibrium quotients from the Benesi-Hildebrand and Creswell-Allred methods. Both procedures are suitable for evaluation by computer, an ICL 1905E processor being used for all calculations.

The computer data-fitting program 'BHCURVEFIT'[217] was employed for processing data applicable to the Benesi-Hildebrand procedure. The data (values for Δ_{obs} and n_B, n_S, M_B, M_S, ρ_B and ρ_S) are fed into the program, which calculates the equation for the best-fit line through a plot of $1/\Delta_{obs}$ against the reciprocal of the concentration of B, $[B]_o$. The program allows the equation to be either linear or quadratic, either at the discretion of the operator or because the computer finds that one form gives a better least-squares fit to the line, and data are printed out showing the difference between the experimental and computed values for $1/\Delta_{obs}$. Weighting factors allowing for the accuracy of each point may thus be introduced. For all the data reported here a linear fit was found to minimise the errors. Using the equation defining the line or curve the computer evaluates the intercept and differential at zero solvent concentration, the reciprocal of the intercept and the ratio of the differential to the intercept defining Δ_c and the equilibrium quotient respectively.

The program used to evaluate the equilibrium parameters from the Creswell-Allred procedure is known as 'COMPLEXICON'[53] and was also devised in this laboratory. The information supplied to the program is similar to that for 'BHCURVEFIT' except that δ_{obs} values are used rather than Δ_{obs}. Therefore a set of data describing δ_{free} may be used, but this is not necessary. The operator supplies guesses of the minimum and maximum values expected for the equilibrium quotient, and also information regarding the accuracy to which it is required. Having been supplied with this information the program is able to choose values for the equilibrium quotient and calculate values for n_{AB}/n_A using equations 1.72., 1.73. and 1.74. The iteration proceeds in order to obtain a value for the equilibrium quotient, to the required accuracy, such that the corresponding values of n_{AB}/n_A and δ_{obs} conform with the linearity of equation 1.68., the slope of the line being equated to Δ_c.

This method, of course, permits different ranges of concentration to be studied, and comparisons of values of Δ_c and the equilibrium quotients obtained over a particular range to be made. Use is made of this possibility in the investigations reported in Chapter 7, although the significance of the values for the equilibrium quotients obtained in this manner are subject to some doubt.

4.3. The Use Of Spin-Lattice Relaxation Times.

In this thesis the measurement of spin-lattice relaxation times will be described as a method for gaining information concerning the mechanism of complex formation and in this respect it is more important initially to study the variation of relaxation times with concentration.

Samples similar to those used in chemical shift procedures will be employed, i.e. keeping the concentration of the solute, A, constant, whilst varying the ratio of B to S. All of the reported work on the use of spin-lattice relaxation times for the study of systems in which molecular association occurs has been directed towards analysis in terms of rotational and translational correlation times, rather than the actual mechanism, but use may be made of some of the conclusions drawn in order to predict the effect of a polar solute on the relaxation processes of other molecules in the equilibrium mixture.

4.3.1. The Nature Of Relaxation Processes And The Effect Of Complex Formation.

The studies made by Anderson[92-94] into the effect of chloroform on the relaxation processes in a benzene solution showed that there was little evidence to be found confirming that a complex was indeed formed. He concluded that a molecular association whose lifetime is short compared with the correlation times applicable to the system, will not affect T_1. Huntress[90], however, has shown that the random motion of chloroform molecules is less in benzene solutions than in the pure liquid and interprets this in terms of the complex formed between chloroform and benzene. Whilst Huntress found that the C_3 motion of chloroform was only slowed by a factor of 1.3 by specific association, the molecular tumbling motion is slowed by a factor of 4, which is consistent with the complex occurring along the symmetry axis of the chloroform and perpendicular to the plane of the benzene ring. It was also proposed that the chloroform and benzene molecules do not slip relative to each other in the complex, and that the C_6 motion of benzene is

unaffected by complex formation. This means, therefore, that any change observed in T_1 values must be due to intermolecular processes, because the rotational intramolecular contribution is the same.

The fact that the relaxation time of benzene is affected by complex formation due to the restriction of translational motion has been demonstrated both by Huntress[90] and Sato and Nishioka[91]. These latter workers have shown that whilst the relaxation time of chloroform is not affected by dilution in benzene, the T_1 of benzene is significantly affected. Sato and Nishioka carried out their studies on effectively single spin systems by observing either $CHCl_3$ or C_6H_6 and varying the apparent mole fraction by addition of the deuterated analogue, whilst the other component was deuterated and kept constant in amount. They have shown that, because of their small magnetogyric ratios, deuterium and chlorine may be considered to contribute negligibly to relaxation processes, and, therefore, for the system proposed for study in this thesis, i.e. $CDCl_3$ - C_6H_6 - C_6H_{12}, the effects of $CDCl_3$ may be neglected except in the way in which it affects the relaxation processes occurring between C_6H_6 and C_6H_{12}. The use by Sato and Nishioka of Hubbard's[114] equation for calculating τ_T (the translational correlation time) precludes quantitative use of their results because the equation refers to spherical molecules only.

The other information available concerning systems of this type is very limited, and it appears that it will be necessary to interpret the results obtained in terms of the models for relaxation processes proposed in Chapter 2, and the mechanism of complex formation suggested in Chapter 7. However, it may be useful in future studies to employ some

of the techniques which have been applied to systems with chemical exchange[96,119-123,218].

4.3.2. The Choice Of Experimental Techniques.

It is evident from the discussions in Chapter 2 that the A.F.P.S. method of measuring spin-lattice relaxation times is accurate, as well as being easy to employ, and will therefore be used for all subsequent investigations reported here. However in the systems to be studied there are two distinct types of protons, and relaxation times must be evaluated according to the equations for two spin systems. The method employed by Hoffman and Forsen[123] is suitable for use here, and is preferable to the more complicated procedure proposed by Powles[108]. There are also other procedures available,[95,118,119], but these offer no higher accuracy in the evaluation of the relaxation times.

For a two-spin system the equations describing the decays of the magnetisations of spins A and B are:[95,97].

$$\frac{dM_z^A}{dt} = \frac{M_o^A - M_z^A}{T_{AA}} + \frac{M_o^B - M_z^B}{T_{BA}} \qquad 4.42.$$

$$\frac{dM_z^B}{dt} = \frac{M_o^A - M_z^A}{T_{AB}} + \frac{M_o^B - M_z^B}{T_{BB}} \qquad 4.43.$$

A method which may be generally applied is to neutralise the time-dependent coupling between M_z^A and M_z^B by means of double irradiation. If an experiment is performed in which a strong irradiating field is employed to saturate signal B equation 4.43. becomes invalid, but equation 4.42. still holds and is simplified because $M_z^B = 0$:

$$\frac{dM_z^A}{dt} = \frac{(M_o^A - M_z^A)}{T_{AA}} + \frac{M_o^B}{T_{BA}} \qquad 4.44.$$

Upon integration this equation becomes:

$$M_z^A = (M_o^A + M_o^B\, T_{AA}/T_{BA})(1 - e^{-t/T_{AA}}) \qquad 4.45$$

or: $$M_z^A = M_\infty^A\,(1 - e^{-t/T_{AA}}) \qquad 4.46.$$

where M_∞^A is the new equilibrium value of M_o^A due to the nuclear Overhauser effect.

If M_z^A is perturbed by an A.F.P. experiment the decay of M_z^A towards M_∞^A will be purely exponential with a time constant T_{AA}, and the data may be processed as for a single spin system. The steady state Overhauser effect is conveniently given by equation 4.47.

$$\eta_\infty^A = T_{AA}M_o^B/T_{BA}M_o^A \qquad 4.47.$$

Thus, by measuring the nuclear Overhauser effect from the relationship:

$$\eta_\infty^A = (M_\infty^A - M_o^A)/M_o^A \qquad 4.48.$$

it is possible to calculate T_{AA} and T_{BA}. A set of experiments similar to those described above in which signal A is saturated enables T_{BB} and T_{AB} to be calculated.

Hoffman and Forsen[123] used this procedure to calculate the relaxation times in formic acid and acetaldehyde, and found that it was significantly more accurate than other methods, the ratios of T_{BA}/T_{AB} correlating well with the theoretical value of M_o^B/M_o^A.

The Overhauser effect may be measured most easily by plotting the value of M_z^A or M_z^B against time, t, after release of the modulation frequencies saturating B or A respectively, and extrapolation of the line, which is not exponential, back to t = o. This is necessary because the value of M_∞

measured under steady state conditions is often subject to some saturation, and is smaller than its optimum value. The peak being monitored is often seen to rise sharply when the modulation frequency is removed, due to this effect.

The measurement of η_∞ in the systems studied here has proved to be difficult in some circumstances because of its small value. The effect is entirely intermolecular, unlike those observed by Hoffman and Forsen, and the small values give rise to large errors in T_{BA} and T_{AB}. Other work in this laboratory, however, has shown that if η_∞^A is small, η_∞^B is usually large, (or vice versa) values up to 0.43 having been obtained for η^{219}. Thus either T_{BA} or T_{AB} can be evaluated accurately from a value of η_∞ which is accurately known, and the other estimated from the relationship $M_o^B/M_o^A = T_{BA}/T_{AB}$.

The methods used to prepare the quantitative samples required for these investigations will be discussed further in Chapter 8, with particular reference to the technique devised to eliminate oxygen from the samples.

4.3.3. Data Processing Procedures.

The calculation of relaxation times from the technique described above is readily carried out with the aid of a least-squares fit computer program.

For single spin systems, T_1 may be calculated from the equation:

$$\ln(M_o - M_z) = \ln M_o - t/T_1 \qquad 4.49.$$

Values of M_o, $M_z(t)$, and t are fed into the computer, which then plots $\ln(M_o - M_z)$ against t, the value of T_1 being given as -1/Slope. It was found to be easier to let the computer count the peaks (values of M_z), and multiply this

number by the field sweep period to obtain each value of t, which need only be relative. The field sweep period was measured accurately to 1×10^{-3}sec. using the Varian frequency counter. This procedure also eliminates the alternative dependence on the recorder time-base, which may be non-linear.

For two spin systems equation 4.49. still applies for the measurement of T_{AA} and T_{BB}, except that M_o is replaced by M_∞. The same least-squares-fit computer procedure was employed to obtain T_{AA} and T_{BB}.

It is apparent from the arguments which have been proposed in Chapters 2, 3 and 4, that based on the nature of the general approach of other workers, it is still difficult to obtain values for T_{BA} and T_{AB} accurately. Even the use of the nuclear Overhauser effect may lead to erroneous results if values of η_∞ are small. It seems necessary, therefore, to develop more sensitive, and hence more accurate, experimental and theoretical procedures to enable the values of these important parameters to be obtained with more certainty, and this essentially involves the consideration of suitable data processing procedures. Two unrefined techniques have been developed, but the results are not yet sufficiently accurate for quantitative use. The techniques do, however, hold promise, and are reported in Appendix 1 for this reason.

4.4. Conclusions.

Within this chapter it has been attempted to show the conditions under which reliable parameters pertaining to the formation of molecular complexes in solution may be obtained. For those relying on chemical shift measurements the ideal concentration range is $x_B = 0.9$ to 1.0, and $x_A < 0.005$.

Concentration scales may be rationalised, as described, to be self consistent, and enable meaningful values of K_x, K_c, K_m and Δ_c to be obtained when the Benesi-Hildebrand procedure is used. The Creswell-Allred procedure enables averaged parameters to be obtained, but gives comparable results to the Benesi-Hildebrand procedure over the thermodynamically valid concentration range. In subsequent studies using chemical shifts the investigations will be directed towards the confirmation of the modifications proposed (Chapter 5) and to determine the validity of the use of the Creswell-Allred procedure to calculate parameters from data obtained over the concentration range $x_B = 0 \rightarrow 1.0$ (Chapter 7).

Procedures have been discussed whereby the measurement of spin-lattice relaxation times may be used to gain information concerning the mechanism of complex formation. Despite the limited amount of work previously carried out on this type of system some basic suggestions have been proposed to enable the initiation of the use of relaxation time measurements, although it is necessary that the initial results be interpreted in terms of previously defined models. It has also been shown in chapter 2 that it is very necessary to remove all traces of oxygen from the samples and investigations will initially be directed towards developing a new method for deoxygenation, and subsequently employing this method for the preparation of quantitative samples. The technique of Hoffman and Forsen will be used to derive spin-lattice relaxation times in two-spin, three-component systems. The calculation of T_{BA} and T_{AB} is considered to be less important than obtaining accurate values for T_{AA} and T_{BB}.

CHAPTER 5

CONFIRMATION OF THE VALIDITY OF RATIONALIZED DATA PROCESSING PROCEDURES.

5.1. Introduction.

The investigations which are to be reported in this chapter are directed primarily towards the confirmation of procedures, and modifications to them, which enable meaningful parameters describing simple molecular interactions to be obtained from chemical shifts.

In the previous chapter the two most widely used methods of processing n.m.r. data were discussed and compared critically. Anomalies were apparent in the results which had previously been obtained by the use of both the Benesi-Hildebrand[45] and Creswell-Allred[46] procedures in their basic forms. These showed, firstly, that the chemical shift, Δ_c, induced in one species of a bimolecular complex appeared to depend on the concentration scale used to process the data, and, secondly, that K, the equilibrium quotient, and Δ_c, appeared to depend on the supposedly inert solvents used for studying the reaction. It was shown[40,41] that these anomalies could be resolved by modifying the expressions for K_x, K_c and K_m so that they were consistent with each other, and also with the analytical procedures used. Account was also taken of the different molecular sizes of the aromatic, B, and inert solvent, S, components. A detailed consideration of the thermodynamic properties of the system indicated that, whilst Whitney[49] has shown that the ranges of concentration which could be studied to give meaningful results for the parameters K and Δ_c are wider than expected, for the reasons given in the preceding chapter, strict control of the concentration range, and also the concentration of

the solute, A, will be observed in order to provide values which have some real significance.

The earlier work depended upon the measurement of chemical shifts at 60MHz on a non-field frequency locked spectrometer, and had fairly high error limits, and therefore precluded the conclusive proof of the validity of the proposed modifications and conditions which should be applied. Chemical shifts reported in this chapter were measured at 100MHz on a Varian HA100D spectrometer operated in the HA field sweep mode (see Chapter 3), and are consequently of a significantly higher standard of accuracy.

5.2. Experimental Considerations.

The interaction between chloroform and $[^2H_6]$ benzene (99.7% isotopic purity) was studied in the solvents cyclohexane, cis-decalin, bicyclohexyl,tetradecane and hexadecane, in each case over a range of aromatic concentration of between 0.9 and 1.0 mole fraction. The five 'inert' solvents were the same as those used previously[40,41,49], cis-decalin and bicyclohexyl being chosen by analogy with the supposedly inert cyclohexane[220], whilst tetradecane and hexadecane were chosen as being probably inert. The reaction is closely related to that used previously, which was that between chloroform and benzene in the same five solvents, under similar conditions of concentration.

The change in observed shifts, Δ_{obs}, is given by the usual equation for the screening contributions due to intermolecular effects:

$$\Delta_{obs} = \Delta\sigma_b + \Delta\sigma_a + \Delta\sigma_w + \Delta\sigma_E + \Delta\sigma_s \qquad 5.1.$$

$\Delta\sigma_b$ is zero because the shifts are internally referenced, and $\Delta\sigma_a$ may justifiably be neglected, as discussed in Chapter 2.

$\Delta\sigma_s$ is the most important contribution, but as also stated in Chapter 2, $\Delta\sigma_W$ and $\Delta\sigma_E$ cannot safely be neglected under conditions of high experimental accuracy. Whilst the refractive indices and dielectric constants (which enter the expressions for σ_W and σ_E) of the five solvents are similar to each other and to that of benzene and $[^2H_6]$ benzene it is not valid to ignore these differences. The values for the refractive index and dielectric constant for each component are shown in Table 5.1. The differences in the refractive indices of benzene and $[^2H_6]$ benzene indicate that equilibrium parameters for the reactions between these two aromatics seperately with chloroform should not be totally similar.

Chemical shift measurements between chloroform and a suitable absorption from the solvent, S, (δ_{obs}) were made on the Varian HA100D spectrometer, for which a lock signal was provided by the 0.3% proton impurity in the $[^2H_6]$benzene. In order to obtain data of high accuracy several supplementary experiments were carried out prior to the investigation of the reaction between chloroform and $[^2H_6]$benzene and these are summarised below:

a. Purity Of Components.

The reagents used for the investigations were of the best commercial purity available, and were checked by both n.m.r. and gas-liquid chromatography. The chloroform was dried over calcium chloride, distilled several times to remove the ethanol used for stabilisation, and stored in the absence of light in a refrigerator.

b. Sample Tubes.

In order to ensure that the sample tubes, supplied by

COMPONENT	n_D^T	$-dn/dt \times 10^3$	REFERENCE	ε^T	$-d\varepsilon/dt \times 10^2$	REFERENCE
cyclohexane	1.4263^{20}	0.54	221	2.0199^{25}	0.23^{+}	229
cis-decalin	1.4810^{20}	0.38^{+}	222	2.19^{20} *	–	–
bicyclohexyl	1.4766^{20}	–	223	2.18^{20} *	–	–
tetradecane	1.4290^{20}	0.41	224	2.04^{20} *	–	–
hexadecane	1.4345^{20}	0.38	225	2.06^{20} *	–	–
chloroform	1.4486^{15}	0.59	226	4.724^{25}	1.63^{+}	230
benzene	1.5011^{20}	0.64	227	2.2628^{30}	0.15^{+}	229
$[^2H_6]$benzene	1.4991^{20}	0.64	228	–	–	–

TABLE 5.1. The refractive indices and dielectric constants of the components used in the investigations.

$^{+}$calculated from data given in the reference.

*calculated from the refractive index.

Loxford Ltd., which were to be used were of good quality, resolution and signal to noise tests were carried out on a random selection of tubes. Resolution was optimised and, using the conventional sample of σ-dichlorobenzene, was found to be equal to that obtained by using a known high quality sample tube supplied with the instrument. Similarly, there was only an insignificant decrease in signal to noise ratio when using the normal 1% ethylbenzene solution to ascertain this parameter. Some tubes, however, had to be discarded because their outside diameters were marginally too large to enable a good fit into the spinner turbine, whilst others were found to be rather brittle after they had been sealed. When samples to be employed in the subsequent investigations were prepared those which showed any cracks were remade.

c. Temperature Stability.

An important factor in these investigations was the long term temperature stability in the vicinity of the sample. The temperature of the probe was monitored using the conventional sample of methanol, and measuring the shift between the methyl and hydroxyl protons. Several periods of testing, in association with colleagues, showed that normally the temperature was maintained to within one degree, or less, of normal (309.5K) for periods of up to twelve hours. The provision of an enclosure for the whole magnet system reduced draughts in the vicinity of the probe, and the variation was subsequently much less pronounced over the same period of time, although the absolute temperature varied slightly from day to day depending upon ambient conditions. This stability was considered to be

adequate, but was checked continually when series of samples were later investigated. As a further precaution, each series of samples were investigated in a single day.

d. Optimisation Of x_A.

Several samples containing varying amounts of chloroform were investigated to determine a realistic value for x_A. The good signal to noise ratio of the spectrometer enabled the amount of solute to be reduced to a mole fraction of 0.001, which is well within the maximum value (determined by Whitney[49]) of 0.005, above which variations in δ_{free} are noticeable. This mole fraction gave an r.m.s. signal to noise ratio of about 3 to 1 (10dB), which was considered to be large enough to enable accurate shift measurements to be made. The signal to noise ratio was improved by the narrow line width of the absorption. Line widths are almost invariably smaller when deuterium (or chlorine) atoms are present in molecules in solution because of the large intramolecular contribution of the nuclear quadrupoles to relaxation processes.

e. Reproducibility Of Chemical Shifts.

The samples used for the preceding experiment were also investigated with respect to the reproducibility of values for δ_{obs}. It was found that for the sample containing a mole fraction of solute equal to 0.001, shifts were reproducible to within ±0.04Hz, for six measurements taken over a period of several hours. This was considered to be adequate for the present purposes. The variation in the shift is surprisingly small since it includes long term alterations in the stabilities of temperature, the oscillators and the frequency counter.

f. Preparation Of Samples.

Samples to be used in the investigations were prepared to a high accuracy as follows: the approximate weights required for each component in each sample were calculated and the actual weights were measured on a balance reading to 10^{-5}g. Figures were taken to be accurate to 10^{-4}g. The total weight of each sample was approximately 10g. Evaporation of the liquids was minimised by the use of syringes to introduce the materials through inert rubber seals, and the sample, when prepared, was immediately transferred to a clean n.m.r. tube and sealed with a small flame.

g. Optimisation Of Experimental Conditions.

A small selection of samples was taken and used to optimise the experimental conditions, which were found to vary considerably from sample to sample, the reason being the wide relative variation in solvent concentration. The 0.3% impurity in the $[^2H_6]$ benzene did not provide a lock signal of sufficient amplitude to be readily monitored on the oscilloscope, and thus the audio amplifier described in Chapter 3 was used to distinguish the lock signal from background noise. It was found that the lock was stable if it was not attempted to sweep quickly through the spectrum, and in order to ensure that the risk of losing the signal was minimised the 100Hz sweep width and the 0.4Hz/s sweep rate were used at all times during these investigations.

The compositions and chemical shifts for each sample are shown in Table 5.2. Each shift is an average of several measurements and is quoted relative to chloroform in the free

TABLE 5.2. The compositions of the mixtures employed in the investigation of the chloroform (A) + $[^2H_6]$benzene (B) reaction in the presence of various inert materials (S), together with the corresponding chemical shifts of chloroform measured relative to the shift of chloroform in the absence of $[^2H_6]$benzene, and the corrected mole fractions of the aromatic component, x_B^{corr}, in the mixtures. An external tetramethylsilane lock was employed in the measurement of each value of δ_{free}.

$10^4\ n_A$/mol	$10^2\ n_B$/mol	$10^3\ n_S$/mol	Δ_{obs}/Hz	x_B^{corr}
S= cyclohexane, δ_{free} = 563.83Hz (309.7K).				
0.4858	3.2945	3.2425	83.10	0.8928
0.4414	3.3195	2.8686	83.34	0.9046
0.5553	3.3165	2.6015	83.59	0.9127
0.4481	3.3531	2.1268	83.97	0.9282
0.3727	3.3891	1.7925	84.54	0.9394
0.3803	3.4180	1.4150	84.60	0.9519
0.4615	3.4523	1.1370	85.17	0.9614
0.3945	3.4985	0.7354	85.44	0.9750
0.4087	3.5367	0.3701	85.81	0.9874

(continued)

TABLE 5.2. (continued).

$10^4\ n_A$/mol	$10^2\ n_B$/mol	$10^3\ n_S$/mol	Δ_{obs}/Hz	x_B^{corr}
S = cis-decalin, δ_{free} = 558.05Hz (309.2K).				
0.3333	3.2076	3.6506	92.12	0.8356
0.3761	3.2423	3.2671	92.94	0.8517
0.3493	3.3090	2.9290	93.38	0.8673
0.3886	3.3412	2.5712	93.91	0.8826
0.2982	3.3507	2.1835	94.48	0.8988
0.3250	3.3869	1.8598	94.78	0.9133
0.4372	3.4205	1.5156	95.09	0.9289
0.3518	3.4955	0.8102	96.36	0.9615
0.3534	3.5262	0.3634	97.08	0.9825
S = bicyclohexyl, δ_{free} = 537.06Hz (309.7K).				
0.3543	3.2072	3.6502	84.84	0.8078
0.6491	3.2444	3.2558	85.73	0.8266
0.4665	3.2784	2.8863	86.33	0.8445
0.3970	3.2805	2.5540	86.82	0.8600
0.4959	3.3503	2.1774	87.28	0.8804
0.3853	3.5213	1.8082	87.59	0.9030
0.3426	3.4224	1.4325	88.16	0.9195
0.3283	3.4582	1.0815	88.96	0.9386
0.3476	3.4922	0.8044	89.22	0.9540
0.3602	3.5287	0.3645	89.47	0.9789

(continued)

TABLE 5.2. (continued).

$10^4\ n_A$/mol	$10^2\ n_B$/mol	$10^3\ n_S$/mol	Δ_{obs}/Hz	x_B^{corr}
S = tetradecane, δ_{free} = 580.83Hz (309.4K).				
0.2948	3.2050	3.5517	85.90	0.7555
0.5687	3.3083	3.1779	87.00	0.7810
0.4833	3.2832	2.8180	87.80	0.7996
0.4665	3.3161	2.4518	88.72	0.8224
0.4339	3.4262	2.1371	89.16	0.8459
0.3409	3.3907	1.7400	90.37	0.8697
0.3124	3.4277	1.3609	91.09	0.8927
0.3702	3.4849	1.0491	92.57	0.9192
0.4213	3.5021	0.7001	93.55	0.9448
0.4079	3.5311	0.3517	94.35	0.9717
S = hexadecane, δ_{free} = 580.53Hz (310.7K).				
0.5009	3.2116	3.5296	84.94	0.7350
0.4146	3.2459	3.1721	85.92	0.7572
0.3769	3.2777	2.8212	87.21	0.7798
0.4875	3.3224	2.4703	88.18	0.8039
0.4959	3.3520	2.1305	89.00	0.8275
0.4515	3.4470	1.4085	91.39	0.8818
0.4037	3.4583	1.0536	92.24	0.9091
0.3258	3.4964	0.7013	93.42	0.9383
0.3375	3.5290	0.3481	94.39	0.9687

state; i.e. according to the equation $\Delta_{obs} = \delta_{obs} - \delta_{free}$. Both δ_{obs} and δ_{free} were measured relative to the sharpest peak arising from each of the inert solvents; no problems were encountered with this, although other workers[40] have preferred to use the aromatic absorption as a reference, which is equally valid[217]. An external tetramethylsilane lock was employed in the measurement of each value of δ_{free}, since an external benzene lock did not enable the chloroform absorption to be observed in the relevant sample. The temperatures at which each series of samples was investigated was measured in the conventional way, described earlier, and are shown in Table 5.2.

Because of the small lock signal several measurements of shifts were found to be necessary; finally good data for the chloroform + $[^2H_6]$ benzene reaction occurring in all five solvents were obtained. An example of the accuracy of the data is shown in Figure 5.1., which is a plot of Δ_{obs} against x_B for the reaction occurring in hexadecane. It should be noted that although in this case the plot is linear, for other solvents it is noticeably curved; it is the <u>continuity</u> of the data points which was taken to signify high accuracy.

5.3. Results.

The data shown in Table 5.2. were processed on an ICL1905E computer, using the previously defined modifications and conditions relevant to the Benesi-Hildebrand procedure, on the mole fraction, molarity and molality concentration scales. The computer program used for the calculations (BHCURVEFIT[217]) was modified such that the concentrations of each component on the scale used were calculated within the program, rather than being read in to the computer. This method requires that only the weights, molecular weights and

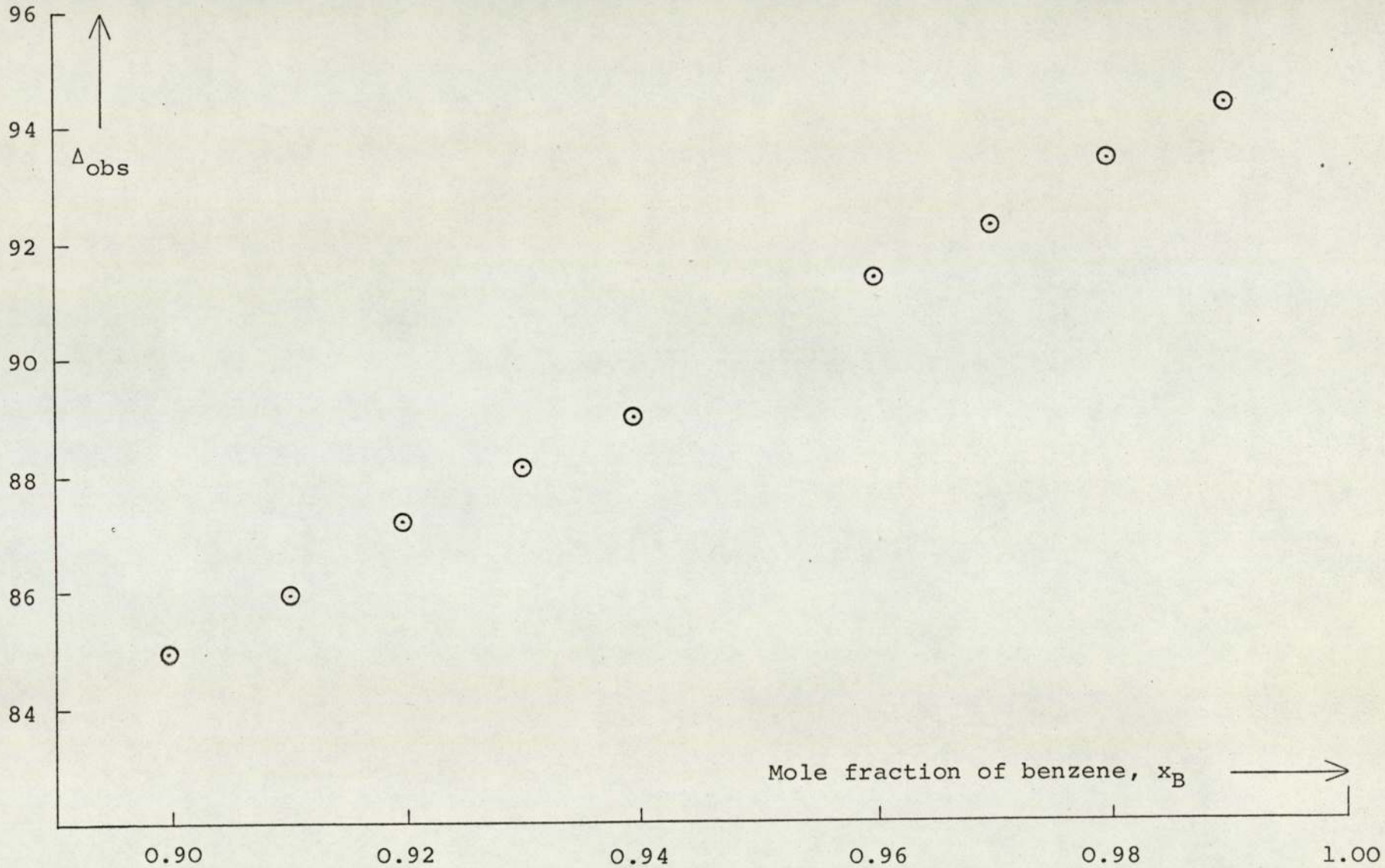


FIGURE 5.1. The relationship between Δ_{obs} and x_B for the chloroform + $[^2H_6]$benzene reaction occurring in hexadecane at 310.7K.

densities of each component in every sample are fed into the program, and considerably reduces the number of calculations required before the computation. The densities for each component at the temperatures relevant to the investigations are shown in Table 5.3.

The concentration of the aromatic component in each sample on each of the three concentration scales is given, neglecting the small amount of solute[40], by equations 5.2., 5.3. and 5.4. respectively:

$$x_B^{corr} = n_B V_B / (n_B V_B + n_S V_S) \qquad 5.2.$$

$$C_B = n_B / (n_B V_B + n_S V_S) \qquad 5.3.$$

$$m_B = n_B / (n_B V_B \rho_B + n_S V_S \rho_B) \qquad 5.4.$$

and calculated by the computer from the analagous equations 5.5., 5.6. and 5.7. respectively:

$$x_B^{corr} = w_B / (w_B + w_S \rho_B / \rho_S) \qquad 5.5.$$

$$C_B = w_B / M_B (w_B / \rho_B + w_S / \rho_S) \qquad 5.6.$$

$$m_B = w_B / M_B (w_B + w_S \rho_B / \rho_S) \qquad 5.7.$$

where w_B and w_S are the weights of the components B and S respectively in each sample, M_B is the molecular weight of B, and ρ_B and ρ_S are the densities of B and S respectively at the relevant temperatures.

If K_x is less than unity, Whitney has shown[49] that the amount of solute, n_A, affects the value of the equilibrium quotient to a small, but noticeable, extent. Consequently modifications to the program include a section which, if K_x is less than one, recalculates the equilibrium quotients

TABLE 5.3. The densities of the various materials used at the temperatures of the investigations.

T/K	$10^{-3}\ \rho_B/kg.m^{-3}$ [a]	SOLVENT, S	$10^{-3}\ \rho_S/kg.m^{-3}$
309.7	0.9299	cyclohexane	0.7634[b]
309.2	0.9305	cis-decalin	0.8846[b]
309.7	0.9299	bicyclohexyl	0.88[c]
309.4	0.9302	tetradecane	0.7514[b]
310.7	0.9287	hexadecane	0.7622[b]

[a] Calculated for 99.7% isotopic purity from the data given by J.A.Dixon and R.W.Schiessler[228] for 100.0% and 99.3% isotopic purity at several temperatures.

[b] Deduced from the data given by J.Timmermans, 'Physico-chemical Constants Of Pure Organic Compounds', Elsevier, Amsterdam, 1965, Volume 2.

[c] As a value at 309.7K is not available from the literature, that provided by the supplier, Phase Separations Ltd., for the mixture of isomers was used, (880 $kg.m^{-3}$ at 298.2K).

from concentration expressions which include the amount of solute present in each sample. For example, the mole fraction of the aromatic component in a sample is then given by equation 5.8:

$$x_B^{corr} = n_B V_B / (n_A V_A + n_B V_B + n_S V_S) \qquad 5.8.$$

For this reason weights, molecular weights and densities for all components were included in the computer input, but the use of this part of the program was not required in these investigations.

In Chapter 4 it was shown that the values for the equilibrium quotients and Δ_c are most meaningful when evaluated at zero solvent concentration, and also that in the case of the molality scale the definition of the concentration must be modified to be consistent with the two others, if the ambiguity of infinite molality, but a finite slope of the Benesi-Hildebrand plot is to be resolved. The concentrations of component B at this point are therefore given by equations 5.9., 5.10. and 5.11. for the mole fraction, molarity and molality scales respectively,

$$x_B^{corr} = 1 \qquad 5.9.$$

$$c_B = 1/V_B \qquad 5.10.$$

$$m_B = 1/V_B\rho_B = 1/M_B \qquad 5.11.$$

which are derived from equations 5.2., 5.3. and 5.4. under the condition that n_S is zero.

Values are thus deduced by the program for the equilibrium quotients K_x, K_c and K_m, together with the associated values for Δ_c by obtaining the best equation for the plot of $1/\Delta_{obs}$ against $1/[B]_o$ (i.e. equations 1.80 - 1.82.,

where $[B]_o$ is the initial concentration of component B) and evaluating the slope and intercept of the line at the points determined by equations 5.9. - 5.11. depending upon the scale on which $[B]_o$ is defined. The iteration to find the best equation for the line will proceed, if necessary, or if commanded, to evaluate an equation which is quadratic, (i.e. it allows for slight curves in the data), but for all the results obtained here a linear fit gave the lowest standard deviation in values for Δ_{obs}.

The final results are shown in Table 5.4., which only includes one value for Δ_c for the reaction in each solvent since these values were exactly the same, irrespective of the concentration scale used for processing the data. The accuracy of the results will be discussed below.

5.4. Discussion.

Table 5.5. shows the values for K_c/K_x and K_m/K_c which, according to the modifications to equation 1.79. proposed in Chapter 4, should equal V_B and ρ_B respectively. Comparison of the relevant values shows remarkably good agreement, and provides strong support for the validity of equations 5.12. - 5.14. for K_x, K_c and K_m respectively.

$$K_x = \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB}) n_B V_B} \qquad 5.12.$$

$$K_c = \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB}) n_B} \qquad 5.13.$$

$$K_m = \frac{n_{AB}\rho_B(n_B V_B + n_S V_S)}{(n_A - n_{AB}) n_B} \qquad 5.14.$$

It should be remembered, however, that these ratios will tend to cancel out experimental errors, and since the

SOLVENT, S	K_x	$10^3\ K_c/m^3.mol^{-1}$	$K_m/kg.mol^{-1}$	Δ_c/p.p.m.[a]	T/K
cyclohexane	2.1938	0.19827	0.18457	1.2541	309.7
cis-decalin	2.4739	0.22371	0.20814	1.3688	309.2
bicyclohexyl	2.9726	0.26866	0.25010	1.2056	309.7
tetradecane	1.9617	0.17739	0.16505	1.4366	309.4
hexadecane	1.9134	0.17368	0.16133	1.4543	310.7

TABLE 5.4. Values of parameters characteristic of the formation of the $[^2H_6]$benzene + chloroform complex in various solvents.

[a] The values obtained for Δ_c were identical for any particular solvent, whichever concentration scale was used for data processing.

SOLVENT, S	$10^4(K_c/K_x)$/ $m^3.mol^{-1}$.	10^4 $V_B/m^3.mol^{-1}$. (calc).	$10^{-3}(K_m/K_c)$/ $kg.m^{-3}$.	10^{-3} $\rho_B/kg.m^{-3}$. (calc).	T/K
cyclohexane	0.9038	0.9048	0.9309	0.9299	309.7
cis-decalin	0.9043	0.9042	0.9304	0.9305	309.2
bicyclohexyl	0.9038	0.9048	0.9309	0.9299	309.7
tetradecane	0.9043	0.9045	0.9304	0.9302	309.4
hexadecane	0.9077	0.9059	0.9289	0.9287	310.7

TABLE 5.5. Values for K_c/K_x and K_m/K_c compared with values for V_B and ρ_B respectively, calculated at the temperatures of investigation of the chloroform + $[^2H_6]$benzene reaction in each of the solvents used.

same values for V_B and ρ_B were used in the computations, a large deviation would be totally unexpected. The comparisons show a significant improvement over previous results[40,41], and, therefore, a high accuracy for the value of the equilibrium quotient should be expected, since the ratios K_c/K_x and K_m/K_c are all within 0.2% of their theoretical values.

Comparisons between the present results and those obtained previously for the chloroform + benzene reaction in the same solvents[40,41,49] show a significant increase (about 50%) in the values for equilibrium quotients determined here, but there is little difference in the mean values for Δ_c. The values for these parameters deduced on the mole fraction scale for both the previous and the present investigations are compared in Table 5.6.

Values of the equilibrium quotients obtained for the two reactions are abnormally high when bicyclohexyl is used as solvent and differ significantly from the mean values for the other systems. This latter observation may be due to the presence of an undetected impurity or to an insufficiently accurate value for its density (see Table 5.3. footnote c.) being used in the computation. However, it is more probable that this spurious result occurs because the bicyclohexyl molecule may be present with three forms of ring bonding which are: axial-axial, equatorial-equatorial and axial-equatorial. In this case the polar nature, polarizability, and dielectric constant of the solvent could affect the number and nature of interactions present in solution so that the direct use of the Benesi-Hildebrand method would be invalidated and could lead to a spurious and high value for K. Serious errors may arise in cases having more than

TABLE 5.6. A comparison of some of the parameters obtained for the chloroform + benzene,[40] and the chloroform + $[^2H_6]$benzene reactions occurring in different inert solvents.

	CHLOROFORM + BENZENE			CHLOROFORM + $[^2H_6]$BENZENE		
SOLVENT, S	K_x [a]	Δ_c/p.p.m. [a]	T/K	K_x [b]	Δ_c/p.p.m. [b]	T/K
cyclohexane	1.51	1.393	306.6	2.1938	1.2541	309.7
cis-decalin	1.73	1.322	306.6	2.4739	1.3688	309.2
bicyclohexyl	1.94	1.275	306.6	2.9726	1.2056	309.7
tetradecane	1.67	1.367	306.6	1.9617	1.4366	309.4
hexadecane	1.70	1.373	306.6	1.9134	1.4543	310.7

[a] Values should be taken to be accurate to the first decimal place only.[49]

[b] Values are probably accurate to the second decimal place, (see text).

one type of complex in solution, either involving differing stoichiometries or the interaction of the solute with more than one seperate species.

There are two distinct reasons for the easily observable differences between the values of the parameters for these two quite similar systems. Firstly, that the replacement of ^{1}H by ^{2}H in benzene could alter the parameters pertaining to the interaction with chloroform directly, or, secondly, that differences in the interaction of benzene and $[^{2}H_{6}]$benzene with the solvents on the non-bonded contributions to chemical shifts could result indirectly in an apparent change of the interaction parameters. Considerations of the accuracy of the data and of the significant difference between the values for K_x and Δ_c for the two systems indicate that both the reasons given above may together explain the observations.

There are also other factors beyond the two proposed above which may have some small influence on these variations, and these are the differences which may be expected to occur via comparison of the systems at different temperatures and solute concentrations. This may explain the variations in Δ_c, which are more prominent for the $[^{2}H_{6}]$benzene + chloroform reaction. The solvent should not affect this parameter. It has been found previously[49,231] that Δ_c does exhibit extremely small variations with temperature, such as those reported here. The effect of the solute concentration is difficult to estimate, but it is possible that it may lead to slightly different values for K and Δ_c by modifying the slope of the Benesi-Hildebrand plot. The effect would, however, almost certainly be small.

The differences referred to cannot be directly due to

the replacement of ^1H by ^2H in benzene because it is reasonable to suppose that the very small differences in bond lengths and molar volumes (0.2%) can be neglected. The volume corrections, V_S/V_B, are, therefore, also very similar in each case. However, it is probable that changes could result in the physical parameters of the molecule which are influenced by electric fields, and interpretation on this basis is quite feasible.

The reasons for these variations are thus rather nebulous in nature, but it does appear that two major factors predominate. Firstly, that difference in K for the same reaction in various solvents may be explained in terms of the non-inertness of the solvents (bicyclohexyl certainly gives rise to anomalous results), and secondly that there is a significant increase in the interaction energy for chloroform with $[^2H_6]$benzene rather than benzene, which arises because of a kinetic isotope effect.

An attempt will now be made to correlate the variations in K with these two major reasons for them, but, because there are so many other effects such as differences in temperature, solute concentration, solvent shape, and activity coefficients, the result must necessarily be rather less than quantitative.

5.4.1. Solvent Effects.

The primary requirement of any solvent is that it should have exactly the same physical properties as the molecules it is replacing in a solution, except, in this case, the ability to form molecular complexes. The impossibility of this is immediately obvious, since to fulfil this requirement the size, shape[232], and more importantly the refractive index and dielectric constant must be the same as those for the

molecule which it is replacing, in order that dispersion and reaction field forces remain constant with the changing composition of the liquid mixture. An allowance has already been made in these investigations for the different sizes of the solvent and aromatic components, but none for the differences and changes in refractive indices and dielectric constants, because it was previously assumed that the small differences in the relevant contributions to chemical shifts would be negligible and within experimental error. However, although the strength of these forces ($\sim$1.5kJ mol^{-1}), are less than that for complex formation ($\sim$4kJ mol^{-1}), they are still of the same order of magnitude. Ideally, therefore, an allowance should be made in the shift data for variations in σ_W and σ_E, but since this is not practicable[80] because of the inadequacies in the theories for these effects, another approach must be adopted. σ_a will be affected to a lesser extent[77], and here attention will be focussed on changes in σ_W and σ_E.

Data for use in the modified Benesi-Hildebrand equation are determined over a finite range of concentration, and thus the influence of the variations in σ_W and σ_E on the plot of $1/\Delta_{obs}$ against $1/[B]_o$ may be reflected in the slope and position of the line for each solvent. The simplest method of illustrating this is to interpret the differences in refractive indices and dielectric constants of each solvent-aromatic combination as a semiquantitative measure of the extent of this variation.

The equations describing the contributions to chemical shifts arising from dispersion and electric field interactions have been discussed in Chapter 2. Both equations 2.21. and

2.23., describing σ_W and σ_E respectively, are of the general form: σ = (variable) x (constant). The variable is solely dependent upon the solvent, and the constant is solely dependent upon the solute. For dispersion interactions the variable term is a function of refractive index, n, and for electric field effects is a function of refractive index and dielectric constant, ε. If, as in this case, the solvent has two components with different values of n and ε, the magnitudes of σ_W and σ_E will vary with the composition of the solvent. The differences in the refractive indices (Δn) and dielectric constants ($\Delta\varepsilon$) for each pair of components (i.e. aromatic and inert solvent) must be eliminated. Using a common solute and several solvents a plot may be made of Δn or $\Delta\varepsilon$ against a parameter dependent upon variations in electronic interactions. Extrapolation to $\Delta n = 0$ or $\Delta\varepsilon = 0$ should enable the calculation of the parameter independent of such effects. As mentioned above, the slope of the Benesi-Hildebrand plot, $1/K_x\Delta_c$ is such a dependent parameter, and may conveniently be used for the extrapolation procedure.

It is reasonable to suppose that variations in σ_W and σ_E with composition may affect both the slope and intercept ($1/\Delta_c$) of the Benesi-Hildebrand plot. However, it is not anticipated that the solvent will affect Δ_c as much as K_x. This is substantiated by the data in Table 5.6.; Δ_c is not greatly affected by procedures other than complex formation. Indeed, a plot of $1/\Delta_c$ against Δn shows no apparent correlation between points, and appears to be completely independent of the inert solvent used.

Dielectric constant data for some of the components used are not available from the literature, but a complete set of refractive indices is readily obtainable. However,

since $\varepsilon \approx n^2$ for non-polar molecules this makes little difference. Employing data from Tables 5.1. and 5.6. graphs of $1/K_x\Delta_c$ against Δn were plotted for both the chloroform + benzene and chloroform + $[^2H_6]$benzene reactions occurring in the five solvents. The plots are shown in Figure 5.2., from which it can be seen that there is some correlation between $1/K_x\Delta_c$ and Δn for each reaction, especially that using $[^2H_6]$benzene. The latter plot shows little scatter from a straight line, and is expected to be of a higher accuracy than the data for the other reaction; because there are few points it was considered unrealistic to calculate a correlation coefficient for these, and its meaning in this context would certainly be difficult to interpret.

Since the ideal solvent has physical properties which are identical to the interacting component which it is replacing in solution, the plot shown in Figure 5.2. provides a means of obtaining a value of $1/K_x\Delta_c$ which is solvent independent. Differences in the electronic interactions occurring between the solvent and aromatic as the concentration is varied may be eliminated by extrapolating to $\Delta n = 0$. Values which result are: for the chloroform + benzene reaction $1/K_x\Delta_c = 0.408$, and for the chloroform + $[^2H_6]$benzene reaction $1/K_x\Delta_c = 0.278$. The mean values for Δ_c for the two reactions (1.364p.p.m. and 1.378p.p.m. respectively) gives rise to solvent independent values for K_x of 1.800 and 2.611 respectively. (The mean values for Δ_c are those calculated after discarding the spurious bicyclohexyl data). The significance of this extrapolation procedure will be discussed further in Chapter 6.

The variation in values of K_x for these two similar systems cannot be accounted for solely by experimental error,

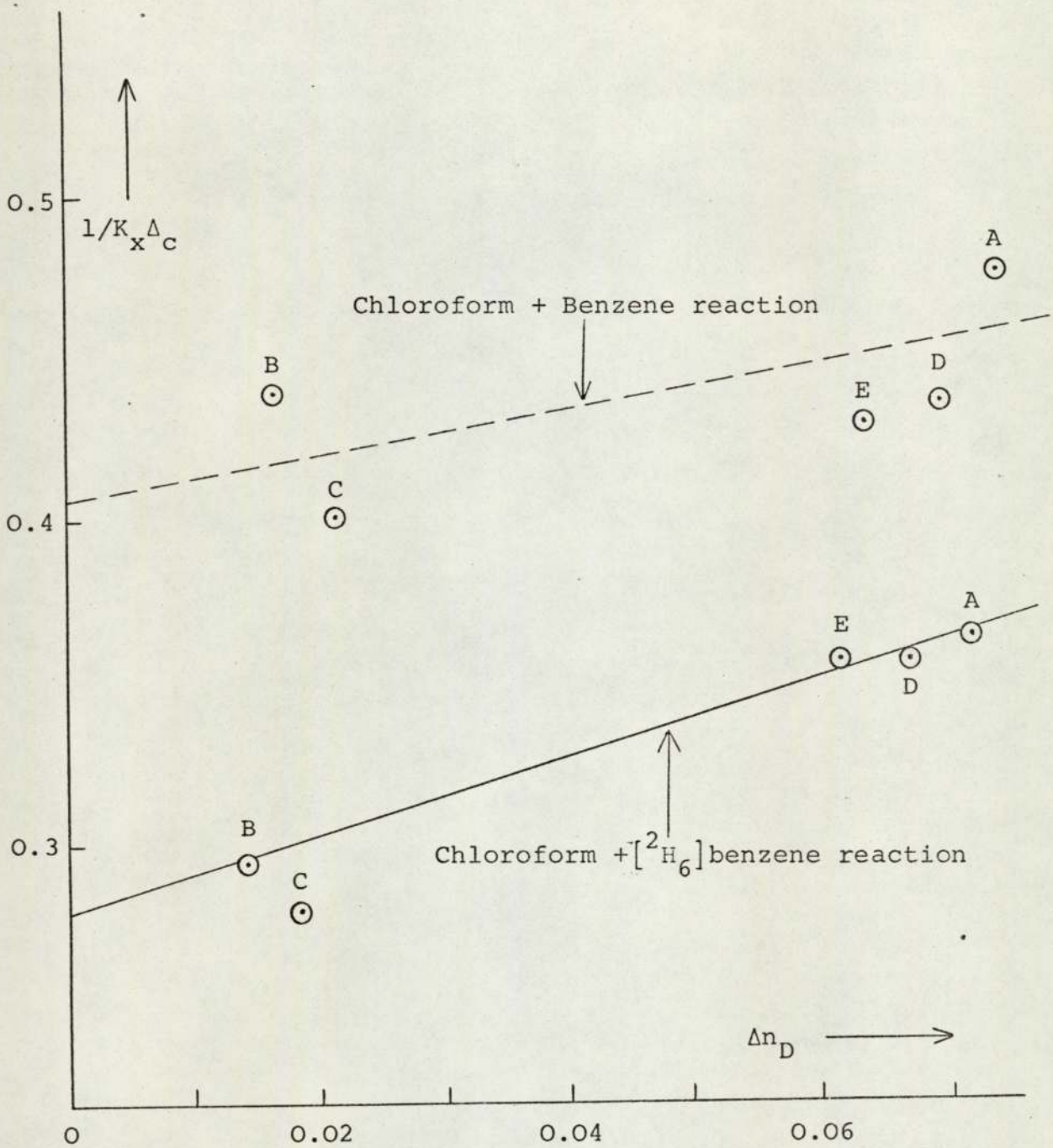


FIGURE 5.2. The relationship between $1/K_x\Delta_c$ and Δn_D for the two reactions chloroform + [$^2H_6$]benzene and chloroform + benzene in the five solvents: cyclohexane (A), cis-decalin (B), bicyclohexyl (C), tetradecane (D) and hexadecane (E).

which may be smaller than 0.02[209], or about 1%. It is apparent, however, from the foregoing argument that the complexes formed in these two systems are very similar in nature, but since the variations in the values for K_x appear to be real, the actual mechanisms of their formation and their relative stabilities must differ. It is therefore reasonable to suppose that kinetic isotope effects may be worthy of consideration.

5.4.2. Isotope Effects In Aromatic Molecules.

Valuable information concerning reaction mechanisms has been provided by studies of the effects on reaction rates of replacing an atom by one of its isotopes. A rigourous theory for these effects has been worked out by Bigeleisen[233], but its discussion here will not result in quantitative explanations because of the variety of effects other than those of isotopic substitution present in the systems under investigation. It is unfortunate that the precise theory of isotope effects is a complicated one, and is difficult to apply to specific examples[234], because when an isotopic substitution is made a considerable number of relatively small effects make themselves felt[235], and for the overall effect to be understood each one must be considered in detail. This would be a prodigious undertaking, and not worthwhile here.

Kinetic isotope effects are usually most apparent when a hydrogen atom is replaced by deuterium, since this substitution corresponds to a large relative change in atomic mass[234]. Many physical properties of protonated and deuterated molecules are very similar, the refractive indices, molar volumes, ionisation potentials and bond strengths only differing by less than 1% (see Table 5.7.) and by a simple

PROPERTY	BENZENE	REFERENCE	$[^2H_6]$BENZENE	REFERENCE
Molar volume/$m^3.mol^{-1}$. at 298.2K	0.8923×10^{-4}	236	0.8910×10^{-4}	228
Refractive index, n_D^{293}	1.5011	227	1.4991	228
dn_D^T/dT	0.64	227	0.64	228
Polarisability: $\alpha_E^{306.6}$	0.001040	237	0.001034	237
$\alpha_M^{306.6}$	0.001057	237	0.001051	237
Moment of inertia, I	The ratio of $I_{C_6H_6}:I_{C_6D_6}$ = 1:1.1664			237
Ionisation potential /eV *	15.44 (H_2)	238	15.48 (D_2)	238
Bond strength /$kJ.mol^{-1}$.*	24.67 (H_2)	235	25.10 (D_2)	235

TABLE 5.7. A comparison of some of the physical properties of benzene and $[^2H_6]$benzene.

* Values for these parameters for both molecules are not available from the literature; those for the hydrogen and deuterium molecules are shown.

n.m.r. experiment involving the dilution of H_2O by D_2O it can be shown that the difference in hydrogen bonding effects is negligible. It is apparent from Table 5.7., however, that those parameters which are affected by atomic mass are significantly altered by the isotopic substitution.

In an exhaustive and definitive study of the benzene molecule Ingold and co-workers[237,239] obtained Raman, infra red and fluorescence spectra of benzene and $[^2H_6]$benzene, and attributed the differences to variations in the zero point energies. They showed, however, that the polarisabilities of each molecule were very similar. They interpreted the fact that Raman bands were broader for benzene as being due to the difference in moment of inertia of the two molecules. Rabinovich and Volokhova[240] have reached similar conclusions.

The reason for changes in reaction rates due to isotopic substitution is that there is a change in the average vibrational energy of the molecule, and, in relation to the present subject, of any complex formed. There is, however, no change in the potential energy surface for the molecule, but a reduction in zero point energy. For example, the dissociation energy of H_2 is 24.67 $kJ.mol^{-1}$, whilst that for D_2 is 25.10 $kJ.mol^{-1}$[235]. If no further factors are significant a reaction involving a bond to hydrogen will occur more rapidly than the reaction involving the same bond to deuterium. Many molecules containing a C - H bond have a vibrational frequency of 2900 - 3000cm^{-1}, but the substitution of hydrogen by deuterium changes the frequency to between 2000 and 2100cm^{-1}, the ratio of these frequencies being approximately equal to the square root of the ratio of the

masses of H and D. This is so because of the appearance of the reduced mass, μ, in the selection rule expression.

Molecular rotation is also altered by isotopic substitution since rotational energy levels are given by an expression including the molecular moment of inertia. If this rises the rotational energy levels are lowered and become closer together. Although relaxation time studies have been carried out on both the systems investigated here[90-94], data are not available to enable the calculation of the times for which both the chloroform-benzene and chloroform-$[^2H_6]$benzene complexes move as a unit, and hence deduce differences in rotational characteristics. These will probably be small[90], and may probably be neglected.

However, if a bond in a molecule involving H or D is not broken, the reaction occurring at another place in the molecule, or only a complex is formed, such as the complexes under investigation in this case, the situation is more complicated since the effect on reaction rates, or equilibrium quotients, is much smaller. The reasons for this are quite subtle.

In the case of a complex where the C-H or C-D bond is not directly involved in interaction there will be hardly any isotope effect. However, a bond which is strengthened will show a reverse isotope effect, the molecule containing deuterium reacting more rapidly in this case[235].

By analogy with theories for activated complex formation[235], isotopic substitution will also affect the position of an equilibrium reaction, and it may readily be deduced that substitution of a heavier atom will always favour formation of a stronger bond, because the zero point energy of the heavy molecule will be relatively lower than

that of the light molecule. Figure 5.3. illustrates this point. The meaning of this in the present context is that there will be a stronger bond, or interaction, between chloroform and $[^2H_6]$benzene than chloroform and benzene. The equilibrium for the reaction $A + B \rightleftharpoons A....B$ will therefore move to the right hand side by a small amount.

The foregoing arguments have been based on kinetic theories. However, current theories of kinetic isotope effects are insufficiently advanced to throw unambiguous light on complex formation. The ensuing argument will therefore be developed by analogy with the results of other workers.

Halein and Ravid[241] have studied HCl-alkylbenzene π - complexes of the nature investigated here, and also some charge-induced dipole complexes such as those occurring in nitration reactions, with respect to isotopic substitution. Their qualitative conclusions are important in this context since they found that deuterated aromatics reacted to give higher equilibrium quotients for this type of reaction than the hydrogenated molecule. For the HCl + benzene reaction they found $K_H/K_D = 0.95$, and for the nitration of benzene $K_H/K_D = 0.87$, where K_H/K_D is the ratio of the equilibrium quotients for nitration of benzene and $[^2H_6]$ benzene respectively. The effect was interpreted as being due to smaller out of plane vibrations and a shorter length for the C-D bond, and concluded that the C-D bond aids the stabilisation of electron deficient systems. While their method of calculating equilibrium quotients for the formation of complexes is subject to some doubt, their qualitative conclusions can be invoked as a valid argument in this case.

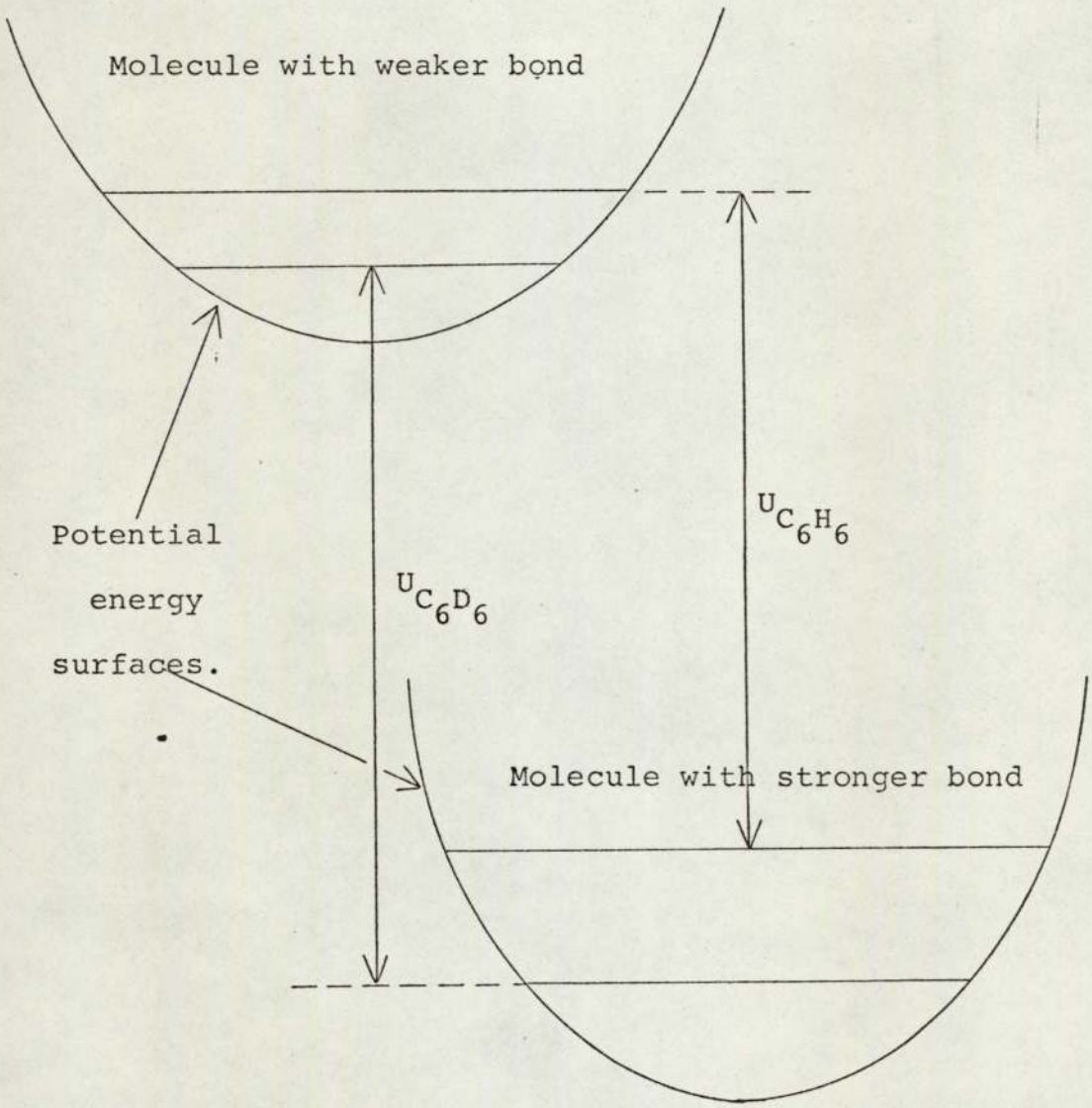


FIGURE 5.3. The effect of isotopic substitution on the position of chemical equilibrium. The difference between the zero-point energies is greater for the molecule with the stronger bond, so that $U_{C_6H_6}$ is less than $U_{C_6D_6}$. The equilibrium for the heavy molecule is therefore in favour of the stronger bond.

A detailed treatment of isotope effects obviously involves a treatment of the vibrational characteristics of the aromatic molecules in both the initial and activated states, and requires a precise knowledge of the potential energy surfaces. Exact treatments have only been carried out for a few simple gas phase reactions, and thus it is only possible to draw qualitative conclusions here.

In order to draw these conclusions a knowledge of K_H/K_D for the reaction under consideration here is necessary, and this can be calculated to be approximately 0.7, which indicates a much larger isotope effect than observed by Halein and Ravid[241]. However, as stated earlier, their results are subject to some doubt, because the HCl-benzene complex exhibits abnormal behaviour, apparently changing the mechanism of its formation above $x_B = 0.5$ from a σ- to a π- complex[231]. Moreover, they deduced the equilibrium constants for benzene nitration from the rates of product formation and this fact leads one to suspect that K_H/K_D for the formation of a complex only (i.e. no actual reaction) is in fact less than 0.87, because as shown above, whilst the C-D bond stabilises the complex more than the C-H bond, it is also stronger. Because H or D is lost in the nitration reaction it is reasonable to suppose that C-H or C-D is in a state of stretching in the activated complex. Consequently, the deuterated molecule will tend to react slower (i.e. the antithesis of Figure 5.3. is that a weakened bond will reflect a faster reaction rate if the lighter isotope is used), although the actual loss of H or D is a very fast, non-rate-determining step.

The reaction studied here is the formation of a similar complex between chloroform and benzene or $[^2H_6]$

benzene. In the latter case the complex is stabilised to a larger extent for at least two reasons (i.e. stronger interaction and increased stabilisation), and since no bond is broken, it is reasonable to suppose that K_H/K_D should be less than 0.87, although it is not possible to give a precise value.

The preceding arguments indicate that whilst Δ_c is very similar for both reactions, the difference between the extrapolated equilibrium quotients, deduced using the previously quoted mean values for Δ_c, (K_x = 1.800 and 2.611 for the reactions of chloroform with benzene and $[^2H_6]$ benzene respectively), is readily explained by the effects of isotopic substitution which are that: (a) the interaction between the solute and the heavier aromatic is stronger, (b) the C-D bond is more electropositive, and shorter, than the C-H bond, and stabilises electron deficient systems, causing the equilibrium to shift to the right.

5.5. Conclusions.

In this chapter an attempt has been made to show that the practical conditions and modifications applicable to the Benesi-Hildebrand method which have been proposed by other workers are valid. Using data of higher accuracy than obtained by them it has been shown that these modifications are justified, and eliminate previous anomalies. Values for Δ_c have been obtained which are independent of the concentration scale used for data processing, and values for the equilibrium quotients K_x, K_c and K_m, deduced on the mole fraction, molar and molal scales respectively, are consistent with the predicted relationship between them to a high order of accuracy.

The variation of equilibrium quotients with the inert solvent used for the study of a particular reaction has been satisfactorily explained in terms of the differences in dispersion and electric field effects of the solvent and aromatic used, and a method for deducing the equilibrium quotient for a particular reaction which is independent of the solvent has been derived. It appears that in order to provide realistic values for K and Δ_c at least three diluting solvents of the saturated hydrocarbon type employed here should be used. There are, nevertheless, still small errors in this procedure because changes in σ_a have been neglected.

Comparisons between the equilibrium quotients for the reaction studied in this chapter and very similar reactions studied by other workers indicate that isotopic substitution effects can be important in studies of molecular interactions. The differences between the equilibrium quotients for the chloroform + $[^2H_6]$benzene reaction (K_x = 2.611) and the chloroform + benzene reaction (K_x = 1.800) have been qualitatively explained on this basis, but it was noted that the nature of each complex was very similar, as indicated by the Δ_c values, and that isotopic substitution only appears to change the stability of the complex.

CHAPTER 6

SOME OBSERVATIONS ON REFERENCING TECHNIQUES.

6.1. Introduction.

In investigations of the type reported in the previous chapter, the difficulty in finding solvents which reflect the properties of aromatic molecules in all respects, except in the ability to form complexes, was the subject of some concern and a method for eliminating solvent effects was proposed, and shown to be effective. There is, however, the related problem of the effect of the choice of reference materials on the studies to be considered. In the past, and in the present investigations, the internal reference technique has been used with some justification. Using the solvent in a three component mixture as the reference, Homer et al[40,220] have shown its effect on observed chemical shifts (of the magnitude measured here) to be small. However, in the light of the conclusions drawn in the preceding chapter, these problems must be reconsidered. It has been noted by Laszlo et al[242] that the arbitrary choice of an internal reference may lead to serious effects in studies of non-polar solutes where the solvent induced shifts are similar to the screening of the reference proton.

The use of reference independent methods[49,243] might be thought to eliminate this difficulty and it was considered to be worthwhile investigating this point in further detail here. The technique developed by Becconsall et al[244] is based on an external reference method, and requires no corrections for differences in bulk susceptibility. The calculated shifts are independent of the chosen reference.

Data was therefore obtained using the reference independent technique. By a comparison of the results obtained

from processing such data with those obtained via the internal reference procedure, some observations can be made concerning the validity of the two procedures.

6.2. The Internal Reference Method.

The nature of the screening contributions to the chemical shift has been described in Chapter 2, and further explanation of the screening terms is not required here. The observed, internally referenced, chemical shift between, say, chloroform and cyclohexane, in a typical three component mixture is given by equation 6.1.

$$\Delta_{obs} = \delta_{obs} - \delta_{free}$$

$$= (\sigma^{CHCl_3} - \sigma^{C_6H_{12}}) - (\sigma^{CHCl_3}_{(free)} - \sigma^{C_6H_{12}}_{(free)}) \qquad 6.1.$$

where:

$$\sigma^{CHCl_3} = \sigma_a^B + \sigma_a^S + \sigma_w^B + \sigma_w^S + \sigma_E^B + \sigma_E^S + \sigma_s^B + \sigma_s^S \qquad 6.2.$$

$$\sigma^{C_6H_{12}} = \sigma_a^{B^1} + \sigma_a^{S^1} + \sigma_w^{B^1} + \sigma_w^{S^1} + \sigma_s^{B^1} + \sigma_s^{S^1} \qquad 6.3.$$

$$\sigma^{CHCl_3}_{(free)} = \sigma_a^{S^{11}} + \sigma_w^{S^{11}} + \sigma_E^{S^{11}} + \sigma_s^{S^{11}} \qquad 6.4.$$

$$\sigma^{C_6H_{12}}_{(free)} = \sigma_a^{S^{111}} + \sigma_w^{S^{111}} + \sigma_s^{S^{111}} \qquad 6.5.$$

The superscripts B and S indicate that the terms apply to the screening induced by the aromatic, B, or the solvent, S, respectively. Therefore, Δ_{obs} is given by equation 6.6.

$$\Delta_{obs} = (\sigma_a^B - \sigma_a^{B^1} + \sigma_a^S - \sigma_a^{S^1} + \sigma_a^{S^{111}} - \sigma_a^{S^{11}})$$

$$+ (\sigma_w^B - \sigma_w^{B^1} + \sigma_w^S - \sigma_w^{S^1} + \sigma_w^{S^{111}} - \sigma_w^{S^{11}})$$

$$+ (\sigma_E^B + \sigma_E^S - \sigma_E^{S^{11}}) + (\sigma_s^B - \sigma_s^{B^1} + \sigma_s^S - \sigma_s^{S^1} + \sigma_s^{S^{111}} - \sigma_s^{S^{11}})$$

6.6.

Normally, justification for the use of the internal reference method to study variations in σ_s^B is based on the fact that all other terms are constant or zero. The latter is supposedly true for all σ_s terms except σ_s^B when the concentration is varied, whilst each individual term varies with the composition of the sample, each term of the type $(\sigma - \sigma^1)$ and $(\sigma^{111} - \sigma^{11})$ will tend to zero., and $(\sigma_E^B + \sigma_E^S - \sigma_E^{S^{11}})$ will also tend to zero.

However, in the light of the proposals made in the previous chapter, it is apparent that the validity of these approximations may be subject to some doubt, and that some, if not all, screening terms could vary with composition. If this is the case Δ_{obs} is more accurately described by equation 6.7.

$$\Delta_{obs} = \Delta\sigma_w + \Delta\sigma_a + \Delta\sigma_E + \sigma_s^B \qquad 6.7.$$

where $\Delta\sigma$ is the variation in screening with mixture composition; according to the work of Homer and Redhead[77], $\Delta\sigma_a$ is usually quite small and may be neglected. Therefore, variations in dispersion and electric field interactions will be reflected in the magnitude of chemical shifts[245]. This will affect the slope of Benesi-Hildebrand plots, and influence the values of K and Δ_c obtained therefrom. These parameters are very sensitive to the slope of the line, a fact which may be readily demonstrated by leaving out slightly erroneous data points from the computer input. This results often in a significant change

in the magnitudes of K and Δ_c.

This approach indicates that an extrapolation procedure of the type mentioned above is valid for deducing reference independent values for the equilibrium parameters, which may be compared with values of K_x and Δ_c obtained from reference independent studies.

6.3. The Reference Independent Method.

The procedure developed by Becconsall et al[244] for obtaining reference independent shifts requires that the sample is composed of a solute (A), in low concentration in a solvent, in this case the mixed solvent B + S. The sample is placed in a sample tube surrounding a coaxial external reference capilliary, containing the same solute, A, at the same concentration in another solvent, which in this case may be S alone. The chemical shift difference between the solute in the two environments is measured, both with the tube perpendicular to the applied field, B_o, and with the axis of the tube parallel to B_o. This procedure, of course, requires two spectrometers.

If the samples can be assumed to be of infinite length, or effectively, that they are long enough to present the same dimensions to the magnetic field, then for perpendicular sample orientation:

$$\sigma_b^{\perp} = 2/3(\pi\chi_v) \qquad 6.8.$$

and for the parallel orientation:

$$\sigma_b^{\parallel} = 4/3(\pi\chi_v) \qquad 6.9.$$

where χ_v is the volume susceptibility of the solvent. Therefore, defining σ_{sol} as the solvent screening contribution to the solute:

$$\sigma_{sol}^{\parallel} = \sigma_b^{\parallel} + \sigma_{loc} = -\ 4/3(\pi\chi_v) + \sigma_{loc} \qquad 6.10.$$

$$\sigma^{\perp}_{sol} = \sigma^{\perp}_{b} + \sigma_{loc} = 2/3\ (\pi\chi_v) + \sigma_{loc} \qquad 6.11.$$

where σ_{loc} is the sum of the local screening terms σ_a, σ_w, σ_s and σ_E.

The relative shifts between the solute in the three-component (x) and two-component mixture (y) are given for each orientation by:

$$\sigma^{\perp}_{sol(y)} - \sigma^{\perp}_{sol(x)} = \frac{2\pi}{3}\left[\chi_{v(y)} - \chi_{v(x)}\right] + \sigma_{loc(y)} - \sigma_{loc(x)} \qquad 6.12.$$

$$\sigma^{\parallel}_{sol(y)} - \sigma^{\parallel}_{sol(x)} = \frac{-4\pi}{3}\left[\chi_{v(y)} - \chi_{v(x)}\right] + \sigma_{loc(y)} - \sigma_{loc(x)} \qquad 6.13.$$

and combining equations 6.12. and 6.13. the reference independent shift is given by:

$$\bar{\Delta}\,{}^{x}_{y} = \sigma_{loc(x)} - \sigma_{loc(y)} = \frac{1}{3}\left[\sigma^{\parallel}_{sol(y)} - \sigma^{\parallel}_{sol(x)} + 2(\sigma^{\perp}_{sol(y)} - \sigma^{\perp}_{sol(x)}\right]$$

$$= \frac{1}{3}(\delta^{\parallel}_{(y-x)} + 2\delta^{\perp}_{(y-x)}) \qquad 6.14.$$

Again using the chloroform-benzene-cyclohexane system as a model, the screening terms $\sigma_{loc(x)}$ and $\sigma_{loc(y)}$ in equation 6.14. are given by equations 6.15. and. 6.16.

$$\sigma_{loc(x)} \equiv \sigma^{CHCl_3}_{(sample)} = \sigma^{B}_{a} + \sigma^{S}_{a} + \sigma^{B}_{w} + \sigma^{S}_{w} + \sigma^{B}_{E} + \sigma^{S}_{E} + \sigma^{B}_{s} + \sigma^{S}_{s} \qquad 6.15.$$

$$\sigma_{loc(y)} \equiv \sigma^{CHCl_3}_{(reference)} = \sigma^{S^+}_{a} + \sigma^{S^+}_{w} + \sigma^{S^+}_{E} + \sigma^{S^+}_{s} \qquad 6.16.$$

The terms in equation 6.16. must be constant since the composition of the mixture is constant. Therefore, the resulting equation for $\bar{\Delta}\,{}^{x}_{y}$ becomes:

$$\bar{\Delta}\,{}^{x}_{y} = (\sigma^{B}_{a} + \sigma^{S}_{a}) + (\sigma^{B}_{w} + \sigma^{S}_{w}) + (\sigma^{B}_{E} + \sigma^{S}_{E}) + (\sigma^{B}_{s} + \sigma^{S}_{s}) - K \qquad 6.17.$$

where K is a constant. Thus, if it is assumed that σ^{S}_{s} is zero and that the terms $(\sigma^{B} + \sigma^{S})$ are constant, $\bar{\Delta}\,{}^{x}_{y}$ only varies

with changes in σ_s^B. However, if these non-self cancelling terms do vary with composition, this technique will in fact be less accurate than the internal reference technique. The values of K and Δ_c obtained by the use of the reference independent technique should certainly be different from those calculated by use of the internal reference method because the $(\sigma^B + \sigma^S)$ terms in the former must be finite, but are minimised by the inclusion of $(-\sigma^{B^1} - \sigma^{S^1})$ terms in the latter method. For the internal reference method, therefore, all terms except σ_s^B will tend to zero.

It may be concluded that whilst the reference independent method is superficially promising for studies of molecular complexes, it may be subject to effects arising from small variations in the screening due to the aromatic and solvent. The internal reference method conceals errors proportional to the difference between electronic forces of these two components; this is the basis of the extrapolation procedure. It is possible, therefore, to compare the two procedures, in the light of these arguments. Since there are minor influences on reference independent shifts, the extrapolation procedure may prove to be more accurate.

6.4. Experimental Considerations And Results.

In order to apply the reference independent method to study the three component chloroform-benzene-cyclohexane system it is necessary to obtain the chemical shifts between chloroform in the sample and the external reference, and for this shift data to be accurate precision capilliary tubes must be used[49]. A precision Wilmad tube was used for the purpose, but was not sealed because of the prohibitive cost of making many samples of this nature. It was assumed that the tight fit

between the capilliary tube and the outer tube would prevent evaporation of the sample, but this was minimised by using a plastic seal, and another such cap was used to seal the reference tube.

There is, however, a major problem to be resolved; since the shift of chloroform, in low concentration in the reference capilliary, is very close to the large benzene absorption, it cannot be observed readily. Whitney[49] suggested the use of $[^2H_6]$benzene to overcome this problem, and although he used it to study the system, his results were not of a high enough accuracy to draw any conclusions concerning the use of the reference independent technique. This was because his measurements at 220MHz were not made on a field-frequency locked spectrometer, unlike those reported here. Whitney also measured the internally referenced shifts of his samples and found that the equilibrium parameters obtained from their analysis were compatible with other results[40,49]. Joyce[243] has resolved the problem by noting that the shift between chloroform and cyclohexane in the reference sample is constant, and can be measured seperately. Therefore, if the shift between chloroform in the three component sample and cyclohexane in the reference capilliary is measured, a simple subtraction enables the shift between the two chloroform environments to be calculated, without negating any assumption of the technique.

The results obtained by Joyce[243] for ten samples, and the reference capilliary, are shown in Tables 6.1. and 6.2. The values of $\delta^{\perp}$ and $\delta^{\parallel}$ were measured on a Varian HA100D spectrometer, described in Chapter 3, and a Varian HR220 spectrometer, with a field-frequency lock system, respectively, the latter being located at the Physico-Chemical Measurements Unit, Harwell.

SAMPLE	$\delta^{\perp}$/p.p.m.				
	~283K	~293K	~303K	~313K	~323K
	(282.0-283.4K)	(293.1-293.8K)	(302.1-302.6K)	(313.7K)	(323.9K)
Reference	5.6466	5.6400	5.6379	5.6366	—
190	4.3085	4.3908	4.4316	4.4539	4.4929
191	4.3001	4.3778	4.4259	4.4443	4.4846
192	4.2906	4.3588	4.4150	4.4326	4.4720
193	4.2837	4.3564	4.4077	4.4272	4.4668
194	4.2729	4.3484	4.3960	4.4165	4.4556
195	4.2660	4.3398	4.3871	4.4079	4.4482
196	4.2535	4.3412	4.3848	4.3951	4.4375
197	4.2439	4.3376	4.3676	—	4.4263
198	4.2326	4.3281	4.3560	—	—
199	4.2265	4.3185	4.3449	—	—

TABLE 6.1. The chemical shifts ($\delta^{\perp}$/p.p.m.) of chloroform measured relative to external cyclohexane on the Varian HA100D spectrometer, at several temperatures. All shifts were measured by M.Joyce.[243]

SAMPLE	T/K (~283)	$\delta^{\parallel}$/p.p.m.	T/K (~293)	$\delta^{\parallel}$/p.p.m.	T/K (~303)	$\delta^{\parallel}$/p.p.m.	T/K (~313)	$\delta^{\parallel}$/p.p.m.	T/K (~323)	$\delta^{\parallel}$/p.p.m.
Reference	284.2	5.6509	295.2	5.6507	303.7	5.6482	313.0	5.6485	323.2	5.6476
190	281.0	4.2900	—	—	302.6	4.4095	311.9	4.4434	322.7	4.5067
191	280.7	4.2680	295.0	4.3430	303.1	4.3945	311.9	4.4218	322.5	4.4836
192	281.1	4.2559	295.0	4.3439	303.2	4.3770	311.7	4.4102	—	—
193	281.0	4.2482	295.1	4.3255	303.3	4.3786	311.8	4.4089	—	—
194	281.2	4.2384	295.0	4.3121	303.3	4.3643	312.3	4.3904	322.5	4.4556
195	281.2	4.2323	294.9	4.3032	303.5	4.3591	312.5	4.3882	322.8	4.4521
196	280.6	4.2130	—	—	303.5	4.3411	312.6	4.3725	323.0	4.4368
197	280.6	4.2007	294.9	4.2772	303.5	4.3320	312.7	4.3627	—	—
198	280.7	4.1883	294.9	4.2649	303.5	4.3198	312.8	4.3545	323.1	4.4161
199	280.7	4.1845	295.0	4.2536	—	—	—	—	—	—

TABLE 6.2. The chemical shifts of chloroform ($\delta^{\parallel}$/p.p.m.) measured relative to external cyclohexane on the Varian HR220 spectrometer at several temperatures. The actual temperature of each sample at the time of measurement is shown.

It may be seen from Tables 6.1. and 6.2. that differences exist in the temperatures of the shifts measured on the two instruments, and in order to overcome this problem, graphs of shift (220MHz) against temperature were plotted for each sample, and values for the shifts at common temperatures (relative to 100MHz) obtained by interpolation[243]. This is justified since the plots are extremely smooth, and show only marginal scatter. The shifts for the reference capilliary were more accurately measured on the HR220 instrument, and are used in all subsequent calculations, since the geometry of the magnetic field does not affect other internal absorptions.

The interpolated values for $\delta^{\perp}$ and $\delta^{\parallel}$ are shown in Table 6.3. at five temperatures, together with values for $\Delta^{\perp}$, $\Delta^{\parallel}$ ($\delta^{\perp} - \delta_{free}$ and $\delta^{\parallel} - \delta_{free}$ respectively) and the reference independent shift, $\bar{\Delta}^{x}_{y}$, calculated from equation 6.18.

$$\bar{\Delta}^{x}_{y} = \frac{1}{3}\left[\Delta^{\parallel} + 2\Delta^{\perp}\right] \qquad 6.18.$$

It is possible to interpolate values for shifts which have not been actually measured at all five temperatures, and these are noted in Table 6.3. The table also includes the values for x_B^{corr} for each sample, the total range of concentration corresponding to the 'correct' condition for use of the Benesi-Hildebrand method.

The results obtained by Joyce[243] for the equilibrium parameters K_x and Δ_c are shown in Table 6.4., assuming the Benesi-Hildebrand plot to be either linear or quadratic. Whilst there are significant variations in the values for each parameter, it is noticeable that the slopes of the plots at zero solvent concentration also vary at each temperature assuming either relationship. It has been appreciated for

TABLE 6.3. Extrapolated shift data deduced for the calculation of reference independent shifts at five temperatures. The corresponding values of x_B^{corr} are also shown.

SAMPLE	$\delta^{\perp}$/ppm.[b]	$\delta^{\parallel}$/ppm.[b]	$-\Delta^{\perp}$/ppm.	$-\Delta^{\parallel}$/ppm.	$-\bar{\Delta}_y^x$/ppm.	x_B^{corr}
Temperature = 283.2K, δ_{free} = 5.6510 ppm.						
190	4.3082	4.3030	1.3428	1.3480	1.3445	0.88922
191	4.3015	4.2833	1.3495	1.3677	1.3556	0.89862
192	4.2910	4.2733	1.3600	1.3777	1.3659	0.91195
193	4.2863	4.2630	1.3647	1.3880	1.3725	0.91794
194	4.2762	4.2510	1.3748	1.4000	1.3832	0.93300
195	4.2713	4.2439	1.3797	1.4071	1.3888	0.94220
196	4.2593	4.2280	1.3917	1.4230	1.4021	0.95718
197	4.2625	4.2169	1.3885	1.4341	1.4037	0.96774
198	4.2510	4.2034	1.4000	1.4476	1.4159	0.98045
199	4.2379	4.1977	1.4113	1.4533	1.4253	0.99382
Temperature = 295.0K, δ_{free} = 5.6500 ppm.						
190	4.3971	4.3635[a]	1.2529	1.2865[a]	1.2641	0.88929
191	4.3846	4.3433	1.2654	1.3067	1.2792	0.89868
192	4.3681	4.3329	1.2819	1.3171	1.2936	0.91201
193	4.3587	4.3245	1.2913	1.3255	1.3027	0.91800
194	4.3553	4.3122	1.2947	1.3378	1.3091	0.93304
195	4.3497	4.3054	1.3003	1.3446	1.3151	0.94224
196	4.3386	4.2893[a]	1.3114	1.3607[a]	1.3278	0.95721
197	4.3437	4.2780	1.3063	1.3720	1.3282	0.96777
198	4.3346	4.2662	1.3154	1.3838	1.3382	0.98046
199	4.3246	4.2536	1.3254	1.3964	1.3491	0.99383

TABLE 6.3. (continued).

SAMPLE	$\delta^{\perp}$/ppm.[b]	$\delta^{\parallel}$/ppm.[b]	$-\Delta^{\perp}$/ppm.	$-\Delta^{\parallel}$/ppm.	$-\bar{\Delta}_y^x$/ppm.	x_B^{corr}
Temperature = 303.2K, δ_{free} = 5.6493 ppm.						
190	4.4341	4.4055	1.2152	1.2438	1.2247	0.88934
191	4.4222	4.3850	1.2271	1.2643	1.2395	0.89873
192	4.4076	4.3743	1.2417	1.2750	1.2528	0.91205
193	4.3958	4.3672	1.2535	1.2821	1.2630	0.91804
194	4.3922	4.3546	1.2571	1.2947	1.2696	0.93308
195	4.3895	4.3481	1.2634	1.3012	1.2760	0.94227
196	4.3721	4.3319	1.2772	1.3174	1.2906	0.95723
197	4.3715	4.3205	1.2778	1.3288	1.2948	0.96778
198	4.3629	4.3098	1.2864	1.3395	1.3041	0.98047
199	4.3547	4.3050[a]	1.2946	1.3443[a]	1.3112	0.99383
Temperature = 313.2K, δ_{free} = 5.6485 ppm.						
190	4.4672	4.4567	1.1813	1.1918	1.1848	0.88941
191	4.4556	4.4395	1.1929	1.2126	1.1995	0.89879
192	4.4420	4.4248	1.2065	1.2237	1.2122	0.91210
193	4.4336	4.4193	1.2149	1.2292	1.2197	0.91809
194	4.4264	4.4064	1.2221	1.2421	1.2288	0.93312
195	4.4198	4.4002	1.2287	1.2430	1.2352	0.94231
196	4.4056	4.3838	1.2429	1.2647	1.2502	0.95726
197	4.3986[a]	4.3723	1.2499[a]	1.2762	1.2587	0.96781
198	4.3905[a]	4.3630	1.2580[a]	1.2855	1.2672	0.98049
199	4.3828[a]	4.3590[a]	1.2657[a]	1.2895[a]	1.2736	0.99383

TABLE 6.3. (continued).

SAMPLE	$\delta^{\perp}$/ppm.[b]	$\delta^{\parallel}$/ppm.[b]	$-\Delta^{\perp}$/ppm.	$-\Delta^{\parallel}$/ppm.	$-\bar{\Delta}_y^x$/ppm.	x_B^{corr}
Temperature = 323.2K, δ_{free} = 5.6476 ppm.						
190	4.4913	4.5080	1.1563	1.1396	1.1507	0.88948
191	4.4837	4.4868	1.1639	1.1608	1.1629	0.89886
192	4.4700	4.4753[a]	1.1776	1.1723[a]	1.1758	0.91216
193	4.4648	4.4713[a]	1.1828	1.1763[a]	1.1806	0.91814
194	4.4538	4.4582	1.1938	1.1894	1.1923	0.93316
195	4.4467	4.4524	1.2009	1.1952	1.1990	0.94235
196	4.4352	4.4358	1.2124	1.2118	1.2122	0.95728
197	4.4244[a]	4.4241[a]	1.2232[a]	1.2235[a]	1.2233	0.96783
198	4.4150[a]	4.4161	1.2326[a]	1.2315	1.2322	0.98050
199	4.4062	4.4127[a]	1.2414	1.2349[a]	1.2392	0.99384

[a] A corresponding shift was not actually measured, and the value is therefore subject to some error.

[b] Calculated by M.Joyce[243] from graphs of shift against temperature.

TABLE 6.4. Results* obtained for the parameters K_x, Δ_c and $1/K_x\Delta_c$ from processing the reference independent shift data for the reaction occurring between chloroform and benzene in cyclohexane according to the Benesi-Hildebrand equation, assuming that the plot is linear (a), and quadratic (b).

T/K	K_x		Δ_c/ppm.		$1/K_x\Delta_c$	
	a	b	a	b	a	b
283.2	1.1083	1.2815	2.7188	2.5428	0.3319	0.3086
295.0	1.1051	1.8958	2.5768	2.0611	0.3512	0.2559
303.2	0.8730	1.6292	2.8280	2.1208	0.4051	0.2894
313.2	0.6934	1.0293	2.1293	2.5213	0.6773	0.3854
323.2	0.5853	1.7180	3.3761	2.9797	0.5060	0.1953

* All results reported in this table were obtained by M.Joyce.[243]

some time that whilst $K_x\Delta_c$ may be constant, the separation of these terms may give rise to anomalies such as those described above[246-8], although it appears that such anomalies often arise due to data inaccuracy.

Ideally the accuracy of the measurements made by Joyce[243] should be assessed by processing the shift data obtained from the samples used for reference independent investigations on an internal reference basis. These results could then be compared with those obtained by Whitney[49] by the use of the internal reference method. Unfortunately, owing to the inadequate reporting of measurements made by Joyce it has not been possible to do this, and only the shifts $\sigma^{CHCl_3}_{(sample)} - \sigma^{C_6H_{12}}_{(reference)}$ and $\sigma^{CHCl_3}_{(reference)} - \sigma^{C_6H_{12}}_{(reference)}$ were available. This data could be processed on an external reference basis, but this requires a knowledge of magnetic susceptibility differences, which are not well documented, although they may be calculated[64], or found experimentally[249]. Even so, as previously mentioned, Whitney did process his data on an internal reference basis and found that results were compatible with those obtained from analysis of the data obtained from a separate series of internally referenced samples.

It appears from plots made by Joyce[243] of $1/\bar{\Delta}\,\frac{x}{y}$ against x_B, that the data is of high accuracy. This is signified by the very small scatter observed in these plots. The reference independent shift data can therefore be used with some degree of confidence.

6.5. Discussion.

The results obtained for K_x and Δ_c by the use of internal reference[49], reference independent[243] and the proposed extrapolation procedures are compared, at similar temperatures,

in Table 6.5. These values are those obtained assuming a linear relationship in the Benesi-Hildebrand equation. Also shown are the thermodynamic parameters ΔG^o, ΔH^o and ΔS^o obtained from the use of the first two techniques. The results shown in Table 6.5. will now be considered, along with those in Table 6.4.

The values of Δ_c deduced by the use of the reference independent technique may be seen to be very high with those obtained by other methods, and are also theoretically higher than expected. Also the apparent and unexpected dependence of Δ_c upon temperature when using this technique is of some concern. The fact that a Van't Hoff plot of the equilibrium quotients obtained by this technique gives rise to an uncharacteristically low value of ΔG^o of only - 0.015 $kJ.mol^{-1}$ certainly throws doubt upon its usefulness in this type of investigation. Additionally, the variation of $1/K_x\Delta_c$ with temperature does not compare well with the almost constant value obtained by Whitney[49] using the internal reference procedure.

The most conclusive evidence for the validity of the internal reference procedure and subsequent extrapolation rather than the reference independent technique may be obtained from a comparison of the calculated values for K_x, Δ_c and $1/K_x\Delta_c$ using each procedure. The value of K_x obtained by extrapolation is, as would be expected, only slightly higher than that obtained by internal reference measurements in cyclohexane or other solvents, but the reference independent value is much lower than this. The Δ_c values are almost exactly opposite in their variation. It is interesting to note that $1/K_x\Delta_c$ is similar for all three methods, but this may be expected from the arguments of other workers[246-8].

TABLE 6.5. The results obtained for K_x, Δ_c and $1/K_x\Delta_c$ by the use of the internal reference,[49] reference independent[243] and extrapolation procedures at similar temperatures, for the chloroform + benzene reaction occurring in cyclohexane. Values of ΔG^o, ΔH^o and ΔS^o obtained by the use of internal reference and reference independent procedures are also shown for the same reaction occurring at 298.2K.

PARAMETER	INTERNAL REFERENCE	REFERENCE INDEPENDENT	EXTRAPOLATION
K_x	1.510	0.873	1.800
Δ_c/ppm.	1.393	2.828	1.364
$1/K_x\Delta_c$	0.4777	0.4051	0.408
T/K	306.6	303.2	306.6
$-\Delta G^o$/kJ.mol^{-1}.	2.155	0.015	—
$-\Delta H^o$/kJ.mol^{-1}.	13.363	17.878	—
$-\Delta S^o$/J.mol^{-1}.K^{-1}.	37.584	59.939	—

Since the values of K_x and Δ_c obtained by the internal reference and extrapolation procedure differ from those obtained by the reference independent method, the proposals made previously are borne out, but may now be explained in more detail, and in practical terms. A further understanding of these differences may be gained by reference to Figure 6.1., and equations 6.6. and 6.17. It is apparent from these equations that, relative to the internal reference procedure, changes in the values of σ_W and σ_E with changing composition are negative. Theoretically, this will give rise to variations in δ_{obs} with x_B as illustrated in Figure 5.1., where $-\delta_{obs}$ is larger at a given value of x_B when the reference independent rather than the internal reference procedure is used. The nature of these influences on experimental data would certainly affect the values of K_x and Δ_c obtained by each method.

As suggested earlier, it is apparent that the extrapolation procedure does allow for differences in contributions due to the electronic interactions between aromatic and solvent molecules, whereas the reference independent method includes contributions which are not minimised by other terms. In the two cases the electronic interactions (σ_W and σ_E contributions) would affect the chemical shifts in opposite ways relative to internally referenced shifts, with the result, concurrent with present observations, that K_x and Δ_c would also change in opposite directions.

The extrapolation procedure discussed in Chapter 5, and compared here with the reference independent technique, appears to be the most meaningful because it inherently accomodates corrections for reference and solvent effects. The reference independent technique, apart from providing results which are

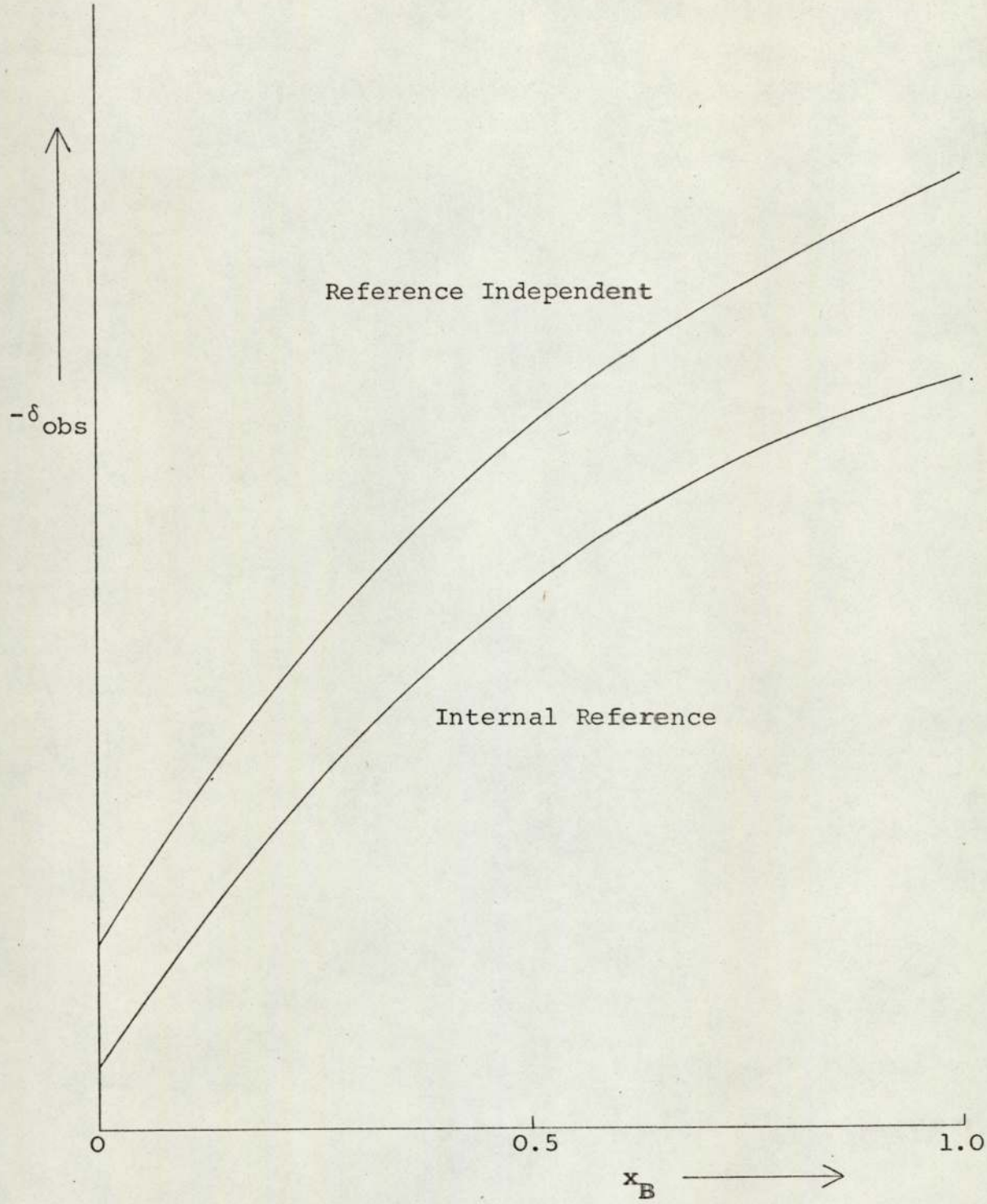


FIGURE 6.1. The proposed differences in the variation of observed aromatic induced shifts, δ_{obs}, with the composition of the mixture, between reference independent and internally referenced measurements.

of questionable significance, only eliminates unwanted effects due to the reference used. The extrapolation procedure, however, does not correct for variations in σ_a with composition, and the scatter observed in Figure 5.2. may be attributed to these.

6.6. Conclusions.

From the proposals and observations made in this chapter it is apparent that the reference independent method is not suitable for the type of investigation reported here. The values for equilibrium and thermodynamic parameters obtained by its use are certainly of questionable significance. The anomalies arise because of finite solvent screening contributions to the observed reference independent shifts, which do not tend to zero as they do when using internally referenced shifts. The variations in K_x and Δ_c can be attributed directly to the additional screening contribution.

The internal reference procedure is based on the assumption that all screening terms except σ_s^B tend to zero. However, when using data of high accuracy it has been demonstrated that σ_w and σ_E terms (and to a lesser extent σ_a terms) may not always cancel. The difference between the observed shifts, and their associated equilibrium parameters, and the 'true' values, which are solely dependent on σ_s^B variations, may be attributed mainly to differences in electronic interactions between aromatic and solvent.

The proposed extrapolation procedure allows for this difference by plotting $1/K_x\Delta_c$ obtained for the reaction in each solvent against the difference in refractive indices, Δn, of the aromatic and solvent components. The arguments concerning the validity of this plot are given in Section 5.4.1. The near linearity of these plots are consistent with theoretical

predictions concerning screening effects on the reference and naturally compare well with results obtained by internally referenced measurements in a single solvent. It is apparent that this extrapolation procedure may give rise to more meaningful results for K_x and Δ_c in these circumstances than those obtained by use of the reference independent method. Some major solvent and reference effects may, therefore, be eliminated by its use to give rise to parameters which depend almost solely upon variations in σ_s^B.

CHAPTER 7

A THEORY FOR COMPLEX FORMATION AND EVIDENCE FOR SHORT RANGE MOLECULAR ORDER IN LIQUIDS.

7.1. Introduction.

In the foregoing chapters it has been shown how chemical shift data must be analysed in order to obtain meaningful equilibrium parameters for the formation of transient molecular complexes. The correct procedure involves the use of small ranges of concentration, which, in principle, does not allow information to be forthcoming concerning the mechanism of such interactions.

However, a considerable amount of data is available for systems studied over the whole concentration range, from $x_B = 0$ to $x_B = 1$. In the following discourse it will be described how this data has been used to attempt to deduce a model for complex formation.

The approximations in the Benesi-Hildebrand[45] approach make it impossible to obtain meaningful values for K_x and Δ_c when it is used to study systems outside the concentration range of $x_B = 0.9$ to 1.0. The Creswell-Allred[46] procedure, however, does, in principle, permit the investigation of liquid mixtures over the complete concentration range. However, only average values, corresponding to particular ranges of composition can be obtained by this method for the reasons given in Section 4.2.1.1. This approach, however, does permit comparisons between different systems, and it has been applied to some of the data mentioned above in order to gain more information about the mechanism of complex formation.

It has been shown[40] that K_x must depend on the composition of the solutions or mixtures studied, and a general theoretical argument may be proposed which shows

that Δ_c must vary similarly. It is possible to show that this variation can be explained in terms of basic molecular interactions within the mixtures, and that at the same time, the bulk parameters pertaining to the molecular interactions are consistent with the molecular basis of the mechanism.

7.2. The Theoretical Approach.

The Creswell-Allred method of data processing depends on equation 7.1. which relates to the Gutowsky-Saika theory of fast exchange[37], as shown in Section 1.13.

$$\delta_{obs} = \frac{n_{AB}}{n_A} \Delta_c + \delta_{free} \qquad 7.1.$$

An iterative computer procedure[53] is employed to select arbitrary values of K_x and calculate values of n_{AB}/n_A from equation 7.2., neglecting $(\gamma^R_{AB}/\gamma^R_A.\gamma^R_B)$.

$$K_x = \frac{n_{AB}(n_A + n_B + n_S V_S/V_B - n_{AB})}{(n_A - n_{AB})(n_B - n_{AB})} \quad \frac{(\gamma^R_{AB})}{(\gamma^R_A.\gamma^R_B)} \qquad 7.2.$$

The iteration proceeds in order to obtain a value for K_x such that the associated values of n_{AB}/n_A and δ_{obs} over a range of concentrations comply with the inherent linearity of equation 7.1. Since it is reasonable to suppose that γ^R_A and γ^R_{AB} are approximately equal[40] and since the chemical shifts are measured over a range of composition, the equilibrium quotient must correspond to $\overline{K}_x$ given by equation 7.3.

$$\overline{K}_x = KC\overline{\gamma^R_B} \qquad 7.3.$$

$\overline{K}_x$ is an average equilibrium quotient for complex formation, and is related to the true constant for the equilibrium process by $\overline{\gamma^R_B}$, which is the average Raoult activity coefficient of the aromatic component, B, in the series of samples studied, and C,

which is a constant. In the iterative computer procedure employed for this type of investigation (i.e. COMPLEXICON[53]), it is necessarily assumed that K_x is a constant for the chosen range of concentrations, and the 'best fit' value of Δ_c which makes equation 7.1. linear is calculated. However at different compositions γ_B^R is different, so calculations must result in different values for K_x assuming that Δ_c is constant over the chosen range of compositions.

It has been indicated by a detailed study of the thermodynamics of liquid mixtures[40] that Δ_c may also vary with their composition. Consequently, if both K_x and Δ_c vary with the composition such iterative procedures of analysis merely provide numbers whose absolute physical meaning is obscure, but which supposedly reflect the magnitude of these parameters.

At a series of different compositions identified by a, b, c...., the actual equations corresponding to equation 7.1. will be:

$$\delta^a_{obs} = \frac{n^a_{AB}}{n_A} \Delta^a_c + \delta_{free} \qquad 7.4.$$

$$\delta^b_{obs} = \frac{n^b_{AB}}{n_A} \Delta^b_c + \delta_{free} \qquad 7.5.$$

$$\delta^c_{obs} = \frac{n^c_{AB}}{n_A} \Delta^c_c + \delta_{free}, \text{ etc.} \qquad 7.6.$$

Therefore, the analysis of the data would correspond to its rationalisation in terms of equation 7.7.

$$\delta^*_{obs} = \frac{n^*_{AB}}{n_A}(\Delta'_c + M^*) + \delta_{free} \qquad 7.7.$$

where M^* represents a variation in the basic shift Δ'_c for a

particular composition. The criterion of this approach is that a plot of δ_{obs} against n^*_{AB}/n_A can only be linear if equation 7.8. holds

$$M^* = Q(n_A/n^*_{AB}) \qquad 7.8.$$

Q is a constant for the chosen value of $\overline{K}_x$ but differs for different ranges of compositions in a similar fashion to $\overline{K}_x$. It is,therefore, possible to relate a known variation in K_x to one in Δ_c because n_A/n^*_{AB} is a function of $\overline{K}_x$, and also to relate this relative variation to the mechanism of the formation of transiently formed molecular complexes.

If a series of reactions between different solutes and the same aromatic component in a common solvent are investigated, variations in $\overline{\gamma}^R_B$ are constant, and may be ignored. This approach permits a direct comparison of the effect of different solutes on variations in $\overline{K}_x$ and Δ_c, and enables the nature of formation of transient molecular complexes to be investigated.

7.3. Data Processing.

Data have been obtained[250,251] for the interactions between methyl iodide, methylene chloride, vinyl cyanide, methylene bromide, dimethylformamide, chloroform, methylene iodide, trichloroethylene and nitroform, seperately with benzene (B) in the presence of cyclohexane (S) as the inert solvent. The data are presented in Table 7.1., and represent investigations carried out over the complete concentration range from x_B = 0 to 1.0. The shifts of each sample were measured at 60MHz on a Perkin-Elmer R10 Spectrometer using the conventional sideband technique for spectral calibration. Only the shifts for one proton (H^1) are used for the vinyl cyanide-benzene interaction; because all three proton shifts were derived from ABC spectral analyses, each should have the

TABLE 7.1. The variation of ^1H chemical shifts (Hz at 60MHz, relative to internal cyclohexane, S) with the initial composition of the reactant mixtures of various polar solutes (A) with benzene (B) at 306.6K.

SAMPLE	$10^4\ n_A$/mol	$10^2\ n_B$/mol	$10^2\ n_S$/mol	$-\delta_{obs}$/Hz
A = methyl iodide.				
A	1.9163	0.0000	2.0425	33.08
B	0.7539	0.1733	1.2723	27.20
C	0.5566	0.2875	0.9942	23.03
D	1.6063	0.8567	1.2680	16.94
E	1.5006	0.9817	1.0039	13.62
F	1.0075	0.9984	0.9955	13.87
G	1.6979	0.9523	0.6061	10.89
H	1.1061	1.2300	0.5010	8.26
I	0.9300	1.3607	0.3219	6.38
J	1.0357	1.5480	0.1562	4.14
A = methylene chloride.				
A	1.6484	0.0000	1.2255	220.27
B	1.5188	0.0836	1.2517	214.72
C	1.0126	0.1235	1.2323	212.40
D	2.1311	0.3128	1.2068	204.40
E	1.4717	0.5397	1.2144	197.82
F	1.6601	0.8713	1.2416	192.58
G	1.9780	1.2310	1.2296	188.64
H	2.6020	1.8405	1.2242	184.81
I	1.8721	1.4095	0.6278	182.00
J	3.6264	2.6457	0.6126	178.90

TABLE 7.1. (continued).

SAMPLE	10^4 n_A/mol	10^2 n_B/mol	10^2 n_S/mol	$-\delta_{obs}$/Hz
A = vinyl cyanide.				
A	19.883	0.0000	4.8002	243.64
B	19.393	0.0910	4.5970	241.90
C	18.884	0.2458	4.5404	239.22
D	18.865	0.3001	4.4077	237.97
E	20.184	0.4085	4.3564	236.54
F	21.409	0.5537	4.2581	234.33
G	22.955	0.9720	3.7526	228.12
H	18.865	1.4780	3.3024	220.85
I	22.691	2.0117	2.7723	215.83
J	21.051	2.4462	2.3644	211.38
K	20.354	3.0254	1.8346	206.49
L	20.071	3.4304	1.5178	203.67
M	19.224	3.6417	1.1859	201.85
N	21.862	3.8851	0.8772	199.04
O	18.074	4.0575	0.7451	198.72
P	20.561	4.2657	0.5886	198.16
Q	20.392	4.3986	0.3724	197.34
R	19.770	4.4150	0.2305	196.48
S	19.223	4.7106	0.0490	195.43

TABLE 7.1. (continued).

SAMPLE	10^4 n_A/mol	10^2 n_B/mol	10^2 n_S/mol	$-\delta_{obs}$/Hz
A = methylene bromide.				
A	0.8743	0.0000	1.2555	199.43
B	1.6279	0.0690	1.2624	194.51
C	1.4553	0.1343	1.2579	190.90
D	1.6854	0.3070	1.2641	183.90
E	1.7199	0.5487	1.2392	177.30
F	2.8934	0.8193	1.2487	173.11
G	2.8359	1.2172	1.2704	168.95
H	3.3190	1.8418	1.2280	164.51
I	1.9270	1.4180	0.6893	162.01
J	3.9000	2.4044	0.6602	158.98

A = dimethylformamide

				α-methyl	β-methyl
A	1.6691	0.0000	1.2457	81.36	78.34
B	1.9837	0.0608	1.2255	77.63	76.65
C	1.6280	0.1258	1.2547	74.37	74.94
D	1.8332	0.3161	1.2536	66.52	71.60
E	2.1205	0.4925	1.2401	61.70	69.50
F	2.3805	0.8416	1.3044	55.35	66.69
G	2.4215	1.2153	1.2288	50.33	64.72
H	3.3929	1.8399	1.2641	46.05	63.19
I	2.4352	1.5182	o.6169	41.61	61.88
J	3.3382	2.4721	0.6299	38.34	60.93

TABLE 7.1. (continued).

SAMPLE	10^4 n_A/mol	10^2 n_B/mol	10^2 n_S/mol	$-\delta_{obs}$/Hz
A = chloroform.				
A	0.7849	0.1650	2.4988	332.56
B	1.2222	0.4615	2.4984	324.45
C	1.9551	0.6323	2.5004	321.23
D	1.6251	0.6285	2.4986	321.13
E	1.1183	0.4160	1.2584	317.16
F	1.0429	1.0271	1.2484	306.01
G	1.5295	1.5295	1.2494	301.43
H	0.9223	1.1813	0.6275	297.15
I	0.7473	1.0956	0.3314	293.47
J	1.2724	1.8868	0.3309	290.84
K	0.9214	1.4353	0.1222	289.19
L	0.8140	1.9047	0.1012	288.43
M	0.8762	1.6586	0.0781	287.41
A = methylene iodide.				
A	1.1126	0.0000	1.2540	137.95
B	1.1985	0.0646	1.2490	133.49
C	1.3665	0.1363	1.2204	129.68
D	1.5756	0.3080	1.2357	123.70
E	1.7063	0.5067	1.2473	117.86
F	1.9826	0.8553	1.2595	112.27
G	2.3858	1.2597	1.2378	108.24
H	2.7218	1.8216	1.2485	104.90
I	1.8705	1.4588	0.6138	101.07
J	3.1736	2.4086	0.6122	98.18

TABLE 7.1. (continued).

SAMPLE	10^4 n_A/mol	10^2 n_B/mol	10^2 n_S/mol	$-\delta_{obs}$/mol
A = trichloroethylene.				
A	1.4232	0.0000	1.2583	291.35
B	1.1720	0.0591	1.2461	288.49
C	1.3471	0.1467	1.2490	285.21
D	1.5602	0.3186	1.2518	279.72
E	1.7657	0.5363	1.2466	274.87
F	2.1006	0.8290	1.2496	270.64
G	2.4050	1.2493	1.2586	266.66
H	3.0900	1.8735	1.2535	263.13
I	2.0016	1.4674	0.6247	259.69
J	3.1128	2.4894	0.6180	256.72
A = nitroform.				
A	3.794	0.000	3.746	339.65
B	1.576	0.010	1.000	331.16
C	1.582	0.031	1.000	318.00
D	1.649	0.064	0.999	303.87
E	1.688	0.111	1.000	290.31
F	2.019	0.334	1.000	265.36
G	3.072	1.000	1.000	249.13
H	6.104	2.999	1.000	242.72
I	1.549	0.899	0.100	240.92
J	3.052	1.899	0.100	240.73

same characteristics with changing composition, as shown by the α- and β- methyl shifts in the dimethylformamide-benzene interaction (See Table 7.2.). H^1 is that proton bonded to the same carbon atom as the cyanide group.

The processing of these data must be done in such a way that small variations in $\overline{K}_x$ can easily be shown. It would be difficult to do this if small ranges of composition were studied in turn since the results would be dependent on the accuracy of a very small number of shift measurements, or alternatively, it would be necessary to measure a large number of shifts for each small increment in composition. It was shown that the data selected did not give good results when processed in the latter manner, there being considerable scatter in the values of $\overline{K}_x$ obtained when plotted against the average incremental composition. The data were, therefore, processed in the following way. For each separate reaction the sets of data obtained (values of n_A, n_B, n_s and δ_{obs} for each sample) were discarded one at a time starting at the $x_B^{corr} = 1$ end of the concentration scale, x_B^{corr} being given by equation 7.9.[40].

$$x_B^{corr} = n_B/(n_B + n_s V_s/V_B) \qquad 7.9.$$

except for the vinyl cyanide-benzene interaction, where x_B^{corr} is given by equation 7.10[251].

$$x_B^{corr} = n_B/[(n_A - 0.005(n_A + n_B + n_s))V_A/V_B + n_B + n_s V_s/V_B] \qquad 7.10.$$

which allows for the higher mole fraction of solute used in that series.

From the remaining data $\overline{K}_x$ and Δ_c were evaluated on an 1CL1905E computer and the results are shown in Table 7.2.;

TABLE 7.2. The corrected mole fractions (x_B^{corr}), of the mixtures, and values of $\overline{K}_x$, Δ_c and $\overline{K}_x\Delta_c$ for the interaction of various polar solutes with benzene in cyclohexane.

SAMPLE	x_B^{corr}	$\overline{K}_x$	Δ_c/ppm.	$\overline{K}_x\Delta_c$/ppm.
A = methyl iodide.				
A	0.0000	—	—	—
B	0.1003	—	—	—
C	0.1913	1.4970	0.7543	1.1292
D	0.3547	1.1244	0.9525	1.0710
E	0.4426	1.1171	0.9533	1.0649
F	0.4498	1.0143	1.0286	1.0433
G	0.5580	1.0518	1.0023	1.0542
H	0.6646	1.0403	1.0098	1.0505
I	0.7686	1.0844	0.9829	1.0659
J	0.8853	1.0790	0.9860	1.0639
A = methylene chloride.				
A	0.0000	—	—	—
B	0.0516	—	—	—
C	0.0756	—	—	—
D	0.1735	1.5651	1.2497	1.9559
E	0.2656	1.2911	1.4639	1.8900
F	0.3633	1.4061	1.3712	1.9280
G	0.4481	1.4349	1.3516	1.9394
H	0.5484	1.4715	1.3292	1.9559
I	0.6430	1.5347	1.2949	1.9873
J	0.7719	1.6144	1.2578	2.0306

TABLE 7.2. (continued).

SAMPLE	x_B^{corr}	$\overline{K}_x$	Δ_c/ppm.	$\overline{K}_x\Delta_c$/ppm.
A = vinyl cyanide.				
A	0.0000	—	—	—
B	0.0157	—	—	—
C	0.0417	—	—	—
D	0.0519	—	—	—
E	0.0699	2.5039	0.8326	2.0847
F	0.0942	2.0818	0.9760	2.0318
G	0.1708	1.4798	1.1385	1.6848
H	0.2631	0.9392	1.9149	1.7985
I	0.3635	1.3314	1.4491	1.9293
J	0.4490	1.3333	1.4475	1.9300
K	0.5624	1.3036	1.4700	1.9163
L	0.6345	1.2808	1.4873	1.9049
M	0.6992	1.3063	1.4687	1.9186
N	0.7624	1.2457	1.5123	1.8839
O	0.7988	1.2676	1.4964	1.8968
P	0.8339	1.3036	1.4721	1.9190
Q	0.8825	1.3513	1.4436	1.9507
R	0.9152	1.3797	1.4364	1.9818
S	0.9625	1.4016	1.4146	1.9827

TABLE 7.2. (continued).

SAMPLE	x_B^{corr}	$\overline{K}_x$	Δ_c/ppm.	$\overline{K}_x\Delta_c$/ppm.
A = methylene bromide.				
A	0.0000	—	—	—
B	0.0426	—	—	—
C	0.0800	—	—	—
D	0.1649	0.9381	1.0758	1.0092
E	0.2646	1.7363	1.1733	2.0372
F	0.3462	1.7398	1.1716	2.0383
G	0.4361	1.6797	1.2000	2.0156
H	0.5467	1.5819	1.2472	1.9729
I	0.6231	1.5533	1.2614	1.9593
J	0.7406	1.5733	1.2521	1.9699
A = dimethylformamide (results obtained from the α-methyl shifts)				
A	0.0000	—	—	—
B	0.0387	—	—	—
C	0.0754	—	—	—
D	0.1700	0.7427	2.2145	1.6447
E	0.2435	1.1064	1.5617	1.7279
F	0.3432	0.9713	1.7367	1.6869
G	0.4444	1.0447	1.6409	1.7142
H	0.5393	1.0539	1.6303	1.7182
I	0.6621	1.0989	1.5837	1.7403
J	0.7556	1.0950	1.5874	1.7382

TABLE 7.2. (continued).

SAMPLE	x_B^{corr}	$\overline{K}_x$	Δ_c/ppm.	$\overline{K}_x\Delta_c$/ppm.
A = dimethylformamide (results obtained from the β-methyl shifts)				
A	0.0000	—	—	—
B	0.0387	—	—	—
C	0.0754	—	—	—
D	0.1700	1.4361	0.5802	0.8332
E	0.2435	1.5746	0.5382	0.8474
F	0.3432	1.1916	0.6674	0.7953
G	0.4444	1.3214	0.6182	0.8169
H	0.5393	1.4219	0.5878	0.8358
I	0.6621	1.6196	0.5402	0.8749
J	0.7556	1.7158	0.5241	0.8993
A = chloroform.				
A	0.0617	—	—	—
B	0.1550	2.8614	0.9083	2.5990
C	0.2005	2.5779	0.9832	2.5346
D	0.1990	2.4680	1.0169	2.5097
E	0.2467	1.4373	1.5306	2.1999
F	0.4490	1.6118	1.4022	2.2601
G	0.5470	1.5390	1.4141	2.2527
H	0.6490	1.5628	1.4325	2.2787
I	0.7630	1.5812	1.4219	2.2483
J	0.8450	1.5805	1.4223	2.2479
K	0.9161	1.6005	1.4120	2.2599
L	0.9457	1.6119	1.4073	2.2684
M	0.9900	1.6644	1.4246	2.3711

TABLE 7.2. (continued).

SAMPLE	x_B^{corr}	$\overline{K}_x$	Δ_c/ppm.	$\overline{K}_x\Delta_c$/ppm.
A = methylene iodide.				
A	0.0000	—	—	—
B	0.0405	—	—	—
C	0.0834	—	—	—
D	0.1686	2.6029	0.7850	2.0433
E	0.2482	1.3153	1.3403	1.7629
F	0.3553	1.3306	1.3284	1.7676
G	0.4512	1.4107	1.2733	1.7962
H	0.5409	1.4316	1.2606	1.8047
I	0.6558	1.4072	1.2745	1.7935
J	0.7562	1.3804	1.2894	1.7799
A = trichloroethylene.				
A	0.0000	—	—	—
B	0.0373	—	—	—
C	0.0875	2.0089	0.6899	1.3859
D	0.1719	0.6025	2.0595	1.2408
E	0.2596	0.7547	1.6803	1.2681
F	0.3505	0.9026	1.4444	1.3037
G	0.4464	0.9436	1.3945	1.3159
H	0.5475	0.9872	1.3481	1.3308
I	0.6544	0.9873	1.3480	1.3309
J	0.7626	0.9911	1.3445	1.3325

TABLE 7.2. (continued).

SAMPLE	x_B^{corr}	$\overline{K}_x$	Δ_c/ppm.	$\overline{K}_x\Delta_c$/ppm.
A = nitroform.				
A	0.0000	—	—	—
B	0.0081	—	—	—
C	0.0246	17.7408	1.3176	23.3753
D	0.0492	13.8814	1.5564	21.6050
E	0.0829	12.2447	1.6833	20.6115
F	0.2124	11.1853	1.7679	19.7745
G	0.4449	10.4980	1.8166	19.0707
H	0.7012	10.3842	1.8237	18.9377
I	0.8679	10.4325	1.8209	18.9965
J	0.9260	10.4310	1.8209	18.9938

graphs were plotted of these parameters against the highest value of x_B^{corr} in the sets of data processed.

Although this method of processing the data is not accurate enough to allow analysis of the results in terms of absolute values of $\overline{K}_x$, because $\overline{K}_x$ is, as mentioned above, only valid in relative terms, and also because the value of $\overline{K}_x$ should be plotted against the average value of x_B^{corr}, which is difficult in this case due to the curvature of the plot, comparisons between the curves may readily be made, and conclusions drawn from them. It is reasonable to suppose, however, that the portions of the curves which are linear reflect a reasonably accurate value of x_B^{corr}, and evidence for this is proposed in a later section of this chapter. The fact that x_B^{corr} is arbitrarily chosen does not affect the ensuing argument.

7.4. Results And Initial Observations.

For each of the nine systems studied the values of $\overline{K}_x$ and Δ_c were found to vary with the range of composition chosen. The variations are typified in Figures 7.1. and 7.2. from which it can be seen that $\overline{K}_x$ and Δ_c are reasonably constant above a certain value of x_B^{corr}, but below this value they vary significantly. The graphs of $\overline{K}_x$ against x_B^{corr} rise from the linear region, whereas for the Δ_c plot, the values fall below the linear portion of the line.

Graphs of K_x against x_B^{corr} of the shape shown in Figures 7.1. and 7.2. have been obtained, also in this laboratory, from studies of molecular complexes using a phase distribution approach[39].

The variations in values of $\overline{K}_x$ are to be expected to some degree because of variations in $\overline{\gamma}_B^R$. However, the onset

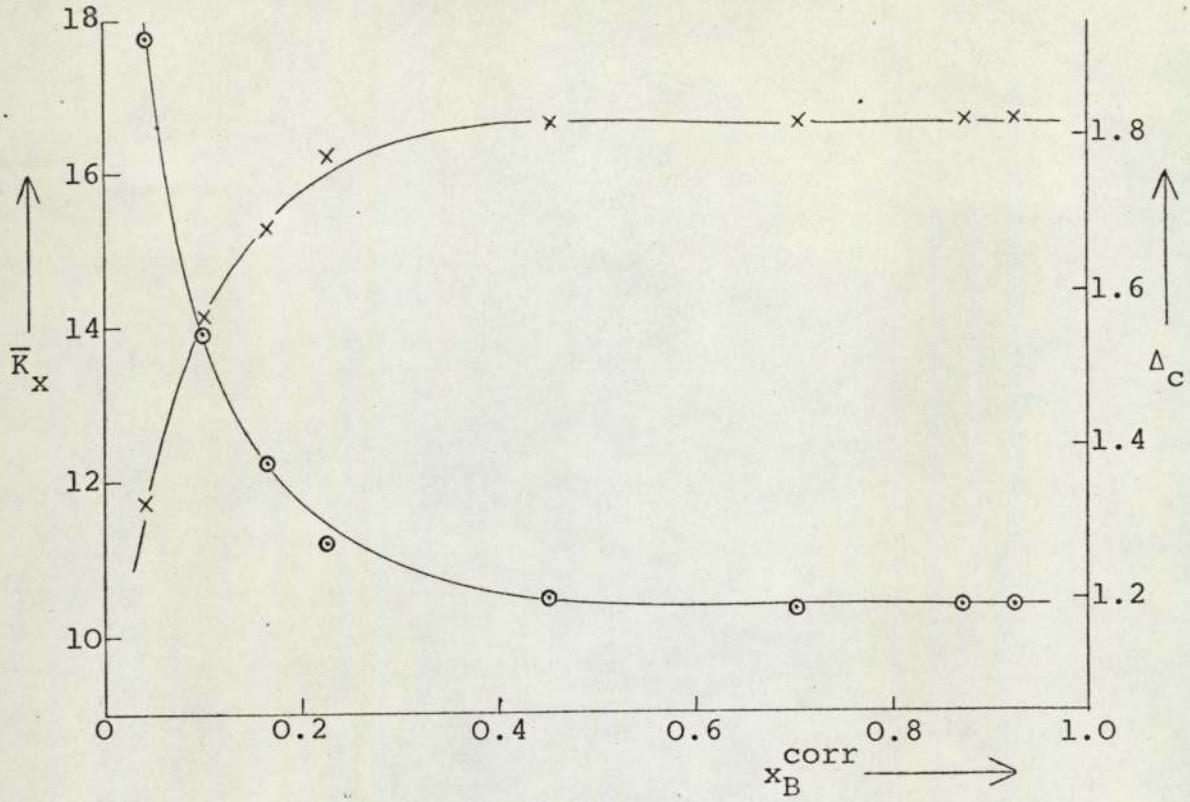


FIGURE 7.1. The variation of $\overline{K}_x$ (⊙) and Δ_c (X) with x_B^{corr} for the nitroform+benzene reaction occurring in cyclohexane at 306.6K.

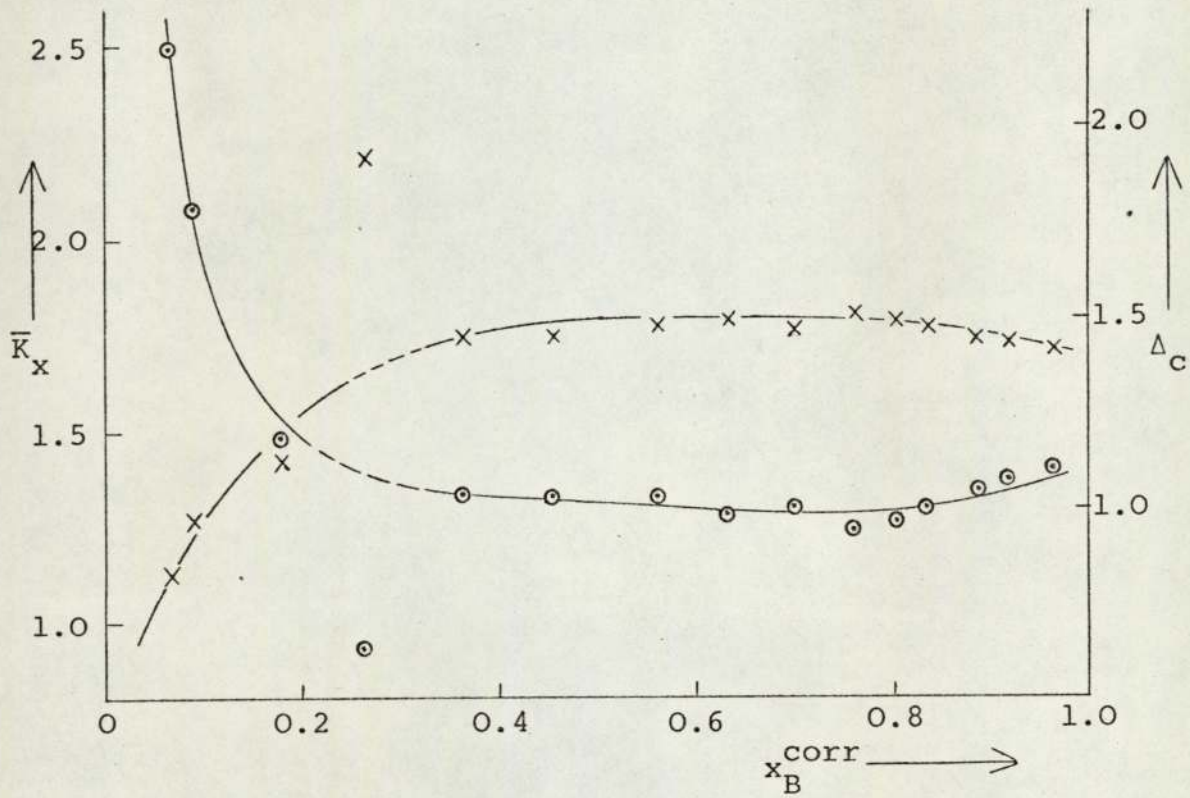


FIGURE 7.2. The variation of $\overline{K}_x$ (⊙) and Δ_c (X) with x_B^{corr} for the vinyl cyanide + benzene reaction occurring in cyclohexane at 306.6K.

of the major variations in $\overline{K}_x$, and also Δ_c, cannot be explained completely by the effect of the variation in $\overline{\gamma}_B^R$. This can be shown by correcting $\overline{K}_x$ for variations in $\overline{\gamma}_B^R$ as follows. The values of $\overline{\gamma}_B^R$ below the chosen values of x_B^{corr} were evaluated from a plot of γ_B^R against x_B^{corr}, which was deduced from the results of Scatchard et al[213-4]. The plots of both γ_B^R and $\overline{\gamma}_B^R$ against x_B^{corr} are shown in Figure 7.3. The data were corrected for $\overline{\gamma}_B^R$ using values from this plot and the graphs of $\overline{K}_x/\overline{\gamma}_B^R$ against x_B^{corr} were replotted, a typical result being shown in Figure 7.4. It is noticeable that this latter graph is still non-linear over part of its range. It is also found that, even when variations in γ_B^R are taken into account, for the different systems $\overline{K}_x$ and Δ_c start to vary from the approximately linear region at significantly different values of x_B^{corr}. The values of x_B^{corr} at the point of deviation ($x_{B(lim)}^{corr}$) are shown in Table 7.3. For all the reactions considered it is interesting to note that a plot of $\overline{K}_x\Delta_c$ against x_B^{corr} (represented in tabular form in Table 7.2.) is also linear over the upper part of the concentration range, thus explaining the unexpected wide ranging linearity of Benesi-Hildebrand[45] plots.

7.5. The Development Of A Theory For Complex Formation.

It is apparent that Δ_c, as well as $\overline{K}_x$, varies with the composition of the liquid mixture, and because a common aromatic and inert solvent were used for all the reactions studied, the point of deviation from linearity of the plots must depend on the polar solute used. An examination of these points of deviation, reported in Table 7.3., shows that there is some relationship between them and the size of the solute, and this is shown in Figure 7.5. This is not altogether unexpected because if the concentration of the solute is very

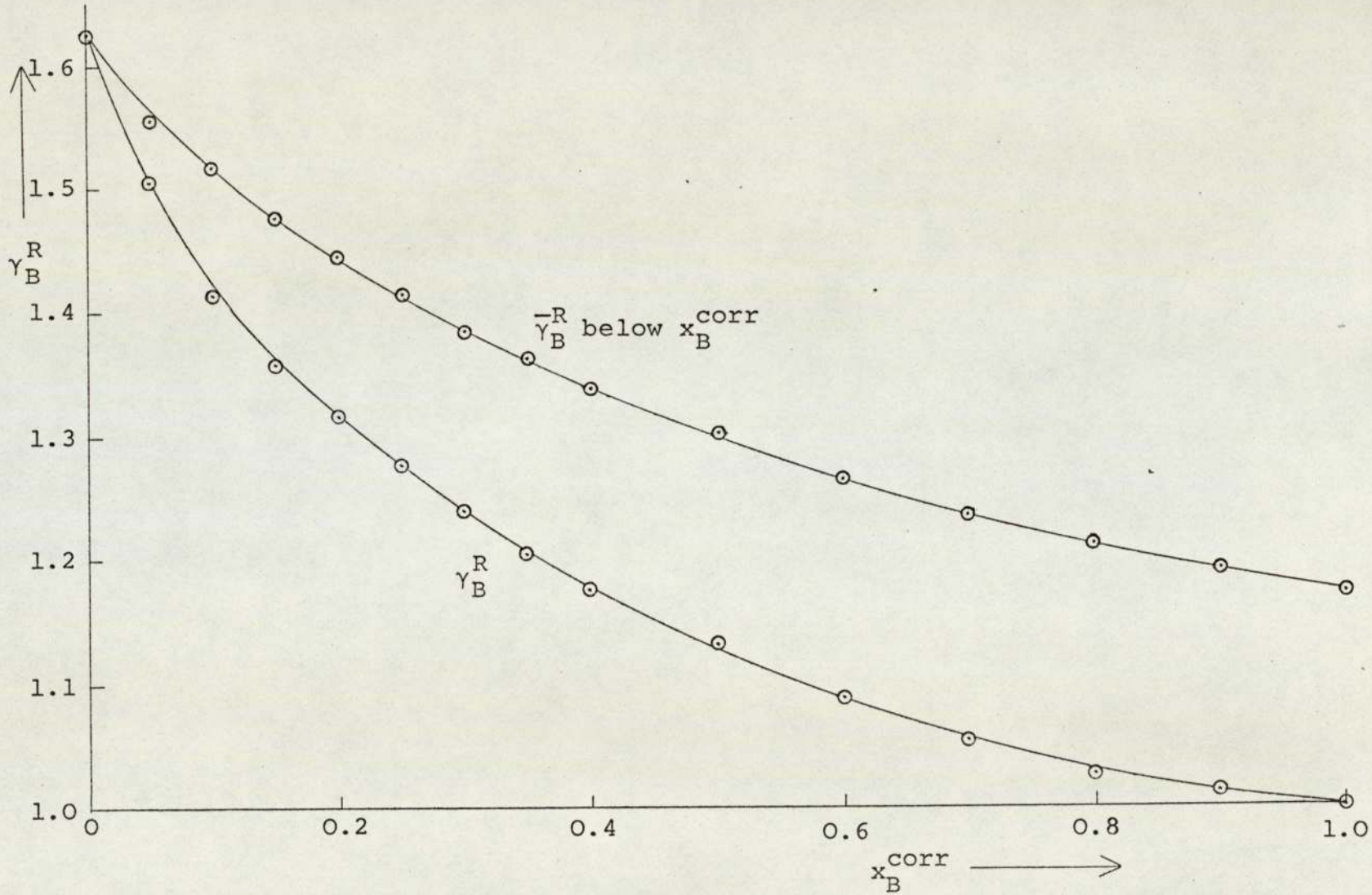


FIGURE 7.3. The variation of γ_B^R and $\bar{\gamma}_B^R$ with x_B^{corr} for the benzene - cyclohexane system.

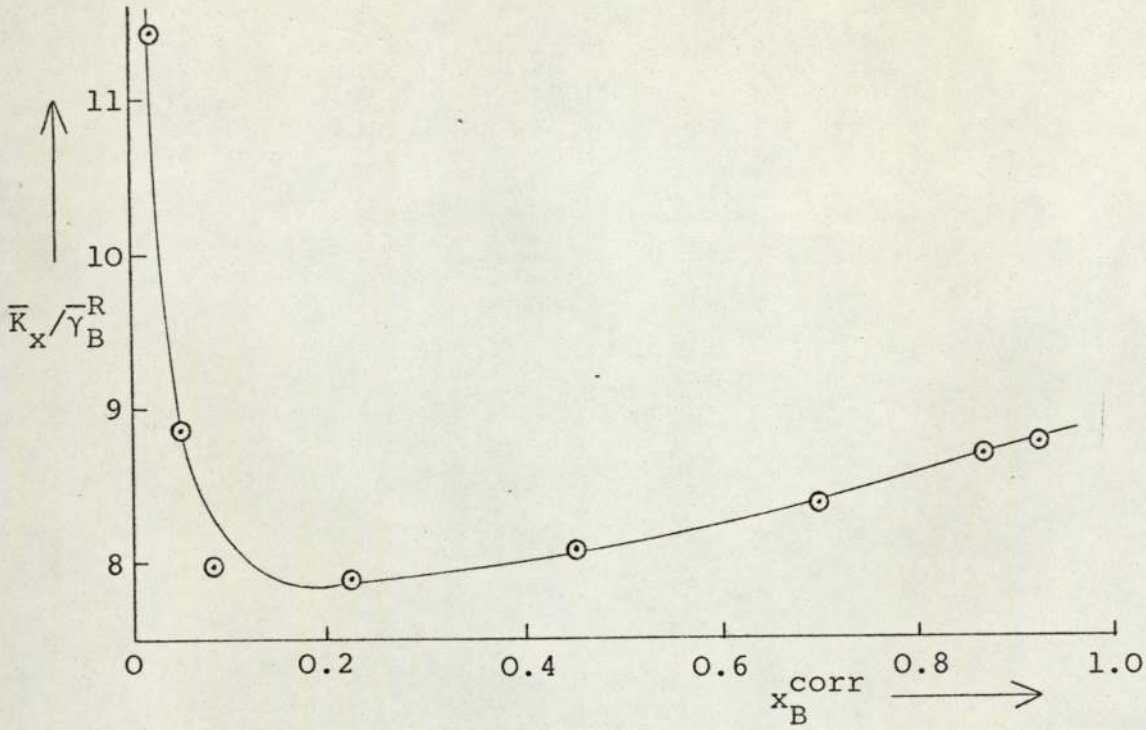


FIGURE 7.4. The variation of $\overline{K}_x/\overline{\gamma}_B^R$ with x_B^{corr} for the nitroform + benzene reaction occurring in cyclohexane at 306.6K.

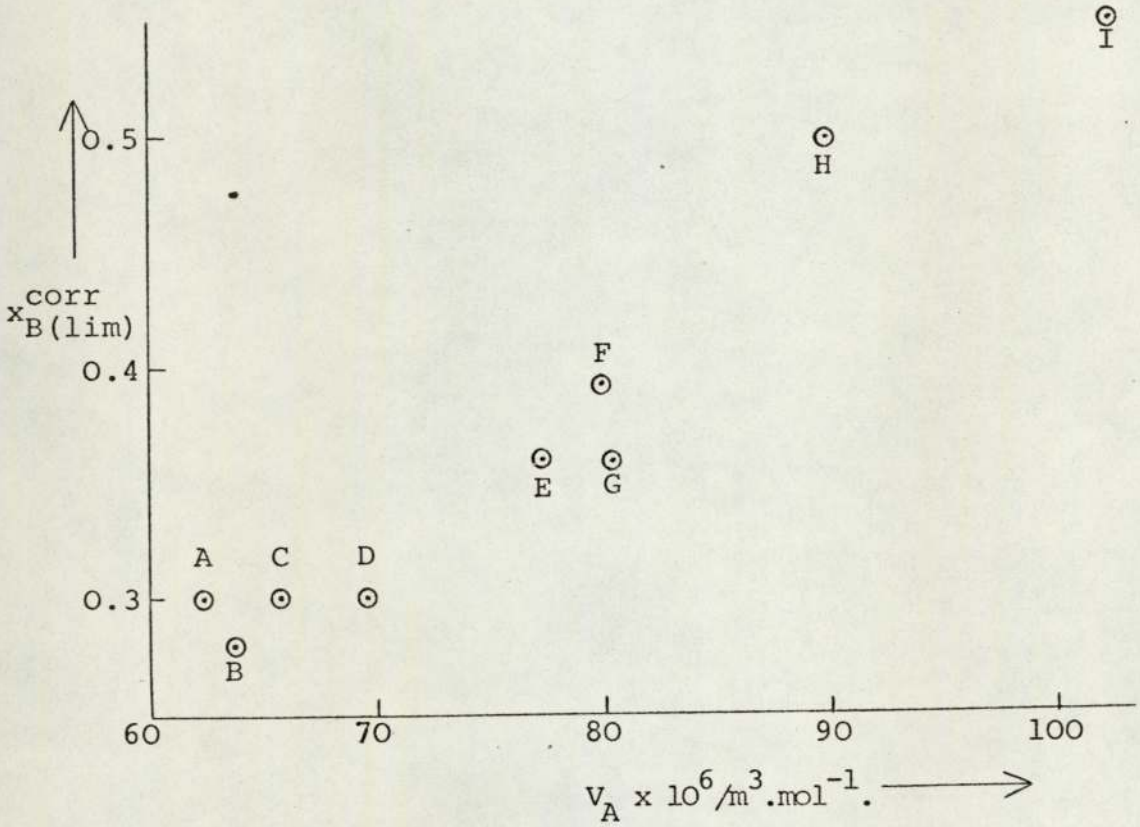


FIGURE 7.5. The variation of $x_{B(lim)}^{corr}$ with the molar volume of the solute, V_A.

Solutes: methyl iodide (A), methylene chloride (B), vinyl cyanide (C), methylene bromide (D), dimethylformamide (E), chloroform (F), methylene iodide (G), trichloroethylene (H), and nitroform (I).

COMPOUND	$V \times 10^6/m^3.mol^{-1}$	$x^{corr}_{B(lim)} \pm 0.02$	$\bar{K}_{x(lim)}$	$\Delta_{c(lim)}$/ppm.	$x^{corr}_{B(lim)} (V_A^{1/3} + V_B^{1/3})^2$ $\times 10^4/m^2.mol^{-2/3}$
Benzene	90.3269	—	—	—	—
Cyclohexane	109.8298	—	—	—	—
Methyl iodide	62.2544	0.30	1.12	0.9533	21.416
Methylene chloride	63.6180	0.28	1.32	1.4367	20.125
Vinyl cyanide	65.8313	0.30	1.33	1.4483	21.798
Methylene bromide	69.7604	0.30	1.74	1.1717	22.198
Dimethylformamide	77.3954	0.36[a]	0.96[a]	1.7367[a]	27.554
		0.36[b]	1.19[b]	0.6667[b]	27.554
Chloroform	80.0349	0.40	1.58	1.4217	30.948
Methylene iodide	80.5527	0.36	1.33	1.3283	27.904
Trichloroethylene	89.8700	0.50	0.97	1.3500	40.185
Nitroform	102.1231	0.55	10.40	1.8233	46.148

TABLE 7.3. Values of the molar volumes, V, for all the compounds used, and the corresponding values of $x^{corr}_{B(lim)}$, $\bar{K}_{x(lim)}$, and $\Delta_{c(lim)}$ for the reactions of the various solutes with benzene, in the presence of cyclohexane, at 306.6K. The values of $x^{corr}_{B(lim)} (V_A^{1/3} + V_B^{1/3})^2$ used in Figures 7.6. and 7.7. are also shown. [a,b] Values deduced from the dimethylformamide α- and β-methyl shifts respectively.

low,(for the reactions studied here the average value of $x_A = 0.012$), it may be anticipated that the polar solute will have a preferential affinity for the aromatic rather than the inert material, and the collision frequency of the complexing molecules will depend on the size of the solute. It is also apparent that the number of aromatic molecules involved in these interactions at different compositions will significantly influence the data from which $\overline{K}_x$ and Δ_c are deduced.

From the data available it is possible to derive a theory which explains these observations and also provides a useful working model.

The bulk medium of the liquid mixture is composed of aromatic and solvent molecules, with corrected mole fractions x_B^{corr} and x_S^{corr}, interspersed with molecules of the polar solute, mole fraction x_A. It was postulated above that solute molecules in low concentration will effectively have a preferential affinity for aromatic molecules, and thus it is reasonable to consider for each molecule of solute a sphere of influence over B, the sphere containing B and S in the same ratio as in the bulk medium. The number of moles of B within each sphere of influence, assuming random distribution of B and S, is given by equation 7.11.

$$n_B' = ZNx_B^{corr}/L \qquad 7.11.$$

where Z is the number of molecules of B and S which can be fitted in one 'solvation' shell round one molecule. N is a constant, greater or less than one, introduced to allow approximately for one occupation of several 'solvation' shells within the defined sphere of influence. Since Z describes a number which includes molecules of B and S, it may be given by equation 7.12.

$$Z = \pi\left[x_B^{corr}\left(\frac{(V_A^{1/3} + V_B^{1/3})^2}{V_B^{1/3}}\right) + x_s^{corr}\left(\frac{(V_A^{1/3} + V_s^{1/3})^2}{V_s^{1/3}}\right)\right] \qquad 7.12.$$

Equation 7.12. is derived from the basic equation[252] (7.13.) for the number of solvent molecules which may surround a solute.

$$Z' = \pi\left(\frac{(V_A^{1/3} + V_B^{1/3})^2}{V_B^{1/3}}\right) \qquad 7.13.$$

There are, within a given liquid mixture, $n_A L$ spheres of influence if the solute is sufficiently dilute, and therefore equation 7.11. must be modified to equation 7.14. to account for this.

$$n_B = n_A Z N x_B^{corr} + n_{BU} \qquad 7.14.$$

where n_{BU} is the number of moles of B uninvolved in complex formation at a particular instant in time. Equation 7.14. may be divided by the total corrected number of moles in the system to give equation 7.15., x_A^{corr} being so small that it may be equated with x_A.

$$x_B^{corr} = x_A x_B^{corr} Z N + x_{BU}^{corr} \qquad 7.15.$$

The preferential affinity of A for B will draw aromatic molecules towards the solute, and as the value of x_B^{corr} increases from zero, the volume in the immediate vicinity of A will be populated mostly by aromatic molecules, these being attracted from the extremes of the sphere of influence. The fraction of B within the total sphere of influence of A may still be described by x_B^{corr}, the solvent molecules occupying the outer part of the sphere. As x_B^{corr} increases the number of aromatic molecules surrounding A will also increase until a limiting value, which may be denoted by $x_{B(lim)}^{corr}$ is reached,

at which concentration the solute is experiencing almost the maximum effects of the aromatic in terms of the equilibrium for complex formation, although a small amount of S may be closely involved with A, i.e. the inert solvent has not been completely confined within the outer part of the sphere of influence of the solute. At this point, therefore, the value of Z will tend to that described by equation 7.13., and equation 7.15 becomes 7.16.

$$x^{corr}_{B(lim)} = x_A x^{corr}_{B(lim)} \pi \left(\frac{(V_A^{1/3} + V_B^{1/3})^2}{V_B^{1/3}} \right) N' + x^{corr}_{BU} \qquad 7.16.$$

where N' is the limiting value of the constant, N. It may appear that x_B^{corr} on the right hand side of equation 7.15. should be equated to unity when applying the above conditions in order to obtain equation 7.16. because the medium surrounding A is nearly all molecules of B. The reason this is not so will be considered below, when this point may be discussed in terms of the results obtained.

Above the limiting value of x_B^{corr}, x_{BU}^{corr} will increase, but parameters affected by the amount of B around A (i.e. $\overline{K}_x$ and Δ_c) will remain reasonably constant and it is possible to equate $x^{corr}_{B(lim)}$ with the value of x_B^{corr} at which $\overline{K}_x$ and Δ_c start to deviate from approximate linearity with aromatic concentration. In equation 7.16. x_A may be kept at a constant value, and it may be postulated that at $x^{corr}_{B(lim)}$ the value of x_{BU}^{corr} is fairly small. A plot of $x^{corr}_{B(lim)}$ against $x^{corr}_{B(lim)}$ $\left[(V_A^{1/3} + V_B^{1/3})^2\right]$ should, under the conditions that x_A is small and constant, be a straight line, with a slope equal to $x_A \pi N' / V_B^{2/3}$ and an intercept of x_{BU}^{corr}.

Figure 7.6. shows that this plot is indeed a straight

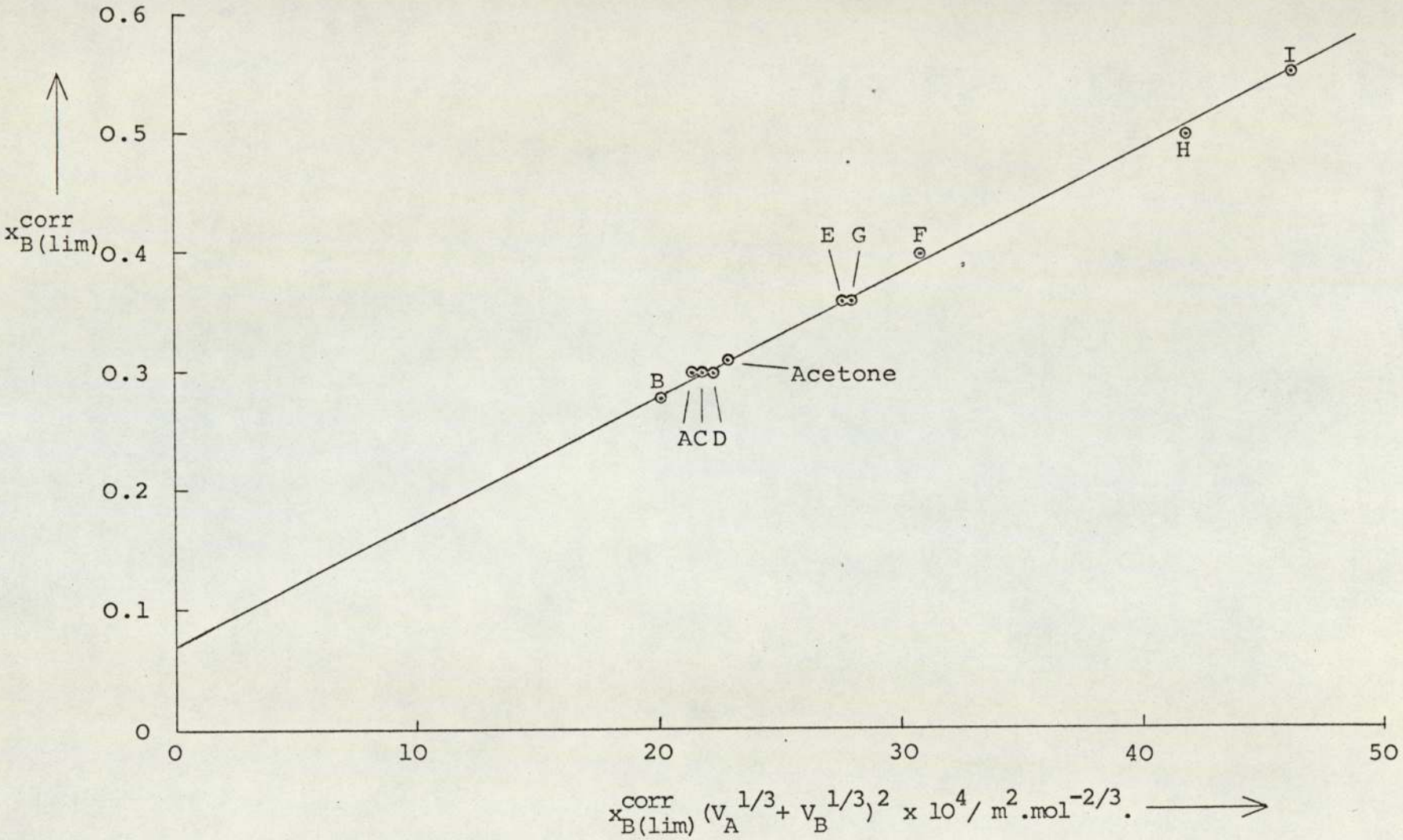


FIGURE 7.6. The plot of $x^{corr}_{B(lim)}$ against $x^{corr}_{B(lim)} (V_A^{1/3} + V_B^{1/3})^2$. A→I see Figure 7.6.

line for the reactions mentioned earlier. Using the average experimental value of $x_A = 0.012$ the slope of the line gives a value of N' equal to 5.5, and the intercept gives a value of 0.07 for x_{BU}^{corr}. 5.5Z benzene molecules corresponds to about two and a half 'solvation' shells, varying slightly depending on the actual solute, and this seems to be a reasonable value, as is that for x_{BU}^{corr}.

The sphere of influence of the solute may, therefore, be estimated to cover five 'solvation' shells, and this indicates that electric field and dispersion interactions are effective over this range, (Section 2.A.3.4.).

7.6. Discussion.

The major point which arises during the development of the above theory is that a detailed consideration of the criteria applied to the system would seem to indicate that the value of $x_{B(lim)}^{corr}$ on the right hand side of equation 7.16. should be equated to unity, and that equation 7.16. should, in fact, be formulated as equation 7.17.

$$x_{B(lim)}^{corr} = x_A \pi \left(\frac{(V_A^{1/3} + V_B^{1/3})^2}{V_B^{1/3}} \right) N' + x_{BU}^{corr} \qquad 7.17.$$

The reasons for this approach arise from the definition of the number of benzene molecules surrounding the solute, given by equation 6.11., which assumes that x_B^{corr} is the fraction of the total number of molecules surrounding the solute which are benzene molecules. However, at $x_{B(lim)}^{corr}$ it has been postulated that the great majority of the molecules surrounding the solute are benzene, and in this case x_B^{corr} (for the shell) would approach unity. If this is true, a plot of $x_{B(lim)}^{corr}$ against $(V_A^{1/3} + V_B^{1/3})^2$ should be a straight line, (i.e. equation 7.17. holds). Figure 7.7. shows, however, that

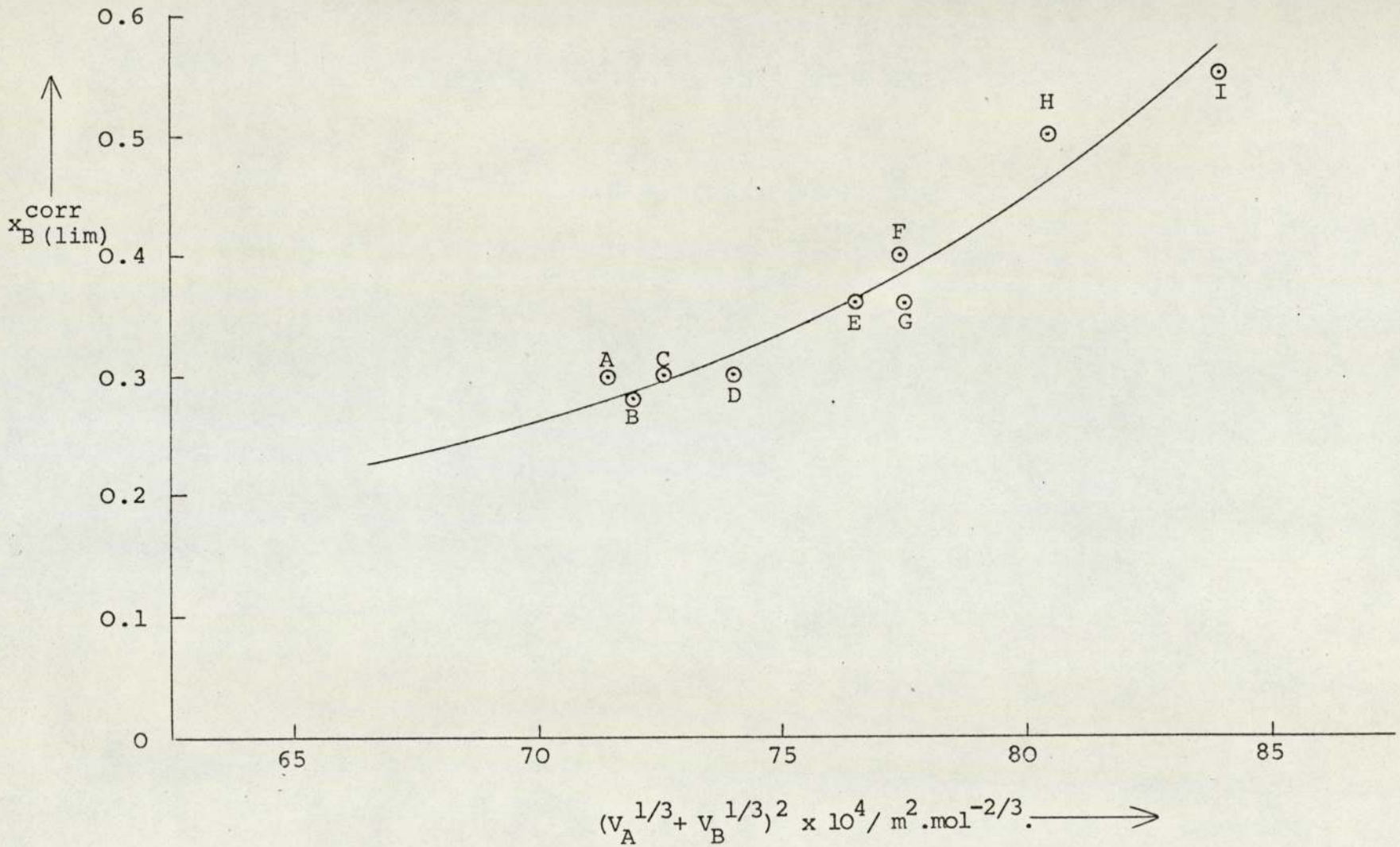


FIGURE 7.7. The plot of $x_{B(lim)}^{corr}$ against $(V_A^{1/3} + V_B^{1/3})^2$. A→I see Figure 7.6.

this plot is a curve, indicating that a variable has not been included. The reason why equation 7.17. does not hold is that the criteria which have been applied have related to the whole sphere of influence of the solute, including the solvent molecules in the outer part of the sphere.

This argument indicates that all the molecules within the sphere of influence of A must be constantly changing positions, and exchanging with those in the bulk medium. If this were not the case equation 7.17. would hold, because the solvent would have no effect on the interaction between A and B. Only by postulating a model on this basis can the use of $x^{corr}_{B(lim)}$ for the bulk medium on the right hand side of equation 7.16. be justified, and the results obtained from its inclusion (and non-inclusion) indicate that a dynamic model of this form is a reasonably accurate representation of the real system.

The implication of these arguments is that molecular complexes arise in the environment of short range ordering of the benzene molecules around the solute, and that as the concentration of benzene is increased, Δ_c varies and increases to some approximately constant value which is governed by the number of benzene molecules influenced by the solute. However, the analytical procedures which led to the theory and model proposed earlier assumed that the complex was entirely bimolecular. A further apparent paradox that requires some discussion is that the observed shift of the solute changes continuously with increasing benzene concentration, whilst Δ_c reaches some limiting value at some point in the concentration range. These problems can be elucidated by a more detailed interpretation of the results in terms of the observed shift

variation, δ_{obs}, with benzene concentration and the short range ordering in the immediate vicinity of the solute, which was postulated above.

The mechanism of complex formation and its interpretation in terms of the δ_{obs} variation is illustrated in a rudimentary fashion in Figure 7.8. The observed shift, measured relative to an internal reference, is conveniently divided into three contributions. The non-bonded contributions of the medium to the screening of molecule A is given by equation 7.18.

$$\sigma^A = \sigma_a + \sigma_w + \sigma_E \qquad 7.18.$$

where the screening terms have their usual significance. The screening contribution to A arising from the formation of a bimolecular complex is considered separately and is denoted by σ_s^A. For the reference solvent, which is non-polar, the non-bonded screening contributions are given by equation 7.19.

$$\sigma^S = \sigma_a' + \sigma_w' \qquad 7.19.$$

The variations of each of the three screening terms σ^A, σ_s^A and σ^S can be deduced qualitatively and are illustrated in Figure 7.8. The right hand side of the schematic equilibria represent the environmental structure around a particular solute molecule, which is sufficiently remote from any other that the left hand side of the equilibrium can be considered as the intervening medium between molecules of type A at any chosen composition. (Five representative compositions are considered in Figure 7.8.). Initially, in the absence of benzene, σ^A and σ^S have some particular finite value and σ_s^A is zero. As the concentration of benzene increases the preferential affinity of A for the aromatic, B, rather than S, results in a clustering of benzene molecules about solute

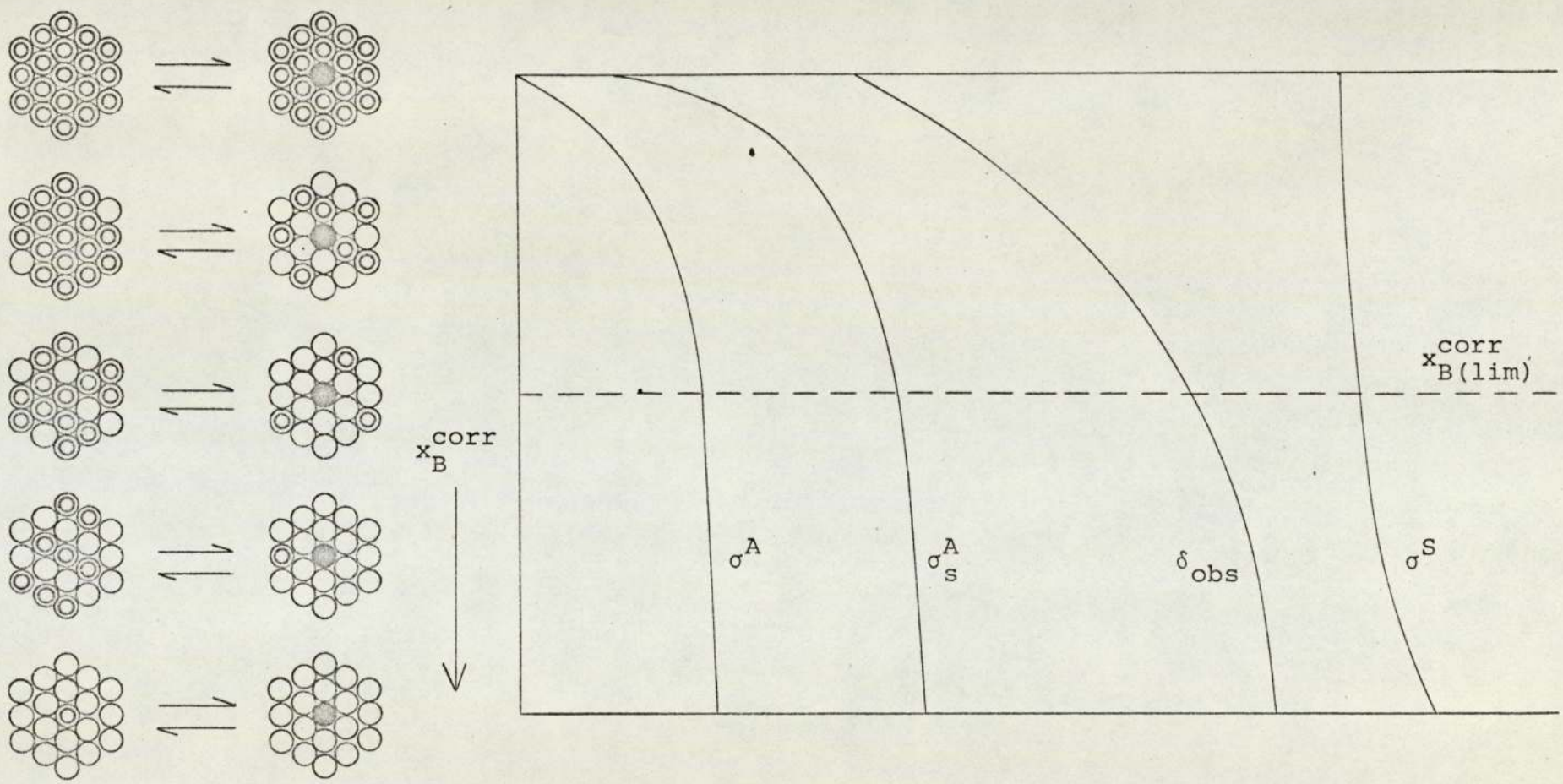


FIGURE 7.8. Schematic representations of the molecular interactions involved in studies of the reaction between A (●) and B (○) in the presence of S (◎) at various mole fractions of the aromatic, B, and their use in the interpretation of contributions to observed chemical shifts.

molecules. The implications of this are that σ^S increases very slowly due to the smaller number of benzene molecules in the vicinity of S outside the sphere of influence of A, whereas σ^A increases rapidly with the increasing benzene concentration about A. Similarly, because of the increased probability of formation of bimolecular complexes, σ_s^A also increases rapidly. These variations continue until the limiting number of benzene molecules, deduced earlier, surround A, in a dynamic (exchanging) situation. After this stage further addition of benzene results in a more rapid variation of σ^S. However, the environment of A can change only to a small extent with the result that both σ^A and σ_s^A can vary only slightly until $x_B^{corr} = 1$ due to equilibration with the environment of S. The observed chemical shift, δ_{obs}, is given by equation 7.20.

$$\delta_{obs} = \sigma^A + \sigma_s^A - \sigma^S \qquad 7.20.$$

where the screenings of isolated molecules are neglected. The variation of δ_{obs} is shown in Figure 7.8. and is as normally observed, thus indicating that the variation of the individual screenings based on the dynamic model proposed earlier may be reasonably accurate.

It should be pointed out that the value of σ_s^A is not equal to Δ_c at $x_B^{corr} = 1$ because even at infinite dilution in the aromatic the screening of A is a time averaged resultant of the screening values in the fully complexed and uncomplexed states. Moreover, the model does not refute the proposed formation of a bimolecular complex, even though its environment consists mostly of randomly oriented benzene molecules.

Further substantial evidence supporting this type of mechanism may be obtained from a consideration of the results

of Whitney[49], who investigated the validity of both the Creswell-Allred and Benesi-Hildebrand methods of data processing at low mole fractions of benzene. In common with the results shown here a wide variation in $\overline{K}_x$ for the chloroform + benzene reaction in cyclohexane was found when using the Creswell-Allred procedure. The concentration range considered was restricted between $x_B = 0$ and $x_B = 0.2$, and if data points with values of x_B higher than 0.3 were included in the computation reasonable values of $\overline{K}_x$ were evaluated, being of a similar magnitude to those values calculated by a Benesi-Hildebrand process at $x_B = 1$; this is also evident from Figures 7.1. and 7.2. An explanation was proposed in statistical thermodynamic terms to show that the changing environment of the complex (and solute) was the overriding factor in accounting for anomalously high values of $\overline{K}_x$ obtained within this low concentration range, and it is interesting to include and reinterpret the relevant parts of his argument here.

Whitney assumed that the only plausible explanation for the calculation of meaningful values of $\overline{K}_x$ at concentrations down to $x_B = 0.35$ was that the activity coefficient ratios in equation 7.2. fortuitously remained constant. He noted that γ_B^R, despite the drastic change in its value in the region from $x_B = 0$ to 0.2, could not alone account for the variations of $\overline{K}_x$ in this range, this latter assumption having been proved here. However, it is desirable to deduce the part played by activity coefficients in the variations, and thus the effect of the changing environment on the values of the activity coefficients of A,B, and the complex AB must be considered.

The equilibrium quotient in this region of concentration

($x_B = 0$ to $x_B = 0.3$) can be derived in statistical terms, and assuming that if A and AB are in low concentration they will only affect the chemical potential of each other and of B insignificantly compared with the effects of those components which are in high concentration, (i.e. B and S). The equilibrium constant is given by equation 7.21.

$$RT\ln K_x = RT\ln K^o + L(bw'_{A,B} + sw'_{A,B} + s'w'_{A,S} - b'w'_{AB,B} - s''w'_{AB,S}) \qquad 7.21.$$

this may be represented in more recognisable thermodynamic terms as equation 7.22.

$$RT\ln k_x = RT\ln K^o + RT\ln \frac{\gamma_A^R \cdot \gamma_B^R}{\gamma_{AB}^R} \qquad 7.22.$$

K^o is the equilibrium constant for the reaction $A + B \rightleftharpoons AB$; b and b' are the number of aromatic molecules surrounding the interactions A-----B and AB----B respectively; s, s' and s" are the number of solvent molecules surrounding the interactions A----B, A----S, and AB----S respectively; and w'_{ij} is defined by equation 7.23.

$$w'_{i,j} = E_{i,j} - \tfrac{1}{2}[E_{i,i} + E_{j,j}] \qquad 7.23.$$

where $E_{i,j}$ is the energy required to bring together one molecule of i and one molecule of j which are initially infinitely separated. Other terms have their previously defined significance.

When x_B is small it may be assumed that the chemical potentials of A and AB are approximately constant[49], but as x_B increases they will be modified, as also will be the parameters b and b', which will increase, and s, s' and s",

which will decrease. The terms $w'_{A,B}$ and $w'_{AB,B}$ in equation 7.21. may be expected to be large compared with $w'_{A,S}$ and $w'_{AB,S}$ respectively, but the former terms will have different values and cannot be expected to change proportionally as x_B increases. Therefore γ_A/γ_{AB} will tend only slowly towards a limiting value dictated by the limiting number of molecules of B which must surround A (or AB) in order to obtain realistic values for $\overline{K}_x$.

This interpretation lends support to the proposals made previously that below a certain value of x_B^{corr}, the calculated values for $\overline{K}_x$ reflect significant changes in the numbers of benzene and cyclohexane molecules surrounding the solute and complex, (i.e. b,b' and s in equation 7.21). However, over a wider concentration range above $x_{B(lim)}^{corr}$ the parameters b and b' will reach a limiting value with the result that the term $\gamma_{AB}^R/\gamma_A^R.\gamma_B^R$ is much less variable, and more consistent results for $\overline{K}_x$ are obtained.

Apart from providing an alternative explanation of the results obtained, and further substantiating the proposed model, this statistical approach further confirms that the method of data processing used can only provide realistic results in the prescribed concentration range (x_B = 0.9 - 1.0). However, the activity coefficient term can be neglected if data at a concentration of benzene above $x_{B(lim)}^{corr}$ are included in the computer input. The values of $x_{B(lim)}^{corr}$ for different solutes are, then comparable directly. However, values of $\overline{K}_x$ and Δ_c deduced from data over a concentration range below $x_{B(lim)}^{corr}$ have no real meaning, and thus, as stated earlier, cannot be plotted accurately against $x_{B(lim)}^{corr}$ because no account can be taken of the variations in activity coefficients.

Within this chapter no allowance has been made for any variations in K_x and Δ_c due to the energetic differences of dispersion and electric field effects between solvent and aromatic. However, this is justifiable since cyclohexane and benzene have been used as solvent and aromatic respectively in all the investigations reported here. Therefore, it should be borne in mind that whilst the arguments proposed in Chapters 5 and 6 are still valid, the values for the equilibrium parameters, above and below $x_{B(lim)}^{corr}$, obtained in the present chapter are still subject to an absolute error relative to the solvent and reference independent results, (Chapters 5 and 6).

7.7. Conclusions.

A theory and working model have been deduced which explain variations with concentration in the parameters relating to the formation of molecular complexes. It is implicit in the proposals that Δ_c, as well as K_x, varies with the composition of the mixtures studied. Variations in the observed chemical shift of the solute are consistent with the model. These facts emphasise that values for K_x and Δ_c are most realistically obtained using equations of the Benesi-Hildebrand type at the limiting condition of $x_B^{corr} = 1$. It is interesting that the model, in addition to explaining many observable facts, is consistent in some respects with that proposed by Engler and Laszlo[253].

The theory has been further substantiated by calculating the values of $x_{B(lim)}^{corr}$ for other solute molecules. For example, its value for the reaction between acetone and benzene at a similar concentration in cyclohexane is 0.31, and comparison with a plot of K_x against x_B^{corr} obtained by a phase distribution method[39] shows that this is a realistic value.

CHAPTER 8

SPIN-LATTICE RELAXATION TIME MEASUREMENTS

8.1. Introduction.

The object of the investigations reported in this chapter is to gain further information concerning the nature and mechanism of formation of the transient complex, AB. The work reported in previous chapters has depended wholly upon the measurement of the n.m.r. chemical shift induced in a solute by an aromatic molecule, but this parameter refers fundamentally to the molecular nature of the interaction. It is from this that the mechanism for complex formation proposed in Chapter 7 has been derived. There appears to be no reason why the short-range ordering effect predicted by this mechanism should not be accepted qualitatively, although further proof of its authenticity is required.

The measurement of spin-lattice relaxation times, T_1, and the related nuclear Overhauser effect, are being used increasingly as aids to the solution of many chemical problems, and lend themselves to the type of problem considered here. The analysis of the data obtained often enables an absolute knowledge of molecular interactions, intramolecular rotations and orientations to be acquired. This is because, whilst T_1 is a bulk n.m.r. parameter, the contributions to its value may readily be analysed in terms of basic molecular interactions, and the structure of liquids. Some methods of analysis have been discussed in Chapter 2. Several workers[90-94] have used relaxation time measurements to study interactions very similar to those reported here. These investigations have been mostly concerned with the chloroform-benzene reaction. Huntress[90] has shown that the C_3 rotation of chloroform is slowed by

a factor of 4 when it is dissolved in benzene, and that the chloroform-benzene complex moves as a unit for periods of time much shorter than that observable by n.m.r. through chemical shift measurements.

It is apparent, therefore, that the measurement of spin-lattice relaxation times may give rise to information which it is not possible to obtain directly from chemical shift data. In the former investigations carried out on the chloroform-benzene complex, diluting solvents of the saturated hydrocarbon type have not been used because it has been thought that proof of the existence of the complex, and changes in rotational characteristics were of primary importance, although dilution with deuterated analogues (i.e. $[^2H_6]$ benzene and $[^2H]$ chloroform) has been invoked as a means for obtaining these primary characteristics. The use of inert solvents which are similar in all respects to benzene, except in the ability to form complexes, should enable variations in relaxation times to be observed, which may be interpreted in terms of the structure of the liquid mixture around the solute with changing composition. Since the object of the present investigations is to confirm the general mechanism proposed in Chapter 7, relaxation studies provide an ideal way of studying the problem. It is important to see if the results of these studies are consistent with those deduced from chemical shift measurement.

The general approach will be to measure relaxation times of benzene and cyclohexane, at compositions ranging from $x_B = 0$ to $x_B = 1$, and then to measure the effect of introducing a polar solute, $[^2H]$ chloroform, on the relaxation times. $[^2H]$ chloroform has been used as a polar solute because, as described previously, (Section 2.B.6.), it will

change the liquid structure by virtue of complex formation, but will not contribute appreciably to the relaxation mechanisms of benzene or cyclohexane. The proposed three component system reduces to one of two spins, which may be analysed by the method of Hoffmann and Forsen[103]. The polar solute can therefore be considered as a non-inert diluent.

There is, however, an important factor in the measurement of relaxation times, and related parameters, which must be considered before attempting measurements on the proposed systems. This is the efficient removal of oxygen from samples whose T_1 values are to be measured, for in a large number of reported cases this does not appear to have been adequately considered. It was noted in Chapter 2 that whilst some workers have obtained values for spin-lattice relaxation times which are consistent with proposed models, others, who have obtained lower values at similar temperatures, have not been able to correlate their results with any model, and have often attempted to show that the model is at fault. Those who have efficiently removed oxygen from their samples, and have consequently obtained realistic T_1 values, have shown that the models are in fact quite insensitive to the small changes which have been proposed by those workers with erroneous results.

The next section of this chapter therefore concerns a method which has been derived to efficiently remove oxygen from samples, and the quantitative preparation of multi-component systems. The results obtained will be compared with previously reported values for T_1, and the accuracy of preparation of quantitative samples will be considered before proceeding to the problem in hand.

8.2. The Preparation Of Samples.

It has long been recognised that the paramagnetic nature of molecular oxygen significantly reduces the values of spin-lattice relaxation times, and attempts to remove the oxygen are normally made by the familiar freeze-thaw degassing procedure, or by passing an oxygen-free gas through the liquid sample. In common with others[129,254,255], it has been found in these investigations that it is difficult to employ these procedures efficiently, and because of their unreliability, chemical means of deoxygenating samples have been investigated. Although some such methods have been reported[254,256] they are extremely tedious to implement, and the reducing power of the reaction is such that only simple hydrocarbons may be deoxygenated in this way. An alternative procedure has therefore been sought which satisfies the following conditions: (a) the materials should be readily obtainable, (b) they should be soluble in a wide variety of liquids, or be capable of use with solvents miscible or immiscible with the liquid under investigation, (c) have low vapour pressures to facilitate the easy removal of the subject material by distillation, and (d) the materials should be capable of use at very low concentration to minimise the potential reduction of the subject material. A compound which has been found to fulfil these requirements is $[Co(bipy)_3](ClO_4)_2$ which, when dissolved with sodium borohydride in a suitable solvent, removes oxygen in a reversible colour-indicating reaction. The use of this compound to remove oxygen from simple compounds will first be discussed, and results obtained by its use compared with those obtained by more conventional techniques. Its use in the preparation of quantitative samples will be discussed in

Section 8.2.2. and 8.2.3. In this context it should be noted that some by-products of the reaction are also paramagnetic and must not be allowed to enter the sample tube.

8.2.1. The Removal Of Oxygen With $[Co(bipy)_3](ClO_4)_2$

The cobalt complex suggested above for use as a deoxygenating compound is easily prepared[257,258] by the addition of hydrated cobalt (II) perchlorate to a solution of 2,2'-bipyridyl in ethanol. The complex precipitates readily, and after filtration is washed with ice-cold ethanol, and dried thoroughly to effect purification. The material has recently been used as a reducing agent in the reduction of nitro - and nitrosobenzene[258] and although its mode of reaction has been discussed at length[258-262] no definite conclusions have been reached. The fact that it efficiently removes oxygen from solution is, however, without doubt.

Depending on the conditions used, the reduction of tris (2,2'-bipyridyl) cobalt (II) or (III) complexes in the presence of perchlorate ions is known to result in the formation of $[Co(I)(bipy)_2](ClO_4)$[259] or $[Co(I)(bipy)_3](ClO_4)$[260]. In low concentrations, the reduction of the Co(II) or Co(III) complex with sodium borohydride in ethanol or aqueous ethanol, gives a homogeneous, oxygen free, blue solution, which is extremely oxygen sensitive. In the presence of oxygen the solution is pale yellow-brown in colour, but may be reduced again in the presence of an excess of sodium borohydride. The oxidation-reduction cycle is not reversible indefinitely.

Addition of a trialkylphosphine to the blue solution enables the isolation of the complex $[Co(I)(bipy)(PR_3)(H)_2](ClO_4)$[261]. By analogy with work on the related rhodium system[258,262], a reactive intermediate such as $Co(bipy)H_2^+$

is thought to be present. This species may lose dihydrogen to give an intermediate which may react with the oxygen molecule. Alternatively an outer sphere mechanism involving oxygen and $Co(bipy)_2^+$ or $Co(bipy)_3^+$ may operate[263].

Whilst there are many other compounds which are classed as 'oxygen-carriers' or, with oxygen, form adducts, they are mostly more complicated, and their modes of reaction are not well understood[264-6]. Although the nature of the chemical reaction which removes oxygen from solution is not well understood for the compound chosen here, the complex is easily made, the reaction is colour-indicating, and as will now be shown, is easily used.

The preparation of deoxygenated samples of pure liquids, liquid mixtures, and solutions of solids have been the subject of considerable interest in the author's laboratory, and equipment has been specially developed for this purpose[219]. Since the $[Co(bipy)_3](ClO_4)_2$ complex and sodium borohydride are not soluble in some of the liquids under investigation, methods have been devised by which such samples may be prepared. There are, therefore, three distinct types of preparation for a single liquid, namely: (a) the deoxygenating compounds dissolve in the liquid, (b) the compounds are soluble in a liquid which is miscible with the sample liquid, and (c) the compounds are soluble in a liquid which is immiscible with the sample liquid.

As previously mentioned, the compounds dissolve readily in ethanol and water, but also in other polar liquids such as acetone, methylene chloride, dimethyl sulphoxide and dimethylformamide. The latter two solvents are ideal for use in case (b) because of their high boiling points, which make distillation of samples easier. The two

preparative techniques (a) and (b) will be considered together because of their similarity.

8.2.1.1. Pure Liquids And Homogeneous Mixtures.

The deoxygenation of pure liquids requires the use of a simple vacuum manifold, with three isolable flasks connected to it in order that its volume may be altered as required (Figure 8.1.). The n.m.r. sample tube is positioned so that liquids of high boiling point, (i.e. low mean free path) may be distilled easily. The manifold is connected to a system dependent on a rotary pump and a mercury diffusion pump, so that a pressure of 10^{-3} torr, at least, may be attained. Two liquid nitrogen traps are used to stop any waste material entering the main pump.

For pure liquids, about 10ml. of the sample is placed into a round-bottomed flask; a magnetic follower, 2mg.(approx) of the cobalt complex and 20mg.(approx) of sodium borohydride are quickly added. The flask is rapidly placed on the vacuum line, the contents frozen with liquid nitrogen, and the excess air extracted. When a good vacuum has been attained, the tap above the flask is reclosed, and the contents of the flask allowed to come to room temperature. Upon changing from the solid to the liquid phase the mixture in the flask becomes intensely blue, indicating the absence of oxygen. Any leakage of air into the flask can be counteracted by the vigourous stirring of the mixture, but oxygen cannot be taken up indefinitely by the cobalt compound. In this case the solution becomes a yellow-brown colour. The sample liquid can, however, be kept in a deoxygenated state for several hours.

The stirring is maintained for about five minutes, after which time the reaction noticeably slows. During this first period bubbles of gas, probably hydrogen[219], are liberated,

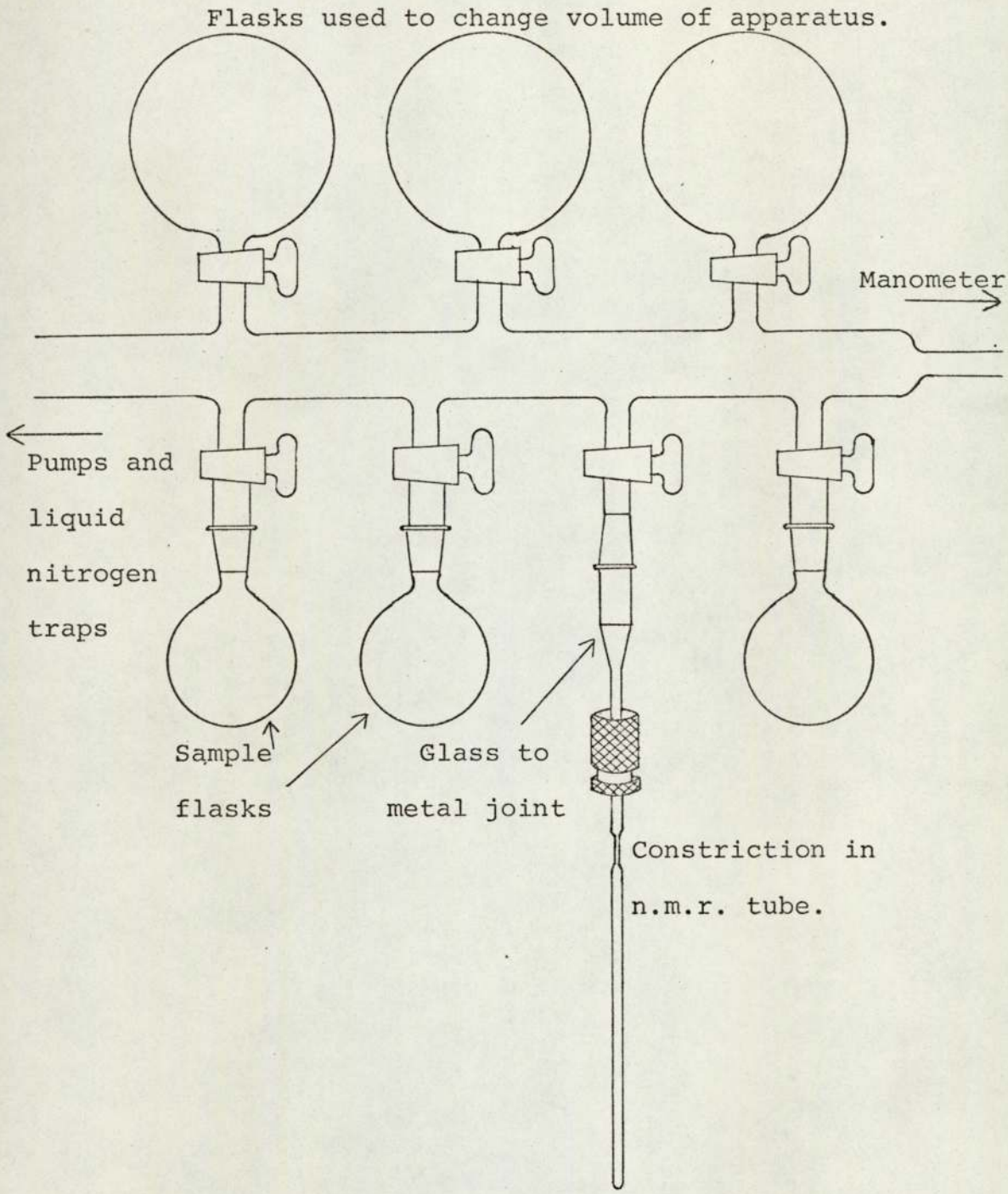


FIGURE 8.1. The apparatus used to chemically deoxygenate pure liquids used for n.m.r. relaxation time studies.

and this gas must be removed so that the sample may be subsequently distilled into the n.m.r. tube. This is most easily done by freezing the mixture, opening the tap above the flask until a reasonable vacuum is attained, closing the tap and allowing the mixture to warm up again. With liquids of a high boiling point it is not always necessary to freeze the mixture.

An n.m.r. tube is connected to the vacuum manifold using a special glass to metal joint with an O-ring seal. The tube is evacuated and warmed to remove any oxygen from its walls. The tap from the manifold to the pump is then closed, and those between the flask and the n.m.r. tube opened. The liquid is thus allowed to distill into the tube, which is cooled to condense the vapour. Continued stirring of the mixture in the flask will help any oxygen leaking into the manifold to be absorbed.

When the required amount of sample has been distilled into the n.m.r. tube, (about 1cm. in length - Section 3.4.5.) the contents are frozen and the tube evacuated. Initially the tube was sealed under vacuum with a pencil flame by collapsing the glass at several points just below the metal to glass joint. However, it was found that in a high proportion of cases the seal was defective or cracked. In order to overcome this problem each tube was constricted and its glass thickened at a suitable point before connecting it to the vacuum manifold. Sealing can then be effected with a single touch of the pencil flame.

Often, the material under investigation is not polar enough to dissolve both the cobalt complex and sodium borohydride, and an intermediate solvent is required, which must dissolve both these compounds, and be either miscible with

the liquid under investigation, or immiscible, forming either homogeneous or heterogeneous mixtures respectively. A required property of such an intermediate solvent include a low vapour pressure, and for most low boiling point hydrocarbons, such as benzene, the addition of a few drops of dimethyl sulphoxide or dimethylformamide enables the deoxygenating compounds to be dissolved. Therefore, for homogeneous mixtures, the experimental procedure is similar to that for a pure liquid. The samples so prepared were not found to contain any traces of the intermediate solvent.

8.2.1.2. Heterogeneous Mixtures.

In some cases it is not possible to find a suitable intermediate solvent which gives rise to the formation of a homogeneous mixture. However, it is possible to use an intermediate solvent immiscible with the sample material; very vigourous stirring enables efficient deoxygenation of the sample. Due to its low surface tension, water was found to be a good intermediate solvent for heterogeneous mixtures; all of the systems studied were lighter than water and comprised the top layer of the mixture, facilitating their easy removal by distillation.

The technique developed for the deoxygenation of a component in a heterogeneous mixture is identical to that for a pure liquid or homogeneous mixture up to the point of the commencement of stirring. Since there are two phases, the mixture must be stirred very vigourously, and for a longer time (10 minutes was usually adequate). The formation of a coarse emulsion enables oxygen to diffuse into the intermediate solvent, and there to be taken up by the cobalt complex.

After stirring the mixture must be allowed to settle

into two layers, after which the distillation into the n.m.r. tube is carried out as before if the top layer is the sample material. Stirring during distillation is impracticable, and thus it is necessary for the settling to occur rapidly.

It was found that, in certain cases, this technique had to be modified to avoid reactions between the deoxygenating compounds and the solvents; for example with carbon tetrachloride, the colours of the solution vary between orange and green. In such cases it was found necessary to first freeze the intermediate solvent(water), with the deoxygenating compounds, then to add the material under investigation, freeze it down, draw off the trapped air, and then allow the two phases to come into contact during the melting process.

8.2.2. The Quantitative Preparation Of Samples.

The quantitative preparation of liquid mixtures, such as the three-component systems proposed earlier in this chapter, may be approached in two distinct ways: firstly by the distillation of liquids from two or more heterogeneous or homogeneous mixtures into a common n.m.r. tube, or, secondly by siphoning a deoxygenated mixture from a flask containing two distinct layers, one layer containing an intermediate solvent and the deoxygenating compounds, and the other the mixture under investigation. These two techniques will now be considered.

8.2.2.1. Distillation.

The design of the vacuum manifold, shown in Figure 8.1., allows several liquids in seperate flasks to be deoxygenated simultaneously. A mixture of the liquids may be prepared in the n.m.r. tube by distilling various amounts into it, making

use of the familiar complete gas transfer operation. The flasks used to change the volume of the apparatus facilitate the calculation of the composition of the mixture because a knowledge of their volume and the pressure allows calculable weights of any liquid to be distilled into the tube. These calculated weights are, however, only approximate. Coupland[219] has attempted to prepare mixtures of benzene and cyclohexane by this distillation technique, but has found it to be quite inaccurate. He has, therefore, developed a siphoning technique, and has designed an apparatus which connects directly to the vacuum manifold in place of the sample flask.

8.2.2.2. A Siphoning Technique.

The apparatus designed by Coupland[219] for the preparation of deoxygenated liquid mixtures and solution of solids is shown in Figure 8.2.. Its main features are the tubes running from the flask to the n.m.r. tube, which is attached to this part of the system rather than directly to the vacuum manifold.

The apparatus is connected to the manifold, and, when a vacuum of about 10^{-3} torr is obtained, the three-way tap is positioned so as to isolate the flask, the 'Rotaflo' taps being closed. The flask is then opened and about 5ml of water is placed in it, together with the previously mentioned quantities of the cobalt complex and sodium borohydride, and a magnetic follower. The mixture becomes intense blue upon the application of a slight vacuum, which is required to remove excess oxygen and dissolved hydrogen[219]. The mixture is then frozen and the three-way tap adjusted as before to isolate the flask, and the sample of accurately known composition (about 10ml.) introduced and frozen. The flask is evacuated, and when the three-way tap is closed, allowed to attain room temperature.

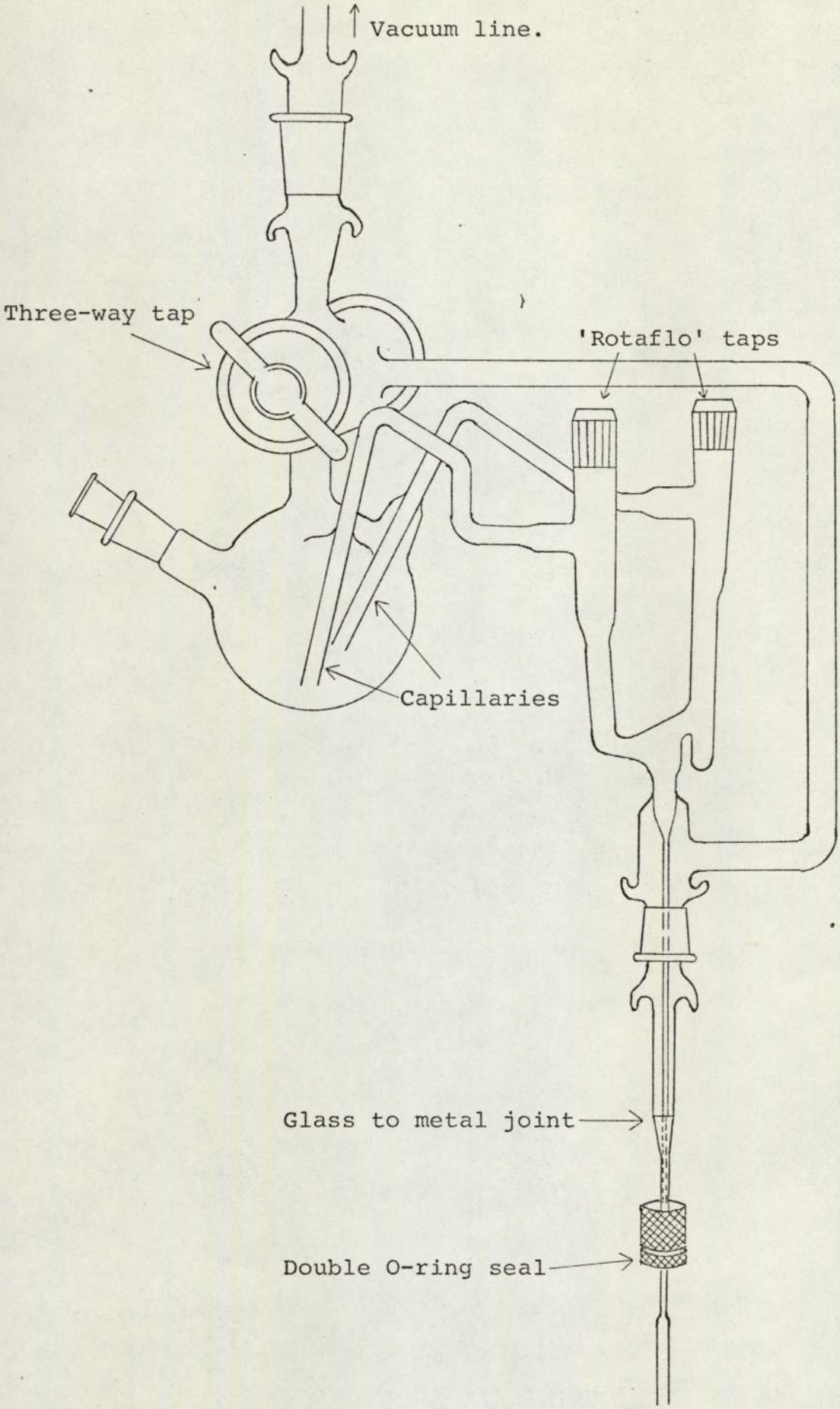


FIGURE 8.2. The siphon apparatus used to chemically deoxygenate samples of liquid mixtures used for n.m.r. relaxation time studies.

When the heterogeneous mixture has liquified the capillary tubes should be in different layers, and a check made to ascertain which tube is in the sample layer. The precise volumes of intermediate solvent and sample may be adjusted so that the tube which terminates in the sample layer is well away from the deoxygenating layer. Vigourous stirring, followed by a short settling period ensures the deoxygenation of the sample.

When the two layers have settled the contents of the flask may be stirred gently to ensure continued deoxygenation of the sample during the following siphon procedure. This is effected by successive cooling and heating of the respective tube near to the 'Rotaflo' tap in order to clear the tube of any unwanted material, and then positioning the three-way tap such that neither the evacuated flask nor the n.m.r. tube are open to the manifold. Subsequent careful opening of the respective 'Rotaflo' tap enables the sample to pass through into the n.m.r. tube, this operation being aided by the excess pressure provided by the production of hydrogen in the flask. When sufficient sample has been collected the 'Rotaflo' tap is closed, and the sample tube sealed as before.

This technique allows samples of liquid mixtures to be prepared quantitatively before they are deoxygenated, and providing that none of the components are soluble in the intermediate solvent layer, they may be transferred efficiently to the n.m.r. tube at the same composition. The accuracy of this preparative technique will be assessed in the following section. It has been used to prepare liquid mixtures of benzene-carbon tetrachloride, benzene-cyclohexane, and benzene-cyclohexane - [^{2}H]chloroform over the concentration range $x_B = 0$ to $x_B = 1$.

8.2.3. The Accuracy Of Sample Preparation And Efficiency Of Oxygen Removal.

In order to assess the accuracy of the preparative techniques described above and the efficiency of oxygen removal from samples, the spin-lattice relaxation times of several common materials have been measured by the A.F.P.S. method. The values obtained from chemically deoxygenated samples are compared with those obtained by the more conventional techniques, such as freeze-thaw degassing, and with those reported by other workers.

The relaxation times reported in this chapter were calculated by a computer using a least-squares fit program based on equation 3.7.,

$$\ln(M_o - M_z) = \ln M_o - t/T_1 \qquad 3.7.$$

which has been discussed in greater detail in Chapter 3. Care must be taken, however, not to include very small values of $\ln(M_o - M_z)$, because these may be subject to a very large percentage error. An example of the linearity of the plots is shown by Figure 8.3. for an experiment on a sample of pure benzene distilled from a heterogeneous mixture, with water as the intermediate solvent.

Preliminary experiments were performed on some simple aromatic molecules in order to assess the relative merits of the new and conventional deoxygenating techniques. The results are reported in Tables 8.1.a. and 8.1.b., where the conditions pertaining to each measurement are reported. It is apparent that the values for spin-lattice relaxation times obtained when the chemical deoxygenating technique is used are significantly longer than those obtained by the use of other conventional methods, and those reported by

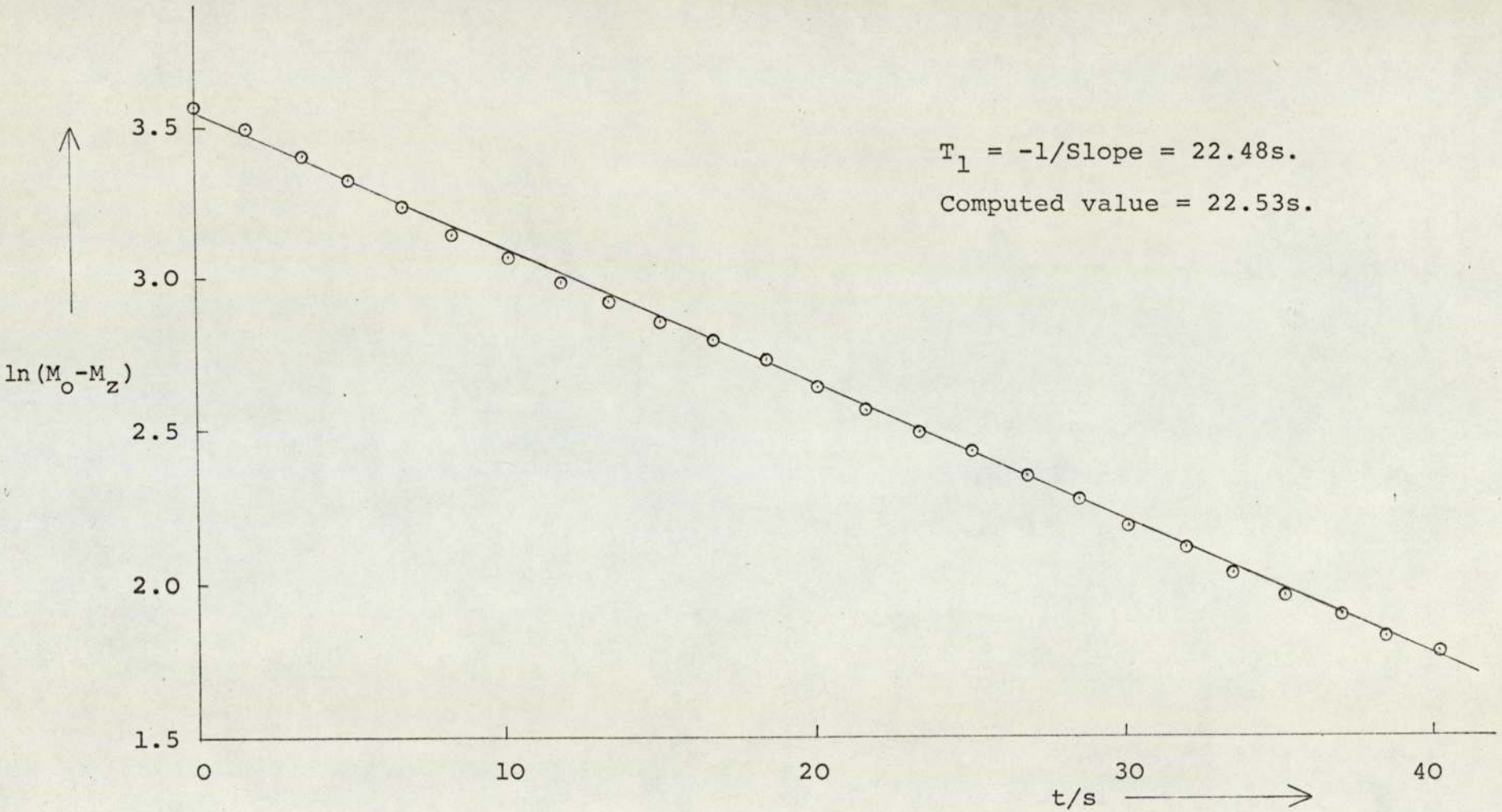


FIGURE 8.3. A plot of $\ln(M_o-M_z)$, measured by the A.F.P.S. technique, for the relaxation of chemically degassed benzene.

TABLE 8.1.a. The spin-lattice relaxation times of benzene measured by the A.F.P.S. technique after degassing by conventional and chemical methods.

DEGASSING TECHNIQUE		T_1/s.[a]
Undegassed		4.82[b]
Freeze-thaw at 10^{-3} torr – 4 cycles		5.47[b]
Freeze-thaw at 10^{-5} torr:[c]	1 cycle	23.60
	2 cycles	21.81
	3 cycles	21.43
	4 cycles	20.79
	5 cycles	17.67
	6 cycles	22.05
Bubbling oxygen-free nitrogen for:	15 minutes	20.85
	30 minutes	20.88
	60 minutes	13.12
Chemical degassing:		
Homogeneous mixture containing dimethylformamide		22.73
		22.76
Homogeneous mixture containing dimethylsulphoxide		23.11
		23.41
Heterogeneous mixture with water		23.01
		24.86
Literature values:[d]	Measured at 303K[108]	22.0
	Measured at 305.1K[133]	18.4
	Measured at 298K[129]	19.3

[a] values measured at ca 309K. [b] average of four values.
[c] the freeze-thaw operations were continuous; samples were removed after each cycle. [d] highest reported values.

SUBJECT MATERIAL	T_1/s [a] UNDEGASSED	T_1/s [a] FREEZE-THAW AT 10^{-3} TORR	T_1/s [a] CHEMICAL METHOD	T_1/s [a] LITERATURE VALUES[b]
Benzene	4.82	5.47	23.31[c]	22.0 at 303K [108]
Toluene[d] - ring	3.76	4.18	21.27[c]	16.0 at 298K [129]
- methyl	3.29	3.50	11.64[c]	9.0 at 298K [129]
p-Xylene[d] - ring	3.43	4.36	16.70[c]	14.0 at 298K [129]
- methyl	3.32	3.88	7.30[c]	7.5 at 298K [129]
Acetone	—	—	17.58[c,e]	15.8 at 298K [102]
Methylene chloride	—	—	36.10[c]	28.5 [166]
Cyclohexane	—	—	7.90[f]	7.2 at 303K [267]

TABLE 8.1.b. The spin-lattice relaxation times of some common materials, measured by the A.F.P.S. technique after degassing by conventional and chemical methods.

[a] Values reported are the average of several measurements at ca 309K. [b] Highest reported values. [c] Distilled from the pure liquid containing the deoxygenating compounds. [d] Ring and methyl T_1 values were measured separately by saturating out the unwanted resonance. [e] The estimated error for 13 determinations is ±0.2s. [f] Distilled from a heterogeneous mixture containing dimethylsulphoxide.

other workers. The values are also more reproducible, and subject to less error, if the chemical method is used.

The errors arising in the measurement of the spin-lattice relaxation time of acetone were shown to be extremely small. For fifteen determinations the error was ±0.4s(2.4%), and for thirteen determinations ±0.2s(1.2%). The reproducibility of T_1 values using the new technique for different samples of the same material was ±0.5s. This small error in measurement may be considered to be negligible in these investigations.

The larger values of T_1 reported here may be due, in part, to the slightly higher temperature at which the measurements were made, because T_1 is almost directly proportional to temperature as long as the material is kept well below its critical point. This has been clearly demonstrated by Powles and Figgins[103]. However, a comparison of the increase in T_1 with temperature by them leaves no doubt that in some cases (e.g. toluene) the increase is due to the more efficient removal of oxygen from the sample.

The use of the syphonation technique to prepare quantitative samples of liquid mixtures necessitates an assessment of the accuracy with which the previously prepared sample is deoxygenated and transferred to the n.m.r. tube. In order to show that this technique is accurate, Coupland[219] has prepared samples of benzene-carbon tetrachloride mixtures, weighed accurately in order to calculate the mole fraction of benzene, x_B. After the measurement of the T_1 of benzene in each, the deoxygenated samples were reopened and their refractive indices measured. The refractive index values were compared with a calibration graph in order to find the mole fraction of benzene in the deoxygenated sample. The

largest error in mole fraction was found to be 0.02, and in nineteen cases was below 0.005, which is within the experimental error of the refractive index measurements. These errors were considered to be negligible.

The efficiency of the siphoning technique was checked by comparing the results obtained by Coupland with those reported by Mitchell and Eisner[267] for the benzene-carbon tetrachloride system. Both sets of results are reported in Table 8.2., and are shown in graph form in Figure 8.4.

The figure shows that relaxation times measured after chemical degassing are almost coincident with the best line through the values reported by Mitchell and Eisner. This best line is, as predicted by the Hill theory[268,269] a slight curve. The results obtained by Coupland for T_1 do, however, tend to be slightly higher for a given mole fraction, but this is easily explained by the difference in the temperatures at which the measurements were made for the two sets of experiments.

It appears that the siphon method for quantitatively preparing deoxygenated samples of liquid mixtures is sufficiently accurate to enable investigations to be carried out with confidence on the benzene-cyclohexane, and benzene-cyclohexane -[^{2}H]chloroform mixtures mentioned earlier.

8.3. A Study Of The Benzene +[^{2}H]Chloroform Reaction In Cyclohexane.

The mechanism for complex formation proposed in the previous chapter was based on the assumption that a polar solute, capable of forming a complex with an aromatic molecule, attracts aromatic molecules from the general aromatic/inert solvent medium in such a way that a cluster or cage of aromatic molecules form around it. It was proposed that these aromatic

TABLE 8.2. The variation in values of T_1 and T_1^{-1} of benzene (B) in benzene-carbon tetrachloride mixtures, measured by Coupland,[219] and Mitchell and Eisner.[267]

	COUPLAND		MITCHELL AND EISNER[c]	
x_B[a]	T_1/s[b]	$T_1^{-1} \times 10^3/s^{-1}$	x_B	$T_1^{-1} \times 10^3/s^{-1}$
0.05	50.50	19.80	0.00	19.5
0.06	53.50	18.69	0.11	22.0
0.07	48.25	20.73	0.22	26.0
0.10	45.50	21.98	0.32	31.5
0.11	44.00	22.73	0.52	36.5
0.12	44.00	22.73	0.615	39.5
0.13	44.00	22.73	0.725	42.5
0.17	39.75	25.16	0.86	47.0
0.17	39.00	25.64	0.95	48.5
0.19	40.25	24.85	1.00	50.0
0.20	39.75	25.16		
0.30	35.00	28.57		
0.42	30.00	33.33		
0.54	26.50	37.74		
0.63	25.75	38.83		
0.68	24.00	41.67		
0.75	24.25	41.24		
0.78	24.50	40.82		
0.89	21.75	45.97		
0.93	21.25	47.06		
1.00	20.75	48.19		

[a] Calculated before deoxygenation. [b] Average values of up to six measurements at 307K. [c] Measured at 303K.

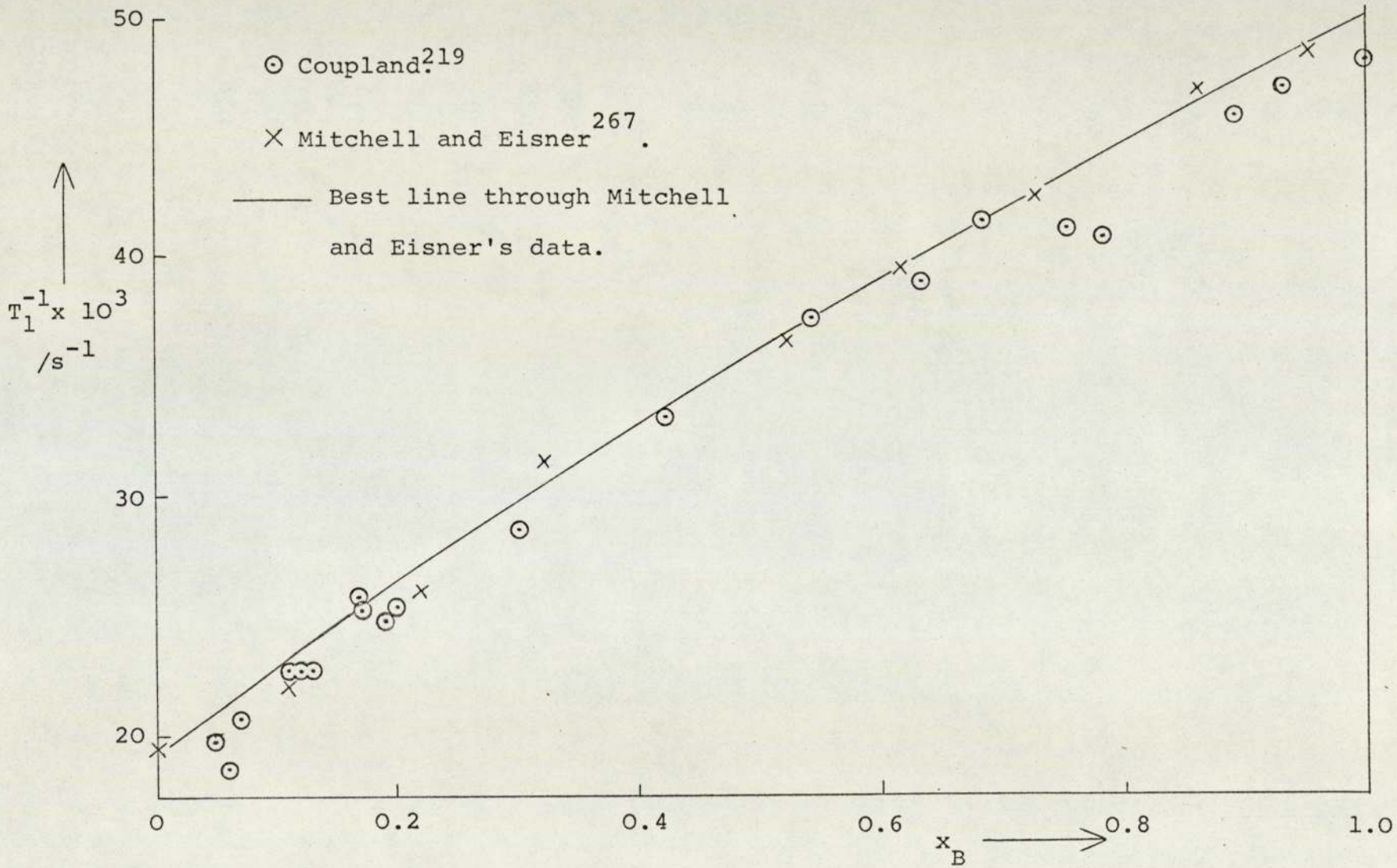


FIGURE 8.4. The variation of T_1^{-1} for benzene with the composition of benzene-carbon tetrachloride mixtures.

molecules exchange with those in the general medium, and also that they may infrequently exchange with an inert solvent molecule. This hypothesis was used to satisfactorily explain experimental observations concerning the variation of equilibrium quotients with the composition of the medium, and the variation of chemical shifts. Since the proposals are based on the fact that the introduction of a polar solute to the general medium disrupts the randomness of the system and changes the translational and rotational characteristics of all the components it is apparent that the spin-lattice relaxation times should be noticeably changed. It is to be expected that the inert solvent will be less affected than the aromatic molecules by the changes in rotation and translation.

Huntress[90], and Sato and Nishioka[91] have attributed the change in the relaxation time of benzene upon the addition of chloroform to a change in the rotational characteristics of the complex relative to the 'free' molecules. The fact that translational correlation times differ only slightly supports the proposed mechanism.

The benzene-cyclohexane -[^{2}H]chloroform system has been chosen as a model system to gain further information for the reasons stated in both this chapter and others. Firstly, therefore, it is necessary to measure the relaxation times of mixtures of benzene and cyclohexane in the composition range $0<x_B<1$, and, secondly, to remeasure them in the presence of chloroform. The composition of the three-component mixtures could not be made the same as for the chemical shift measurements because the effect on the relaxation times could not be seen when x_A was less than 0.01. This is because of the reduced sensitivity of T_1 values to

changes in the environment, compared with the effect upon chemical shifts (e.g. see Figure 8.4.). The use of [^{2}H] chloroform in such high concentration introduces the possibility of solute-solute association, but this will be discussed in the next section.

The samples used for these investigations were carefully weighed out into flasks in a similar fashion to those used for chemical shift measurements. They were chemically deoxygenated by the syphon method, and samples 1cm in length were sealed into the n.m.r. tube. The sample tubes were checked for leaks and cracks, and then, after being allowed to equilibrate in the probe of the Varian HA100D spectrometer, A.F.P.S. experiments were immediately performed on them, as described in Chapter 3. The resonance due to the component not being studied was saturated by connecting an auxiliary oscillator to the modulation input on the r.f. unit. The frequency of this oscillator was not found to be critical within about 20Hz.

The relaxation times of each peak in each sample were calculated from the variation in the peak heights, recorded on the Hellige galvanometer recorder, with time. Rather than depending upon the recorder time base to measure the time of each peak, the sweep period of the linear sweep unit was measured to within 0.1% and the relative event times of each peak were calculated by the computer. A knowledge of absolute time relative to the initial pulse is not required for the A.F.P.S. method.

The data are reported in Tables 8.3.a., 8.3.b. and 8.3.c., and are shown in graph form in Figures 8.5. and 8.6. The value of the nuclear Overhauser effect was measured for some of the samples, where its magnitude allowed, but although

TABLE 8.3.a. The variation of the spin-lattice relaxation times of benzene (B) and cyclohexane (S) with the composition of the benzene-cyclohexane mixtures.

SAMPLE	x_B	BENZENE T_1/s[a]	CYCLOHEXANE T_1/s[a]
A	0.0000	–	7.90
B	0.1045	17.40	8.45
C	0.2046	17.25	9.15
D[b]	0.3069	18.50	9.70
E	0.3972	18.45	9.75
F[b]	0.4935	18.95	10.30
G	0.5977	19.30	10.60
H[b]	0.6987	19.40	11.45
I	0.7974	20.20	11.80
J	0.8969	20.30	12.50
K	1.0000	20.70	–

[a] Values were measured at ca 307K, and are the average of several measurements, quoted to an accuracy of 0.05s.

[b] Samples were prepared and the relaxation times were measured by A.Coupland.[219]

SAMPLE	$n_A \times 10^2$	$n_B \times 10$	$n_S \times 10$	x_A	x_B	BENZENE T_1/s [a]	CYCLOHEXANE T_1/s [a]
A[b]	0.775	0.1370	1.1553	0.0566	0.1000	18.90	8.60
B[b]	0.672	0.2609	1.0612	0.0484	0.1878	19.05	9.40
C[b]	0.664	0.3671	0.7897	0.0543	0.3001	19.50	9.80
D	0.537	0.3582	0.6835	0.0490	0.3270	20.00	10.00
E	0.562	0.4715	0.5934	0.0501	0.4206	20.20	10.80
F	0.562	0.7005	0.3858	0.0492	0.6131	20.70	12.10
G	0.602	0.9307	0.2093	0.0502	0.7754	21.60	12.70
H	0.642	1.0733	0.1081	0.0515	0.8617	21.40	12.75

TABLE 8.3.b. The variation of the spin-lattice relaxation times of benzene and cyclohexane with the composition of the three-component benzene (B) - cyclohexane (S) - [^{2}H]chloroform (A) mixtures, where the mole fraction of chloroform, x_A, is 0.05.

[a] Values were measured at ca 307K and are the average of several measurements, quoted to an accuracy of 0.05s. [b] Samples prepared and relaxation times measured by A.Coupland.[219]

SAMPLE[a]	$n_A \times 10^2$	$n_B \times 10$	$n_S \times 10$	x_A	x_B	BENZENE T_1/s [b]	CYCLOHEXANE T_1/s [b]
I	1.057	0.1104	0.9296	0.0923	0.0963	19.20	8.90
J	1.044	0.2386	0.7620	0.0945	0.2159	19.95	9.55
K	1.064	0.3457	0.6936	0.0928	0.3017	20.30	10.10
L	1.198	0.4440	0.6039	0.1026	0.3802	20.60	10.55
M	1.436	0.7481	0.5822	0.0974	0.5076	21.20	11.30
N	1.208	0.7324	0.4214	0.0947	0.5746	21.20	11.80
O	1.386	0.9584	0.3165	0.0980	0.6780	21.60	12.50
P	1.524	1.2030	0.1687	0.1000	0.7893	21.70	12.80
Q	1.387	1.2323	—	0.1012	0.8988	22.20	—

TABLE 8.3.c. The variation of the spin-lattice relaxation times of benzene and cyclohexane with the composition of the three-component benzene (B) - cyclohexane (S) - [^{2}H]chloroform (A) mixtures, where the mole fraction of [^{2}H]chloroform, x_A, is 0.10.

[a] Samples prepared and relaxation times measured by A.Coupland.[219] [b] Values were measured at ca 307K and are the average of several measurements, quoted to an accuracy of 0.05s.

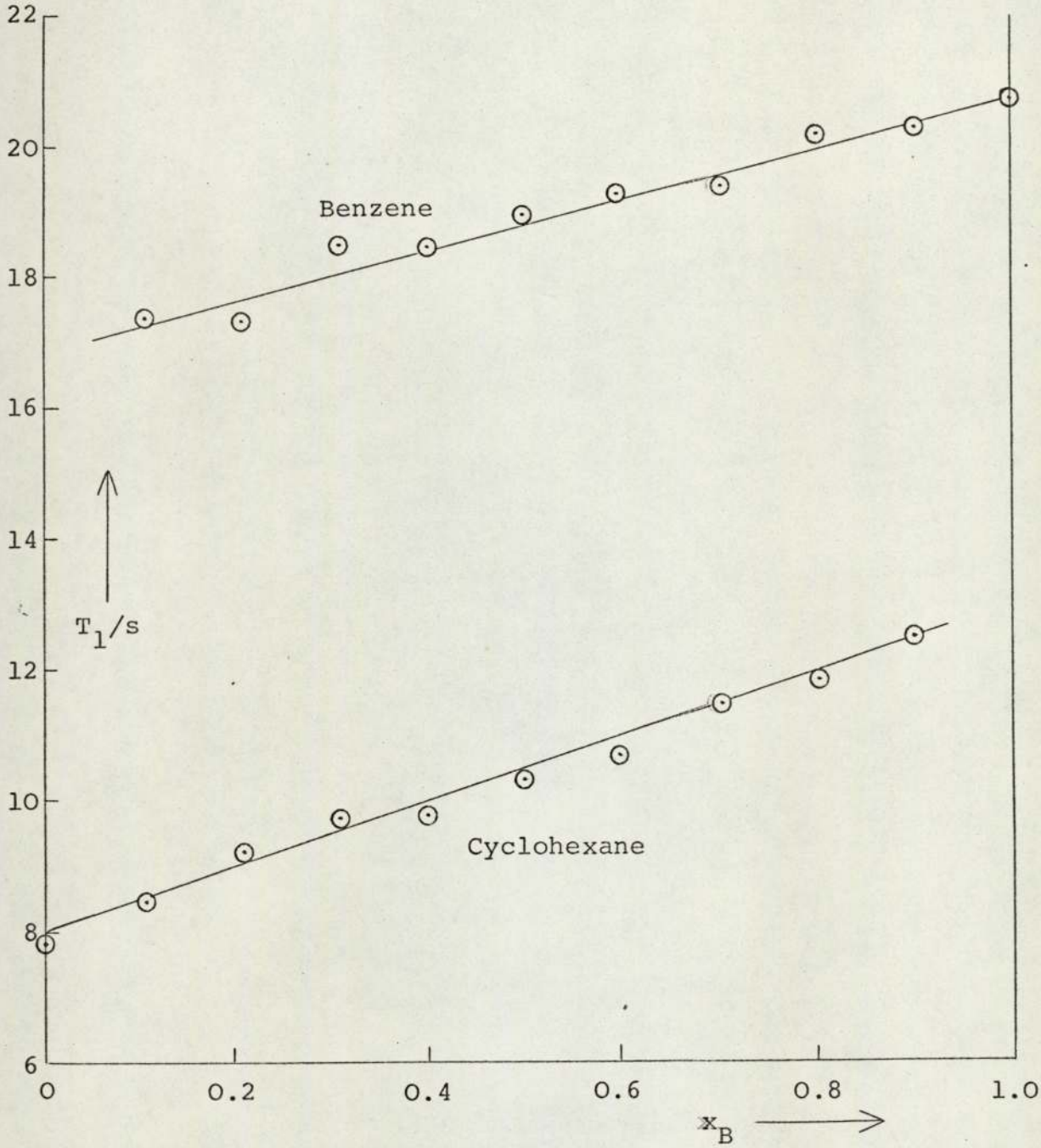


FIGURE 8.5. The variation of the spin-lattice relaxation times of benzene and cyclohexane in benzene-cyclohexane mixtures with the composition of the mixture.

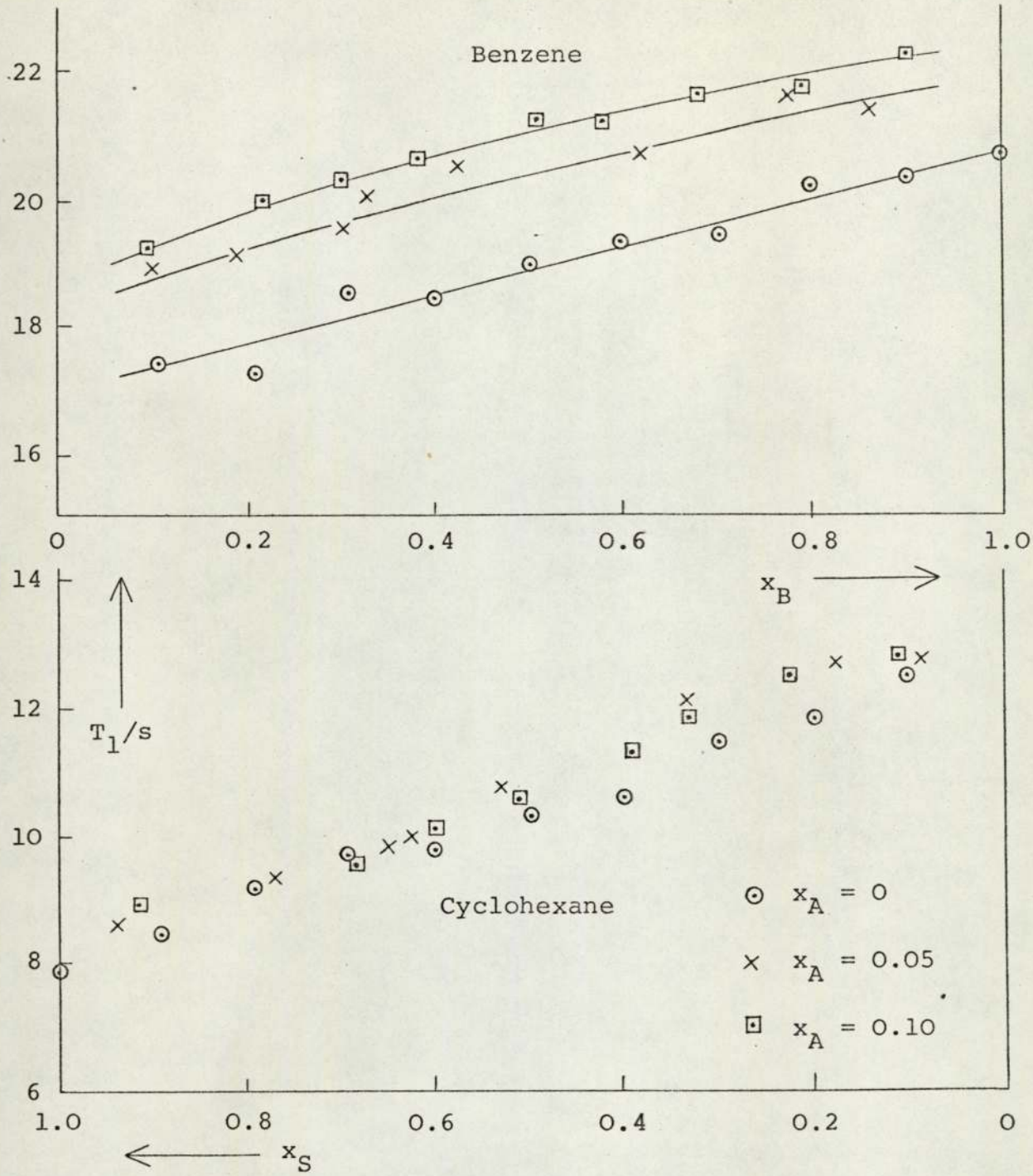


FIGURE 8.6. The variation of the spin-lattice relaxation times of benzene and cyclohexane with their mole fractions, x_B and x_S respectively, in two-component mixtures and in three-component mixtures with [^{2}H]chloroform, mole fraction x_A.

the values were generally consistent with the proposed mechanism they were neither accurate nor reproducible enough to warrant detailed analysis (see Appendix).

8.4. Discussion.

The differences between Figures 8.5. and 8.6. are readily noticeable. The variations of the spin-lattice relaxation times of both benzene and cyclohexane in the two-component mixtures are almost linear in nature; the plot for benzene rises with increasing benzene concentration, and that for cyclohexane falls with increasing cyclohexane concentration. Since the viscosity of the mixtures varies little with composition[91], it may be supposed that the variations referred to above are due entirely to differences in intermolecular contributions to the relaxation time, because the rotational characteristics of the molecules will remain unchanged. The change in values of T_1 with composition appears to depend on the number of protons per unit volume, and given a randomly distributed mixture, this assumption appears to be justified by the linearity of the plots. Sato and Nishioka[91] have also noted this dependence. This is further substantiated by the results for the benzene-carbon tetrachloride system shown in Figure 8.4. In the latter case the relaxation time of benzene increases with increasing carbon tetrachloride concentration (i.e. decreasing proton density).

The results obtained for the benzene-cyclohexane system appear to be self-consistent, reflecting the supposed random state of the liquid mixture, and the interactions occurring in it. The results obtained from studies of three-component systems can, therefore, be compared directly with those for two-component systems with a reasonable degree of confidence.

Figure 8.6. shows the effect of the addition of varying amounts of [^{2}H]chloroform on the spin-lattice relaxation times of benzene and of cyclohexane over the composition range $0<x_B<1$. It is noticeable that the T_1 values of benzene are higher when chloroform is added to the mixture, and appear also to depend on solute concentration. On the other hand, the addition of chloroform to the mixture has little effect on the relaxation times measured for cyclohexane; the plots are almost identical below $x_B = 0.4$. It is also interesting to note that the T_1 values for benzene are increased even at very low values of x_B. These observations will now be considered in detail, and the reasons for them will be discussed with reference to their likely origin.

The effect of [^{2}H]chloroform on the spin-lattice relaxation times of benzene and cyclohexane may be thought to originate in four different ways. It is possible that all four of these effects contribute to the observed variations, or that some have negligible effect.

Firstly, the solute acts as a diluent of the benzene-cyclohexane mixture, and will reduce the proton density within the sample. For the reasons stated earlier (Section 2.B.6.), however, it will not affect the <u>nature</u> of the relaxation processes between benzene and cyclohexane; neither will it provide additional relaxation processes. [^{2}H] chloroform is similar in size to carbon tetrachloride, and its diluting effect would, therefore, be expected to be very similar. The enhancement of the T_1 values of benzene with the solute concentration is to be expected if the observations are due to a dilution effect.

The benzene-carbon tetrachloride system is, therefore, a comparable system in this context, and corrections for

dilution may be made to the data obtained from three-component systems by reference to this. At a mole fraction of carbon tetrachloride of 0.05, the relaxation time of benzene rises by about 0.5s, and for a mole fraction of 0.1, the enhancement is about 1.0s. These values may be used to correct the T_1 values of benzene at each solute concentration in the three-component mixtures, and the resulting plot is shown in Figure 8.7. The data thus obtained for each [^{2}H]chloroform concentration gives rise to plots which are coincident within experimental error, but they still show a real increase over the plot of T_1 values for benzene in the absence of chloroform. The validity of these plots is subject to some doubt because it is inherently assumed that each [^{2}H]chloroform molecule is surrounded entirely by benzene, even at low values of x_B. Figures 8.4. and 8.5. show that the dilution effect of cyclohexane is much less than that of carbon tetrachloride. Therefore, the correction for the dilution effect of [^{2}H]chloroform is the maximum which could be used. It is also probable that, for low concentrations of benzene, the correction which has been applied is too large, because the solute is not completely surrounded by the aromatic but also by the solvent under such circumstances. Moreover, the ensuing arguments will justify the approach used.

This correction shows that, whilst the dilution effect of [^{2}H]chloroform accounts for part of the observed enhancement of benzene spin-lattice relaxation times when this solute is present, there is still a real effect due to some other factor.

The second effect which must be considered is the self-association of the solute molecules, which may play

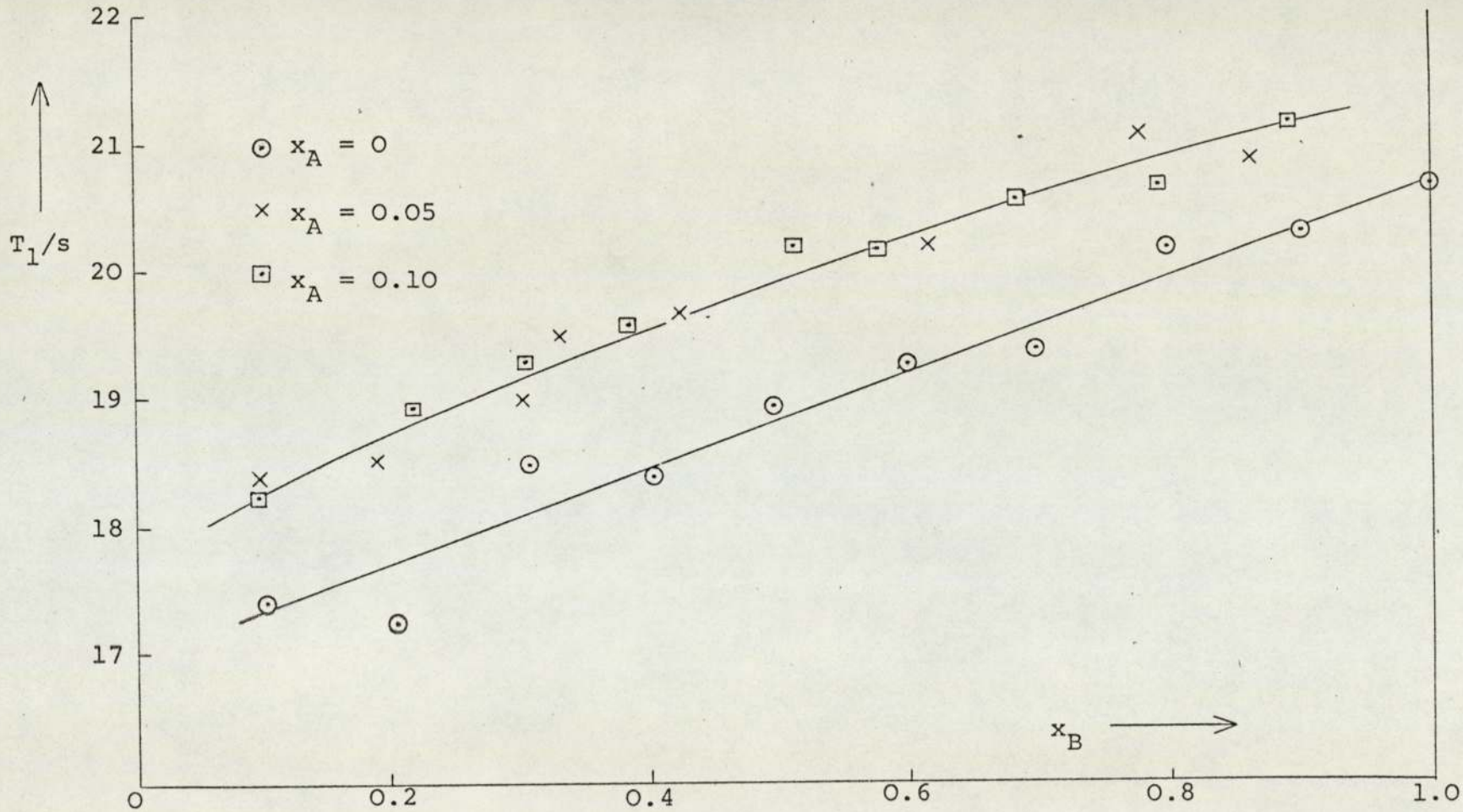


FIGURE 8.7. The variation of the spin-lattice relaxation time of benzene, corrected for dilution, in benzene-cyclohexane-[^{2}H]chloroform mixtures, compared with that in benzene-cyclohexane mixtures.

some part in the observed relaxation time enhancement. The addition of [^{2}H]chloroform to mixtures of benzene and cyclohexane in concentrations of up to 0.1 mole fraction, raises some doubts as to the validity of comparing the results reported in this chapter with those obtained from chemical shift investigations. The use of such high concentrations is not practicable for chemical shift studies because of the sensitivity of the measurements to the self-association of chloroform, but for spin-lattice relaxation studies its effect may be less important[91]. Indeed, most workers in this field have used 1:1 benzene-chloroform mixtures, because the use of such high solute concentrations gives rise to large variations in T_1 values. Jumper, Emerson and Howard[270] have calculated the self association constant (K_x) of [^{1}H]chloroform to be approximately 0.16, which is an order of magnitude smaller than that for the chloroform-benzene association. Sato and Nishioka have measured T_1 values for chloroform in benzene and carbon tetrachloride, and have shown that these values do not change over their experimental concentration range despite the vastly different nature of the two solvents. Therefore, the self-association constant of the chloroform molecule is not large enough to affect the proton spin-lattice relaxation of chloroform in solution. Likewise, it is unlikely that the relaxation mechanisms of benzene and cyclohexane will be affected to a large extent because of [^{2}H]chloroform self-association. Certainly, in view of the magnitude of the self-association constant, any contributions due to this effect will be within the experimental error limits for the variations in T_1 reported here.

Self-association plays a large part in chemical shift measurements because in that case observations concern the

effect of a large amount or aromatic on a small amount of solute. In the present investigations the effect of a slightly larger amount of solute on a high proportion of benzene and cyclohexane is being studied. Thus, the time-average of 'free' and complexed states will result in less noticeable effects of [^{2}H]chloroform on the relaxation times of benzene and cyclohexane.

A third factor which may explain the observed variations is the effect of actual complex formation, (i.e. the effect of the reaction $A + B \rightleftharpoons A.....B$, considered independently of the environment of the reaction). It has been shown that there is a slight change in the rotational characteristics of benzene and [^{2}H]chloroform in the complex relative to the uncomplexed molecules[91]. Huntress has attributed the differences in relaxation times of neat benzene and benzene in [^{1}H]chloroform solution to the restriction of random motion of the chloroform molecule. Sato and Nishioka[91] have concluded that the complex does move as a unit, and that its lifetime is probably of the order of 10^{-12}s. Anderson's theory[92-94] predicts that a complex of this lifetime will not modulate molecular motion, the correlation time for which is of the order of 10^{-10}s. This does not conflict with Huntress's view[90] that the tumbling motion of chloroform is slowed by a factor of four, because the correlation time for this motion is 10^{-12}s., short enough to be affected by complex formation. It appears, therefore, that the effect of chloroform upon the rotational motion, and hence relaxation time, of benzene may be negligible. The arguments proposed earlier concerning the effect of time-averaging of 'free' and complexed states on spin-lattice relaxation times are also valid in this context,(i.e. the effect of complex

formation on T_1 values will not be so important as its effect on chemical shifts). It is reasonable to assume, therefore, that the formation of 1:1 complexes specifically may be discounted as the whole cause of the observed enhancement of benzene relaxation times by [^{2}H]chloroform.

The fourth, and last, factor which must be considered is the mechanism of complex formation. Here, it is necessary to consider the effect of the environment of the solute, and of the complex, on relaxation times. The model proposed in Chapter 7 suggested that, even when in low concentration in a three-component mixture, the benzene molecules tend to cluster round the solute. The effect of this will be to cause a local decrease in proton density (by the exclusion of cyclohexane) around the solute, and hence a rise in the T_1 value for benzene. This will, of course, average with the relaxation time of the benzene in the bulk medium, on which further comment will be made below. The model appears to be sufficiently accurate to explain the observed variations in the relaxation times of benzene.

However, it should be remembered that in these investigations the concentration of solute is higher than that used in Chapter 7, where the model was suggested. In fact, it is high enough not to allow a limiting value for equilibrium parameters to be reached (i.e. there is no corresponding concentration to $x^{corr}_{B(lim)}$ defined in Chapter 7). This effectively means that there is no bulk medium. All molecules in the mixture will be involved in the 'solvation' shell of at least one solute, because the value of x_A is such that the 'solvation' spheres may be expected to overlap. However, cyclohexane will still be excluded from the immediate proximity of the solute molecules, and will tend

to behave as a bulk medium. Relaxation times will, therefore, not be averaged between the two environments. If this were so, wide variations in the enhancement of the relaxation times of benzene should be observed. This is not observed in Figure 8.7., which, therefore, supports the proposals concerning the bulk medium and the model for complex formation.

The proposed model explains the variations in T_1 for benzene satisfactorily by predicting changes in proton density, but it is also necessary to consider the plots observed for cyclohexane, (Figure 8.6.). These plots show that T_1 values for cyclohexane are not seriously affected by the addition of [^{2}H]chloroform. It appears from this observation that cyclohexane is not intimately involved with the solute. This is expected from the predictions of the model, but the model also suggests that, if benzene and cyclohexane molecules are being partially separated by the effects of the solute, the proton density of the 'pseudo bulk medium" is higher. The spin-lattice relaxation time of cyclohexane should, therefore, be lower than observed at low values of x_B, and approach the plot for benzene-cyclohexane mixtures at high values of x_B. The reasons for this are, however, readily explained. Firstly, because of the high concentrations of solute used, the cyclohexane is not so completely separated from the benzene as may be expected. The second, and probably the most important factor, is that the plots shown in Figure 8.6. are not corrected for dilution by the solute. This correction would certainly lead to lower T_1 values, but unfortunately data is not available so that this may be done. If the observed curves could be corrected in this way the resulting plot would be similar to that proposed above.

It appears that major effects observed here may be

explained in terms of the proposed model, together with dilution. The effect of the preferential affinity of the solute for aromatic molecules is to raise the benzene relaxation time and to lower the cyclohexane relaxation time, because of local changes in proton density. Dilution of the mixture by the solute raises both sets of relaxation times to those observed in Figure 8.6.

Finally, it is evident from the variations of benzene proton relaxation times with the composition of the mixture that, even when in low concentration, the relaxation time is affected to a larger extent than would be expected by dilution alone. This supports the theory that benzene, rather than cyclohexane, is preferentially attracted to the solute molecule.

8.5. Conclusions.

Investigations have been carried out concerning the use of spin-lattice relaxation times in the study of the formation of molecular complexes in liquids. A method has been devised by which samples used in these investigations have been easily and efficiently deoxygenated by chemical means. Its use for the quantitative preparation of multi-component samples has been studied, and its accuracy has been proved.

Investigations into the effect of a polar solute, [^{2}H]chloroform, upon the spin-lattice relaxation times of benzene and cyclohexane in mixtures of these compounds, ranging in composition from $x_B = 0$ to $x_B = 1$, have shown that a major change occurs in the structure of the liquid mixture. The results are generally consistent with the model proposed in Chapter 7 of this thesis. A qualitative approach has shown that benzene molecules cluster round

each solute molecule, and that it is possible for cyclohexane molecules to enter the 'solvation shell' occasionally. The most important results of these investigations point to the fact that, upon the introduction of a polar solute to a liquid, part or all of which is capable of interacting specifically with the solute, the randomness of the system is seriously perturbed. The extent of this effect could not be satisfactorily explained unless the concept of a solvent cage model, or similar hypothesis, is invoked. It is apparent, however, that much more work should be carried out on this problem, with a view to a more quantitative approach.

CHAPTER 9

GENERAL CONCLUSIONS

9.1. General Conclusions.

The investigations which have been reported in this thesis have been carried out with the intention of clarifying some aspects of the transient complexes formed between polar aliphatic solutes and aromatic molecules, and confirming previously proposed methods by which these may be studied. The results of these investigations have shown that the data processing procedures are valid and have enabled meaningful values of parameters characteristic of these interactions to be obtained. There can be little doubt that the values of these parameters are more meaningful, and have more significance than those obtained previously. Consequently, a better understanding of the nature of the complexes and the mechanism of their formation has emerged.

The rationalisation of data processing techniques proposed elsewhere[40,41] has been examined critically using data of high accuracy. The modifications proposed by other workers have been shown to be reliable. The use of these procedures, which are self-consistent, and also consistent with the molecular basis of fast exchange equations, has resulted in values being obtained for both the equilibrium quotients and the aromatic induced shift which, when calculated using the Benesi-Hildebrand equation under strict conditions of concentration, are in full agreement with theoretical predictions. The use of data of high accuracy in this section of the work has enabled some observations to be made concerning the effect of inert solvents on the equilibrium parameters K and Δ_c. An extrapolation procedure has been proposed which

enables differences in dispersion and electric field effects between the solvent and aromatic molecules to be eliminated, thus making the method independent of both solvent and reference. The results so obtained have been compared with those calculated by a reference independent technique, and have proved to be more accurate than the latter. The reference independent technique provides equilibrium parameters which still include some effects of major screening contributions arising from the solvent.

The effect of isotopic substitution upon the equilibrium interaction has also been discussed. The differences in values for K and Δ_c for the two reactions benzene + chloroform and $[^2H_6]$benzene + chloroform have been attributed to differences in the level of stabilisation of the complex by C-H and C-D bonds.

The proof of the validity of the modified Benesi-Hildebrand equation show that much of the data which has previously been obtained are invalidated because they were obtained over the whole concentration range, (i.e. $0<x_B<1$). However, appropriate reinterpretation of these superficially invalid data was found to be useful for investigating the proposed[39,40] variations of equilibrium parameters with sample composition. Using data for several solutes each in the same aromatic (benzene) and inert solvent (cyclohexane), the variation was established and interpreted. The nature of the variation observed was quantified and used to deduce a mechanism for complex formation, based on a solvent cage model. The variation of chemical shifts with sample composition was shown to be consistent with the predictions of the model. However, since chemical shifts reflect averaged solute

environments, it was thought necessary to justify this mechanism by the use of an alternative technique. The measurement of spin-lattice relaxation times was chosen for this purpose because, although T_1 is a bulk parameter, it may be readily analysed in terms of basic molecular interactions and molecular motions.

The preparation of samples used for relaxation time studies was shown to be generally difficult if normal deoxygenating techniques were used. A versatile chemical procedure was developed, which enables reproducable results to be obtained, and which facilitates the preparation of samples containing more than one component. Comparisons with other techniques showed the procedure to be a very efficient method for removing oxygen, and the accuracy of the multi-component sample preparation technique was shown to be of a high order.

The investigations into the mechanism of complex formation using spin-lattice relaxation times were approached in a similar way to the measurement of chemical shifts. The variation of T_1 over the range of composition $0<x_B<1$ was measured for benzene and cyclohexane in mixtures of $[^2H]$ chloroform, benzene and cyclohexane. $[^2H]$chloroform was used as a polar solute in order to reduce the system to one of two spin types, and because it acts as a non-inert diluent. The results obtained from these studies showed general concurrence with the previously proposed solvent cage model, and provided further proof of its authenticity.

9.2. Some Suggestions For Future Research.

The conclusions which have been drawn during this thesis show that, whilst it is now possible to obtain values for K

and Δ_c accurately from chemical shift measurements, the use of spin-lattice relaxation times may, in future, prove to have more value. Using this technique it may be possible to investigate, in detail, the true nature of complex formation. A knowledge of the way in which complexes are formed between simple molecules will certainly lead to a better understanding of other interactions occuring in some more important systems, especially the biological and pharmaceutical systems which are of considerable current interest.

In this thesis the reported work on spin-lattice relaxation times has shown that even a qualitative treatment is of worthwhile value. Investigations based on quantitative methods and interpretation would yield much more information. In this way, the use of the equations applicable to systems with chemical exchange may prove to be useful. Those derived by McConnell[96], and Hoffman and Forsen[120-123] may be of special interest. The technique of deuteration may also prove to be useful: for example, a study of the chloroform-benzene-[$^2H_{12}$]cyclohexane system in a similar way to the system reported in Chapter 8 would prove to be complementary to the conclusions drawn from the investigations reported therein, because variations in T_1 values for chloroform could be observed.

The use of the nuclear Overhauser effect is becoming increasingly important in the solution of structural and stereochemical problems. In the context of molecular interactions it will, no doubt, be an extremely valuable parameter. Similarly, a knowledge of the parameters T_{BA} and T_{AB} in Solomon's equations[95] will enable a clearer and more precise knowledge to be obtained about interactions occurring between

different molecules in solution. Of particular interest will be the relaxation interactions relevant to the aromatic-solvent, solute-aromatic and solute-solvent pairs. The calculation of the magnitude of these interactions will enable the basic solvent cage model proposed in this thesis to be considerably refined, and, perhaps, provision may be made in the equations describing the model for the dynamic nature of the molecular constituents of the liquid in which such interactions occur.

The use of the chemical shift in the context of molecular complexes may be of interest, if only used for the investigation of solvent effects. The results reported in Chapters 5 and 6 show that solvent effects, especially those arising from dispersion and electric field contributions, are significant. It is apparent that much work needs to be done so that these effects can be accurately assessed and allowed for in subsequent calculations. However, it appears that this is of less importance than the continued examination of molecular complexes by the use of spin-lattice relaxation times, and related parameters.

APPENDIX

METHODS FOR THE EVALUATION OF RELAXATION TIMES IN TWO-SPIN SYSTEMS.

A.1. Introduction.

The basic equations[75] describing the relaxation characteristics of a system of two spins have been discussed in Chapter 2, and the method used by Hoffmann and Forsen[123] to evaluate the relaxation times in these equations has been investigated in Chapter 4. Preliminary experiments, undertaken to assess the accuracy of Hoffmann and Forsen's method were not promising. Using a sample of chemically deoxygenated toluene the satisfactory values for T_{AA} and T_{BB} of 17.79s and 9.84s respectively were measured. (Spin A refers to the ring protons, and spin B to the methyl protons). However, the steady state Overhauser effects, η_{∞}^{A} and η_{∞}^{B}, were found to be 0.115 and 0.086 respectively. Using the relationships shown in Section 4.3.2. (equations 4.47 and 4.48.), values for T_{BA} and T_{AB} of 92.82s and 189.60s respectively were calculated. The ratio of T_{BA}: T_{AB} is theoretically equal to the ratio of the number of protons of B to the number of protons of A, i.e. M_{o}^{B}: M_{o}^{A}. For toluene, this ratio is 0.6, but the experimental results give a ratio of 0.49. Similar discrepancies existed between theoretical predictions and experimental results for samples of p-xylene.

These errors are possibly due to inaccuracies in measurements of η_{∞}, which are much smaller than those measured by Hoffmann and Forsen[123]. Consequently, it appears that much care would be required to obtain accurate results, even if η_{∞} is large. Therefore it was decided that the equations for two-spin systems should be re-examined in order that a more

accurate and reliable procedure could be derived.

Two distinct methods of analysis have been attempted, both being based on Solomon's equations[95] which are reproduced here for convenience.

$$\frac{dM_z^A}{dt} = \frac{M_o^A - M_z^A}{T_{AA}} + \frac{M_o^B - M_z^B}{T_{BA}} \qquad \text{A.1.}$$

$$\frac{dM_z^B}{dt} = \frac{M_o^A - M_z^A}{T_{BA}} + \frac{M_o^B - M_z^B}{T_{BB}} \qquad \text{A.2.}$$

The two methods will now be discussed, but it should be pointed out that the results obtained by their use by the author have not been accurate enough to warrant their inclusion in the relevant parts of this thesis. However, both the procedures are promising, and are included here for this reason. Indeed, Cooke[271] has shown that, by suitable modification of the computing procedures employed, more realistic results may be obtained.

It is apparent that equations A.1. and A.2. refer solely to two nuclear types, either contained in the same molecule, or two different molecules (i.e. a liquid mixture), which are distributed in a molecularly isotropic liquid. However, in this thesis, the prime consideration is that of specific molecular interactions, and therefore allowance should be made in these equations for chemical exchange phenomena.

McConnell[96] has considered the case of a single type of resonant nucleus, which is allowed to exchange between different environments. He has obtained reasonable results for the effect of such exchange on relaxation times by constructing pseudo-fast-exchange equations, and defining

different time constants for the nucleus in each environment. Hoffmann and Forsen[120-123] have considered similar systems. However, it is difficult to extrapolate these ideas to systems of two spins, which, even without the complicating factor of chemical exchange, have proved difficult to investigate for the reasons given previously. The author is of the opinion that, at present, more importance lies in obtaining reasonable results for T_{AB} and T_{BA}. Only when these can be accurately measured will the real effects of chemical exchange on relaxation times be estimated for systems containing two or more types of resonant nuclei.

A.2. Method 1.

It is obvious from a consideration of Solomon's equations (A.1. and A.2.), that a knowledge of T_{AA}, dM_z^A/dt, $M_o^A - M_z^A$ and $M_o^B - M_z^B$ at a given time enables the calculation of T_{BA}. Similarly a knowledge of T_{BB} and dM_z^B/dt enables the calculations of T_{AB}.

T_{AA} and T_{BB} may be found easily by the method due to Hoffmann and Forsen, which is described in Chapter 4. In order to find the other variable parameters it is necessary to perform an A.F.P.S. experiment on both resonances at once if the use of the apparently unreliable N.O.E. method is to be avoided. The data obtained may then be fitted by a computer to a polynomial equation for the decay, which may be differentiated to give dM_z^A/dt and dM_z^B/dt, and may also be used to calculate values for $M_o^A - M_z^A$ and $M_o^B - M_z^B$ at any given time. These calculated values may then be used to obtain values for T_{BA} and T_{AB}. Samples of toluene and p-xylene were used to test the method, but the results were not encouraging. For toluene, the ratio of T_{BA} to T_{AB} was found to vary between

0.14 and 0.35 depending upon the time chosen to calculate the variables, and for p-xylene the ratio varied between 0.5 and 0.7 (theoretical value 1.5).

There are two main reasons for this variation. Firstly, when comparing the decays of the magnetisations of two coupled spins, the relative time scale between them is important, although, as for A.P.F.S. experiments performed on single-spin systems, the absolute time scale is unimportant. Since there is a finite time lag between the two resonances when the pulse is applied, the time scales are different for the two resonances. In order to overcome this problem saturation-recovery experiments (described in Section 3.4.2.) were performed on toluene and p-xylene. Using this technique the time scales are the same because M_o^A and M_o^B are initially zero. The ratios obtained for T_{BA}/T_{AB} for toluene and p-xylene varied between 0.14 and 1.2, and 0.3 and 2.0 respectively. Whilst the theoretical values now fall within these ranges, the results are certainly not of useable accuracy.

The second reason for the variations have been communicated to the author by Cooke[271]. Cooke has found that the type of procedure used in the computer program to fit a polynomial to the decay curve is not totally suitable in these circumstances. This is because the polynomial coefficients are deduced on the basis of the diagonal of a matrix. If the data points are evenly spaced the polynomial is not accurate unless the data is of a linear nature, because equal spacing of data in the matrix diagonal occurs; this results in the procedure not being able to iterate properly on the data. Unfortunately, shortage of time did not allow other more suitable procedures to be tried.

A.3. Method 2.

This procedure is more complicated than the method described above, as it involves the integration of equations A.1. and A.2., and interpretation of the double exponential equation obtained in terms of the polynomial describing the decays of M_o^A and M_o^B after suitable perturbation (i.e. an adiabatic fast passage or saturation). Equations A.1. and A.2. may be written:

$$\frac{dM_z^A}{dt} = -\frac{M_z^A}{T_{AA}} - \frac{M_z^B}{T_{BA}} + \left(\frac{M_o^A}{T_{AA}} + \frac{M_o^B}{T_{BA}}\right)$$

$$\frac{dM_z^B}{dt} = -\frac{M_z^A}{T_{AB}} - \frac{M_z^B}{T_{BB}} + \left(\frac{M_o^A}{T_{AB}} + \frac{M_o^B}{T_{BB}}\right) \qquad \text{A.3.}$$

which may be written:

$$\frac{dx}{dt} = ax + by + c$$

$$\frac{dy}{dt} = dx + ey + f \qquad \text{A.4.}$$

By shifting the origin of the axes of the coordinates (x,y) to the intersection (h,k) of the lines:

$$ax + by + c = 0$$

$$dx + ey + f = 0 \qquad \text{A.5.}$$

new coordinates (X,Y) are defined in which equations A.4. become:

$$\dot{X} = \alpha X + \beta Y$$

$$\dot{Y} = \gamma X + \delta Y \qquad \text{A.6.}$$

where $X = x - h$ and $Y = y - k$. It is found that $h = M_o^A$ and $k = M_o^B$; thus A.4. becomes:

$$\dot{X} = aX + ah + bY + bk + c$$

$$\dot{Y} = dX + dh + eY + ek + f \qquad \text{A.7.}$$

or, since

$$(ah + bk + c) = (dh + ek + f) = 0$$

$$\dot{X} = aX + bY$$

$$\dot{Y} = dX + eY \qquad \text{A.8.}$$

These two first order simultaneous differential equations have the solution:

$$X = A_1 e^{k_1 t} + A_2 e^{k_2 t}$$

$$Y = B_1 e^{k_1 t} + B_2 e^{k_2 t} \qquad \text{A.9.}$$

where k_1 and k_2 are the roots of:

$$(k - a)(k - e) - bd = 0 \qquad \text{A.10.}$$

or, in this case!

$$(k + 1/T_{AA})(k + 1/T_{BB}) - 1/T_{AB}T_{BA} = 0 \qquad \text{A.11.}$$

For this quadratic equation the following conditions apply:

$$k_1 + k_2 = - 1/T_{AA} - 1/T_{BB}$$

$$k_1 k_2 = 1/T_{AA}T_{BB} - 1/T_{AB}T_{BA} \qquad \text{A.12.}$$

from which it is apparent that T_{AB} and T_{BA} still may not be separated.

Equations A.9. may be expanded to:

$$M_z^A = A_1 e^{k_1 t} + A_2 e^{k_2 t} + M_o^A$$

$$M_z^B = B_1 e^{k_1 t} + B_2 e^{k_2 t} + M_o^B \qquad \text{A.13.}$$

which may in turn be expanded into a polynomial. Assuming that k_1 and k_2 are negative, a convergent series may be formed; for example:

$$M_z^A = A_1(1 - k_1t + (k_1t)^2/2! \text{------})$$

$$+ A_2(1 - k_2t + (k_2t)^2/2! \text{------})$$

$$+ M_o^A \qquad \text{A.14.}$$

which is of the form:

$$x = P_o - P_1(t) + P_2(t^2) - P_3(t^3) \text{ ----}$$

where:

$$P_o = A = A_1 + A_2 + M_o^A \qquad \text{A.15.}$$

$$P_1 = B = -(A_1k_1 + A_2k_2) \qquad \text{A.16.}$$

$$P_2 = C = (A_1k_1^2 + A_2k_2^2)/2 \qquad \text{A.17.}$$

$$P_3 = D = -(A_1k_1^3 + A_2k_2^3)/6 \qquad \text{A.18.}$$

$$P_4 = E = (A_1k_1^4 + A_2k_2^4)/24 \qquad \text{A.19.}$$

Multiplying A.16. by k_1 and adding A.17:

$$Bk_1 + C = Ak_2(k_2 - k_1) \qquad \text{A.20.}$$

Multiplying A.16. by k_2 and adding A.17:

$$Bk_2 + C = Ak_1(k_1 - k_2) \qquad \text{A.21.}$$

Multiplying A.18. by k_1 and adding A.19:

$$Dk_1 + E = Ak_2^3(k_2 - k_1) \qquad \text{A.22.}$$

Multiplying A.18. by k_2 and adding A.19:

$$Dk_2 + E = Ak_1^3(k_1 - k_2) \qquad \text{A.23.}$$

Therefore:

$$(Bk_1 + C)k_2^2 = Dk_1 + E \qquad \text{A.24.}$$

and:

$$(Bk_2 + C)k_1^2 = Dk_2 + E \qquad \text{A.25.}$$

Thus, adding A.24. and A.25.:

$$(k_1 + k_2)(Bk_1k_2 - D) - 2E + C\,(k_1 + k_2)^2 - 2Ck_1k_2 = 0 \qquad \text{A.26.}$$

and, subtracting A.24. and A.25.:

$$(Bk_1k_2 + D) + C(k_1 + k_2) = 0 \qquad \text{A.27.}$$

Rearrangement of equations A.26. and A.27. gives:

$$k_1k_2 = (D^2 - CE)/(C^2 - BD) \qquad \text{A.28.}$$

and:

$$k_1 + k_2 = (CD - BE)/(C^2 - BD) \qquad \text{A.29.}$$

Comparison with equations A.12. shows that k_1 and k_2 are roots of the equation:

$$k^2(C^2 - BD) + k(CD - BE) + (D^2 - CE) = 0 \qquad \text{A.30.}$$

from which the roots k_1 and k_2 can be calculated. In order that the series is to be convergent, k_1 and k_2 must both be negative, as stated earlier.

Multiplying A.15. by k_2 and adding A.16.:

$$A_1 = (k_2(A - M_o^A) + B)/(k_2 - k_1) \qquad \text{A.31.}$$

Multiplying A.15. by k_1 and adding A.16:

$$A_2 = (k_1(A - M_o^A) + B)/(k_1 - k_2) \qquad \text{A.32.}$$

Similarly, using the second of equations A.13. expressions may be found for k_1, k_2, B_1 and B_2. k_1 and k_2 should be defined by the same equation as A.30. The accuracy of the two sets of values serves as a check.

In equations A.13., parts of the equations may be considered as solutions for M_z. This is certainly true for the case where M_z^B or M_z^A is reduced to zero by saturation. Thus:

$$M_z^A = A_1 e^{k_1 t} + M_o^A = A_2 e^{k_2 t} + M_o^A \qquad \text{A.33.}$$

$$M_z^B = B_1 e^{k_1 t} + M_o^B = B_2 e^{k_2 t} + M_o^B \qquad \text{A.34.}$$

$$dM_z^A/dt = k_1 A_1 e^{k_1 t} = k_2 A_2 e^{k_2 t} \qquad \text{A.35.}$$

$$dM_z^B/dt = k_1 B_1 e^{k_1 t} = k_2 B_2 e^{k_2 t} \qquad \text{A.36.}$$

Substituting in A.3., it is found that:

$$T_{BA} = (B_1 A_2 - B_2 A_1)/(A_1 A_2)(k_2 - k_1) \qquad \text{A.37.}$$

and:

$$T_{AA} = - T_{BA} A_2/(B_2 + T_{BA} A_2 k_2) \qquad \text{A.38.}$$

Similarly:

$$T_{AB} = (A_1 B_2 - A_2 B_1)/(B_1 B_2)(k_2 k_1) \qquad \text{A.39.}$$

and:

$$T_{BB} = - T_{AB} B_2/(A_2 + T_{AB} B_2 k_2) \qquad \text{A.40.}$$

Thus, all four relaxation times are defined in terms of A_1, A_2, B_1, B_2, k_1 and k_2.

It is apparent from the foregoing derivation that, if a computer is used to fit a polynomial equation to the decays of the magnetisations of spins A and B, this may be interpreted, in terms of the polynomial coefficients, to give values for T_{BA} and T_{AB}, as well as T_{AA} and T_{BB}.

The results which have been obtained by this method are, however, not immediately encouraging. Occasionally, negative values for relaxation times have been calculated. This absurdity is, as with Method 1, attributed[271] to the nature of the curve-fitting procedure employed.

Unfortunately, it has not been possible to try other curve fitting procedures, but Cooke[271] has done this, and although his method is, as yet, unrefined, it results in the calculation of more reasonable values for all parameters. Indeed, the values for T_{AA} and T_{BB} calculated by Cooke, using this approach, are very similar in magnitude to those reported in Chapter 8.

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Molecular Complexes

Part 10.[1]—Theory for Complex Formation and Nuclear Magnetic Resonance Evidence for Short Range Molecular Order in Liquids

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For reactions of the type $A+B \rightleftharpoons AB$ occurring in the presence of an inert solvent, S, it is shown that the aromatic induced n.m.r. chemical shift, Δ_c, varies with the composition of the mixtures studied in a similar fashion to the equilibrium quotient, K_x. This is explained in terms of a model based on short range order in liquids, which allows aromatic molecules, B, to be preferentially attracted to the solute, A, in the form of solvation shells; experimental and theoretical justification of this is given. The cage model used to describe the formation of bimolecular complexes requires that a polar solute (A) exchanges rapidly between a limiting number of aromatic molecules in the solvation shells, which in turn exchange with molecules in the surrounding medium. The model is used to explain the variation in observed shifts caused by complex formation.

Nuclear magnetic resonance studies of molecular complexes, often involving aromatic molecules with a polar molecule (solute) in an inert solvent, have been the subject of considerable interest for several years.[2, 3] The main parameters pertaining to the formation of these complexes are the equilibrium quotient, K_x, and the chemical shift, Δ_c, induced in the solute in the complex. The main problem with investigations of this type has been the absence of wholly dependable data processing procedures for obtaining K_x and Δ_c. As a result, the values for K_x and Δ_c that have been reported may be of questionable significance. It is not surprising, therefore, that a reasonable model for the complex formation has not been forthcoming. Recently,[4] it has been shown that K_x (an equilibrium quotient devoid of activity coefficients) must depend on the composition of the solution or mixture studied. We now wish to demonstrate that Δ_c must vary similarly, and from this variation derive a model for the formation of complexes.

DATA PROCESSING

1. GENERAL CONSIDERATIONS

Several procedures are available for processing n.m.r. data but most, if not all, neglect the influence of activity coefficients in equilibrium expressions. A critical examination of the effect of this on the widely used Benesi–Hildebrand [5] and Creswell–Allred [6] procedures has been discussed fully elsewhere.[4, 7] The approximations in the Benesi–Hildebrand approach make it impossible to obtain values for K_x and Δ_c over the whole concentration range. However, the alternative procedure to which we now confine our attention does permit this in principle, but in fact only average values, corresponding to a particular range of compositions, can be obtained.

The Creswell–Allred method depends on the familiar equation [8] (1)

$$\delta_{obs} = \frac{n_{AB}}{n_A}\Delta_c + \delta_{free} \tag{1}$$

where δ_{obs} is the observed chemical shift, and δ_{free} the chemical shift of the uncomplexed solute from the reference; n_{AB} is the equilibrium number of moles of complex AB, and n_A is the initial number of moles of solute, A. An iterative procedure [9] is employed which selects arbitrary values of K_x and calculates values of n_{AB}/n_A from eqn (2)

$$K_x = \frac{n_{AB}(n_A + n_B + n_S V_S/V_B - n_{AB})}{(n_A - n_{AB})(n_B - n_{AB})}\left(\frac{\gamma^R_{AB}}{\gamma^R_A \cdot \gamma^R_B}\right) \tag{2}$$

neglecting $(\gamma^R_{AB}/\gamma^R_A \cdot \gamma^R_B)$; in eqn (2) γ^R_i is the Raoult activity coefficient of species i, n_B and n_S are the initial numbers of moles of aromatic, B, and inert solvent, S, respectively and V_B and V_S are the molar volumes of B and S respectively. The iteration proceeds in order to obtain a value for K_x such that the corresponding values of n_{AB}/n_A and the observed shifts over a range of concentrations conform with the linearity of eqn (1). Since shifts over a range of concentration are measured (and it is reasonable to suppose that γ^R_A and γ^R_{AB} are approximately equal [4]), the equilibrium quotient in fact must correspond to $\overline{K}_x$ given by eqn (3)

$$\overline{K}_x = \underline{K}C\overline{\gamma^R_B} \tag{3}$$

$\overline{K}_x$ is an average equilibrium quotient for complex formation, and is related to the true constant by $\overline{\gamma^R_B}$, which is the average Raoult activity coefficient of the aromatic component in the samples studied, and C, which is a constant. In the iterative procedures employed, e.g. COMPLEXICON,[9] it is assumed that K_x is a constant for a chosen range of concentrations, and the " best " value of Δ_c that makes eqn (1) linear is calculated. For different ranges of composition $\overline{\gamma^R_B}$ is different, so calculations must result in different values for $\overline{K}_x$ assuming that Δ_c is constant for the chosen range.

Recent work [4] has indicated that Δ_c may vary with the composition of liquid mixtures. Consequently, if K_x and Δ_c both vary with composition iterative procedures of analysis merely provide numbers, supposedly reflecting the magnitude of these parameters but whose physical meaning is obscure. In fact, at a series of different compositions identified by a, b, c . . ., the actual equations corresponding to eqn (1) will be:

$$\delta^a_{obs} = \frac{n^a_{AB}}{n_A}\Delta^a_c + \delta_{free} \tag{4}$$

$$\delta^b_{obs} = \frac{n^b_{AB}}{n_A}\Delta^b_c + \delta_{free} \tag{5}$$

$$\delta^c_{obs} = \frac{n^c_{AB}}{n_A}\Delta^c_c + \delta_{free}, \text{ etc.} \tag{6}$$

Therefore, the analysis must correspond to a rationalisation of the data in terms of the eqn (7)

$$\delta^*_{obs} = \frac{n^*_{AB}}{n_A}(\Delta'_c + M^*) + \delta_{free} \tag{7}$$

where M^* represents a variation in the basic shift Δ_c'. Obviously a plot of δ^*_{obs} against n^*_{AB}/n_A can only be linear if eqn (8) holds;

$$M^* = Q(n_A/n^*_{AB}) \tag{8}$$

Q is a constant for the chosen value of $\overline{K}_x$ but differs for different ranges of concentrations considered, as does $\overline{K}_x$. It is, therefore, possible to relate a known variation in K_x to one in Δ_c because n_A/n^*_{AB} is a function of $\overline{K}_x$.

2. APPLICATIONS

RESULTS

To test the suggestions made we have obtained data [10] for the interaction between methyl iodide, methylene chloride, vinyl cyanide, methylene bromide, dimethylformamide, chloroform, methylene iodide, trichloroethylene and nitroform, separately with benzene (B) in the presence of cyclohexane (S) as the inert solvent. The data are presented in table 1. In comparisons between features of these reactions in this series, variations of γ^R_B at any particular concentration are eliminated since this parameter is constant for a given concentration in all systems (i.e. it is possible to make comparisons between sets of data).

The data were processed using COMPLEXICON [9] in the following manner. From the sets of data obtained (values of n_A, n_B, n_S and δ_{obs} for each sample) sets were discarded one at a time starting at the $x^{corr}_B = 1$ end of the scale [$x^{corr}_B = n_B/(n_A+n_B+n_SV_S/V_B)$]. For the remaining data the values of $\overline{K}_x$ and Δ_c were evaluated. Even at the low mole fraction end of the scale there were usually enough data sets to give accurate values of $\overline{K}_x$ and Δ_c. Graphs were plotted of $\overline{K}_x$ and Δ_c against the highest value of x^{corr}_B in the set of data processed.

TABLE 1.—THE VARIATION OF ^{1}H CHEMICAL SHIFTS (HZ AT 60 MHZ RELATIVE TO INTERNAL CYCLOHEXANE) WITH THE INITIAL COMPOSITION OF REACTANT MIXTURES OF VARIOUS POLAR SOLUTES WITH BENZENE AT 306.6 K

solute	moles of solute $\times 10^4$	moles of benzene $\times 10^2$	moles of cyclohexane $\times 10^2$	$-\delta_{obs}$/Hz
methyl iodide	1.9163	0.0000	2.0425	33.08
	0.7539	0.1733	1.2723	27.20
	0.5566	0.2875	0.9942	23.03
	1.6063	0.8567	1.2680	16.94
	1.5006	0.9817	1.0039	13.62
	1.0075	0.9984	0.9955	13.87
	1.6979	0.9523	0.6061	10.89
	1.1061	1.2300	0.5010	8.26
	0.9300	1.3607	0.3219	6.38
	1.0357	1.5480	0.1562	4.14
methylene chloride	1.6484	0.0000	1.2255	220.27
	1.5188	0.0836	1.2517	214.72
	1.0126	0.1235	1.2323	212.40
	2.1311	0.3128	1.2068	204.40
	1.4717	0.5397	1.2144	197.82
	1.6601	0.8713	1.2416	192.58
	1.9780	1.2310	1.2296	188.64
	2.6020	1.8405	1.2242	184.81
	1.8721	1.4095	0.6278	182.00
	3.6264	2.6457	0.6126	178.90

TABLE 1—*continued*

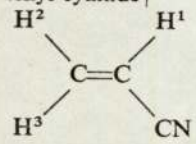
solute	moles of solute $\times 10^4$	moles of benzene $\times 10^2$	moles of cyclohexane $\times 10^2$	$-\delta_{obs}$/Hz	
vinyl cyanide† 	19.883	0.0000	4.8002	243.64	
	19.393	0.0910	4.5970	241.90	
	18.884	0.2458	4.5404	239.22	
	18.865	0.3001	4.4077	237.97	
	20.184	0.4085	4.3564	236.54	
	21.409	0.5537	4.2581	234.33	
	22.955	0.9720	3.7526	228.12	
	18.865	1.4780	3.3024	220.85	
	22.691	2.0117	2.7723	215.83	
	21.051	2.4462	2.3644	211.38	
	20.354	3.0254	1.8346	206.49	
	20.071	3.4304	1.5178	203.67	
	19.224	3.6417	1.1859	201.85	
	21.862	3.8851	0.8772	199.04	
	18.074	4.0575	0.7451	198.72	
	20.561	4.2657	0.5886	198.16	
	20.392	4.3986	0.3724	197.34	
	19.770	4.4150	0.2305	196.48	
	19.223	4.7106	0.0490	195.43	
methylene bromide	0.8743	0.0000	1.2555	199.43	
	1.6279	0.0690	1.2624	194.51	
	1.4553	0.1343	1.2579	190.90	
	1.6854	0.3070	1.2641	183.90	
	1.7199	0.5487	1.2392	177.30	
	2.8934	0.8193	1.2487	173.11	
	2.8359	1.2172	1.2704	168.95	
	3.3190	1.8418	1.2280	164.51	
	1.9270	1.4180	0.6893	162.01	
	3.9000	2.4044	0.6602	158.98	
				α methyl	β methyl
dimethylformamide	1.6691	0.0000	1.2457	81.36	78.34
	1.9837	0.0608	1.2255	77.63	76.65
	1.6280	0.1258	1.2547	74.37	74.94
	1.8332	0.3161	1.2536	66.52	71.60
	2.1205	0.4925	1.2401	61.70	69.50
	2.3805	0.8416	1.3044	55.35	66.69
	2.4215	1.2153	1.2288	50.33	64.72
	3.3929	1.8399	1.2641	46.05	63.19
	2.4352	1.5182	0.6169	41.61	61.88
	3.3382	2.4721	0.6299	38.34	60.93
chloroform	0.7849	0.1650	2.4988	332.56	
	1.2222	0.4615	2.4984	324.45	
	1.9551	0.6323	2.5004	321.23	
	1.6251	0.6285	2.4986	321.13	
	1.1183	0.4160	1.2584	317.16	
	1.0429	1.0271	1.2484	306.01	
	1.5295	1.5295	1.2494	301.43	
	0.9223	1.1813	0.6275	297.15	
	0.7473	1.0956	0.3314	293.47	

TABLE 1—*continued*

	1.2724	1.8868	0.3309	290.84
	0.9214	1.4353	0.1222	289.19
	0.8140	1.9047	0.1012	288.43
	0.8762	1.6585	0.0781	287.41
methylene iodide	1.1126	0.0000	1.2540	137.95
	1.1985	0.0646	1.2490	133.49
	1.3665	0.1363	1.2204	129.68
	1.5756	0.3080	1.2357	123.70
	1.7063	0.5067	1.2473	117.86
	1.9826	0.8553	1.2595	112.27
	2.3858	1.2579	1.2378	108.24
	2.7218	1.8216	1.2485	104.90
	1.8705	1.4588	0.6138	101.07
	3.1736	2.4086	0.6122	98.18
trichloroethylene	1.4232	0.0000	1.2583	291.35
	1.1720	0.0591	1.2461	288.49
	1.3471	0.1467	1.2490	285.21
	1.5602	0.3186	1.2518	279.72
	1.7657	0.5363	1.2466	274.87
	2.1006	0.8290	1.2496	270.64
	2.4050	1.2493	1.2586	266.66
	3.0900	1.8735	1.2535	263.13
	2.0016	1.4674	0.6247	259.69
	3.1128	2.4894	0.6180	256.72
nitroform	3.794	0.000	3.746	339.65
	1.576	0.010	1.000	331.16
	1.582	0.031	1.000	318.00
	1.649	0.064	0.999	303.87
	1.688	0.111	1.000	290.31
	2.019	0.334	1.000	265.36
	3.072	1.000	1.000	249.13
	6.104	2.999	1.000	242.72
	1.549	0.899	0.100	240.92
	3.052	1.899	0.100	240.73

† Only the shifts for one proton (H^1) are used for the vinyl cyanide–benzene interaction; because all three proton shifts were derived from ABC spectral analyses, each should have the same deviation characteristics, as shown in the dimethylformamide–benzene interaction.

For each of the nine systems studied the values of $\bar{K}_x$ and Δ_c were both found to vary with the range of composition chosen. The variations are typified in fig. 1 from which it can be seen that $\bar{K}_x$ and Δ_c are reasonably constant above a certain value of x_B^{corr} but below this vary significantly. The graphs of $\bar{K}_x$ against x_B^{corr} rise from the linear region, whereas for the Δ_c plot, the values fall below the linear portion. The variations in values of $\bar{K}_x$ are to be expected to some degree because of variations in in $\gamma_B^{\bar{R}}$,[11] but we find that for the different systems $\bar{K}_x$ and Δ_c start to vary from the approximately linear region at quite different values of x_B^{corr}. The values of x_B^{corr} at the point of deviation are shown in table 2 for all of the reactions considered. Graphs of K_x against x_B^{corr} of the shape shown in fig. 1 have been obtained also in this laboratory from studies of molecular complexes using a phase distribution approach.[1]

It is interesting to note that a plot of $\overline{K}_x\Delta_c$ against x_B^{corr} is also linear above a certain point, thus explaining the unexpected wide ranging linearity of Benesi–Hildebrand [5] plots.

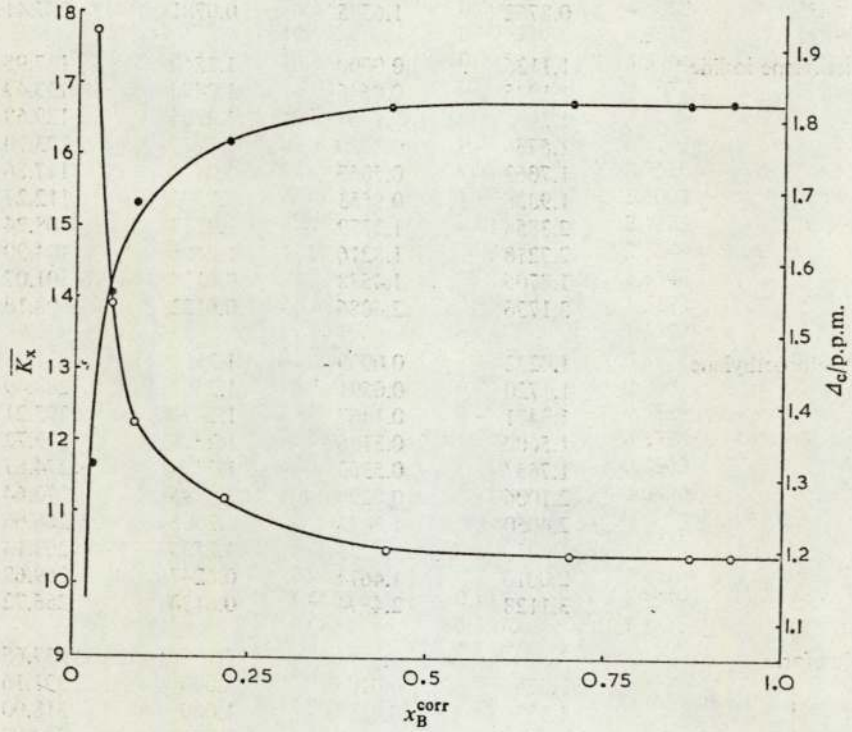


FIG. 1.—Variation of $\overline{K}_x$ (○) and Δ_c (●) with x_B^{corr} for the nitroform + benzene reaction occurring in cyclohexane at 306.6 K.

TABLE 2.—VALUES OF THE MOLAR VOLUMES, V, FOR ALL COMPOUNDS USED, AND THE CORRESPONDING APPROXIMATE VALUES OF $x_{B(lim)}^{corr}$, $\overline{K}_{x(lim)}$, AND $\Delta_{c(lim)}$ FOR THE REACTIONS OF THE VARIOUS SOLUTES WITH BENZENE, IN THE PRESENCE OF CYCLOHEXANE AT 306.6 K

compound	$V \times 10^6$/m^3 mol^{-1}	$x_{B(lim)}^{corr} \pm 0.02$	$\overline{K}_{x(lim)}$	$\Delta_{c(lim)}$/Hz
benzene	90.3269	—	—	—
cyclohexane	109.8298	—	—	—
methyl iodide	62.2544	0.30	1.12	57.2
methylene chloride	63.6180	0.28	1.32	86.2
vinyl cyanide	65.8313	0.30	1.33	86.9
methylene bromide	69.7604	0.30	1.74	70.3
dimethylformamide	77.3954	0.36	0.96 [a] 1.19 [b]	104.2 [a] 40.0 [b]
chloroform	80.0349	0.40	1.58	85.3
methylene iodide	80.5527	0.36	1.33	79.7
trichloroethylene	89.8700	0.50	0.97	81.0
nitroform	102.1231	0.55	10.40	109.4

[a] $\overline{K}_{x(lim)}$ and $\Delta_{c(lim)}$ from the dimethyl formamide α-methyl shifts. [b] $\overline{K}_{x(lim)}$ and $\Delta_{c(lim)}$ from the dimethylformamide β-methyl shifts.

DISCUSSION

The onset of the major variations in $\overline{K}_x$, and hence Δ_c, cannot be explained completely by the effect of the variation in $\overline{\gamma}_B^R$. This can be shown by correcting $\overline{K}_x$ for variations in $\overline{\gamma}_B^R$; the values of $\overline{\gamma}_B^R$ below the chosen values of x_B^{corr} were evaluated from

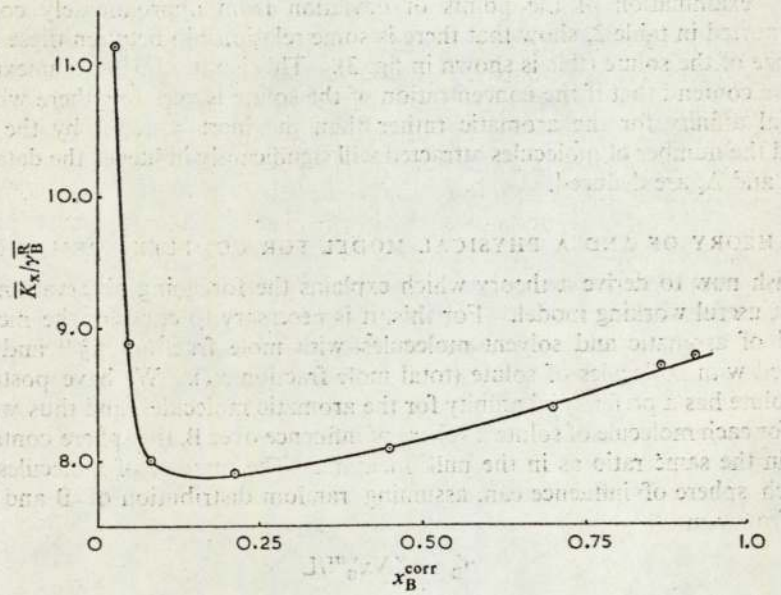


FIG. 2.—Variation of $\overline{K}_x/\overline{\gamma}_B^R$ with x_B^{corr} for the nirtoform + benzene reaction occurring in cyclohexane at 306.6 K.

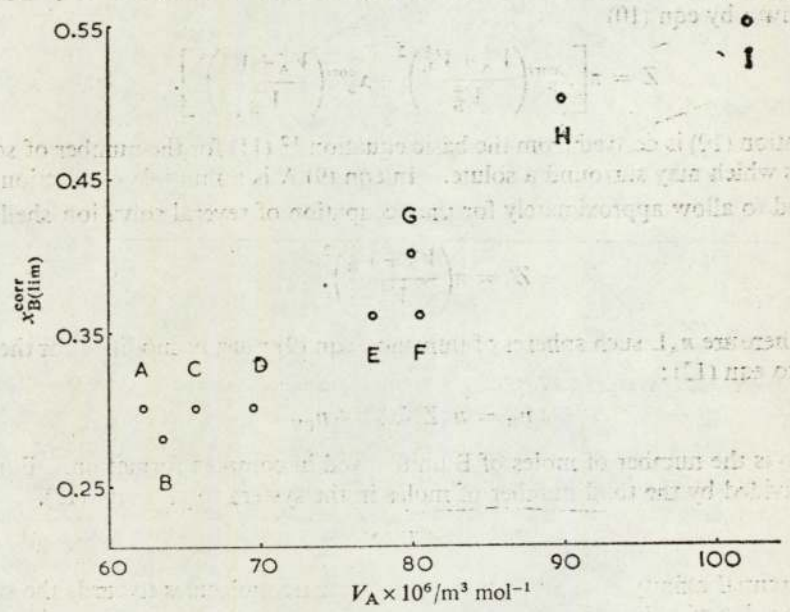


FIG. 3.—The variation of $x_{B(lim)}^{corr}$ with the molar volume (V_A) of the solute. A, methyl iodide; B, methylene chloride; C, vinyl cyanide; D, methylene bromide; E, dimethylformamide; F, chloroform; G, methylene iodide; H, trichloroethylene; I, nitroform.

a plot of γ_B^R against x_B, which was deduced from the results of Scatchard *et al.*[11] A typical plot, in fig. 2, of $\overline{K}_x/\overline{\gamma}_B^R$ against x_B^{corr} is still non-linear over part of its range.

It is apparent, therefore, that Δ_c in fact varies with the composition of the liquid mixture. Because a common aromatic, and inert solvent, was used for all the reactions studied the point of deviation obviously depends upon the polar solute used. A cursory examination of the points of deviation from approximately constant values, reported in table 2, show that there is some relationship between these points and the size of the solute (this is shown in fig. 3). This is not altogether unexpected because we contend that if the concentration of the solute is very low there will be a preferential affinity for the aromatic rather than the inert material by the polar solute and the number of molecules attracted will significantly influence the data from which $\overline{K}_x$ and Δ_c are deduced.

THE THEORY OF AND A PHYSICAL MODEL FOR COMPLEX FORMATION

We wish now to derive a theory which explains the foregoing observations and provides a useful working model. For this, it is necessary to consider the medium, composed of aromatic and solvent molecules, with mole fractions x_B^{corr} and x_S^{corr}, interspersed with molecules of solute (total mole fraction x_A). We have postulated that the solute has a preferential affinity for the aromatic molecules, and thus we may consider for each molecule of solute a sphere of influence over B, the sphere containing B and S in the same ratio as in the bulk medium. The number of molecules of B within each sphere of influence can, assuming random distribution of B and S, be deduced from eqn (9)

$$n'_B = ZNx_B^{corr}/L \tag{9}$$

where Z is the number of molecules of B (and S) which can be fitted in one solvation shell round one solute molecule. Since Z is composed of molecules of B and S, it may be given by eqn (10)

$$Z = \pi\left[x_B^{corr}\left(\frac{V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}}}{V_B^{\frac{1}{3}}}\right)^2 + x_S^{corr}\left(\frac{V_A^{\frac{1}{3}}+V_S^{\frac{1}{3}}}{V_S^{\frac{1}{3}}}\right)^2\right]. \tag{10}$$

This equation (10) is derived from the basic equation [12] (11) for the number of solvent molecules which may surround a solute. In eqn (9) N is a multiple or fraction of Z, introduced to allow approximately for the occupation of several solvation shells.

$$Z' = \pi\left(\frac{V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}}}{V_B^{\frac{1}{3}}}\right)^2. \tag{11}$$

Because there are $n_A L$ such spheres of influence, eqn (9) must be modified for the bulk medium to eqn (12);

$$n_B = n_A ZNx_B^{corr} + n_{BU} \tag{12}$$

in this n_{BU} is the number of moles of B uninvolved in complex formation. Eqn (12) may be divided by the total number of moles in the system to give eqn (13).

$$x_B^{corr} = x_A x_B^{corr} ZN + x_{BU} \tag{13}$$

The preferential affinity of A for B will draw aromatic molecules towards the solute, and as the value of x_B^{corr} increases from zero, the volume in the immediate vicinity of A will be populated mostly by aromatic molecules, until x_B^{corr} reaches a limiting value, $x_{B(lim)}^{corr}$, at which point the solute is experiencing almost the maximum effects of the

aromatic in complex formation even though a small amount of S may be involved with A. At this point, therefore, the value of Z will tend to that described in eqn (11), and eqn (13) becomes (14)

$$x^{\text{corr}}_{\text{B(lim)}} = x_{\text{A}} x^{\text{corr}}_{\text{B(lim)}} \pi \left(\frac{V_{\text{A}}^{\frac{1}{3}} + V_{\text{B}}^{\frac{1}{3}}}{V_{\text{B}}^{\frac{1}{3}}} \right)^2 N' + x_{\text{BU}} \tag{14}$$

where N' is the limiting value of the constant N. Above the limiting value of $x_{\text{B}}^{\text{corr}}$, x_{BU} will increase, but parameters affected by the amount of B around A (i.e., $\bar{K}_x$ and Δ_c) will remain approximately constant and we may therefore equate $x^{\text{corr}}_{\text{B(lim)}}$ with the value of $x_{\text{B}}^{\text{corr}}$ at which $\bar{K}_x$ and Δ_c start to deviate from approximate linearity. In eqn (14) x_{A} may be designed to be a constant, and it may be postulated that at $x^{\text{corr}}_{\text{B(lim)}}$ the value of x_{BU} is a small constant. A plot of $x^{\text{corr}}_{\text{B(lim)}}$ against $x^{\text{corr}}_{\text{B(lim)}}[(V_{\text{A}}^{\frac{1}{3}} + V_{\text{B}}^{\frac{1}{3}}]^2$ should therefore be a straight line, with slope equal to $x_{\text{A}}\pi N'/V_{\text{B}}^{\frac{2}{3}}$ and intercept x_{BU}.

Fig. 4 shows that this plot is indeed a straight line for the reactions mentioned earlier. Using the average experimental value of $x_{\text{A}} = 0.012$ the slope yields a value of N' equal to 5.5 which corresponds to about two and a half solvation shells, and a value of x_{BU} of 0.07, both of which are reasonable values.

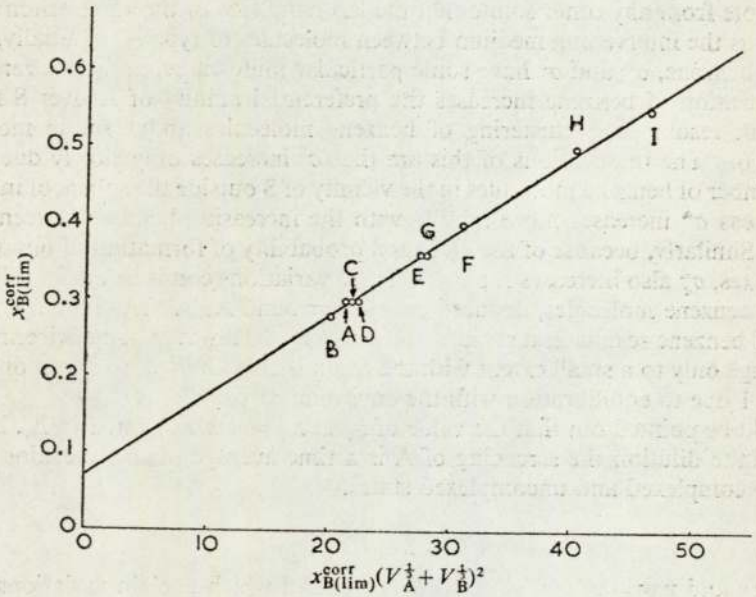


FIG. 4.—The plot of $x^{\text{corr}}_{\text{B(lim)}}$ against $x^{\text{corr}}_{\text{B(lim)}}\,(V_{\text{A}}^{\frac{1}{3}} + V_{\text{B}}^{\frac{1}{3}})^2$. A-I, see fig. 3.

AN EXPLANATION OF CHEMICAL SHIFTS IN TERMS OF THE PROPOSED MODEL FOR COMPLEX FORMATION

The implication of the foregoing arguments is that the molecular complex arises from short range ordering of the benzene molecules around the solute. However, the analytical procedures which led to this model assumed that the complex was entirely bimolecular. These conflicting concepts are accompanied by a further apparent paradox. This is that if Δ_c reaches a limiting value, how can the observed shift of A change with a further increase in benzene concentration? These problems can be elucidated by speculation on the detailed mechanism of complex formation in terms of the observed shift variation, δ_{obs}, and the short range ordered complex proposed earlier.

The observed shift, measured relative to an internal reference S, is conveniently divided into three contributions as in eqn (15)

$$\delta_{obs} = \sigma^A + \sigma_c^A - \sigma^S \tag{15}$$

where σ^A and σ^S are the non-bonded contributions of the medium to the screening of A and S respectively, and σ_c^A is the contribution to A by B in the bimolecular complex. The variation in each of these three screening terms can be appreciated by reference to (I).

(I)

Effectively, the right hand side of the schematic equilibrium represents the environmental structure around a particular solute molecule A at $x_B^{corr} = 0$, which is sufficiently remote from any other solute that the left hand side of the equilibrium can be considered as the intervening medium between molecules of type A. Initially, in the absence of benzene, σ^A and σ^S have some particular finite value, and σ_c^A is zero. As the concentration of benzene increases the preferential affinity of A over S for the aromatic, B, results in a clustering of benzene molecules about solute molecules (r.h.s. of (I)). The implications of this are that σ^S increases only slowly due to the smaller number of benzene molecules in the vicinity of S outside the sphere of influence of A, whereas σ^A increases more rapidly with the increasing benzene concentration about A. Similarly, because of the increased probability of formation of bimolecular AB complexes, σ_c^A also increases rapidly. These variations continue until the limiting number of benzene molecules, deduced earlier, surround A. After this stage further addition of benzene results in a rapid variation of σ^S. However, the environment of A can change only to a small extent with the result that both σ^A and σ_c^A can only vary until $x_B = 1$ due to equilibration with the environment of S.

It should be pointed out that the value of σ_c^A at $x_B = 1$ is not equal to Δ_c, because even at infinite dilution the screening of A is a time average of the screening values in the fully complexed and uncomplexed states.

CONCLUSIONS

A theory and working model have been deduced which explain variations in the parameters relating to the formation of molecular complexes. It is implicit in our proposals that Δ_c as well as K_x varies with the composition of the mixtures studied and values for these are most realistically obtained using equations of the Benesi–Hildebrand type at the limiting condition $x_B^{corr} = 1$. It is interesting that in addition to explaining many observable facts, our model, deduced by theoretical arguments, is consistent in some respects with that proposed by Engler and Laszlo.[13]

One of us (A. R. D.) thanks the S.R.C. for a Research Studentship.

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Molecular Complexes. Part XIII.[1] Confirmation for Methods proposed for rationalizing the Processing of Data obtained from Nuclear Magnetic Resonance Studies

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Molecular Complexes. Part XIII.[1] Confirmation for Methods proposed for rationalizing the Processing of Data obtained from Nuclear Magnetic Resonance Studies

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The interaction between chloroform and [$^2H_6$]benzene in a variety of inert solvents has been investigated, and the chemical shift data processed using the mole fraction, molar, and molal concentration scales, rationalized, as described previously, to be consistent with the Benesi–Hildebrand method of analysis. It is shown that values obtained for Δ_c for any system are independent of the concentration scale used for its evaluation, and that the values obtained for K_x, K_c, and K_m are theoretically compatible.

RECENT investigations [2,3] in this laboratory have been directed towards rationalizing methods of processing data obtained from n.m.r. studies of molecular complexes formed in reactions of the type (1) occurring in

$$A + B \rightleftharpoons A \cdots B \qquad (1)$$

the presence of a supposedly inert solvent, S.[4] Fundamentally two types of procedures are generally used for processing data, namely, those based on the Benesi–Hildebrand [5] and Creswell–Allred [6] methods. These two procedures have been critically compared [2,3] in the light of apparent anomalies concerning the results obtained therefrom. These anomalies were (*a*) that the chemical shift, Δ_c, induced in one species of the complex appeared to depend on the concentration scale used to process the data and (*b*) that K, the equilibrium quotient, and Δ_c appeared to depend on the supposedly inert solvents used for studying the reaction. It has been shown how these anomalies can be resolved.[2,3] However, the earlier work depended on the measurement of chemical shifts with comparatively high error limits, being measured at 60 MHz on a non-field-frequency locked spectrometer. We now present confirmation for the procedures proposed previously using data of a higher accuracy than that available previously.

THEORY

Both the Benesi–Hildebrand and the Creswell–Allred methods of data processing depend on the Gutowsky–Saika [7] theory of fast exchange in the form of equation (2)

$$\delta_{obs} = n_{AB}(\delta_c - \delta_{free})/n_A + \delta_{free} \qquad (2)$$

where δ_{obs}, δ_c, and δ_{free} are the chemical shifts, from an arbitrary reference, of the solute (A) in a given sample, in the fully complexed situation, and in the uncomplexed, or free state, respectively, and n_{AB} and n_A are the equilibrium and initial numbers of moles of complex and solute respectively.

It has been suggested [2,3] that the two anomalies quoted above can be avoided (*a*) by rationalizing the use of properties (concentrations on different scales) pertaining to samples in bulk with the molecular basis of equation (2), and (*b*) by using data processing procedures, *e.g.* the Benesi–Hildebrand method, under the correct thermodynamic conditions, this being necessary because it is known [2,8] that the equilibrium quotient, K, is dependent on the range of concentration over which the interaction between solute (A) and aromatic substrate (B) is studied.

The n.m.r. analogue of the Benesi–Hildebrand method of data processing depends on equation (3), where $\Delta_{obs} = \delta_{obs} - \delta_{free}$, K and $[B]_0$ are respectively the equilibrium quotient (devoid of activity coefficients and thus wrongly considered to be independent of the composition of the reacting mixture) and the initial concentration of B appropriate to the scale used, and Δ_c is the chemical shift induced in A by B in the A $\cdots$ B complex.

$$\frac{1}{\Delta_{obs}} = \frac{1}{K[B]_0\Delta_c} + \frac{1}{\Delta_c} \qquad (3)$$

There are three familiar concentration scales which can be used to describe $[B]_0$, namely, the mole fraction, molarity, and molality scales. Of these it has been suggested [2,3] that the first and last must be modified to account for the molecular basis of equation (2). Additionally, the equilibrium quotients for each scale must be defined for conditions relating to the validity of the Benesi–Hildebrand equation (*i.e.* when $[B]_0 \gg [A]_0$, and activity coefficients can be neglected), and should be given as in equations (4)—(6) respectively. From these definitions the relationships, given in equation (7), between equilibrium quotients on the three concentration scales chosen may be deduced.

$$K_x = \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB})n_B V_B} \qquad (4)$$

$$K_c = \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB})n_B} \qquad (5)$$

$$K_m = \frac{n_{AB}\rho_B(n_B V_B + n_S V_S)}{(n_A - n_{AB})n_B} \qquad (6)$$

$$K_x V_B = K_c = K_m/\rho_B \qquad (7)$$

[1] Part XII, J. Homer and M. C. Cooke, *J.C.S. Faraday II*, in the press.

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[3] J. Homer and P. M. Whitney, *J.C.S. Faraday I*, 1973, **69**, 1985.

[4] See *e.g.* L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry,' Holden-Day, San Francisco, 1964; R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, New York, 1969 and references therein.

[5] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1948, **71**, 2703.

[6] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, 1962, **66**, 1469.

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[8] J. Homer and M. C. Cooke, *J.C.S. Faraday I*, 1973, **69**, 1990.

The evaluation of each of the equilibrium quotients by the well proven Benesi–Hildebrand method, or the equivalent alternatives, has indicated [2,3] the validity of the above relationships. We now confirm these indications by studies on a different interaction, namely [$^2H_6$]benzene + $CHCl_3$, closely related to that investigated before.[2]

TABLE 1

The compositions of the mixtures employed in the investigation of the chloroform (A) + [$^2H_6$]benzene (B) reaction in the presence of various inert materials (S), together with the corresponding chemical shifts of chloroform, measured relative to the shift [a] of chloroform in the absence of [$^2H_6$]benzene

$10^4 n_A$/mol	$10^2 n_B$/mol	$10^3 n_S$/mol	Δ_{obs}/Hz
S = Cyclohexane			
0·4858	3·2945	3·2425	83·10
0·4414	3·3195	2·8686	83·34
0·5553	3·3165	2·6015	83·59
0·4481	3·3531	2·1268	83·97
0·3727	3·3891	1·7925	84·54
0·3803	3·4180	1·4150	84·60
0·4615	3·4523	1·1370	85·17
0·3945	3·4985	0·7354	85·44
0·4087	3·5367	0·3701	85·81
S = *cis*-Decalin			
0·3333	3·2076	3·6506	92·12
0·3761	3·2423	3·2671	92·94
0·3493	3·3090	2·9290	93·38
0·3886	3·3412	2·5712	93·91
0·2982	3·3507	2·1835	94·48
0·3250	3·3869	1·8598	94·78
0·4372	3·4205	1·5156	95·09
0·3518	3·4955	0·8102	96·36
0·3534	3·5262	0·3634	97·08
S = Bicyclohexyl			
0·3543	3·2072	3·6502	84·84
0·6491	3·2444	3·2558	85·73
0·4665	3·2784	2·8863	86·33
0·3970	3·2805	2·5540	86·82
0·4959	3·3503	2·1774	87·28
0·3853	3·5213	1·8082	87·59
0·3426	3·4224	1·4325	88·16
0·3283	3·4582	1·0815	88·96
0·3476	3·4922	0·8044	89·22
0·3602	3·5287	0·3645	89·47
S = Tetradecane			
0·2948	3·2050	3·5517	85·90
0·5687	3·3083	3·1779	87·00
0·4833	3·2832	2·8180	87·80
0·4665	3·3161	2·4518	88·72
0·4339	3·4262	2·1371	89·16
0·3409	3·3907	1·7400	90·37
0·3124	3·4277	1·3609	91·09
0·3702	3·4849	1·0491	92·57
0·4213	3·5021	0·7001	93·55
0·4079	3·5311	0·3517	94·35
S = Hexadecane			
0·5009	3·2116	3·5296	84·94
0·4146	3·2459	3·1721	85·92
0·3769	3·2777	2·8212	87·21
0·4875	3·3224	2·4703	88·18
0·4959	3·3520	2·1305	89·00
0·4515	3·4470	1·4085	91·39
0·4037	3·4583	1·0536	92·24
0·3258	3·4964	0·7013	93·42
0·3375	3·5290	0·3481	94·39

[a] An external tetramethylsilane lock was employed in the measurement of each value of δ_{free}.

EXPERIMENTAL

The interaction between chloroform (at low and constant mole fraction of 0·001) and [$^2H_6$]benzene (99·7% isotopic purity) was studied in the solvents cyclohexane, *cis*-decalin, bicyclohexyl, tetradecane, and hexadecane, in each case over a range of aromatic concentration between 0·9 and 1·0 mole fraction. Chemical shift measurements between chloroform and a suitable absorption from the solvent S (δ_{obs}) were made at 100 MHz on a Varian HA100D spectrometer in the field sweep mode, for which a lock signal was provided by the 0·3% proton impurity in the [$^2H_6$]benzene. The low concentration of benzene used for the lock signal was insufficient to provide a signal which could readily be monitored on the oscilloscope in the usual manner, and so the 2·5 kHz lock signal was monitored using an audio amplifier to distinguish this signal from background noise aurally.

RESULTS

The concentrations and shifts for each sample are shown in Table 1. The temperature of the samples was determined in the conventional way by measuring the shift between the methyl and hydroxy-protons of methanol.

TABLE 2

Densities of the various materials used, at the temperatures of the investigations

T/K	$10^{-3}\rho_B$/kg m^{-3} [a]	Solvent, S	$10^{-3}\rho_S$/kg m^{-3}
309·8	0·9299	Cyclohexane	0·7634 [b]
309·3	0·9305	*cis*-Decalin	0·8846 [b]
309·8	0·9299	Bicyclohexyl	0·88 [c]
309·5	0·9302	Tetradecane	0·7514 [b]
310·8	0·9287	Hexadecane	0·7622 [b]

[a] Calculated for 99·7% isotopic purity from the data given by J. A. Dixon and R. W. Schiessler, *J. Amer. Chem. Soc.*, 1954, **76**, 2197, for 100 and 99·3% isotopic purity at several temperatures. [b] Deduced from the data given by J. Timmermans, 'Physico-chemical Constants of Pure Organic Compounds,' Elsevier, Amsterdam, 1965, vol. 2. [c] As a value at 309·8 K is not available from the literature, that provided by the supplier, Phase Separations Ltd., for the mixture of isomers was used (880 kg m^{-3} at 298·3 K).

The data were processed on an ICL 1905E computer using the modified [2,3] Benesi–Hildebrand method of evaluation. The densities used in the computations are shown in Table 2, for each component studied. It should be pointed out that serious errors can arise from using the Benesi–Hildebrand method in conditions where several complexes of different stoicheiometry coexist in solution. However, in the present work such errors are unlikely because chloroform can only complex with one benzene molecule in the energetically favoured orientation, and the concentration ratios are such that the binding of two chloroform molecules on opposite sides of a single benzene molecule is highly unlikely.

DISCUSSION

The values deduced for K_x, K_c, K_m, and Δ_c for each of the systems studied are shown in Table 3. The values obtained for Δ_c are the same for any particular solvent, irrespective of the concentration scale used for processing the data.

Table 3 also shows values for K_c/K_x and K_m/K_c which according to equation (7) should equal V_B and ρ_B respectively. Comparisons of the relevant values show remarkably good agreement, and provide strong support for the validity of using equations (4)—(6) for K_x, K_c, and K_m respectively.

Comparisons between the present work and that carried out previously [2,3] show a significant (*ca.* 50%) increase in the values for equilibrium quotients determined here. There is also a significant decrease in the values for Δ_c. Whilst it is possible that the replacement of hydrogen by deuterium in benzene could alter the parameters pertaining to the interaction with chloroform directly, it is more probable that differences in the interaction of benzene and [$^2H_6$]benzene with the solvents used could result indirectly in an apparent change in the interaction parameters.

A further comparison between the benzene [2,3] and [$^2H_6$]benzene results shows that for both sets the values for the equilibrium quotients for the bicyclohexyl system are abnormally high, and differ significantly from the mean value for the other systems. This may be due to the presence of an undetected impurity or to an insufficiently accurate value for its density (Table 2, footnote *c*) being used in the computation. However, it is more likely that the effect occurs because the bicyclohexyl molecule may be present with three forms of ring bonding, *viz.*, axial–axial, equatorial–equatorial, and axial–equatorial. In this case the polar forms, polarizability, and dielectric constant of the solvent could affect the number and nature of interactions present in solution so that the direct use of the Benesi–Hildebrand method would be invalidated and could lead to a spurious and high value for K.

TABLE 3

Values of parameters characteristic of the formation of the [$^2H_6$]benzene + chloroform complex in various solvents

Solvent, S	K_x	10^3K_c/m^3 mol^{-1}	K_m/kg mol^{-1}	Δ_c(p.p.m.) [a]	$10^3(K_c/K_x)$/ m^3 mol^{-1}	10^3V_B/ m^3 mol^{-1} (calc.)	$10^{-3}(K_m/K_c)$/ kg m^{-3}	$10^{-3}\rho_B$/kg m^{-3} (calc.)	T/K
Cyclohexane	$2{\cdot}1_{938}$	$0{\cdot}19_{827}$	$0{\cdot}18_{457}$	$1{\cdot}2_{541}$	0·09038	0·09048	0·9309	0·9299	309·8
cis-Decalin	$2{\cdot}4_{739}$	$0{\cdot}22_{371}$	$0{\cdot}20_{814}$	$1{\cdot}3_{688}$	0·09043	0·09042	0·9304	0·9305	309·3
Bicyclohexyl	$2{\cdot}9_{726}$	$0{\cdot}26_{866}$	$0{\cdot}25_{010}$	$1{\cdot}2_{056}$	0·09038	0·09048	0·9309	0·9299	309·8
Tetradecane	$1{\cdot}9_{617}$	$0{\cdot}17_{739}$	$0{\cdot}16_{505}$	$1{\cdot}4_{366}$	0·09043	0·09045	0·9304	0·9302	309·5
Hexadecane	$1{\cdot}9_{134}$	$0{\cdot}17_{368}$	$0{\cdot}16_{133}$	$1{\cdot}4_{543}$	0·09077	0·09059	0·9289	0·9287	310·8

[a] The values obtained for Δ_c were identical for any particular solvent, whichever concentration scale was used for data processing.

It can be concluded that the present work substantiates the previous [2,3] suggestions for rationalizing procedures for processing n.m.r. data obtained from studies of molecular complex formation. Moreover, it appears that these procedures facilitate the detection of meaningful differences between the values of K and Δ_c for quite similar reactions. However, it does appear that to provide reliable values for these two parameters at least two diluting solvents of the saturated hydrocarbon type employed here should be used.

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Removal of Oxygen from Samples used in Nuclear Magnetic Resonance Studies of Spin–Lattice Relaxation Times

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Summary It is demonstrated that conventional degassing procedures for the removal of oxygen from samples used in n.m.r. studies are unsatisfactory, and a versatile chemical alternative is described.

THE measurement of spin–lattice relaxation times, T_1, and particularly the dependent Nuclear Overhauser Effect, N.O.E., are being used increasingly as aids in the solution of chemical problems. It has long been recognized that molecular oxygen significantly reduces the values of T_1 and the N.O.E., and attempts to remove it are normally made by the familiar freeze–thaw degassing procedure or by passing oxygen-free gas through the sample. In common with others[1,2] we have found that it is difficult to employ these procedures efficiently and we now describe a simpler and more effective chemical method.

Air-saturated benzene has a T_1 value of 4·6 s, as measured by the a.f.p.[3] procedure. Repeated freeze–thaw degassing of the same sample in a vacuum line operating at a typical pressure of 10^{-3} torr increases the value to 5·5 s; similarly small increases of less than 1 s in the T_1 values of other compounds are achieved. We have employed the same method at *ca.* 10^{-5} torr to increase the value of T_1 to the order of the widely quoted (e.g. ref. 4), but probably incorrect, value of *ca.* 19 s. Despite taking all reasonable precautions to ensure the success of the degassing technique the values of T_1 obtained are quite irreproducible. Similarly, bubbling oxygen-free nitrogen through the sample, and sealing it under this gas also provides low and irreproducible values for T_1.

Because of the difficulties and unreliability of these procedures we have investigated chemical means of deoxygenating samples. Although some such methods have been reported[1,5] they are extremely tedious to implement. We have, therefore, sought an alternative procedure employing readily obtainable materials that obey the three criteria, (i) they should be soluble in a wide variety of solvents and be capable of use with liquids immiscible with the primary solvent, (ii) have low vapour pressures to

TABLE. A comparison between the ^{1}H T_1 values of physically and chemically degassed compounds.

Compound	T_1/s Literature	T_1/s This work (309 K)
Benzene	19·3[4]	23·6[a]
Toluene Ring	16·0[4]	22·2[b]
CH_3	9·0[4]	11·9[b]
p-Xylene Ring	14·0[4]	16·7[b]
CH_3	7·5[4]	7·3[b]
Acetone	15·8[8]	17·6[c,d]
Methylene chloride	28·5[9]	36·1[d]

[a] Four samples were prepared, two by distillation under reduced pressure (10^{-3} torr) from a previously stirred heterogeneous mixture with water containing $[Co^{II}(bipy)_3](ClO_4)_2$ and sodium borohydride and two from a homogeneous solution containing dimethyl sulphoxide. [b] Distilled under reduced pressure from a previously stirred homogeneous mixture with dimethyl sulphoxide containing the deoxygenating compounds. [c] The estimated experimental error for 13 determinations is ±0·2 s. [d] Distilled under reduced pressure directly from a homogeneous solution containing the deoxygenating compounds.

facilitate their easy removal from the subject material by its distillation, and (iii) remove oxygen in a reversible colour indicating reaction. The compound we have found to fulfil these requirements is $[Co^{II}(bipy)_3](ClO_4)_2$[6] with sodium borohydride. In an oxygenated homogeneous mixture these give a pale yellow-brown solution which changes on the removal of oxygen to an extremely oxygen sensitive intense blue solution. If solutions are subsequently oxidised by dioxygen they may be reduced again in the presence of excess sodium borohydride, but the oxidation–reduction cycle may not be reversed indefinitely.

We have used the two compounds mentioned above at extremely low concentrations (to minimize potential reduction of the sample) in hetero-and homo-geneous mixtures to deoxygenate several materials the T_1 values of which are well documented.[7] The values we have obtained by the a.f.p. method, using a Varian HA100D spectrometer, are compared in the Table with possibly the longest literature times available. It is apparent that our values are significantly longer than those of other workers, by up to 7 s, and that our method of degassing samples is, in addition to being simple, reproducible and much more efficient than those reported previously.

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Phase Diagrams of Binary Mixtures of Liquid Crystals

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Phase Diagrams of Binary Mixtures of Liquid Crystals

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Summary Preliminary studies indicate that some mixtures of liquid crystal compounds may exhibit unusual features in their phase diagrams.

PREVIOUS investigations of mixtures of liquid crystals have shown that the nematic mesophase to isotropic liquid transition temperatures often vary linearly with the composition of the mixtures, but can show regular deviations from linearity.[1-6] Normally, dissimilar compounds show more deviation from linearity than similar compounds,[1,7,8] but in all cases the curves are reported to be continuous. Recently, a theory for nematic–isotropic phase transitions has been developed which explains very satisfactorily the regular experimental data.[9] In contrast to the nematic–isotropic change, the solid-nematic phase diagrams usually exhibit a eutectic, and not a smooth curve.[2-4]

In the course of studying mixtures of liquid crystals suitable for the n.m.r. investigation of solutes partially orientated in the nematic mesophase we have encountered some compounds whose phase diagrams indicate some differences from those normally found. Whilst our observations are incomplete we report our empirical findings in order that they may aid the theoretical understanding of phase changes in mixtures of liquid crystals.

The compounds used in the investigations were 4,4′-dimethoxyazoxybenzene (A), azoxybenzene (B), 4,4′-di-n-hexyloxyazoxybenzene (C), 4-n-pentyloxybenzoic acid (D), 4-n-hexyloxybenzoic acid (E), and 4-n-octyloxybenzoic acid (F), and the binary mixtures studied were A–B, A–C, D–E, D–F, E–F, A–D, A–E, A–F, C–D, C–E, and C–F. Some of these mixtures show regular or near regular phase diagrams and little further comment will be passed on them.

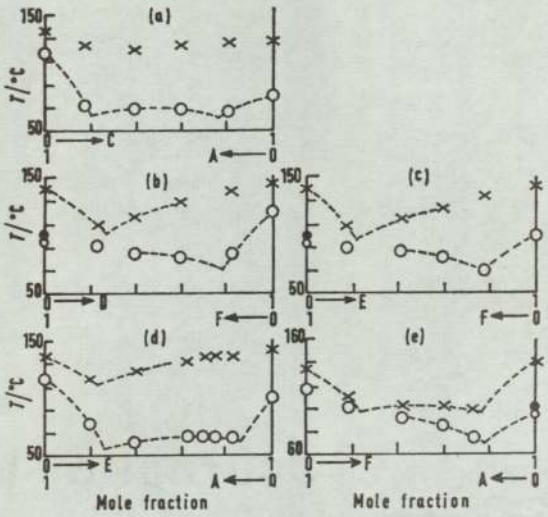

FIGURE. *Phase diagrams of binary mixtures of some liquid crystals. Solid-nematic (or smectic), smectic–nematic, and nematic–isotropic transitions are symbolised by* ○, ●, *and* × *respectively. Broken lines are used merely to illutrate the possible interpretations of the phase changes referred to in the text and should not be taken as accurate assessments of eutectic points.*

The accuracy of our experimental procedure was assessed by studying mixtures of A and B, for which data have been reported previously;[8] the maximum error in our data corresponds to $\pm 2°C$.

Mixtures of C and A showed [Figure (a)] the normal negative deviation from the ideal (linear) nematic-isotropic phase change, as established previously.[1] The present data show that a regular curve cannot be drawn for the solid–nematic transition, but indicate 'eutectic' points.

The 4-n-alkoxybenzoic acids were also examined. These compounds largely owe their nematic character to their ability to exist as dimers.[10] In view of this it is expected that mixtures of them should show double eutectics indicating the formation of weak compounds between unlike acids. In the Figure, (b) and (c), the solid–nematic data clearly show one eutectic with the possibility of a second. More interesting than these observations, however, is that in the Figure, (b) and (c), the nematic–isotropic phase lines appear to show well defined 'eutectics,' in complete contrast to that for D–E mixtures which may be represented by a smooth curve; it is interesting that in the last case the compounds involved have similar lengths.

For the binary mixtures between three 4-n-alkoxybenzoic acids and two 4,4′-di-n-alkoxyazoxybenzenes, strong evidence for eutectics in the solid–nematic phase line was found for the A–E and A–F mixtures [Figure, (d) and (e)]. So far as the nematic–isotropic transition is concerned Figure (e) provides strong evidence for a double eutectic and Figure (d) may be interpreted as showing a regular phase change but arguably shows a eutectic.

Recently, Bernheim and Shuhler have reported phase diagrams for a limited number of liquid crystal mixtures.[11] In common with us, they found that the solid–nematic transition is lowered in temperature over a rather wide range of composition. However, they did not comment on the irregularities in the nematic–isotropic phase diagrams which are quite prominent in two of the four binary mixtures studied by them and concur with our observations. Consequently, despite the limited data available, it appears that some mixtures of liquid crystals may show unusual discontinuities in the nematic–isotropic transition, and that further investigations of them are necessary.

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