NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC STUDIES OF THE ROLE OF STERIC EFFECTS IN MOLECULAR INTERACTIONS USING RATIONALISED DATA PROCESSING PROCEDURES.

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by

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SUMMARY

The n.m.r. technique has been used extensively to study the molecular interactions between aliphatic molecules (solutes) and aromatic solvent molecules. Several problems have become apparent regarding the evaluation of data determined from such studies, namely that the equilibrium quotient (K) and the full aromatic solvent induced shifts (Δ_c) are found to depend on the concentration scale and inert diluent used, regardless of the data processing method. In this thesis, therefore, an attempt has been made to devise a thermodynamically valid data processing technique which overcomes these shortcomings. By the application of a correction for the difference between the molar volume of the aromatic and the inert solvent to the Benesi-Hildebrand data processing method, rationalised results have been shown to be obtained using both the mole fraction and molal scales. The use of the molarity scale has also been validated.

The new data processing method was used to determine the equilibrium quotients and excess shielding values at different temperatures pertaining to the interactions of chloroform (solute) with benzene and alkylated benzenes. Values of ΔG^o, ΔH^o and ΔS^o were subsequently calculated. From a consideration of these data it would appear that the approach of the solute to the aromatic is sterically hindered by substituents of greater bulk than three methyl groups. Such substituents in fact tend to exclude the solute.

Finally, as a result of a study of a reference independent shift technique, a new method of determining magnetic susceptibilities to an accuracy of better than 1% was devised.

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CONTENTS

Page

CHAPTER 1

Some Theoretical Considerations of Nulcear Magnetic Resonance Spectroscopy.

CHAPTER 2

CHAPTER 3

Some Comments on the Origin of the Chemical Shift.

CHAPTER 4

A Thermodynamically Correct Method of Processing Data Obtained from N.M.R. Studies of Molecular Complexes.

CHAPTER 5

A Variable Temperature Study of the Interactions of Chloroform with Benzene and Various Alkyl Substituted Benzenes.

Page

CHAPTER 6

The Application of a Reference Independent Shift Technique to Equilibrium Studies.

CHAPTER 7

A New Nuclear Magnetic Resonance Method for Determining Magnetic Susceptibilities.

CHAPTER 8

ILLUSTRATIONS

CHAPTER 1. SOME THEORETICAL CONSIDERATIONS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY.

1.1 Introduction

The presence of hyperfine splitting in atomic spectra led Pauli[1] to suggest, in 1924, that certain nuclei possess angular momentum and thus a magnetic moment, which interacts with the atomic orbital electrons. In the presence of an applied magnetic field such magnetic moments adopt specific orientations and it is possible to observe transitions occurring between nuclear energy levels associated with the orientations, by irradiation with a suitably rotating magnetic field. The nuclear energy levels are quantised as a direct consequence of the influence of a field on the nuclear magnetic moment which has (2I + 1) observable component values. The spin quantum number, I, can assume any multiple value of $\frac{1}{2}$. Stern and Gerlach[2,3] showed that the measurable values of an atomic magnetic moment are discrete by a beam experiment. Subsequently, the small magnetic moment of the hydrogen nucleus was determined[4] using a beam of hydrogen molecules directed through a steady magnetic field. The molecular beam method was developed further by passing the beam successively through two oppositely inclined magnetic fields of similar gradients, the first to separate it into (2I + 1) beams corresponding to the allowed energies and the second to refocus them on to a detector. The application of an oscillating field, between the original two, induced transitions between the nuclear energy states and resulted in a decrease in efficiency in refocussing the beam at the detector.[5]

It was not until 1945 that n.m.r. signals in bulk materials were detected, at which time two independent groups of researchers, Purcell, Torrey and Pound[6], and Bloch, Hansen and Packard[7] obtained n.m.r. signals from bulk samples of paraffin and water respectively. The observations were accomplished with main magnetic fields of about 1 tesla which necessitated oscillating field frequencies in the range of 10^5 to 10^8 Hz. The n.m.r.

technique is now accepted as being invaluable for the study of certain nuclear properties and in the determination of molecular structure$^{8-10}$.

When discussing the theory of n.m.r.spectroscopy in the subsequent sections, it is convenient to consider firstly the behaviour of an isolated nucleus in a magnetic field, from which the basic equation for resonance can be derived, and then classical and quantum mechanical treatments of resonance criteria. Nuclear energy level distribution, relaxation and saturation effects will be discussed with respect to assemblies of similar nuclei. Finally, the effect of the environment of nuclei will be considered when dealing with chemical shift, spin-spin coupling and exchange phenomena.

1.2 Nuclei in a Magnetic Field

For nuclei, which possess magnetic moments and the associated angular momenta, it is convenient to express their magnetic properties in terms of a constant, the magnetogyric ratio γ , defined in the expression,

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

Hence it can be seen that the magnetic moment and angular momentum are related as parallel vectors (figure 1.1). Quantum mechanics require that the angular momentum is strictly quantised such that the maximum measurable component of the angular momentum must be an integral or half integral multiple of $\hbar$, governed by the value of I. The number of components is limited to (2I + 1) so that the component along any selected direction will have values I,(I - 1) .. (-I + 1), -I in terms of $\hbar$ units. Similarly, μ, is quantised such that the observable components are $m\mu/I$, where m, the magnetic quantum number, has values from +I,(I - 1),.. (-I + 1), -I. In the absence of an applied field, the different levels are degenerate, but in an external field become separated into the predicted (2I + 1)

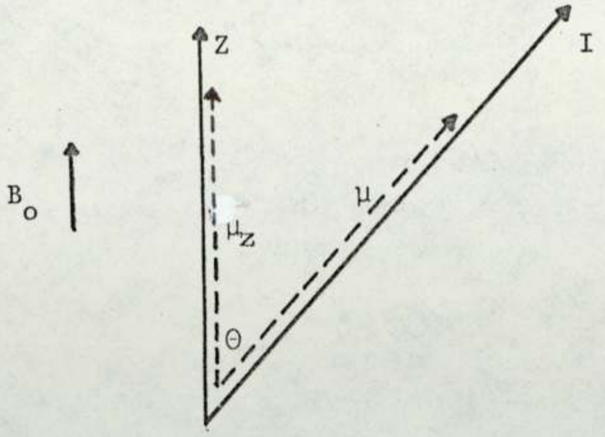


Figure 1.1. The relationship between the magnetic moment μ and the spin angular momentum, I.

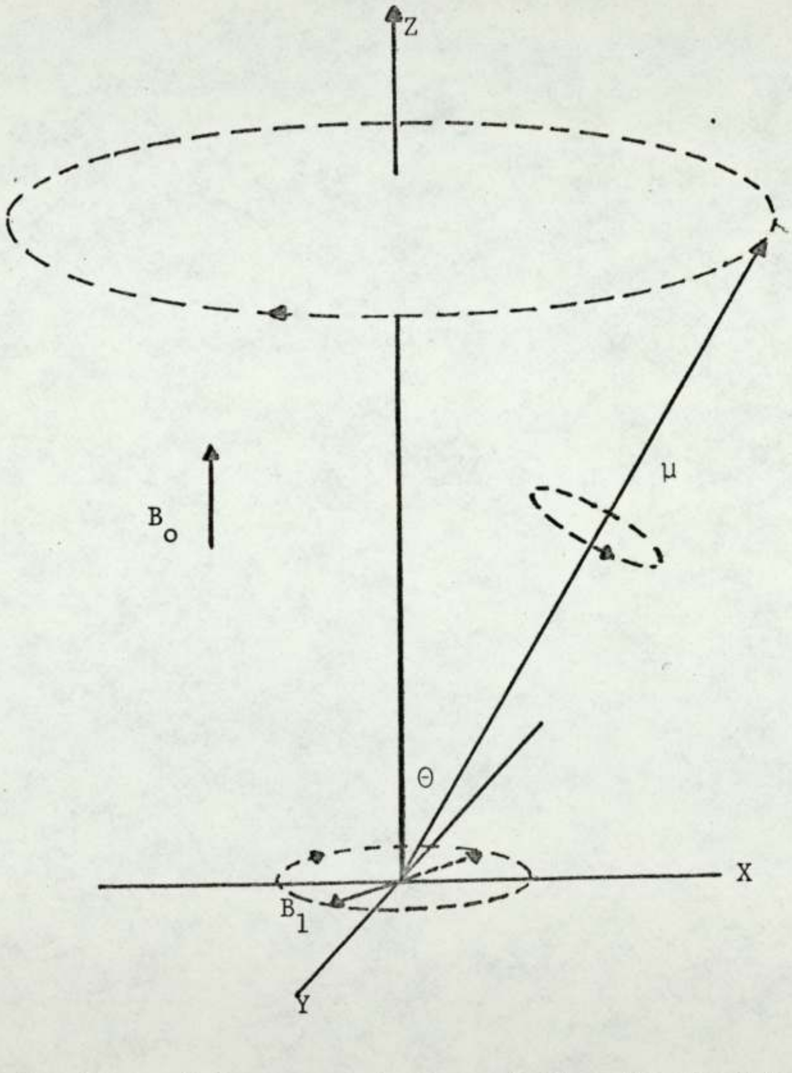


Figure 1.2. Vectorial representation of the classical Larmor precession.

states analogous to the Zeeman splitting of electronic levels. A nucleus in a uniform magnetic field B_o, applied in the z-direction has an energy E_z, relative to that in zero field E_o, given by

$$E_z = -\vec{\mu}_z B_o \qquad \text{.... 1.2}$$

The total energy E is therefore given as

$$E = E_o + E_z = E_o - \vec{\mu}_z B_o \qquad \text{.... 1.3}$$

The allowed nuclear energy levels will thus be $E_o - m\mu B_o/I$, and hence the adjacent levels have an energy separation of $\mu B_o/I$. The selection rule governing transitions is $\Delta m = \mp 1$[11], and so only transitions between successive levels are of importance and for these to occur the Bohr frequency condition must be obeyed, giving the basic n.m.r. equation

$$\nu = \frac{\mu B_o}{I\hbar} = \frac{\gamma B_o}{2\pi} \qquad \text{.... 1.4}$$

1.3 Resonance Criteria

1.3.1 The Classical Concept of Nuclear Resonance

The mechanism of absorption of energy by nuclei can be described by classical means. If a spinning charged particle is placed in a magnetic field of strength B_o, with its magnetic moment at an angle Θ to the direction of the applied field it will experience a torque $\bar{L}$ trying to align it parallel with B_o. From simple magnetic theory[12]

$$\vec{L} = \frac{dp}{dt} = \vec{\mu} B_o = \gamma \vec{p} B_o \qquad \text{.... 1.5}$$

where dp/dt is the rate of change of angular momentum and $\vec{\mu}$ is the magnetic moment. If the angular momentum vector $\vec{p}$ is rotated with an angular velocity ω_o, the rate of change of $\vec{p}$ is given as

$$\frac{dp}{dt} = \vec{p}\omega_o \text{ and hence } \omega_o = \gamma B_o \qquad .... 1.6 - 1.7$$

and the precessional angular velocity and frequency (the Larmor precessional frequency) are governed solely by the value of the imposed static field B_o. This is the Larmor equation which may be rewritten in terms of the precession frequency ν_o

$$\nu_o = \frac{\gamma B_o}{2\pi} \qquad .... 1.8$$

If a co-ordinate system is set up rotating with the Larmor angular frequency ν_o and if there is no other magnetic field acting, the magnetic moment μ, will remain stationary. If another smaller constant magnetic field B_1 is applied perpendicular to B_o (figure 1.2), but rotating about the B_o direction, then B_1 will also be rotating within this frame, provided the angular frequency of B_1 is not the same as ν. The effect of B_1 is to exert a torque μB_1 on the nucleus tending to tip the nuclear moment towards the plane perpendicular to B_o. Whilst B_1 is moving in the rotating frame, the direction of the torque will vary rapidly and only a slight wobbling perturbation of the steady precessional motion will be observed. If,however, the field B_1 is rotating at the Larmor frequency, then it will behave as a constant field and the torque, always being in the same direction will cause large oscillations in the angle between μ and B_o. Therefore, if the rate of rotation of B_1 is varied through the Larmor frequency, the oscillations will increase and be greatest at that frequency, and will manifest themselves as a resonance phenomenom. Normally, the oscillating magnetic field is obtained by applying a radiofrequency voltage to a coil surrounding the sample, arranged such that the field produced can be regarded as the superimposition of two contra-rotating fields. Only the component having the correct sense will synchronise with the precessing magnetic moment; the other component will have no effect. A purely classical picture, such as this, only predicts an absorption of energy.

1.3.2 A Quantum Mechanical Treatment of Nuclear Magnetic Resonance.

When a nucleus of magnetic moment μ, is placed in a magnetic field the Hamiltonian for the system is given by

$$\mathcal{H} = -\mu \cdot B_0 \qquad \text{.... 1.9}$$

and as $\mu = \gamma\hbar I$, then

$$\mathcal{H} = -\gamma\hbar B_0 \cdot I \qquad \text{.... 1.10}$$

The expectation values of the operator I are m; hence the expectation values of E , that is the energy levels of the system, are

$$E = -\gamma\hbar m B_0 \qquad \text{.... 1.11}$$

The application of an oscillating magnetic field constitutes a perturbation suitable to produce transitions between energy levels. The necessary direction of this field can be deduced from the properties of spin operators and eigen functions appropriate to a nucleus of spin I.

A set of spin angular momentum operators I_x, I_y, I_z and I^2 can be defined. If for simplicity, nuclei of spin $I = \frac{1}{2}$ are considered, the only two possible energy states are $\pm \frac{1}{2} \gamma\hbar B_0$, the corresponding eigen functions of which are usually denoted as α and β . The probability of a transition occurring between the two spin states when the oscillating magnetic field is applied along the z-axis is given by

$$P_z \propto (\alpha|I_z|\beta)^2 = 0 \qquad \text{.... 1.12}$$

Hence this arrangement of steady and oscillating fields cannot result in a transition. However, if the oscillating field is applied along the x-axis then

$$P_x \propto (\alpha|I_x|\beta)^2 = \tfrac{1}{4}\hbar \qquad \text{.... 1.13}$$

A similar finite transition probability is obtained if the oscillating field is applied along the y-axis. The energy change when such a transition takes place is

$$\Delta E = \gamma\hbar B_0 \qquad \ldots\ldots 1.14$$

and thus the frequency of the oscillating magnetic field must be

$$\nu = \frac{\Delta E}{h} = \frac{\gamma B_0}{2\pi} \qquad \ldots\ldots 1.15$$

For the general case of a nucleus of spin I, the transition probability[13] between two energy levels m and m^1 is given by

$$P^1 \propto (\Psi_m|I_x|\Psi_{m^1})^2 \qquad \ldots\ldots 1.16$$

which is non-zero only when $m = m^1 \pm 1$, and hence the selection rule for nuclear transitions is given as $\Delta m = \pm 1$.

1.4 Nuclear Energy Level Distribution

The probabilities of transitions occurring between the various accessible levels, by emission or absorption of energy, are identical, the effect of spontaneous emission of energy being negligible[14]. To enable the observation of nuclear resonance signals, there must be a nett change in the distribution of nuclei between the various allowed energy levels. In the absence of a secondary field B_1, there is a Boltzman distribution of nuclei between the various energy levels. Thus the number, n_i of nuclei in a particular level with energy E_i, at thermal equilibrium at a temperature T is given by

$$\frac{n_i}{n} = \frac{e^{-\Delta E_i/kT}}{\Sigma_i e^{-\Delta E_i/kT}} \qquad \ldots\ldots 1.17$$

As there are (2I + 1) possible states and as $\mu B_0/IkT$ is small under normal conditions, the probability P of the nuclei being in a given energy state

E_i is

$$P^i = \frac{1}{(2I+1)} (\exp(m\mu B_{o/IkT})) \simeq \frac{1}{(2I+1)} (1+m\mu B_{o/IkT}) \qquad .... \ 1.18$$

Thus for a nucleus of spin $I = \frac{1}{2}$, the probabilities of a nucleus being in the upper or lower states are respectively

$$P^{\mathrm{upper}} = \frac{1}{2}(1 - \frac{\mu B_o}{kT}) \ ; \quad P^{\mathrm{lower}} = \frac{1}{2}(1 + \frac{\mu B_o}{kT}) \qquad .... \ 1.19 - 1.20$$

Examination of equations 1.19 and 1.20 shows the desirability of the main field being as large as possible; not only are the energy levels more widely spaced but also the sensitivity is increased since the excess population of the ground state is increased.

The observation of an n.m.r. signal requires that there is an excess of nuclei in the lower energy state. To maintain this condition, nuclei must return from the excited to the ground state. However, when a radio-frequency field of large amplitude is applied, the excess number of nuclei in the lower state will tend to zero and the system is said to be saturated- a phenomenom which has no analogy in optical spectroscopy.[14,15]

1.5 Saturation

This phenomenon shows itself primarily as a reduction in signal intensity and broadening of the resonance line and, if the spectrum consists of several lines, it is possible that they may be affected non-uniformly by saturation. A facet of saturation is the possibility of multi-quantum transitions,[16] that is absorptions which do not obey the quantum rule $\Delta m = \pm 1$[11]. A qualitative treatment will now be presented for an assembly of nuclei having $I = 1/2$. Before the radio-frequency is applied, the rate of change of the excess population per unit volume is given by

$$\frac{dn}{dt} = \frac{n_{eq} - n}{T_1} \qquad \text{.... 1.21}$$

where n_{eq} is the value of n when the spin system is in equilibrium (thermal) with its surroundings and T_1 is a relaxation time. When the radiofrequency corresponds to the Larmor frequency, the amount of change in the excess population is 2nP, where P is the probability per unit time for a transition between the two energy levels under the influence of irradiation. Hence,

$$\frac{dn}{dt} = \frac{n_{eq} - n}{T_1} - 2nP \qquad \text{.... 1.22}$$

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

$$\frac{n_s}{n_{eq}} = (1 + 2PT_1)^{-1} \qquad \text{.... 1.23}$$

A value of P can be obtained from standard radiation theory[17]; the probability of a transition in unit time between two states having quantum numbers m and m^1 is given as

$$P_{m \rightarrow m^1} = \tfrac{1}{2}\gamma^2 B_1^{\,2} \, |(m \, |I \, |m^1)|^2 \delta \, (\nu_{mm^1} - \nu) \qquad \text{.... 1.24}$$

B_1 is the amplitude of the r.f. field rotating in the correct sense perpendicular to the static field B_o, and $(m|I|m^1)$ is the appropriate element of the nuclear spin operator matrix. $\delta(\nu_{mm^1} - \nu)$ is the Dirac delta function which is strictly zero for all values except $\nu_{mm^1} = \nu$, thus predicting an infinitely sharp absorption or emmission line. Since this is unreal, the function is replaced by a function $g(\nu)$ given by

$$\int_o^\infty g(\nu)d\nu = 1 \qquad \text{.... 1.25}$$

For $I = \frac{1}{2}$, equation 1.24 reduces to

$$P = \frac{1}{4}\gamma^2 B_1^{\,2} g(\nu) \qquad \text{.... 1.26}$$

and therefore, $$\frac{n_s}{n_{eq}} = (1 + \tfrac{1}{2}\gamma^2 B_1{}^2 g(\nu)\, T_1)^{-1} \qquad \ldots.\ 1.27$$

The right hand side of equation 1.27 is usually denoted by Z and called the saturation factor. Saturation is greatest for the radiofrequency which gives the shape function $g(\nu)$ its maximum value, and if a further relaxation time is introduced (T_2), such that

$$T_2 = \tfrac{1}{2} g(\nu)\max \qquad ,\ldots\ 1.28$$

then $$Z_o = (1 + \gamma^2 B_1{}^2 T_1 T_2)^{-1} \qquad \ldots.\ 1.29$$

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

1.6 Relaxation Phenomena

In the absence of any mechanism to counteract saturation effects,the use of the n.m.r. technique would be severely limited. However, there are processes operating which tend to restore the original distribution of energy levels, following the absorption of energy from the radiofrequency field. This equilibration is produced by relaxation processes, of which there are two principal types.

1.6.1 Spin-lattice relaxation

It was shown in section 1.4 that the distribution of nuclei between energy levels before a field is applied can be described by a Boltzman type function. In the presence of an applied field, this type of function is still applicable, but now there is a rise in temperature to the so called spin temperature, T_s. Nuclear spins invariably interact with their surroundings, but because the interaction is usually small, it is possible to distinguish between the spin and lattice temperatures. Hence this small interaction does enable a thermal equilibrium to be established eventually between the nuclear spins and their environment.The resultant temperature will be close to that of the lattice since the heat capacity of the spin system is negligible compared with that of the lattice except at very low temperatures. The flow of heat from the nuclei to the lattice opposes the reduction of the population of the lower energy state by radio-frequency absorption. This heat flow approach does not however explain the mechanism of the process.

A qualitative explanation may be given by considering that molecules, undergoing random rotational, vibrational and translational motion, produce rapidly fluctuating magnetic fields which any nucleus present will experience. If the time varying magnetic field has a component whose frequency is synchronous with the precessional frequency of a neighbouring nucleus, then that nucleus will experience an r.f. capable of inducing a transition, preferentially a stimulated emission of energy from the spin system rather than an absorption, thus transferring energy to the surrounding lattice.

When a field is first applied to the system, the spin-lattice process takes a finite time, the spin-lattice relaxation time, to equilibrate the distribution of nuclei in the various available energy levels. This may be quantified as follows. If n_1 and n_2 are the number of nuclei per unit volume in the upper and lower states respectively, it is possible to evaluate the rate of change of the excess number of nuclei per unit volume, given by n, as a function of time. If P_1 and P_2 are the upward and downward transition probabilities respectively (for the interaction of a nucleus with other molecular degress of freedom), then at equilibrium, in the presence of a magnetic field, the total number of upward and downward transitions are equal; thus

$$n_1 P_1 = n_2 P_2 \qquad \text{.... 1.30}$$

Re-arranged and using equation 1.17

$$\frac{P_2}{P_1} = \frac{n_1}{n_2} = \exp(-2\mu B_{o/kT}) \simeq (1 - 2\mu B_{o/kT}) \qquad \text{.... 1.31}$$

Provided that the interaction is small compared with the total energy of the system, that is the temperature is invariant, then P_2/P_1 is independent of n_2/n_1. Let

$$P_2 = P(1 + \frac{\mu B_o}{kT}) \quad ; \quad P_1 = P(1 - \frac{\mu B_o}{kT}) \qquad \text{.... 1.32 - 1.33}$$

where P is the mean of P_2 and P_1.

The rate of change of the population is therefore,

$$\frac{dn_1}{dt} = \frac{-dn_2}{dt} = n_2P_2 - n_1P_1 \qquad \text{.... 1.34}$$

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

$$\frac{dn}{dt} = 2(n_2P_2 - n_1P_1) \qquad \text{.... 1.35}$$

Substituting from equations 1.32 - 1.33 gives

$$\frac{dn}{dt} = -2P((n_1 - n_2) - (n_1 + n_2)\frac{\mu B_o}{kT}) = -2P(n - n_{eq}) \qquad \text{.... 1.36}$$

where n_{eq} is the number of excess nuclei in the lower state at equilibrium. Integration of equation 1.36 leads to

$$n - n_{eq} = (n_o - n_{eq}) \exp (-2Pt) \qquad \text{.... 1.37}$$

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

$$T_1 = 1/2P \qquad \text{.... 1.38}$$

thus giving

$$n - n_{eq} = (n_o - n_{eq}) \exp (-t/T_1) \qquad \text{.... 1.39}$$

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

1.6.2 Spin-Spin Relaxation

In addition to interacting with the lattice, magnetic nuclei can interact among themselves.The local field from a precessing nucleus has oscillating and static components and the former produce a magnetic field oscillating at its Larmor frequency which may induce a transition in an identical neighbouring nucleus. A simultaneous reorientation of both nuclei results, there being an interchange of energy between the pair, whilst the total energy of the nuclear system is preserved. This mechanism produces no change in the overall population of the energy levels. It should be noted than only identical nuclei are capable of spin-spin exchange. Any phase coherence of the precessing nuclei is lost in a time T_2 which is generally referred to as the spin-spin relaxation time.

The n.m.r. phenomena have been described thus far in terms of assemblies of isolated nuclei; it is however possible to consider the phenomena in terms of the behaviour of collections of nuclei as a whole, that is in terms of bulk properties.

1.7 N.M.R. in Macrosamples

In a macrosample, all spin states will be occupied to different extents, and in an applied field an assembly of magnetic nuclei will have a magnetic susceptibility which can be described by

$$\chi_o = M/B_o \qquad \text{.... 1.40}$$

where χ_o is the static susceptibility, B_o is the applied field and M is the moment per unit volume of the substance, or nuclear magnetisation. The interaction of M with a r.f. field has been quantitatively elaborated by Bloch.[18-20]

The equation of motion for a single nuclear magnetic moment is

$$\frac{d\vec{\mu}}{dt} = \gamma(\bar{\mu} \times B) \qquad \text{.... } 1.41$$

Similarly, for an assembly of weakly interacting moments contained in unit volume, the equation of motion is

$$\frac{d\vec{M}}{dt} = \gamma(\vec{M} \times B) \qquad \text{.... } 1.42$$

In the usual magnetic resonance experiment, the three components of B are not all constant but have the values

$$B_x = B_1 \cos \omega t \qquad \text{.... } 1.43$$

$$B_y = -B_1 \sin \omega t \qquad \text{.... } 1.44$$

$$B_z = B_o \qquad \text{.... } 1.45$$

B_x and B_y together represent an r.f. field of amplitude B_1, rotating in a plane normal to the static field. Assuming there are no other interactions, then

$$\frac{dM_x}{dt} = \gamma(M_y B_o - M_z B_y) = \gamma(M_y B_o + M_z B_1 \sin \omega t) \qquad \text{.... } 1.46$$

$$\frac{dM_y}{dt} = \gamma(-M_x B_o + M_z B_x) = \gamma(M_x B_o + M_z B_1 \cos \omega t) \qquad \text{.... } 1.47$$

$$\frac{dM_z}{dt} = \gamma(M_x B_y - M_y B_x) = \gamma(-M_x B_1 \sin \omega t - M_y B_1 \cos \omega t) \qquad \text{.... } 1.48$$

In the absence of B_1, M has only the z-component as the individual nuclei themselves then have random phases which result in the x and y components averaging to zero. When the radiofrequency field is zero, equilibrium conditions exist and thus M_z is equal to M_o, the static magnetisation. If thermal equilibrium does not exist, as is the case after the resonant condition has been passed, then M_z approaches M_o exponentially with a characteristic time, T_1, the rate being

$$\frac{dM_z}{dt} = \frac{M_o - M_z}{T_1} \qquad \text{.... } 1.49$$

Bloch called T_1 the longitudinal relaxation time, as it determines the approach to equilibrium of the component M_z, which is parallel to B_o. M_x and M_y only differ from zero if a group of nuclei happen to be in phase, but any phase coherence is lost in a time of the order of the Bloch transversal relaxation time, T_2. Bloch assumed that the rate of approach of M_x and M_y to equilibrium was exponential and was given by

$$\frac{dM_x}{dt} = \frac{-M_x}{T_2} \; ; \quad \frac{dM_y}{dt} = \frac{-M_y}{T_2} \qquad \text{.... 1.50 - 1.51}$$

Thus combined equations 1.46- 1.48 and 1.49 - 1.51 leads to the Bloch equations for describing the actual behaviour of the macroscopic sample during an n.m.r. experiment (figure 1.3).

$$\frac{dM_x}{dt} = \gamma(M_y B_o + M_z B_1 \sin \omega t) - \frac{M_x}{T_2} \qquad \text{.... 1.52}$$

$$\frac{dM_y}{dt} = \gamma(M_z B_1 \cos \omega t - M_x B_o) - \frac{M_y}{T_2} \qquad \text{.... 1.53}$$

$$\frac{dM_z}{dt} = \gamma(-M_x B_1 \sin \omega t - M_y B_1 \cos \omega t) + \frac{(M_o - M_z)}{T_1} \qquad \text{.... 1.54}$$

The solution of the Bloch equations is simplified if they are referred to a set of axes rotating with the frequency of the field B_1. The frame rotates with variable frequency ω, exact resonance occurring when $\omega = \omega_o$. The component of M along and perpendicular to the direction of B_1 is identified as u (in-phase component of M), and v (out-of-phase component of M) respectively (figure 1.4). The relationship between the two components are

$$M_x = u\cos \omega t - v \sin \omega t; \quad M_y = -u\sin \omega t - v \cos \omega t \qquad \text{.... 1.55 - 1.56}$$

Substituting 1.55 and 1.56 into the Bloch equation, noting that $\gamma B_o = \omega_o$, gives

$$\frac{du}{dt} + \frac{u}{T_2} + (\omega_o - \omega)v = o \qquad \text{.... 1.57}$$

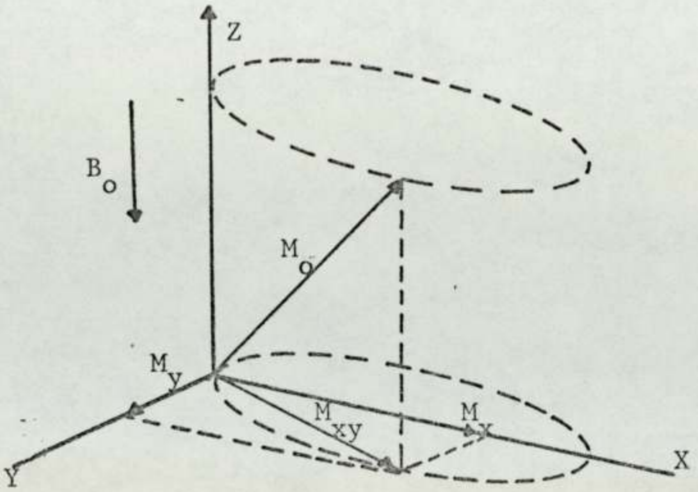


Figure 1.3. The magnetisation vector M_o amd its components in a system of rotating co-ordinates.

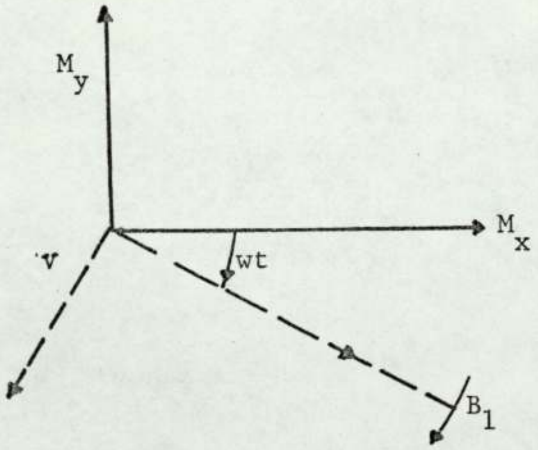


Figure 1.4. Transverse components of the magnetic moment referred to fixed axes (full lines) and axes rotating with the r.f. field (dotted lines).

$$\frac{dv}{dt} + \frac{v}{T_2} - (\omega_o - \omega)u + \gamma B_1 M_z = 0 \qquad .... 1.58$$

$$\frac{dM_z}{dt} + \frac{(M_z - M_o)}{T_1} - \gamma B_1 v = 0 \qquad .... 1.59$$

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

$$u = M_o \gamma B_1 T_2^{\,2} (\omega_o - \omega)/D; \; v = -M_o \gamma B_1 T_2/D \qquad .... 1.60 - 1.61$$

$$M_z = M_o(1 - T_2^2(\omega_o - \omega)^2)/D \qquad .... 1.62$$

where, $D = 1 + T_2^{\,2}(\omega_o - \omega)^2 + \gamma^2 B_1^{\,2} T_1^{\,2} T_2^{\,2}$ 1.63

From equation 1.61, it may be deduced that when B_1 is about 10^{-7} tesla and T_1 and T_2 no greater than a few seconds, the absoption or 'v-mode' signal should be proportional to $\gamma B_1 T_2/(1 + T_2^{\,2}(\omega_o - \omega)^2)$. This describes a Lorentzian line shape[18,21] as shown in figure 1.5. At the centre when the resonance condition is exactly fulfilled $\omega_o - \omega = 0$, the signal height is proportional to $\gamma \dot{B}_1 T_2$. In certain cases it is preferable to use the dispersion or 'u-mode' signal, and this is shown is figure 1.6. The in-phase and out-of-phase magnetisations are also described in terms of the Bloch susceptibilities χ' and χ''.

For high resolution spectroscopy, the absorption spectra are usually looked at. The area under an absorption curve can be obtained by the integration of the v term over all values of $(\omega_o - \omega)$. The result is directly proportional to χ_o which from equation 1.40 is a direct function of the number of nuclei per unit volume. Hence the area under each resonance is a direct indication of the number of nuclei of a particular type undergoing resonance.

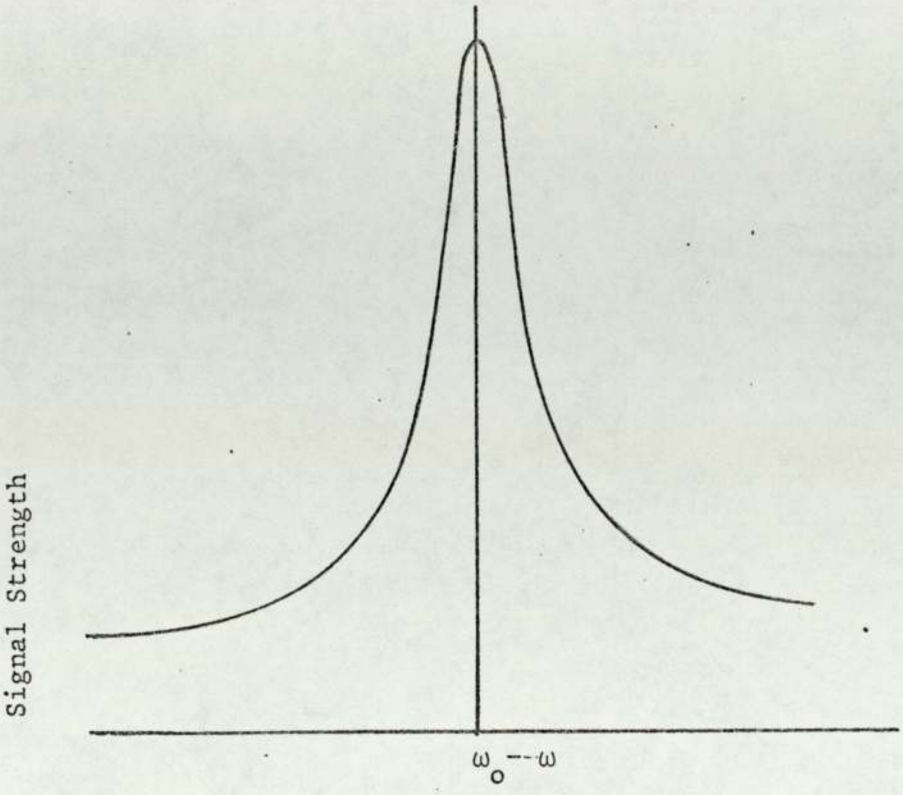


Figure 1.5. Absorption line shape (V-mode or χ") for n.m.r. resonance.

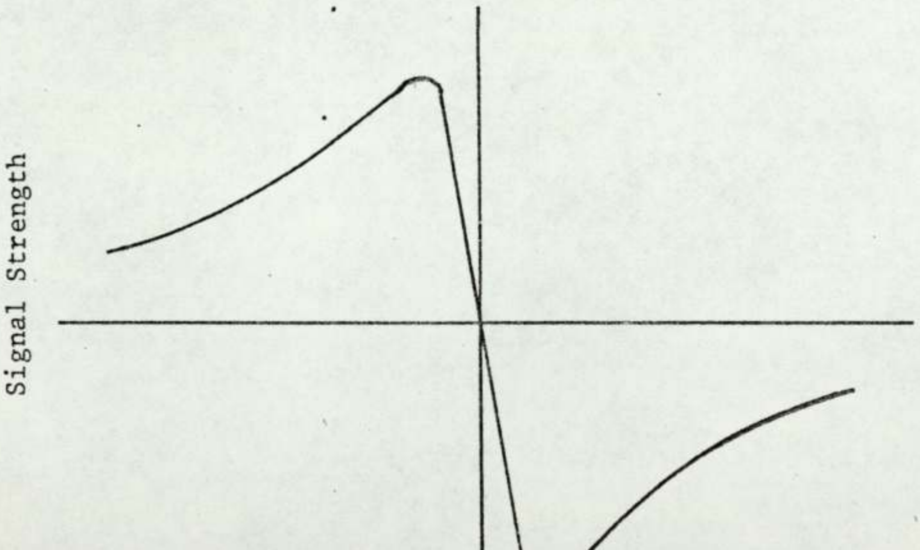


Figure 1.6. Dispersion line shape (u-mode or χ') for n.m.r. resonance.

1.8 Factors Affecting Line Shape.

It has been shown that a nuclear magnetic absorption line can be approximately represented by a Lorentzian curve.[18,21] A quantum mechanical approach to n.m.r. predicts an infinitely sharp absorption line, however, for identical nuclei, absorption occurs over a small but finite frequency range due to several line broadening effects. The width of the line is defined as its width at half-height expressed in terms of the applied field or frequency. The various factors affecting line shape will now be discussed.

1.8.1 Spin-Lattice Relaxation

The existence of the spin-lattice relaxation mechanism places some uncertainty on the life-time of the nucleus in a particular energy state. Heisenberg's Uncertainty Principle quantifies energy and time as

$$\Delta E \, \Delta t \simeq \hbar \qquad \ldots . \; 1.64$$

but as $\Delta E = h\Delta\nu$ 1.65

it follows that

$$\Delta\nu \fallingdotseq \frac{\hbar}{2T_1 h} \qquad \ldots . \; 1.66$$

i.e.

$$\Delta\nu = \frac{1}{4\pi T_1} \qquad \ldots . \; 1.67$$

where T_1 is the spin-lattice relaxation time. It is self-evident from equation 1.67 that small values of T_1 produce great uncertainty in $\Delta\nu$ and hence line broadening.

1.8.2 Spin-Spin Relaxation

In a similar manner to spin-lattice relaxation, this phenomenon leads to uncertainty in the frequency at which resonance will occur, with the resultant widening of the observed absorption.

1. 8. 3 Spontaneous Emmision

Purcell[14] found that the effect of spontaneous emmission on the life-time of the upper state and hence the line-width, was negligible.

1. 8.4 Magnetic Dipole Interaction

The magnetic environment of a nucleus may be modified by fields produced by the magnetic moments of neighbouring nuclei in fixed positions, the rotating components resulting in spin-spin relaxation broadening and the static components in magnetic dipole broadening. The static field of a nucleus a distance r from the nucleus under consideration, and lying on a line inclined at an angle Θ to the magnetic dipole axis, is given by

$$B_{stat} = -\frac{\mu}{r^3}(1 - 3\cos^2\Theta) \qquad \text{.... 1.68}$$

Therefore, in a solid sample, if amorphous, the resultant local fields can have any values between $\pm 2\mu/r^3$. This secondary field will result in resonance occurring over a range of fields and the line will be consequently broadened[23]. Where random motion is possible, as in liquids and gases, the molecular motion of the nuclei ensures that the average field experienced by any nucleus due to its neighbours is averaged to zero, and thus this type of broadening is only experienced by solid samples.

1. 8.5 Electric Quadrupole Effects

Nuclei of spin greater than ½ possess non-spherical nuclear charge distributions, resulting in their having quadrupole moments, Q. Nuclei do not have electric dipole moments and so the energy of any nucleus is independent of its orientation in a uniform electric field. However, when an electric field gradient exists, the quadrupoles undergo precession which displaces the nuclear magnetic levels. The interaction of nuclear quadrupoles with the electric field gradient, which may arise from both inter- and intra-molecular effects, offers an additional relaxation method. Hence, nuclei with quadrupole moments frequently exhibit very short spin-lattice relaxation times and the observed absorption lines are correspondingly broad.

1. 8.6 Other Causes of Line Broadening

Inhomogeneity of the magnetic field B_o over the sample volume will cause line broadening due to resonance occurring, not at a specific field strength, but over a range of field as different portions of the sample experience the resonance condition at slightly different times. Rapid spinning of the sample partially overcomes this problem.

The steady state solution of the Bloch equations assumes that equilibrium has been attained between the applied radiofrequency and the nuclear magnetisation M. In practice, the time taken to reach equilibrium is appreciable and thus a restriction is placed upon the rate at which resonance is traversed. The static nuclear magnetisation is reduced to Z_oM_o in the steady state, where Z_o is the saturation factor. If the resonance line is entered too rapidly, the signal will be strong at first and then become weaker as the magnetisation is reduced, leading to a distortion of the line shape.

Another transient effect encountered with narrow resonance bands, observed for liquids in a homogeneous field, manifests itself as relaxation "wiggles" or "ringing"[23]. These are damped oscillations which follow the resonance line when it is swept rapidly and originate from the inability of the nuclear magnetisation to follow the changing applied field. After the resonance has been traversed, a magnetic moment persists in the plane at right angles to the main field for as long as a group of nuclei continue to precess in phase, inducing a signal in the detector at the precessional frequency whose amplitude decays at a rate proportional to T_2. After the resonance line has been passed, the precessional and radio-frequency differ slightly, so that the two signals interfere with one another to give rise to a low frequency beat signal[24].

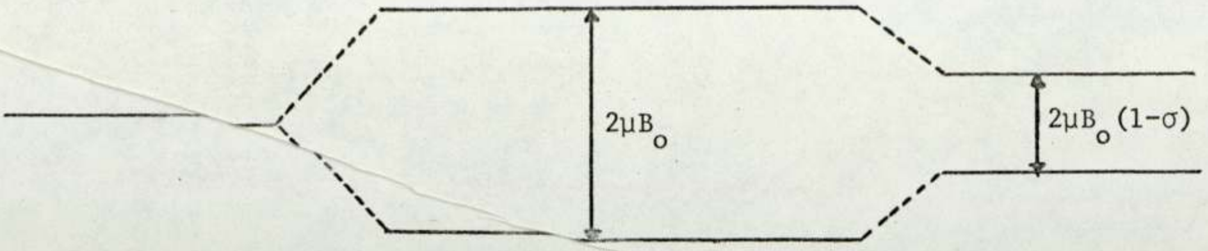
The effect of saturation on line shape has been discussed in section 1.5. Too high an r.f. power will cause a reduction in signal height accompanied by line broadening until eventually the signal will become unobservable due to there no longer being an excess population of nuclei in the lower energy state.

1.9 General Comments on Chemical Shift

Knight[25] observed that the relative position of the resonance line for certain metals and metal salts depended upon the chemical environment of the nuclei, and the phenomenon was given the name, the chemical shift. A chemical shift is observed when two or more nuclei of the same isotopic species have different resonance conditions, a separate absorption usually being observed for each distinct group with an intensity proportional to the number of nuclei in the group. The chemical shift is directly proportional to the applied field strength and arises from small inter- and intramolecular contributions to the actual field experienced by a particular nucleus. These effects may be represented by the expression

$$B = B_o(1 - \sigma) \qquad \text{.... 1.69}$$

where B is the true field experienced, B_o is the applied field and σ is a dimensionless number known as the shielding co-efficient or constant. The modification of B_o changes the Zeeman splitting and, for a specific case of $I = \frac{1}{2}$, this is illustrated below.



If two isotopically similar species in environments i and j have shielding co-efficients, σ_i and σ_j, respectively, then for the same value of B_o, the chemical shift δ_{ij} is given by

$$\delta_{ij} = \sigma_i - \sigma_j \qquad \ldots. \ 1.70$$

The measurement of absolute chemical shifts requires the comparison of the resonant frequencies of the nuclear species in a particular environment with that of the same nucleus devoid of all electrons. As this is not possible, chemical shifts are measured relative to a reference compound, which for proton spectra is usually tetramethyl silane (TMS), and are then conveniently described as the dimensionless number δ.

$$\delta = \frac{B - B_r}{B_r} \times 10^6 \text{ ppm} \qquad \ldots. \ 1.71$$

where B is the resonant field of the nucleus under observation and B_r that for the reference compound. Alternatively, since B is proportional to the frequency ν, for resonance, equation 1.71 may more conveniently be defined as

$$\delta = \frac{(\nu - \nu_r) \times 10^6}{\text{oscillator frequency}} \text{ ppm} \qquad \ldots. \ 1.72$$

where ν and ν_r are the frequencies corresponding to B and B_r in equation 1.71.

Chemical shifts measured relative to TMS are often quoted on the τ scale[26], which gives TMS at infinite dilution in carbon tetrachloride an arbitrary value of $\tau = 10$ ppm. The value of any other resonance is given by

$$\tau = 10 + \delta \qquad \ldots. \; 1.73$$

which dictates that most proton resonances have a positive τ value.

As a large part of this thesis depends on the measurement of chemical shifts, a detailed and critical discussion of the significance and origin of screening contributions is given in Chapter 3.

1.10 Spin-Spin Coupling

Using high resolution instruments it is often found that the chemically shifted peaks are themselves multiplets[27]. Gutowsky and McCall[28] found that such splitting may arise in any molecule containing two or more nuclei which resonate at different resonant conditions. The magnitude of the splitting is known as the coupling or spin-spin interaction constant (J_{AX}) and is quoted in Hz (as it is field independent)[29]. Analysis of such multiplet spectra show them to be of two types, namely first and second order. Spectra in which the chemical shift is large compared with the coupling constant are called first order. When this condition is not obeyed, i.e. $\delta \simeq J$, the spectra are designated second order.

A classification system using the symbols A, B, C ... X, Y, Z to characterise individual nuclei within the nuclear spin system has been devised. Magnetically equivalent nuclei, i.e. nuclei with the same chemical shift and coupled equally to any other resonant nuclei in the molecule, are denoted with the same symbol, whilst nuclei with chemical shift equivalence but not magnetic equivalence, although refered to by the same letter are distinguished from one another by primes. Non-equivalent nuclei of the same species separated by chemical shifts similar in magnitude to the coupling constants are denoted by the letters A,B,C. Similar non-equivalent nuclei in the same molecule but with a large chemical shift from the first set are denoted by the letters X, Y and Z.

To discuss spin-spin coupling fully it is necessary to consider all possible magnetic interactions.[30] These fall into two groups; namely electron-orbital, orbital-spin, spin-spin and spin-external field interaction, and nuclear-electronic-electronic nuclear interactions. It has been proposed[31,32] that the multiplets arise from an interaction between neighbouring nuclear spins which is proportional to their scalar product I(1).I(2) where I(1) and I(2) are nuclear spin vectors. Unlike the direct interaction of the magnetic dipole, an energy of this sort is not averaged to zero by the molecular motions. Ramsey and Purcell[33] interpreted this effect as arising from an indirect coupling mechanism via the bonding electrons in the molecule. A nuclear spin tends to orient the spins of the nearby electrons and consequently the spins of the other nuclei. Ramsey has given a general expression for spin-spin splitting but it is difficult to evaluate even in simple cases. Approximate calculations, however, show that this electron spin mechanism is the most important contribution although in general all magnetic interactions could play some part. To afford some simplification only the less complex first order spectra will now be considered.

For a set of n_A equivalent nuclei of type A and n_X equivalent nuclei of type X, a first order coupling treatment states that the resonance line for A is split into $(2n_XI_X + 1)$ equally spaced lines and the resonant line for X into $(2n_AI_A + 1)$ lines. Hence spin-spin coupling is a mutual effect such that any nucleus which causes splitting of any resonance must itself show splitting of the same magnitude and the number of lines depends on the number of nuclei in the group to which it is coupled. The relative intensities of the peaks comprising the multiplet structure are given by the n^{th} polynomial co-efficients, i.e. for $I = \frac{1}{2}$, the binomial co-efficients are

$$1,\ n,\ \frac{n(n-1)}{2},\ \frac{n(n-1)(n-2)}{3},\ \ldots..$$

where n is the number of magnetically equivalent nuclei producing the splitting.

The relative intensities can be explained by considering a nucleus with spin = $\frac{1}{2}$, having the possible spin states $m = \frac{1}{2}$, α, and $m = -\frac{1}{2}$, β. For a group containing three nuclei, e.g. CH_3, the following spin configurations are possible.

	ααα	ααβ	αβββ	βββ
		αβα	βαβ	
		βαα	ββα	
Total spin	+3/2	+1/2	-1/2	-3/2

By the interactions previously discussed, an adjacent nucleus "sees" four energy states corresponding to four values of the total spin. The spin ± 1/2states are three times as numerous as the spin ±3/2 states and thus the quartet observed has the relative intensities 1:3:3:1.

1.11 Chemical Exchange Phenomena

If a resonant nucleus, X, can exist in two environments I and II, say, in each of which it alone would produce singlet absorptions with shifts δ_I and δ_{II}, two discrete absorptions will be observed if the lifetimes of the two states, τ_I and τ_{II}, are long compared with $2\pi(\delta_I - \delta_{II})$; the shifts are in Hz. On the other hand, if the lifetimes are short compared with $2\pi(\delta_I - \delta_{II})$ a single absorption will be seen. For intermediate lifetimes broad absorptions due to the merging of the two singlets will be seen. When the two lifetimes are short, Saika and Gutowsky[34] have defined the precise time-average shift (δ obs) as

$$\delta_{obs} = P_I \delta_I + P_{II} \delta_{II} \qquad \text{.... 1.74}$$

where $$P_I = \frac{\tau_I}{\tau_I + \tau_{II}} \qquad \text{.... 1.75}$$

and $$P_{II} = \frac{\tau_{II}}{\tau_I + \tau_{II}} \qquad \text{.... 1.76}$$

i.e. P_I and P_{II} are the fractions of time spent by X in the environments I and II.

1.12 Investigations to be Carried Out in this Thesis

Many molecular interactions can be studied by making use of the chemical exchange phenomena; charge-transfer, H-bonding, dipole-dipole and dipole-induced dipole interactions have recently been studied. Investigation of the postulated dipole-induced dipole interactions between the polar solute, chloroform and various aromatic solvents forms the basis of this thesis. It is evident from equation 1.74 that the magnitude of the observed solute time-average shift will depend on the time that the chloroform spends in the free and complexed states. Hence, the measurement of the observed shift as a function of sample composition enables the equilibrium parameter pertaining to the interactions to be determined using one of several data processing methods based on equation 1.74. The equilibrium quotients so calculated will, however, be in terms of bulk concentrations rather than time fractions. Several anomalies have been found in the results obtained from the application of such data processing methods and hence in this thesis an attempt will be made to produce a more satisfactory data processing procedure. In addition, the application of the reference independent shift method preposed by Becconsall[129] to equilibrium studies will be investigated.

CHAPTER 2. EXPERIMENTAL METHODS FOR THE OBSERVATION OF HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA.

2.1 Introduction

The fundamental requirement for the observation of the nuclear magnetic resonance signal for a nucleus i is that equation 2.1 is obeyed.

$$\nu_i = \frac{\gamma B_o(1 - \sigma_o)}{2\pi} \qquad \ldots\ldots 2.1$$

For the resonant condition to be achieved either ν or B_o may be varied whilst the other is kept constant. Spectrometers employing both modes of operation are used currently. They incorporate the following basic features:- a high intensity magnetic field possessing high stability and homogeneity, a probe containing an r.f. transmitter (and receiver) coil, a system of field or frequency sweeping, an r.f. source of high stability, an r.f. receiver and amplification system, and presentation facilities. These basic features will be discussed in general terms and then the spectrometers used in these studies will be described in detail with particular regard to their modes of operation.

2.1.1 The Magnet

The stationary magnetic field B_o may be derived from either a permanent or electro-magnet, both of which are available operating at field strengths in the range 1 - 2.5 tesla. The electromagnet has the advantage of a high degree of flexibility which enables the field to be varied, so that several isotopes can be studied at one frequency without additional equipment and spectra can be observed at different field strengths and frequencies (this sometimes assists in spectral analysis). With permament magnets, the observation of different nuclei necessitates the use of separate audiofrequency oscillators tuned to the appropriate frequency for each nuclear type. Permanent magnets do , however, have the advantages of ease of operation, reliability, resolution stability and negligible running costs.

Superconducting magnets capable of homogeneous fields up to 5 tesla are available but due to the expense and elaborate technology required to maintain the temperature of the conducting wire at 10K, using liquid helium, they are scarce. Use has been made of this type of spectrometer (the S.R.C. 220 MHz instrument) but the details of its operation will not be further discussed.

To achieve highly resolved spectra, a high field homogeneity is required. To attain this in a pole gap of 10-20 mm., the poles, which are usually of 130-150 mm. diameter, should be optically flat[35], strictly parallel, and metallurgically uniform. Both permanent and electromagnets are capable of an intrinsic homogeneity of 1 in 10^6 which may be improved by the use of Golay or shim coils. The shim coils are situated in pairs on the faces of the magnet. Adjustment of stable d.c. currents passing through them produces a field gradient in a specific direction, which can be used to counteract any inherent inhomogeneity in the basic field of the magnet.

When the sample is placed between the poles it experiences a field varying by an amount ΔB_o. If the sample is spun sufficiently rapidly, it behaves as if it were experiencing the time average field $(B_o \pm \frac{1}{2}\Delta B_o)$ all the time. This effect becomes appreciable when the time for one revolution of the sample is equal to or less than $2/(\gamma \Delta B_o)$ where γ is the magnetogyroscopic ratio. Thus, if the sample is spun at such a speed that the period is short, line-widths as small as 0.05Hz or less, which are comparable with naturally occurring line-widths, can be observed.

To enable accurate shift measurements to be made, the magnetic field has to be stable (as does the radiofrequency). Permanent magnets are totally enclosed in thermostatted enclosures, which reduces field drift. Electromagnets require correction for slight variations in the current producing the magnetic field. This is conveniently done by field-frequency lock systems. Both types of spectrometer usually employ some form of field compensator to minimise field variations due to external sources. Field variations produce a voltage in the field compensator pick-up coils, in or near the magnet pole pieces, or at a nominal field node. This voltage is used to apply the necessary correction through an additional set of coils (buckout coils) wound on the pole pieces.

2.1.2. The Radiofrequency Oscillator

The field strengths possible with commonly used magnets place a limit of about 100 MHz on the radiofrequency for the observation of H^1 and F^{19} resonances. Radiofrequency sources capable of the necessary stability utilise carefully thermostatted crystals from which the frequency required can be obtained by multiplication of selected harmonics. The radiofrequency power delivered to the probe should have a constant level and this is generally achieved by incorporating an automatic gain control as the final stage of the r.f. unit, prior to its output being fed to the probe via an attenuator system. Spectrometers using just one crystal to produce different frequencies, or a separate crystal for each frequency, are employed.

2.1.3. The Detection System

The sample holder, or probe, is fixed on an adjustable mounting to enable the optimum position in the main magnetic field to be sought. The probe contains the r.f. coils wound about a glass former, an air turbine for sample spinning and often linear sweep coils; a preamplifier is usually directly connected to the probe. Two types of detection system are in general use. These will be fully discussed when the spectrometers employing them are considered.

2.1.4. Magnetic Field Sweep

Theoretically either the main field or the r.f. may be varied whilst the other remains constant, but practically it has often been found more convenient to vary the field whilst maintaining the r.f. at a steady value. The field sweep may be produced from the output of a sawtooth generator, which is amplified and then fed to two small Helmholtz coils usually mounted on the outside of the probe body. The spectrum can be swept repeatedly and, by varying the time base and the output of the sawtooth generator, the rate of recurrent sweep and its amplitude can be controlled. A slow sweep can be derived from the flux stabiliser by the application of a d.c. current. This results in a linearly varying false correction to the applied field. Alternatively, a slow sweep can be derived, for example, from the motor driven potentiometer linked to the recorder which is used to produce a permanent record of the spectrum. The field or frequency sweep corresponds to the x-axis of the recorder, whilst the y-axis is connected to the detector output, hence displaying the intensity of the n.m.r. signal. To facilitate the optimisation of the spectrometer controls, an oscilloscope is often employed to display the spectrum before a permanent record is made.

2.2 Perkin-Elmer R.10 Spectrometer

This spectrometer, capable of observing H^1 resonances at 60.004MHz, utilizes a permanent magnet of 1.4092 tesla with pole pieces of about 125 mm. diameter and a pole gap of approximately 25 mm. The magnet is in a thermally insulated container, thermostatted to maintain the temperature at 306.56K ± 0.001K, thus minimising temperature induced field drifts. Rapid magnetic disturbances are nullified by a field compensator which has a sensing element situated at the magnetic field node outside the cabinet. Coarse adjustment of the magnet strength is made by means of a mechanical shunt, but the actual optimisation of the field contours in the probe gap is obtained by nine pairs of Golay coils. An additional pair of coils allows computer controlled field shifts to be made when necessary. The basic arrangement of the spectrometer is shown in figure 2.1.

The spectrometer employs a single coil detection system, utilising a twin-T bridge. The bridge circuitry is housed in a mu metal box attached directly to the probe unit, which is held between the magnetic pole pieces by a rigid aluminium bar.

Purcell, Pound and Torrey[6] used the single coil detection system in conjunction with a bridge circuit in the first successful n.m.r experiment. It involves the measurement of the effect of the n.m.r. absorption and/or dispersion signal on the transmitter coil itself. The twin-T bridge[36] has been adopted for high resolution n.m.r. spectrometers as it gives good stability of bridge balance which is essential if a mixture of 'u' and 'v' mode signals is to be avoided. The twin-T bridge consists of two almost identical circuits in parallel, one circuit containing the sample coil and the other a dummy coil. The small absorption or dispersion signal appears as an out-of-balance e.m.f. across the bridge. The unwanted dispersion signal can be suppressed by taking advantage of the fact that the 'u' and 'v' mode signals differ

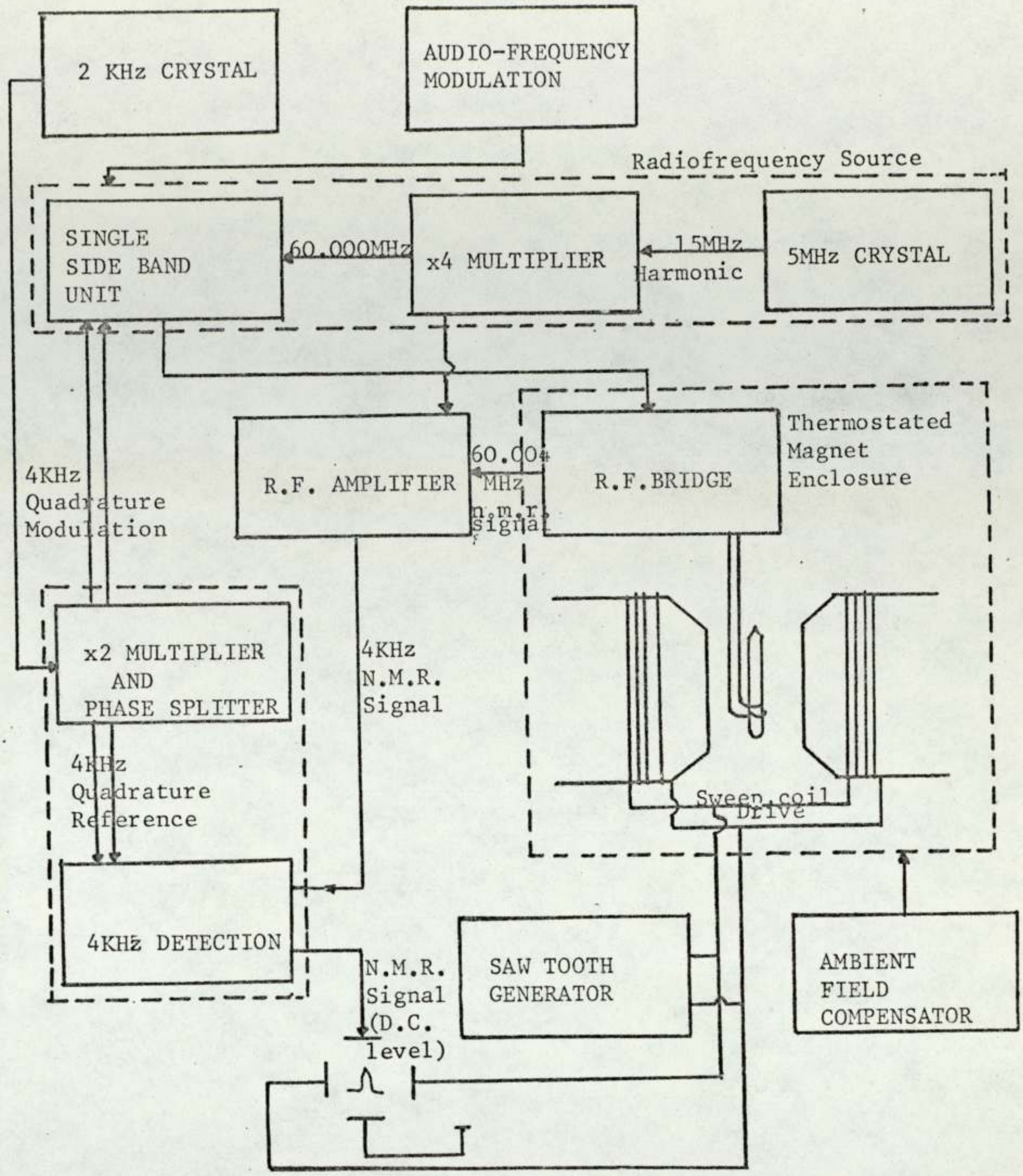


Figure 2.1. Schematic diagram of the Perkin-Elmer R.10 N.M.R. Spectrometer.

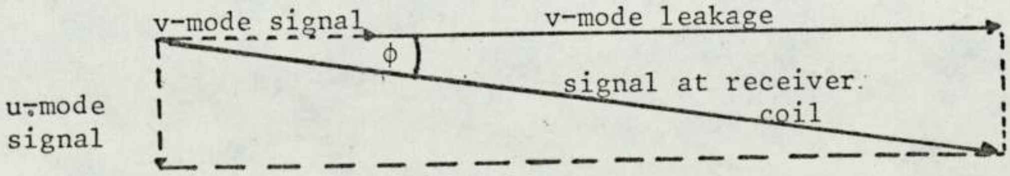


Figure 2.2. Suppression of the u-mode component of the magnetisation vector by adding in-phase leakage to the v-mode component.

in phase by $\pi/2$ rad. The bridge may be partially off-balanced so that some of the transmitter signal is leaked through in phase with the absorption signal so as to swamp the dispersion mode signal (fig. 2.2). As long as the vector sum of the absorption and out-of-balance transmitter signal is large in comparison with the dispersion signal, Φ will be small and hence, as the 'v' mode is proportional to sin ϕ, it will be insignificant.

A sawtooth generator provides the field sweep and the time base for the oscilloscope presentation. Alternatively, the field sweep may be derived from a potentiometer synchronised with the rotation of the recorder drum.

2.2.1 N.M.R. Signal Detection

The r.f. signal for proton resonance studies is derived from a thermostatted quartz crystal controlled oscillator operating at 5MHz with a high harmonic content. The second harmonic (15MHz) is selected and multiplied up to 60.000MHz. A single side-band mode of operation is employed rather than using the actual r.f. produced by multiplication of the crystal frequency. This system, together with ultimate phase detection, produces a very stable base line. A single side-band frequency of 4KHz greater than the fundamental frequency (60.000MHz) is generated in a single side-band unit (SSB), in which the carrier is modulated by two 4KHz signals in quadrature. Signals at the upper side-band frequency, the carrier and lower side-band frequency are generated but these latter two components are suppressed. The single side-band output is then fed, via an automatic gain control amplifier, to give a very stable output level and an attenuation system to the input of a twin-T bridge network. When a sample is placed in the probe, the phase and amplitude of the r.f. signal are adjusted to give a null reading across the bridge, care being taken to avoid a resonant condition. When a resonant condition is reached the inductance of the coil changes producing a bridge imbalance, the resulting signal being fed to an r.f. amplifier where (at 60.004 MHz) it is combined with a signal at the carrier frequency (60.000MHz). The mixed signal passes through a diode detector whose output is the beating 4KHz signal which contains the required n.m.r. signal characteristics. This signal is fed into an audiophase detector supplied with a reference 4KHz signal derived from that supplying the side-band unit. A d.c. signal is produced across the detector output corresponding to the n.m.r. signal, whose phase may be effectively varied. The reference phase is adjusted manually to obtain the desired mode of presentation. The output from this unit is fed to either an oscilloscope or a pen recorder. This system produces a stable n.m.r. signal superimposed on a d.c. level. The standing d.c. signal from the phase detector is reduced to zero by means of a y-axis back-off system so that the n.m.r. signal can be integrated if required.

The quality of the final signal can be improved by the use of filters, which can be selected to improve the signal-to-noise ratio. An integral of the final signal can be obtained by simply feeding the output signal to a d.c. amplifier connected across a condenser. The integral is of great use as the area under the n.m.r. absorption signal is directly proportional to the number of nuclei involved. For routine work, a permanent record of the spectrum is made on pre-calibrated charts which are mounted in the same relative position on a drum.

2.2.2 Spectral Calibration

The measurement of accurate line frequencies relies on the use of the conventional audio side-band modulation technique. In the case of the R.10 spectrometer, the r.f. is generally modulated by a known frequency to give an inverted representation of the portion of the spectrum under observation displaced to either side of the original by the modulation frequency. By the use of a suitably remote single sharp absorption as a reference (internal or external), a series of inverted sharp lines of accurately known frequency separation from the fundamental may be drawn on either side of the portion of the spectrum of interest. The exact position of all lines relative to the reference may be obtained by interpolation. When used carefully this method has the advantage of accommodating field drifts. Cyclohexane was usually used as the reference in the studies reported here. The frequencies used were derived from a Muirhead Wigan D890A Oscillator and checked to an accuracy of ± 0.01Hz using a Venner 3336 counter. Shift measurements to an accuracy of ± 0.1 Hz can be achieved.

2.2.3 The Variable Temperature Probe

To enable shift studies to be conducted at temperatures other than 306.56K, a variable temperature probe is available, allowing any temperature from 133K to 473K to be readily obtained and automatically maintained. The probe consists of a small Dewar flask surrounded by a water jacket maintained at 306.56K. The sample when placed inside the Dewar is effectively insulated from the surrounding environment. To raise the temperature of the sample, air is drawn through a large electrically heated copper block and passed to the probe. To lower the temperature below that of the magnet a supply of liquid nitrogen droplets and gas, boiled from the liquid, is mixed with dry air and the mixture heated to obtain the desired temperature. A platinum resistance thermometer, within 5mm of the r.f. coil, monitors the sample temperature by means of a bridge circuit and allows automatic correction to the pre-set temperature to be made. A copper-constantan thermocouple, incorporated within the probe, allows the accurate temperature (±0.05K) to be determined.

2.3. The Varian HA100D Spectrometer

This spectrometer, capable of observing proton resonances at 100MHz utilises an electromagnet designed for maximum field homogeneity at a field intensity of 2.349 tesla and is equipped with a manually operated field trimmer to compensate for gradual changes in the field homogeneity along the y-axis. The magnet current can be adjusted from zero to a maximum value for various magnetic field requirements. Solid state amplifier and passgate circuits regulate the current against ±10% line voltage variations. The magnet is maintained at 303K by cooling with thermostatted water the two low-impedance coils, mounted in a trunnion support yoke. The pole cap covers (which contain the Golay coils) and yoke insulation jacket insulate the pole pieces and yoke from the effect of ambient air temperature changes helping to maintain the magnetic field. Magnetic field drifts are automatically corrected by a field compensator. The application of a d.c. current to this unit provides a slow to extremely slow linear sweep. In addition this spectrometer utilises a field-frequency lock system whose operation will be described in a subsequent section.

2.3.1. The Probe

The probe contains coils for sweeping the polarising magnetic field, B_o, a transmitter coil for producing the rotating field B_1, a receiver coil for detecting the n.m.r. signal and two sets of paddles for adjusting the leakage between the transmitter and receiver coils. The receiver coil, which is placed in proximity to the sample, is wound on an inset so that the magnetic axis of the coil is parallel to the longitudinal axis of the sample. The transmitter coil is wound in two sections that surround the receiver coil so that the axes of the coils are perpendicular. A Faraday shield, located between the two coils, reduces the electrostatic coupling to a minimum. The sweep coils are located in annular slots on the side of the probe, at a considerable distance from the transmitter and receiver coils, with their magnetic axes parallel to the transverse axis of the probe. The probe itself is milled from a single aluminium forging to produce maximum stability. The operation of the cross-coil detection system utilised will now be discussed.

2.3.2 The Detection System

The crossed coil detection system was employed by Bloch, Hansen and Packard[7] in the first nuclear induction detection system. The two coils are at approximately right angles to each other. Any lack of orthogonality will cause the coils to couple and hence induce voltage leakage in the receiver coil. Skew mounting of the receiver coil and the mounting of a semi-circular sheet of metal, a paddle, in the radiofrequency field, ensures that the r.f. flux can be adjusted to give the necessary controlled finite leakage, and also allows the mode of n.m.r. signal detected to be selected. The dispersion signal is suppressed by introducing a finite amount of leakage from the transmitter coil in-phase with the absorption signal. The leakage voltage serves as a reference for the absorption signal and suppresses the unwanted mode. The degree required depends on the signal strength and may be adjusted to give a suitable leakage-to-signal ratio.

2.3.3 The Linear Sweep Unit

The linear sweep unit provides the linear sweep when connected to the d.c. coils of the probe. A phantastron oscillator furnishes a saw-tooth voltage which is applied to one of two push-pull amplifiers to modulate a 50KHz signal applied separately from a 50KHz oscillator. The 50KHz component in the output of this push-pull amplifier is π rad out of phase with the 50KHz carrier. The two outputs are mixed and amplified to provide the necessary linear d.c. sweep.

2.3.4 The Field-Frequency Lock System

Field-frequency control is a system whereby the spectrometer r.f. and the magnetic field strength at the sample are held in constant proportion. In an internal lock system, a reference material is added to all the samples studied so that the analytical and reference materials are subject to the same applied magnetic field. An error signal is derived from the dispersion mode signal of the reference compound to drive the servo-loop for field-frequency stabilisation. A simplified block diagram of an internal lock system is shown in figure 2.3.

All r.f. signals are modulation side-band responses derived by magnetic field modulation, at audiofrequencies, of the carrier. These signals may be separated one from another in phase-sensitive detectors referred to the relevant modulation frequencies. The mode of the signal, dispersion or absorption, can be set by the audiofrequency reference phase applied to the synchronous detector. The reference phase of the control channel synchronous detector is set for pure dispersion mode, a shape that is well suited for use as an error signal to pull the magnetic field back into resonance, should either the field or

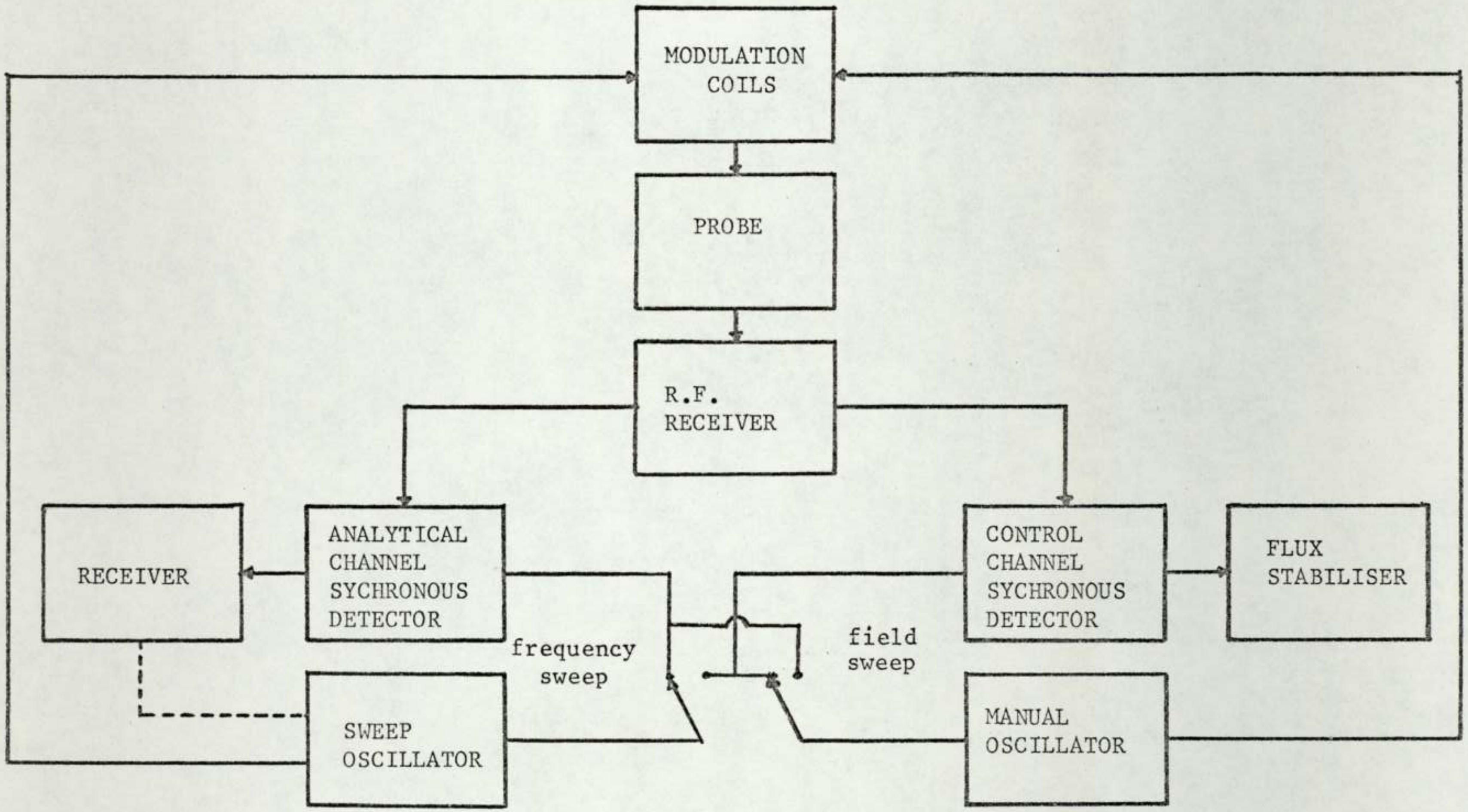


Figure 2.3. Simplified internal lock system.

frequency drift. The error signal, which may be monitored on an oscilloscope, operates through the field compensator. The rest of the n.m.r. spectrum can be examined by the use of a separate signal channel.

In the frequency sweep mode the control channel operates with B_o fixed and a constant modulation frequency, whilst the analytical channel modulation frequency is swept in a linear fashion through the desired region of the spectrum, the frequency control being mechanically linked to the horizontal motion of the recorder arm. Since the movement of the recorder arm from left to right corresponds to decreasing modulation frequency, frequency-sweep spectra are obtained by using the high frequency set of modulation side-bands to excite resonances, so that the lines in the spectrum appear in the conventional order as if the magnetic field had been swept from low to high field. The application of a third audiofrequency in this mode of operation enables double-resonance experiments to be conducted.

The analytical channel in the field sweep mode operates at a constant modulation frequency (derived from the manual oscillator), whilst the control channel modulation frequency is swept linearly using the low-frequency modulation side-bands. When the recorder arm is swept, the lock signal tends to move off resonance, generating a finite d.c. error signal that drives the main magnetic field in a linear fashion so as to hold the lock signal at resonance. The field-sweep mode has the advantage that phase changes with sweep of the observed spectrum are less marked.

The spectrometer has five possible sweep widths. When the recorder arm reaches the indicator mark on the right hand side of the chart, the sweep oscillator is at 2500 Hz. If the manual oscillator is at 2500 Hz also, then the lock signal is at the same point on the chart. However, it is often necessary to examine an expanded portion of the spectrum far removed from the lock, and this may be accomplished by off-setting the manual oscillator above or below 2500 Hz, thus displacing the lock signal to the left or right of the indicator mark. When changing from field to frequency sweep, the phase of the dispersion signal is automatically inverted so as to have the correct sense for regulation.

There are two modes of n.m.r. system operation, namely the HR and HA modes, the latter mode using the field-frequency lock system. The two modes will now be discussed.

2.3.5. The HR Mode

In the HR mode, the stability of the base line of the spectrometer output is enhanced by means of field modulation and a phase sensitive detection system. The r.f. unit shown in figure 2.4 is used. This unit consists of a highly stable fixed frequency transmitter and a high gain superheterodyne receiver isolated by a buffer amplifier to eliminate frequency shifts with load variations. The r.f. from the transmitter section passes via a push button switch attenuator to the probe. In the HR mode of operation, a 2.5 KHz modulator in the integrator/decoupler unit energises the probe a.c. coils to modulate the magnetic field in the region of the sample. As the total magnetic field is swept through the resonance line, an amplitude modulated signal is obtained. The n.m.r. signal from the low noise pre-amplifier in the probe is fed to the first of two stages of r.f. amplification. The r.f. signal is then mixed with the local oscillator frequency (95MHz) in the

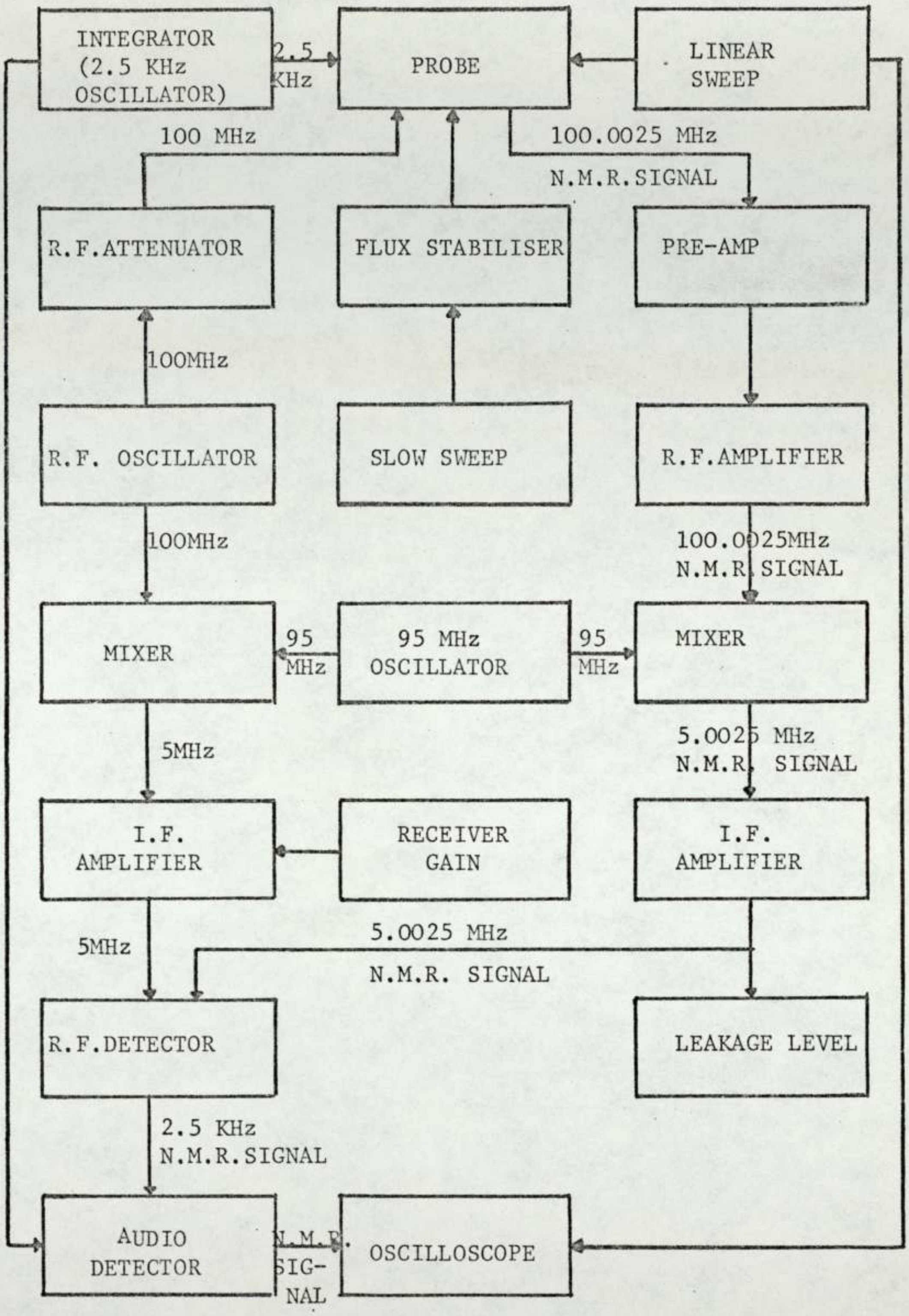


Figure 2.4 Schematic diagram of the Varian HA 100D N.M.R. Spectrometer (HR mode of operation).

mixer (A) resulting in an IF (nominally 5 MHz) signal being passed to the first of two stages of amplification. Receiver gain is accomplished by varying the bias in the two stages. A 5 MHz reference signal, derived from mixing the transmitter frequency (100 MHz) and the local oscillator frequency (95 MHz) in mixer (B) is fed to the other IF amplifier. The two IF amplifier outputs are applied to a detection system to produce a signal at 2.5 KHz, which is phase sensitive detected by reference to the 2.5 KHz modulation signal. The reference may be adjusted so that only the absorption component of the system is detected. The d.c. output signal is amplified for spectral or integral display on a recorder or oscilloscope. The signal-to-noise ratio is improved by an R.C. circuit before display on the recorder. Thus audiofrequency components of the n.m.r. signals are created and detected whilst discriminating against changes in the a.c. levels at the output of the r.f. detector due to probe balance fluctuations, minor r.f. changes and troublesome r.f. leakage.

2.3.6 The HA Mode

In the HA mode, the stability of the magnetic field is enhanced by the use of a field-frequency lock unit, the Internal Reference Proton Stabilization Unit, which provides n.m.r. stabilization by furnishing audiogain and phase detection in both signal and control channels between the r.f. unit, the recorder and the magnet stabilizing circuits. The unit consists of a transmitter section and a receiver section contained on printed circuit cards (figure 2.5).

The transmitter section contains two audiofrequency oscillators; a sweep oscillator and a manual oscillator. The oscillators are identical in nature and perform similar functions, both being modified Wein Bridge

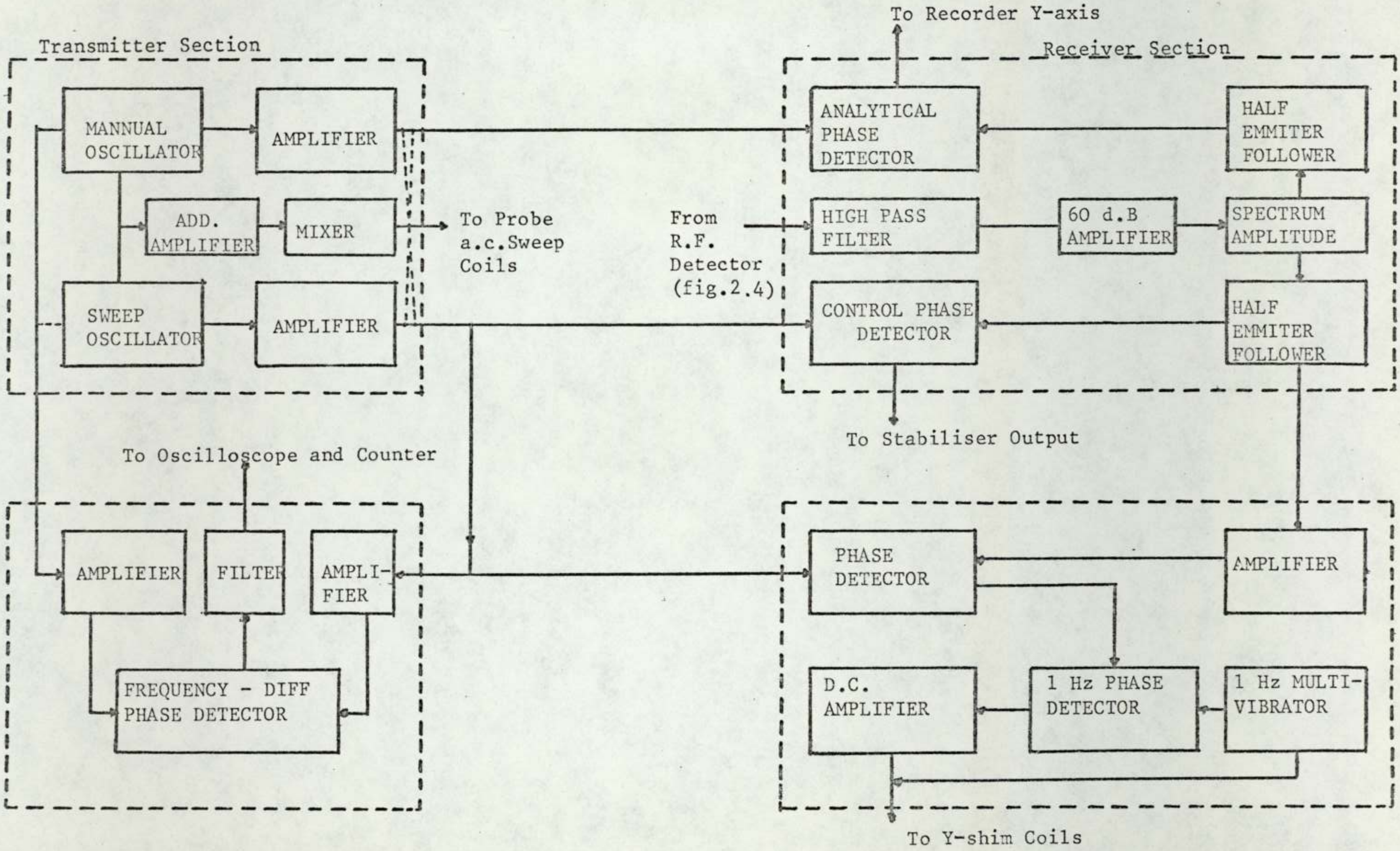


Figure 2.5 Schematic diagram of the Varian HA100D N.M.R. Spectrometer (HA mode of operation)

oscillator circuits. The sweep oscillator is tuned for 50, 100, 250, 500 and 1000 Hz ranges, whilst the manual oscillator has two frequency ranges, 1500 - 2500 Hz and 2500 - 3500 Hz. Amplifiers with thermistor stabilized outputs provide the necessary gain for the oscillators.

Both of the oscillator outputs may be switched to the Frequency Difference Phase Detector to enable the frequency difference between them to be determined. Depending on the mode of operation, either the manual or the sweep oscillator output is applied as reference voltage to this unit. This reference voltage is amplified and shaped into a square wave, then applied to the switching gear which compares the phase of the reference and analytical signals to produce a differential frequency for application to an oscilloscope or frequency counter. Alternatively, the control signal frequency may be compared with an external oscillator frequency, such as the one used for decoupling, by the appropriate switching.

The outputs of the sweep and manual oscillators before application to the a.c. sweep coils of the probe are added, amplified and filtered. The audiosignals that result modulate the 100 MHz carrier and the resultant signals are processed in the receiver section in a similar manner to that described in section 2.3.5. The input signals to the receiver are first amplified and then filtered to remove spinner noise; the "Spectrum Amplitude" controls the signal level in this amplifier. The signals are then separated into two channels - (1) the control channel which provides audiogain, phase detection and filtering of the control resonance, and (2) the analytical channel which performs the same functions for the analytical sample resonances. Impedance matching of the control and analytical signals to their respective amplifiers and phase detectors is provided by two separate emitter follower circuits.

The control signal is applied to the control amplifierand phase detector through the "Field-Frequency" switch. The reference phase detection is supplied by either the manual or sweep oscillator depending on the mode of operation. The detected coherent side-band resonance is coupled through the "Lock-On" switch to the Stabilization Filter circuit card. The Stabilization Filter provides low-pass filtering for the d.c. control signal which is then applied to the Flux Stabiliser to complete the control loop.

The analytical channel output from the emitter follower is applied to the audio-amplifier and phase detector. The reference frequency for phase detection is obtained either from the manual or sweep oscillator depending on the mode of operation. The detected coherent side-band resonance is coupled through the Integrator/Decoupler unit where it is amplified and/or integrated and then applied to the recorder circuits.

2.3.6.1 The Autoshim Facility

In the HA mode, the homogeneity of the magnetic field may be optimised by the use of this facility. The autoshim (automatic homogeneity) control adjusts the y-axis shim coil current in response to an amplitude change in a control signal. Initial homogeniety adjustments must be accurate for effective autoshim control. Since the magnetic field homogeneity must be optimum to maintain maximum n.m.r. signal amplitude, a change in the environmental conditions requires adjustment of the y-axis homogeneity. Any change in the y-axis shim coil current reduces signal amplitude slightly and thus affects the system's resolution.

Minute amplitude changes may be detected more easily when the signal is modulated at a slow rate (1 Hz). A 1 Hz square wave generated in a symmetrical multivibrator modulates the y-axis shim current. The shim coil field in turn modulates the n.m.r. signal. When the shim current is at optimum value, no modulation of the n.m.r. signal is detectable as no change occurs in the signal amplitude. However, if the shim current is less than optimum, a modulation of the n.m.r. signal is detected as the square wave sweeps the current beyond the optimum value. The same effect results when the shim current is greater than optimum, except that a phase change occurs in the modulation. The signal modulation is phase detected to obtain a d.c. voltage which is then fed to the shim coils to maintain the current at optimum value.

2.3.7 Spectral Calibration

A flat bed recorder is employed with calibrated charts. Spectra are recorded across the chart at any one of five selected sweep rates. Accurate shift measurements (± 0.05 Hz) are obtained using a Varian 4315A frequency counter by putting the signal monitor switch to "Sweep" or "Man. oscillator frequency" and thus effectively counting the two audio-modulation frequencies. Chemical shifts can thus be determined by measuring and taking the difference between the sweep frequencies of the two absorptions involved.

2.3.8 XL 100 Variable Temperature Accessory

The variable temperature accessory automatically controls the sample temperature for analytical studies in the temperature range 153K to

473K. The sample is placed in a temperature controlled nitrogen gas stream which maintains the selected operating temperature of the sample. During operations below ambient temperature, the nitrogen gas is cooled by liquid nitrogen, then the gas is heated to the selected temperature by a heater in the probe. When operating at ambient temperatures and above, the nitrogen gas flows directly into the probe for heating to the selected temperature. The temperature is controlled by a bridge circuit containing a controller and sensor. As the heated nitrogen flows past the sensor, the temperature sensitive element presents a value of resistance that maintains the bridge balance. A change in the temperature control settings or in the sensor resistance alters the bridge balance and results in a change in the heater current. The nitrogen gas temperature is increased or decreased accordingly and effects a change in the sensor resistance. The bridge balance is regained, the heater current resumes a steady value and the temperature is stabilised. The current circuits maintain the temperature within ± 1K for 5mm tubes at the sensor and regulate the temperature at the sample to ± 2K.

This accessory was modified to enable variable temperature studies to be conducted on 0.181" tubes. Thus samples prepared for use with the Perkin-Elmer R.10 spectrometer could also be run on the 100MHz instrument.

CHAPTER 3. SOME COMMENTS ON THE ORIGIN OF THE CHEMICAL SHIFT.

3.1 Introduction.

It was briefly stated in Chapter 1 that the actual field (B_i) experienced by a nucleus i when placed in an external field (B_o), differs from the applied static field by an amount which was designated σ_i, the screening constant, thus

$$B_i = B_o(1 - \sigma_i)$$

It is the purpose of this chapter to elaborate on the physical significance of the screening constant and to elucidate the quantitative approaches that have been suggested to explain the magnitude of σ.

The screening constant can be regarded as the sum of the intermolecular and intramolecular effects. The principle concern of the studies in this thesis is molecular interactions in solution, requiring the determination of the chemical shift of a common solute in different environments, and consequently it is the intermolecular terms which are of greatest importance here. For completeness, however, the origin of both inter- and intra-molecular constributions will be discussed, the emphasis being on the former. Before considering intramolecular effects, it is worthy of note that the calculation of either of these terms directly is very difficult, so attention will be directed to the concepts implicit in these.

3.2 Intramolecular Effects (σ^{intra})

Lamb[37] considered intramolecular shielding to originate from the current induced in a spherically symmetrical electron distribution about a nucleus by an applied field, the current generated producing an associated field which opposes the applied field. This approach, although adequate on an atomic scale, was unsuitable for nuclei in a molecule due to the lack of spherical symmetry of the electron charge cloud. Ramsey,[38,39] using a second order perturbation theory, calculated the first full treatment of the shielding co-efficient of a nucleus in a molecule, but it was limited by the condition that the molecule in the absence of an applied magnetic field has no resultant electron or electron orbital angular momentum. His equation consisted of two terms. The first term gave a positive contribution to the shielding and is known as the diamagnetic term. It is similar to the Lamb expression for atoms and in fact when averaged over all directions becomes equal to it. The second term, the paramagnetic term by analogy with the Van Vleck[40] equation for diamagnetic susceptibility, gave a negative contribution. The calculation of σ is not generally practicable as it would require a knowledge of the wave functions of excited states which are not usually known.

By analysis of Ramsey's approach it has been possible to attach almost classical significance to several contributions to intramolecular screening. Saika and Slichter[41] suggested splitting the total intramolecular screening into three parts, (a) a diamagnetic contribution for the atom in question, (b) a paramagnetic term for the same atom, and (c) the contribution for electrons of other atoms. It is now generally accepted that the total intramolecular screening experienced by a nucleus can be described more completely by division into four contributions, and given as

$$\sigma_A = \sigma_{dia}^{AA} + \sigma_{para}^{AA} + \Sigma_{A \neq B}\, \sigma_{AB} + \sigma_{deloc} \qquad \ldots.\ 3.2$$

Each of these terms will be considered in turn.

3.2.1 The Diamagnetic Term (σ_{dia}^{AA})

This term includes the effect which formed the basis of the Lamb theory. The diamagnetic electron currents induced in atom A produce a field, which opposes the applied field at the nucleus A and whose magnitude is proportional to the electron density around the nucleus. If the electron circulation is not uniform, a paramagnetic contribution to the shielding arises.

3.2.2 The Paramagnetic Term (σ^{AA}_{para})

The applied field, B_o, is regarded as inducing a mixing of the ground and excited states to generate this term. It may be physically envisaged as arising from the hindrance of the Larmor precession by different local fields, produced by the lack of axial symmetry of the electron cloud, with respect to the applied field direction. Theoretically it is difficult to evaluate as the exact form of the excited and ground state wave-functions are seldom known exactly. It is found[42] that only if the excited states correspond to an electron transfer between s and p orbitals does it contribute to the local paramagnetic currect; therefore, if the electrons localised on the nucleus are in a pure s-state, this term is zero.

3.2.3 The Interatomic Term ($\Sigma_{A \neq B} \ \sigma_{AB}$)

This term corresponds to term (c) of the Saika and Slichter treatment and arises principally from the so called anisotropic effect. When substituents with different principal components of the magnetic susceptibility are placed in a magnetic field, magnetic moments are induced along the principal axes of the substituents. The associated secondary field produced by these induced (sometimes called equivalent) dipoles at the nucleus are the origin of this effect. The calculation of the magnitude of the effect is simplified by assuming point magnetic dipoles acting at the neighbouring atoms or bonds. The magnitude of the total effect at a particular nucleus is dependent on the nature of the neighbouring atoms or bonds, the distance between the point dipole and the nucleus (r), and the angle between r and the induced dipole direction (Θ). The effect of the anisotropy of an axially symmetrical bond can be calculated by this approach, using the McConnell[43] equation.

$$\sigma_A = \frac{(\chi_{11} - \chi_{\perp})(1 - 3\cos^2\Theta)}{3r^3} \qquad \text{.... 3.3}$$

where χ_{11} and $\chi_{\perp}$ are the components of the magnetic susceptibility of the bond (longitudinal and transverse respectively to the axis of the bond).

3.2.4 Delocalised Electron Term (σ^{deloc})

This term is physically not unlike the Lamb theory but on a molecular scale. In molecules in which the electrons are delocalised over several nuclei, e.g. aromatic molecules, the electrons are considered to circulate in fixed orbitals in a plane at some time average angle to the applied magnetic field. The secondary fields induced oppose the applied field and result in different nuclei being screened to different degrees. Nuclei in the vicinity of the symmetry axis of the loop are shielded whilst those lying in the plane are deshielded.

All these intramolecular effects can produce a complex spectrum for a molecule which would, neglecting the effects and being a collection of chemically equivalent nuclei, be expected to give a single absorption band. The importance of the different terms varies from molecule to molecule. With proton shieldings it is bond anisotropy, that is the variation of $\Sigma_{A \neq B}$ σ^{AB}[44], that is thought to be important in observed chemical shift differences, whilst with fluorine shieldings[45] the polarity of the bonds is thought to be of over-riding importance, the electric fields produced by such bonds being important in altering σ^{AA}_{dia} and σ^{AA}_{para}.

3.3 Intermolecular Effects (σ^{inter})

This term accounts for the screening arising from the presence of solvent molecules surrounding the molecule containing the nucleus whose screening is being evaluated, and hence many authors have used the term "solvent effects" for these screenings. In a similar manner to intramolecular effects, the solvent intermolecular effect can be simplified by splitting into several contributions, namely

$$\sigma^{\text{inter}} = \sigma_b + \sigma_w + \sigma_a + \sigma_E + \sigma_c \qquad \text{.... 3.4}$$

where the various terms refer to the effects of the bulk magnetisation of the medium (σ_b), van der Vaals interactions (σ_w), anisotropy in the susceptibilities of the surrounding molecules (σ_a), the effect on an electrically polar solute of the reaction field of the solvent which is induced by the solute (the direct effect of a polar solvent may also contribute) (σ_E), and specific solute-solute or solute-solvent interaction (σ_c).

Numerous theories have been postulated to enable the individual terms of equation 3.4 to be calculated. The separation of the terms $\sigma_a + \sigma_E + \sigma_w$, however, poses a problem, for whilst isotropic solvent studies provide some information concerning σ_w alone, for both anisotropic polar and non-polar solvents, the only information which can be deduced relates to $\sigma_a + \sigma_w + \sigma_E$ and $\sigma_a + \sigma_w$ in the respective cases. Notwithstanding the implicit difficulties, numerical expressions for all three terms individually have been advanced which have given reasonable calculated values for them. It must be noted that all such expressions contain empirical constants in the guise of shape and scaling factors of some form, which must cast some doubt on their validity. The major cause of difficulty lies in the assumption that the orientation of the solvent molecules with respect to each other and the solute are completely random or random within limits.

The existance of directionally dependent molecular interactions negates this basic assumption.

Differences of any of the terms of equation 3.4 for two nuclei can affect the σ^{inter} contribution. These differences may be appreciable for two nuclei in different environments and are thus particularly important when using an external reference for the measurement of chemical shifts. For this experimental situation all of the terms often contribute significantly to the observed shift. These effects will be largely (but not completely) eliminated by the use of an internal reference. In the investigations to be discussed subsequently, the majority of the studies have been conducted using an internal reference, and hence for these studies, although it is realised that all the solvent effects may make small contributions to the shifts of the nuclei under consideration, those differential contributions other than σ_c have been neglected; thus the observed shifts can be taken as a direct measure of the σ_c term. For externally referenced studies a correction for the bulk susceptibility term (σ_b) is needed to enable the screening originating from solute-solvent interactions to be determined. Accepting this, only the terms σ_b and σ_c need to be discussed in detail, the other terms in the shielding expression being briefly treated in physical terms.

3.3.1 The Magnetic Susceptibility Term (σ_b)

In an applied magnetic field solvent molecules undergo a diamagnetic polarisation which produces an additional screening at the resonant nucleus, designated σ_b. The work of Dickinson[46] on the effect of adding paramagnetic ions to solutions forms the basis of present day understanding of σ_b. He considered the resonant nucleus to be at centre of a small spherical cavity.

Assuming that both the applied field and the magnetisation ($M = \chi_v B_o$) are homogeneous over the sample, equation 3.5 was derived for the induced field B^1,

$$B^1 = \left(\frac{4\pi}{3} - \alpha + g\right) M \qquad \ldots.\ 3.5$$

and the corresponding equation for σ_b must then be

$$\sigma_b = \left(\alpha - g - \frac{4\pi}{3}\right) \chi_v \qquad \ldots.\ 3.6$$

where χ_v is the volume susceptibility of the substance, $4\pi M/3$ is the magnetic field due to induced magnetic dipoles on the surface of the sphere, $-\alpha M$ is the diamagnetic field (α being a shape factor) and gM the magnetic field due to the material within the sphere. Some workers suggested that when an external reference was used, the difference in the shieldings of the solute and the reference due to differences in their respective volume susceptibilities could be explained in terms of equation 3.6. Frost and Hall[47] considered the full implications of the arrangement in which the n.m.r. tube containing the sample is transversely disposed to the direction of the applied field and the reference material is contained in either a spherical or cylindrical glass tube positioned co-axially within the n.m.r. tube. One such arrangement is shown in figure 3.1. If nuclei A and B resonate at B_A^o and B_B^o respectively, the actual field experienced by the respective nuclei are

$$B^T_B = B^o_B \left(1 - \alpha_4 \chi_g^1 + \alpha_3\chi_g^1 - \alpha_3\chi_B + \frac{4\pi}{3}\chi_B\right) \qquad \ldots.\ 3.7$$

and

$$B_A^T = B_A^o\left(1 - \alpha_4\chi_g^1 + \alpha_3\chi_g^1 - \alpha_3\chi_B + \alpha_2\chi_B - \alpha_2\chi_g + \alpha_1\chi_g - \alpha_1\chi_A + \frac{4\pi\chi_A}{3}\right) \qquad \ldots.\ 3.8$$

The observed chemical shift between A and B (δ^o_{B-A}) can hence be related to the true shift (δ^T_{B-A}) by combination of equations 3.7 and 3.8.

$$\delta^T_{B-A} = \delta^o_{B-A} + \left(\frac{4\pi}{3} - \alpha_2\right)\chi_B + (\alpha_2 - \alpha_1)\chi_g + \left(\alpha_1 - \frac{4\pi}{3}\right)\chi_A \qquad \ldots.\ 3.9$$

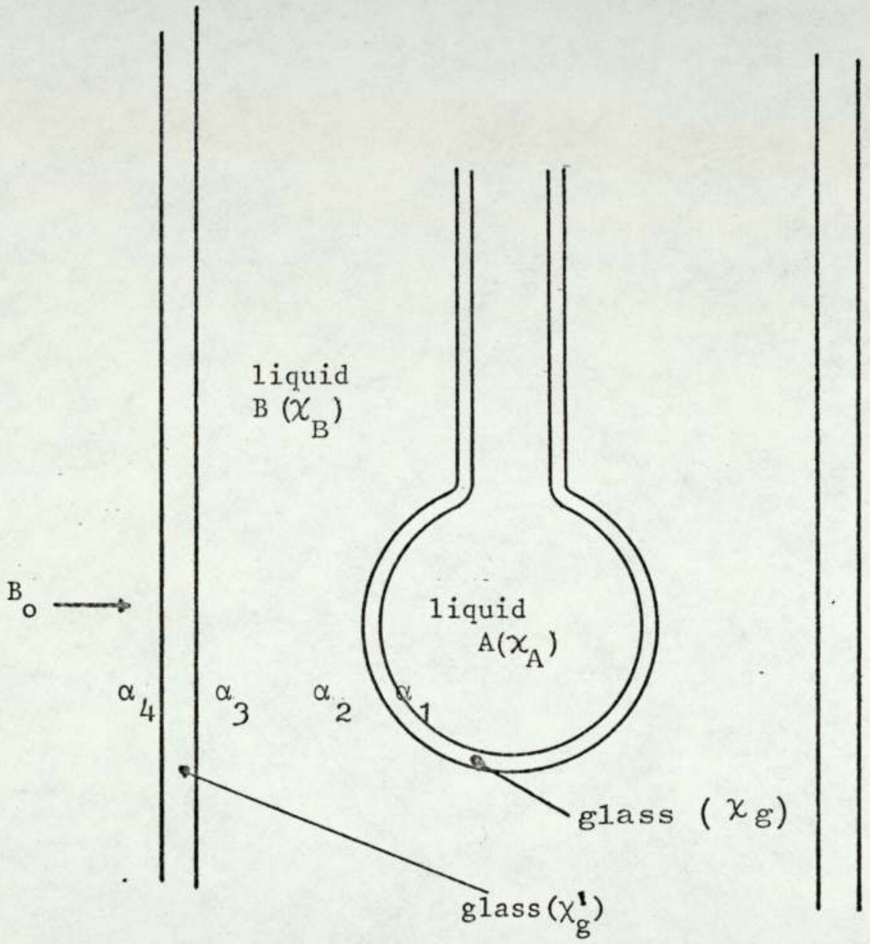


Figure 3.1. Cross-section of a n.m.r. external reference cell system.

For a perfectly spherical reference vessel $\alpha_1 = \alpha_2 = 4\pi/3$ and the true shift equals the observed shift. For a cylindrical reference vessel equation 3.9 reduces to

$$\delta^T_{B-A} = \delta^o_{B-A} + \frac{2\pi}{3} (\chi_A - \chi_B) \quad \text{.... 3.10}$$

The shift correction of mixtures is the implicit concern here. Normally, the volume susceptibility of a mixture of A and B is expressed[8] as

$$\chi_{AB} = \chi_A \Phi_A + \chi_B \Phi_B \quad \text{.... 3.11}$$

where Φ_i and χ_i are the volume fractionsand susceptibilities of i. Experimentation has shown this equation to be applicable to perfect mixtures only. Broersma[48], by classical experimentation,has shown however that deviations due to non-ideality are likely to be only of the order of 0.006 ppm, which can be considered insignificant. It is therefore possible to accurately evaluate the σ_b contribution provided the volume susceptibilities are known within the desired limits of experimental accuracy.

3.3.2 The Van der Waals Term (σ_w)

The van der Waals or dispersion forces between molecules perturb the electronic structure of the molecules and thus lead to a change in the nuclear screening constant[49]. Two effects may contribute to this:- (a) distortion of the electronic environment of the nucleus due to the varying electric dipoles of each molecule polarising an adjacent molecule. (the distortion is an expansion and the diamagnetic screening is thus diminished, resulting in a paramagnetic shift),and (b) departures from the equilibrium solvent configuration will lead to a buffeting of the solute and have a time dependent distortion of the electronic structure. This also leads to a paramagnetic shift. Repulsive effects are often taken to be negligible. Homer and Huck[50] have calculated the magnitude of σ_w in the nitroform-aromatic-cyclohexane system. In the concentration range from almost pure cyclohexane to pure aromatic, the difference between the calculated screening of the solute and the reference never exceeded about 0.002 ppm. Thus in this work, on analogous systems, the $\Delta\sigma_w$ contribution can be considered negligible.

3.3.3 The Reaction Field Term (σ_E)

A polar solute molecule polarises its liquid surroundings and the polarisation results in a reaction field, E, at the solute. If E correlates with $\vec{\mu}$ for the solute, the component of the reaction field E_z in the solute along an X-H bond that does not possess spherical symmetry will either decrease or increase the electron density at the proton, depending on the direction of E. Shifts proportional to E are therefore to be expected. A square field E^2 at the nucleus destroys the normal electron distribution about it usually leading to a low-field shift proportional to E^2. The magnitude of the σ_E contribution can thus be expressed[9]

$$\sigma_E = -C - AE_z - BE^2 \qquad \text{.... 3.12}$$

where A and B are constants pertaining to the nature of the bond and resonant nucleus respectively. It has been calculated[51] that for hydrogen, $C = 2 \times 10^{-5}$, $A = 2 \times 10^{-12}$, and $B = 10^{-18}$ esu. Work done in this laboratory suggests that for systems similar to those reported in the present investigation, differences in this term are insignificant.

3.3.4 The Anisotropy Term (σ_A)

The origin of this term is the anisotropy of the magnetic susceptibility of the solvent molecules concerned. The magnitude of this effect in the absence of any specific solute-solvent interactions is greatly affected by the average configuration of the nearest solvent neighbours with respect to the solute. The distribution of orientations of solvent molecules surrounding the solute molecule may be non-random at small distances because of the latter's presence, and this results in a time-averaged non-zero susceptibility tensor which leads to screening at the nucleus of the solute molecule.[52] Possible causes for this non-randomness, which have recently been discussed include electric dipolar interaction,[53-57] size and shape of the solute[58-60] and steric crowding in condensed aromatics.[61]

3.3.5 The Specific Association Term (σ_c)

This term is introduced to encompass the screening contributions of specific molecular interactions, a term used to include a multitude of effects, the most commonly recognised of which include H-bonding, charge transfer, dipole-dipole, and dipole-induced dipole interactions. Of particular interest here are the polar solute-aromatic solvent interactions. The mechanism by which benzene is able to produce differential solvent shifts in the proton resonances of the same molecule have been widely interpreted in terms of a benzene-solute collision complex.[62,52] The term collision complex is meant to imply a short-lived orientation of the benzene molecule that has been generated by dipole-induced dipole or other weak interactions. It is the intention in the subsequent chapters to study similar complexes, formed transiently by the interaction of chloroform with a variety of aromatic compounds according to the general reaction,

$$A + B \rightleftharpoons AB \qquad \ldots\ 3.13$$

where A is chloroform and B is the aromatic. The characteristics of the complexes AB will now be discussed, firstly considering the effect of complex formation on the appearance of the spectrum.

3.3.5.1 The Effect of Complex Formation on the Appearance of the Spectrum

The life-time of the chloroform-aromatic complex is such that the two absorptions which would be expected for the chloroform proton in the free and complexed states are not observed (see section 1.11). A single absorption which is the time-average of the two is observed. Taking the chloroform-benzene interaction as an example, the spectrum will be of the form depicted in figure 3.2. The magnitude of δ_{obs} will depend on the relative time that the chloroform spends in the free and complexed states. The measurement of this parameter as a function of concentration enables the equilibrium parameters pertaining to the interaction to be determined using one of several data processing methods available.

Unfortunately these data processing methods are generally based on fallacious assumptions and the erroneous use of different concentration scales and ranges. Therefore any conclusions concerning the characteristics of such complexes which have been drawn from results obtained by the use of such data processing methods are to be treated with suspicion. Bearing this in mind, a consideration of such conclusions may prove useful but not critical. It is the intention in the subsequent chapter to overcome these shortcomings and produce a thermodynamically valid data processing method from which meaningful parameters and conclusions can be drawn.

Several attempts have been made to determine the screening resultant from ring current effects, and if it can be assumed that no appreciable distortion of the π-cloud occurs, then such models may be quantitatively useful in explaining observed changes in solute chemical shifts.

3.3.5.2 The Aromatic Induced Shifts due to Ring Current Effects

It is evident that with aromatic solvent systems the shift changes of the solute result from the presence of the conjugated π-system of the

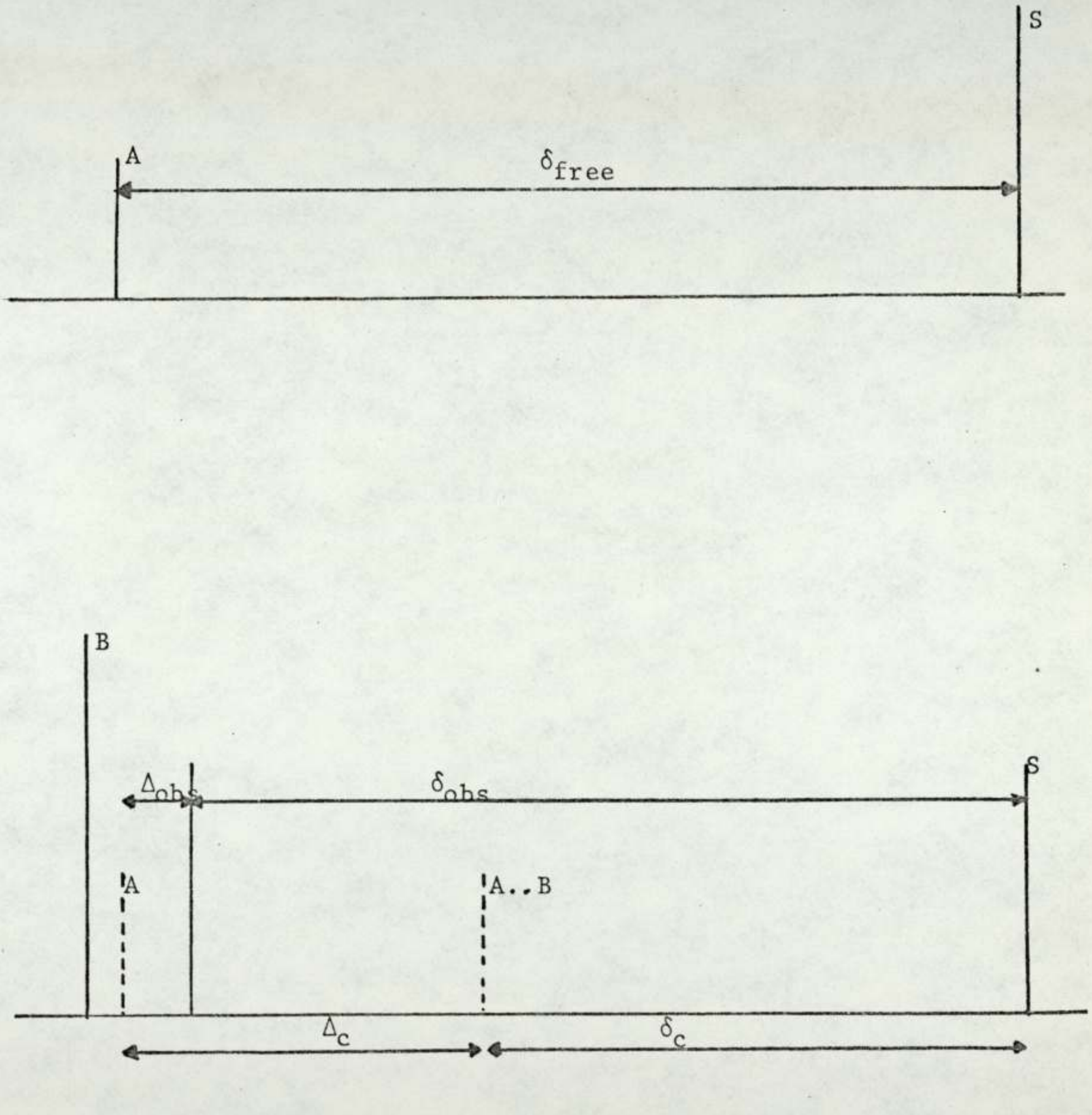


Figure 3.2. Schematic spectra showing the effect of the chemical shift of a species A due to the reaction with B according to $A + B \rightleftharpoons A..B$. An inert solvent S is employed as diluent and internal reference.

aromatic molecule. A rigorous treatment involving the consideration of the shape of the π-orbitals would be extremely complicated and thus a number of simpler models have been contrived and have had varying degrees of success.

Following Pauling,[63] Pople[64] considered the π-electrons to move in the carbon plane, producing a ring currect of magnitude (I).

$$I = \frac{ne^2 Bo \cos\Theta}{4\pi mc} \quad .... \; 3.14$$

where n is the number of circulating π-electrons, m is the electron mass, c the velocity of light and cosΘ a term allowing for the time-averaged orientation of the ring with respect to the $B_o(z)$ direction. If the current is considered to act as a point dipole ($\bar{m}$), acting at the centre of the ring, $\bar{m}$ is given by

$$\bar{m} = \frac{ne^2 a^2 B_o \cos\Theta}{4mc^2} \quad .... \; 3.15$$

where a is the aromatic ring radius. The screening experienced by an aromatic proton, a distance R from the ring centre is thus

$$\sigma_{hor} = \frac{ne^2 a^2 \cos^2\Theta}{4mc^2 R^3} \quad .... \; 3.16$$

The calculated value of -1.83ppm compares favourably with the experimentally determined value of -1.48ppm[65] (the chemical shift difference between benzene and the olefinic proton resonance of 1,3 cyclohexadiene, a molecule similar to benzene but not possessing delocalised π-electrons). Considering the delocalised π-cloud of benzene above and below the plane of the ring, as being more accurately represented as two point dipoles situated on the six-fold axis and separated by a distance 2d, Pople's treatment was extended. The resultant screening was resolved into horizontal and vertical components, the horizontal component being expressed as

$$\sigma_{hor} = \frac{ne^2a^2\cos^2\Theta}{4mc^2(R^2 + d^2)} \left[\frac{3d^2}{R^2 + d^2} - 1\right] \qquad \ldots.\ 3.17$$

By the use of simple electrostatic theory this treatment can be extended to derive an expression for the shielding on the six-fold axis at a point a distance R_1 from the plane of the ring.

$$\sigma_{vert} = \frac{ne^2a^2\cos\Theta}{4mc^2} \left[\frac{1}{((R_1 - d)^2 + a^2)^{3/2}} + \frac{1}{((R_1 + d^2)^2 + a^2)^{3/2}}\right] \qquad \ldots.\ 3.18$$

For a value of d = 0.64Å , equation 3.17 gives a value of σ_{hor} = -1.35ppm, which is a considerable improvement on the single dipole model.

A more rigorous treatment by Waugh and Fessenden,[66] involving elliptical integrals, considered the current to circulate in a loop of radius equal to that of the aromatic ring. When the π- electrons were considered to circulate in the ring plane, the poor result of -2.7ppm for σ_{hor} was obtained. Good agreement resulted, however, when the electrons were considered to circulate in two loops, above and below the aromatic plane, in a manner anologous to the two point dipole treatment of Homer and Huck.[50] Johnson and Bovey[65] have extended the treatment, and have shown that if 2d is taken as 0.918 ring radii (1.28Å) the calculated shifts for a wide range of aromatics are in excellent agreement with the observed results.

Tables have been published,[9] based on Johnson and Bovey calculations, giving the shielding values at various co-ordinates (p,z) around the aromatic. Experimental values of the induced chemical shift may be obtained by the method given in chapter 4 and these may be used in conjunction with such tables to obtain structures for the complex. It is intended to use this procedure to obtain approximate time-averaged structures for a series of chloroform-substituted benzene complexes.

It should be noted that recently[68] it has been suggested that 17% of the observed shift difference between benzene and cyclohexadiene is due to other electric effect differences than the presence of a π-cloud. Thus the inferences from the Johnson and Bovey tables will have to be treated with caution. Furthermore, when considering alkylated benzenes it is apparent that the effects of alkyl substituents on the aromatic and on the solute in the complex have to be considered. For the purposes of subsequent work, the anisotropy effects of the carbon-carbon and carbon-hydrogen bond of the benzene nucleus will be assumed to be constant, but the effects of the alkyl substituent C-C bond anisotropy will be calculated using equation 3.3. The effects of substituents on the ring current of the aromatic has been shown[69] to be no greater than 0.01 ppm and will therefore be ignored. It is appreciated that as a result of these assumptions only qualitative inferences will be justified.

3.3.5.3 The Stoichiometry of the Complex

It is generally assumed that many complexes have 1 : 1 stoichiometry. Justification for this comes mainly from cryoscopic studies. For example, these studies show that the chloroform-toluene[70] and chloroform-mestylene[71] systems, definitely form 1 : 1 molecular complexes and, therefore by inference, probably associate in a 1 : 1 ratio in solution. Much work in this field has been based on the well-known Benesi-Hildebrand[72] equation

$$\frac{1}{\Delta_{obs}} = \frac{1}{K[B]\Delta_c} + \frac{1}{\Delta_c}$$

which will be discussed further in chapter 4. Some reference will be made to the conclusions of these works but it should be appreciated that by and large they have been reached by improper use of the equation.

It has been suggested that the linearity of a plot of $1/\Delta_{obs}$ against the reciprical of mole fraction was evidence in itself for 1 : 1 stoichiometry. However, Johnson and Bowen[73] have demonstrated that such linear Benesi-Hildebrand plots are not substantiative evidence. Baker and Wilson[74] have used a modified form of the Benesi-Hildebrand equation, whereby plots should give straight lines of slope n, where n is the number of molecules of benzene complexed with each molecule of solute, the intercept being $\log_{10}K_c$. The fortuitous use of the molar scale apart, the method has several limitations, not the least being the use of too large a concentration range (the importance of using the molar scale and restricting the concentration range studied form the subject of chapter 4). The limitations are (1) the failure to incorporate in the mathematical treatment a term quantifying the probability that if the stoichiometric state 1 : n is predominant - states 1 : (n - 1), 1 : (n - 2) etc will inevitably be present; (2) the lack of any proven non 1 : 1 stoichiometric states with which to test the treatment and (3) the dubious extrapolation of shifts to 0.0K to obtain Δ_c. The authors' treatment showed several systems to be of more complex stoichiometry than 1 : 1, but no further proof was offered and the systems chosen were not well documented.

Orgel and Mulliken[75] proposed that ΔH^o, the heat of formation of a complex, should be a constant if a simple 1 : 1 complex was formed. ΔH^o may be determined from the variation of the equilibrium quotient with temperature in the following way:-

It is known that

$$\Delta G^o = -RT\ln K_x \quad \ldots. \ 3.19$$

and that

$$\left[\frac{\delta(\Delta G^{o}/T)}{\delta(1/T)}\right]_{p} = \Delta H^{o} \qquad \ldots .\ 3.20$$

Thus combining equations 3.19 and 3.20

$$-R\left[\frac{\delta(\text{In}K_{x})}{\delta(1/T)}\right]_{p} = \Delta H^{o} \qquad \ldots .\ 3.21$$

Inspection of equation 3.21 shows that a plot of $\text{In}K_x$ against 1/T should give a linear plot of gradient $-\Delta H^o/R$ at any temperature if ΔH^o is independent of temperature, which is the pre-requisite for the formation of a 1:1 complex only, or a series of isomeric 1:1 complexes. If complexes with other than 1:1 stoichiometry are present, they would be expected to form by consecutive association and hence, in such cases, each ΔH^o will differ, resulting in non-linear plots. This method has been extensively used in this laboratory and the equilibrium quotients obtained at different temperatures have resulted in linear plots being obtained. However, the data processing method used in many of these studies was that suggested by Creswell and Allred,[76] the unacceptability of which will be discussed in chapter four.

3.3.5.4 The Nature of the Interaction

In three thorough and definitive studies Klink and Stothers[55-57] have reported strong evidence that the solute dipole induces a transient dipole in the aromatic as a result of which the interaction may be considered to be of a dipole-induced dipole nature. Homer and Cooke[77] have reached similar conclusions. A similar mechanism has also been postulated by Schneider[78] to explain the large $\Delta^{\text{neopentane}}_{\text{benzene}}$ value for alkyl-X and vinyl-X solutes (where X = CN, CHO, NO_2, Cl), the benzene ring lying as far away as possible from the region of negative charge. The large diamagnetic shift of the methyl groups observed ($\Delta^{\text{neopentane}}_{\text{benzene}}$ = 0.94ppm) is expected from the known large anisotropy of the benzene ring. Huck[67] considered the transient dipole to originate from the promotion of an aromatic π-electron to a π_p^* anti-bonding orbital.

Schneider supported his dipole model by plotting the observed shifts for a series of polar (CH_3X) molecules against μ/v, where μ is the dipole moment and v the molar volume of the various solutes used. Linear plots resulted. The molar volume is introduced as, after rotational averaging, this parameter will determine the mean distance of closest approach to the benzene molecule.

It is evident that the degree of electronic anisotropy induced is important. Genuine charge-transfer drastically alters the screening effects resultant from the π-electron circulation in the vicinity of the ring. Work done in this laboratory on the p-xylene-nitroform system suggests that complete charge-transfer does not occur. The peak assigned to the complex in the ultra-violet region had an extinction co-efficient of about 50. A genuine charge-transfer band is usually denoted by a value of about 10,000.[79] By analogy, therefore, it is reasonable to assume that the complexes studied here and in subsequent chapters are predominantly dipole-induced dipole in nature.

3.3.5.5 The Strength of the Interaction

The concept of a transient 1 : 1 association at least provides a useful working hypothesis for themodynamic measurement of the strength of the interaction. If the equilibrium has any significance at all, the shifts induced by the aromatic should be temperature dependent. This has been shown to be true for aliphatic[80-83] and aromatic[55-57,62,84-85] solutes. Plots of $\ln K_x$ against 1/T have enabled the parameters ΔS^o, ΔH^o, and ΔG^o to be calculated from equations3.19, 3.21 and 3.22.

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \qquad \ldots\ 3.22$$

The subsequent calculation of heats of formation for benzene-solute interactions of the order of $4KJ.mole^{-1}$ has been taken to demonstrate the weak nature of the interaction. It is open to discussion as to which parameter (ΔH^{o} or ΔG^{o}) provides the best measure of the interaction strength.

The heat of formation has generally[77,86,87] been used as a measure of the strength of the complex without any deep-seated reasoning. From a thermodynamic standpoint ΔG^{o}, the Gibb's Free Energy, which may be envisaged as a measure of the feasibility of the reaction occurring, provides a better correlation. The invariance of ΔH^{o}, and to a smaller extent ΔS^{o}, with temperature has been demonstrated in this laboratory. It would appear, therefore, that the function ΔG^{o}, whose temperature dependence is demonstrated in equation 3.22, offers the most rational measure of the probability of a reaction occurring.

Berkeley and Hanna[88] suggested that,after allowance has been made for aromatic ring current effects, Δ_c, the shift of the complex, was the parameter to be used to indicate the strength of the solute-aromatic interaction. Work done in this laboratory suggests that Δ_c is only marginally temperature dependent. It is evident that any parameter that purports to measure the strength of the interaction must be temperature dependent; the degree of association or complex contact time is so dependent, increasing gradually as the temperature is decreased. Δ_c, as has been discussed in section 3.3.5.2 does not exactly reflect the ring current. Even so, Δ_c may be of some use as a measure of the distance of closest approach, the temperature insensitivity being explained in terms of a constant solute-solvent separation R, but a variation of possible orientations with temperature (section 3.3.5.6). A knowledge of R enables the interaction energy to be calculated by the method proposed by Homer and Cooke,[77] and thus Δ_c may indirectly reflect the strength of the interaction. The significance of Δ_c will be further discussed in a subsequent chapter.

3.3.5.6 The Stereochemistry of the Interaction

It is possible to visualise two extremes of configuration for 1:1 benezene-solute complexes, these being (1) a planar model and (2) a model in which the interacting proton situated on the molecular dipole axis of the solute is on the six-fold axis of the benzene ring. Anderson[89] has found that solvent shifts of some 1,3 dioxans are highly dependent on the size of the axial substituent in the five-position and a non-planar solute-solvent complex accounts for the observed shifts. Similarly, the solvent shifts of adamantyl halides[82] are best understood in terms of a non-planar model. Certain proton shifts in 5α-andostran-11-one[90] are best reported by a time-averaged picture in which the benzene ring is steeply inclined with respect to the plane of the steroid ring. Other evidence for this oblique model is forthcoming from the analysis of the infra-red spectra of benzene-bromine complexes. Hassel,[92] however, has determined that the structure of the benzene-bromine complex in the crystalline state is best represented by the six-fold model (2).

It has been suggested that,as benzene is twice as polarisable in the plane of the ring as along the six-fold axis , a planar type orientation is to be preferred. Rigorous calculations however, assuming all other factors to be equal, show that the interaction of a dipole with the aromatic ring is approximately twice that with the dipole acting along the six-fold axis, as when it adopts a planar structure. Steric considerations apart, it is therefore justifiable to assume that the solute will adopt configuration(2) shown in figure 3.3.

Such a static model, however, cannot account for the variation of interaction energy with temperature, as was demonstrated by Homer and Huck[67]. If, on time-average, such a static model is correct, the interaction energy will be temperature independent. It would appear more realistic to assume that the solute molecules adopt a restricted continuum of orientations slightly off the six-fold axis, which on time-average gives the static model. The solute molecule can be considered to adopt a series of orientations relative to the aromatic molecule or, on time-average to be undergoing a wobbling motion about the aromatic perpendicular axis. Such a model will be temperature sensitive owing to changes in the semi-angle (α) of the prescribed cone of motion of the solute (figure 3.4). Further evidence for the time-average cone model, which is forthcoming from a consideration of entropy effects, will be considered in detail in a later section when the necessary experimental results are available. It should be noted from figures 3.3 and 3.4 that, if the model is accepted, as the temperature increases there is a greater chance of the solute proton lying off the axis, but at the same distance from the plane of the ring, hence being slighly less shielded, as is found experimentally. The model can also be used to explain how the interaction energy[77,93] decreases with increasing temperature due to slight increases in the angle between the solute dipolar axis and the aromatic six-fold axis.

Correlation time studies of deutero-chloroform-benzene and chloroform-deutero-benzene systems have shown[94] the orientation of the molecules to be anisotropic. The tumbling motion of chloroform in benzene was found to be four times slower than in pure chloroform, presumably due to closer packing and association along the C_3 axis, the C_3 motion being unchanged. This was

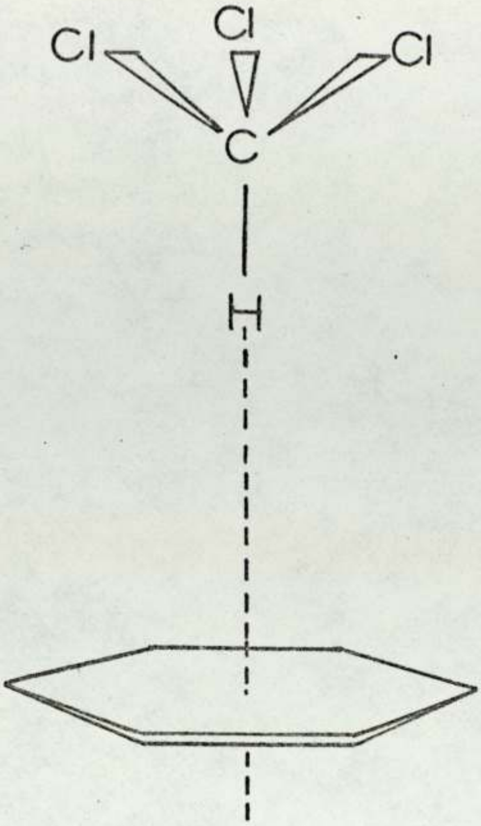


Figure 3.3. Preposed structure for the chloroform-benzene complex.

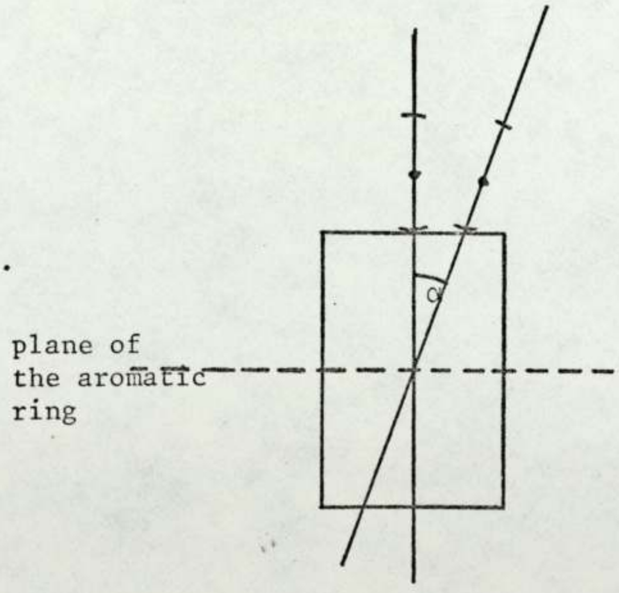


Figure 3.4. Preposed structure for the chloroform-benzene complex, showing the effect of tilting as the temperature is raised, α is the semi-angle of the cone of possible orientations.

interpreted as the formation of a complex along the symmetry axis of the chloroform perpendicular to the plane of the benzene ring. Following more recent correlation time studies[95] on the chloroform-benzene system, some doubt has been expressed as to the validity of regarding the complex as a discrete entity at all. Rothschild[95], in fact, found that the molecular moeties of the complex experienced a relatively large degree of rotational and translational motion, the translational trapping indicating that contributions to translational displacements in which the complex moved as a whole were insignificant. The rotational motion of benzene molecules dissolved in chloroform was not distinguishable from that in pure benzene. He stated that the average life-time, molecular trapping time, of the chloroform-benzene entity was of the order of 10^{-11} to 5×10^{-11} secs. The inherent anisotropy, generating the effective intermolecular forces, is assumed to be partially averaged out by fast orientational motions of all the molecules. Whilst not accepting the conclusions of the author, it is evident that the proposed model needs modification. The complex needs to be regarded as transient, the chloroform undergoing rapid jumps from one aromatic molecule to another, and adopting a configuration in each case, such that the solute proton is in the previously preposed cone of motion. The response time of the n.m.r. technique is such that only a time-averaged spectrum is observed of the solute in the free and complexed isomeric states, and thus the parameters determined relate to an average of several isomeric 1 : 1 complexes. The method of determining these parameters forms the subject of the following chapter.

CHAPTER 4. A THERMODYNAMICALLY CORRECT METHOD OF PROCESSING DATA OBTAINED FROM N.M.R. STUDIES OF MOLECULAR COMPLEXES.

4.1 Introduction

Within this chapter, the principal concern is the n.m.r. studies of 1:1 molecular complexes formed in reactions of the type:-

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

occurring in a supposedly inert solvent S. The reaction is studied by assuming that the chemical shift associated with A, present in a small fixed amount, is modified when the concentrations of B and S are varied. The observed shift is given by equation 4.2.

$$\delta_{obs} = \frac{n_{AB}}{n_A} (\delta_c - \delta_{free}) + \delta_{free} \qquad \ldots 4.2$$

or alternatively

$$\Delta_{obs} = \frac{n_{AB}}{n_A} \Delta_c \qquad \ldots 4.3$$

where δ_{free} is the shift of uncomplexed A, δ_c is the corresponding shift of the complex, n_A is the number of moles of A (free and complexed) and n_{AB} that of the complex at equilibrium, and

$$\Delta_{obs} = \delta_{obs} - \delta_{free} \; ; \; \Delta_c = \delta_c - \delta_{free}$$

If the interaction of chloroform (A) with benzene (B) in cyclohexane[52,97-99] (S) is considered as an example, the upfield shift of the chloroform proton, measured with respect to the cyclohexane, decreases as the ratio of B to S increases. From this shift variation with concentration it is possible to determine the parameters characterising the equilibrium. The increased screening of A originates from the screening magnetic field induced from the circulation of the π - electrons of the aromatic induced by the applied field B_o. It is assumed that the π - electron circulation is unchanged in the complex and thus the shielding of the solute proton (Δ_c) can be used to calculate the geometry of the complex (section 3.3.5.2) Generally the concentration of the polar solute, A, is kept low and constant to avoid the possibility of self-association.

The determination of Δ_c, which it is supposed is characteristic of the complex formed, requires the determination of n_{AB}/n_A in equation 4.2. This is not usually possible because of the transient nature of the complex, and the value of Δ_c and the associated value of the equilibrium quotient for reaction 4.1 are obtained by the use of a form of equation 4.3 and an extrapolation method due originally to Benesi and Hildebrand[72] (I), or by the use of equation 4.2 and an iterative data processing method due to Creswell and Allred[76] (II). The value of Δ_c so obtained should be independent of the concentration scale and the data processing method used for its evaluation. However, it has become a matter of considerable concern that apparent anomalies concerning the value of Δ_c and the equilibrium quotients have been found.[100-103] The most significant of these are (a) that when a particular set of experimental data is processed, the value of Δ_c obtained is found to depend on the concentration scale employed in the processing method, and (b) that when a particular reaction is studied in different supposedly inert solvents, different values of Δ_c and the various equilibrium quotients are obtained (negative values for the quotient have been found in some cases). Therefore, it is the intention within this chapter to consider the thermodynamics of solution reactions and hence produce a rational data processing method which, when used over the "correct" concentration range, is independent of scale and gives consistant results with different inert solvents. Methods (I) and (II), which are widely used for data processing, will first be discussed.

4.2 The Benesi-Hildebrand and Creswell and Allred Methods of Data Processing

The Benesi-Hildebrand (BH) method of data processing requires that (i) the initial concentration of one component, A, is very much smaller than that of the second component, B, and (ii) it is possible to construct an equilibrium quotient for reaction 4.1, all terms of which are known and which may, therfore, be free of activity co-efficients of all sorts, and moreover, which is independent of the concentration of B over an appreciable concentration range. The equilibrium quotient may be expressed in mole fraction, molar or molal terms, as shown in equations 4.4, 4.5 and 4.6 respectively.

$$K_x = \frac{x_{AB_{eq}}}{x_{A_{eq}} \, x_{B_{eq}}} = n_{AB} \, \frac{(n_A + n_B + n_S - n_{AB})}{(n_A - n_{AB})(n_B - n_{AB})} \qquad \ldots.\ 4.4$$

where n_i is the number of moles of i.

$$K_c = \frac{c_{AB_{eq}}}{c_{A_{eq}} \, c_{B_{eq}}} = n_{AB} \, \frac{(n_A - n_{AB})V_A + (n_B - n_{AB})V_B + n_S V_S + n_{AB} V_{AB}}{(n_A - n_{AB})(n_B - n_{AB})} \qquad \ldots.\ 4.5$$

where V_j is the molar volume of j

$$\text{and} \quad K_m = \frac{m_{AB_{eq}}}{m_{A_{eq}} \, m_{B_{eq}}} = n_{AB} \, \frac{(M_S)}{(n_A - n_{AB})(n_B - n_{AB})} \qquad \ldots.\ 4.6$$

where M_S is the mass of the solvent S in Kg. Applying criterion (i), equations 4.4, 4.5 and 4.6 reduce to equations 4.7, 4.8 and 4.9.

$$K_x \simeq \frac{n_{AB}(n_B + n_S)}{(n_A - n_{AB})(n_B)} \quad \ldots.\ 4.7$$

$$K_c \simeq \frac{n_{AB}(n_B V_B + n_S V_S)}{(n_A - n_{AB})(n_B)} = \frac{n_{AB}(V)}{(n_A - n_{AB})(n_B)} = \frac{n_{AB}}{(n_A - n_{AB})c_B} \quad \ldots.\ 4.8$$

$$K_m \simeq \frac{n_{AB}M_S}{(n_A - n_{AB})n_B} = \frac{n_{AB}}{(n_A - n_{AB})m_B} \quad \ldots.\ 4.9$$

where V is the molar volume of the solution. Hence it is expected that

$$K_x = \frac{K_c}{V} = \frac{K_m}{M_S} \quad \ldots.\ 4.10$$

It follows from equation 4.2 that

$$\frac{1}{\Delta_{obs}} = \frac{(n_B + n_S)}{n_B K_x\ \Delta_c} + \frac{1}{\Delta_c} \quad \ldots.\ 4.11$$

and $$\frac{1}{\Delta obs} = \frac{V}{n_B K_c \Delta_c} + \frac{1}{\Delta_c} \quad \ldots.\ 4.12$$

and $$\frac{1}{\Delta_{obs}} = \frac{M_s}{n_B K_m \Delta_c} + \frac{1}{\Delta_c} \quad \ldots.\ 4.13$$

Equations 4.11, 4.12 and 4.13 are the n.m.r. analogues of the Benesi-Hildebrand equation. If K_x, K_c and K_m are independent of $(^{n}B/(n_B + n_s))$, $(^{n}B/V)$ and $(^{n}B/^{M}s)$ respectively, it follows that plots of Δobs^{-1} against these concentration parameters will give straight lines yielding Δ_c and K_x, K_c and K_m respectively.

Scott[100] and Foster[104] have rearranged equation 4.11 to give equations of the form

$$\frac{n_B}{(n_B + n_S)\ \Delta_{obs}} = \frac{1}{K_x\ \Delta_c} + \frac{n_B}{(n_B + n_S)\Delta_c} \quad \ldots.\ 4.14$$

and,

$$\frac{\Delta_{obs}(n_B + n_S)}{n_B} = K_x \Delta_c - K_x \Delta_{obs} \qquad \text{.... 4.15}$$

Appropriate plots once again are used to determine K_x and Δ_c. Analogous equations exist for the molar and molal scale equilibrium parameters; it is to be expected that the same conditions apply to these equations.

The Creswell and Allred treatment is less assumptive that the BH method in that criterion (i) is not applicable. Combining equation 4.2 and 4.4 gives the appropriate equation,

$$\delta_{obs} = \Delta_c \left[\frac{K_x n_B + K_x n_A + n_S \pm \sqrt{((K_x n_B + K_x n_A + n_S)^2 - 4K_x n_A n_B)}}{2K_x n_A} \right] + \delta_{free} \qquad \text{.... 4.16}$$

A similar equation can be obtained in terms of K_c and K_m. Consideration of equation 4.2 indicates that a plot of δ_{obs} against n_{AB}/n_A should give a straight line. Values of n_{AB}/n_A are calculated for selected values of K_x and it is assumed that the "correct" value of K_x has been obtained when a straight line results. A computer program has been devised in this laboratory to facilitate the matriculation.[105]

To determine the circumstances in which condition (ii) is satisfied the thermodynamics of the system must be considered in detail.

4.3 The Thermodynamics of the System

4.3.1 Low Concentration Studies

The value of the equilibrium constant will be independent of the concentration of the reactants if the solute species are present in small concentrations, as the solution will be ideal and the Henry activity coefficients of all active species will be unity. The chemical potential of each species at equilibrium may then be represented by the equations.

$$\mu_i = \mu_i^{\Theta} + RT\ln x_i \qquad \ldots 4.17$$

where $\mu_i^{\Theta} = \lim_{x_i \to 0}(\mu_i - RT\ln x_i)$

$$\mu_i = \mu_i^{c} + Rt\ln c_i \qquad \ldots 4.18$$

where $\mu_i^{c} = \mu_i^{\Theta} + RT\ln V_m$

$$\mu_i = \mu_i^{m} + RT\ln m_i \qquad \ldots 4.19$$

where $\mu_i^{m} = \mu_i^{\Theta} + RT\ln M_s$

where V_m is the molar volume, c_i is the molarity of i, M_s the molar mass of species S in Kg and m_i is the molarity of i. Statistical thermodynamics predicts that for equations 4.17, 4.18 and 4.19 to be valid, each species (i) must be so dilute that in solution each molecule of i is completely surrounded by molecules of solvent S. If all the components are at such low concentration, as dictated by equation 4.17, the reaction isotherm requires that the appropriate quotient is given by:

$$RT\ln K_x' = RT\ln \frac{x_{AB_{eq}}}{x_{A_{eq}}\, x_{B_{eq}}} = \mu_A^{\Theta} + \mu_B^{\Theta} - \mu_{AB}^{\Theta} = -\Delta G^{\Theta} \qquad \ldots 4.20$$

where ΔG^{Θ} is the standard free energy change at infinite dilution i.e. the free energy change resulting from the formation of one molecule of complex, completely surrounded by S, from one molecule of A and one molecule of B, both completely surrounded by S. Similarly on the molar and molal scales, the appropriate equilibrium quotients are defined by:

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

$$= -\Delta G_c^{\ominus} \qquad \ldots 4.21$$

$$RT\ln K_m' = RT\ln \frac{m_{AB_{eq}}}{m_{A_{eq}}\, m_{B_{eq}}} = \mu_A^{\ominus} + \mu_B^{\ominus} - \mu_{AB}^{\ominus} + RT\ln M_s = -\Delta G + RT\ln M_s$$

$$= -\Delta G_m^{\ominus} \qquad \ldots 4.22$$

$\Delta G_c^{\ominus}$ and $\Delta G_m^{\ominus}$ are only of mathematical consequence; any attempt at a physical interpretation is futile. It can be seen that under those conditions , although K_x' is dependent on the chemical potentials as defined by equation 4.17, K_c' and K_m' are dependent also on molar volumes and molecular weights respectively. Studies under these conditions are unlikely to be possible because of the sensitivity of most n.m.r. spectrometers and thus an alternative concentration range must be considered. The effect of a larger concentration of, say, B on the equilibrium quotient expressions must be discussed.

The values of $\mu_A^{\ominus}$ and $\mu_{AB}^{\ominus}$ will be expected to be slightly changed to $\mu_A^{\ominus'}$ and $\mu_{AB}^{\ominus'}$ as there is now a finite chance that some position around the molecule will be occupied by molecule B. The chemical potential of B will be described by the equation

$$\mu_B = \mu_B^{\ominus} + RT\ln \gamma_B^H + RT\ln x_B \qquad \ldots 4.23$$

where γ_B^H is the Henry activity co-efficient of B. The mole fraction equilibrium quotient can therefore be expressed as:

$$RT\ln K_x = \mu_A^{\ominus'} - \mu_{AB}^{\ominus'} + \mu_B^{\ominus} + RT\ln \gamma_B^H \qquad \ldots 4.24$$

Similarly, for the molar scale, the appropriate quotient will be given by the expression:

$$RT\ln K_c = \mu_A^{\ominus'} - \mu_{AB}^{\ominus'} + \mu_B^{\ominus} + RT\ln\gamma_B^{H} + RT\ln V'_m \qquad ..4.25$$

where V'_m is the new value of V_m, which will change with each value of c_B. On the molal scale, μ_B^{m} will now be described by:

$$\mu_B^{m} = \mu_B^{\ominus} + RT\ln \frac{M_S}{1 + m_B M_S} \qquad ...4.26$$

so that K_m is given by the equation:

$$RT\ln K_m = \mu_A^{\ominus'} - \mu_{AB}^{\ominus'} + \mu_B^{\ominus} + RT\ln\gamma_B^{H} + RT\ln \frac{M_S}{1+m_B M_S} \qquad ..4.27$$

From equations 4.24, 4.25 and 4.27 it is evident that the respective equilibrium quotients are no longer independent of the concentration of B and, therefore, the use of the Benesi-Hildebrand equation and the Creswell and Allred procedure is negated, as condition (ii) is not being satisfied. The failure of studies in this concentration range, therefore, leads to the consideration of the remaining range, in which say, one component, B is at a very high concentration whilst the other two components, A and S, are at a very low concentration.

4.32 High Concentration Studies

It is reasonable to suppose that relatively small amounts of A and AB in the mixture will have very little effect on the fugacity of B, and therefore, the fugacity depends only on the relative amounts of B and S. The chemical potential of B can be described over the whole mole fraction range by the equation

$$\mu_B = \mu_B^{o} + RT\ln\gamma_B^{R} + RT\ln x_B \qquad ...4.28$$

where μ_B^{o} is the chemical potential of pure B at the same temperature and γ_B^R is the Roault Activity co-efficient of B. A plot of the fugacity of B against $n_B/(n_B + n_S)$ will be as depicted in figures 4.1 or 4.2, the activity co-efficient being given by the ratio ac/bc. It is evident that the shape of the plot is immaterial as in both cases, as x_B approaches unity, the value of the Roault activity co-efficient approaches unity. Thus as $x_B \rightarrow 1$, expression 4.28 reduces to:

$$\mu_B = \mu_B^o + RT\ln x_B \qquad \ldots 4.29$$

As $x_B = V_{BS}C_B$, where V_{BS} is the molar volume of the mixture, it follows that, as $\gamma_B^R \rightarrow 1$ on the molar scale,

$$\mu_B = \mu_B^o + RT\ln V_{BS} + RT\ln c_B + RT\ln \gamma_B^R \qquad \ldots 4.30$$

It would appear that μ_B will be independent of concentration on the molar scale only if V_{BS} is independent of composition, a condition which will only be met when the partial molar volumes of B and S are the same. The molal expression has not been considered, as it is unsatisfactory because, as $x_B \longrightarrow 1$, then $m_B \longrightarrow \infty$.

It follows that activity co-efficient free expressions for the equilibrium quotient require that μ_B and μ_{AB} be similarly independent of concentration; in statistical terms there are reasonable grounds for considering these two terms constant as x_B tends to unity. Assuming the forces between A and B, and A and S to be identical, A will be surrounded by some molecules of B (say b) and some molecules of S (say s) and thus the value of $\mu_A^{\Theta''}$ will be given approximately by the statistical expression

$$\mu_A^{\Theta''} = \mu_A^{\ o} + w = \mu_A^{\ o} + Lbw_{AB} + Lsw_{AS} \qquad \ldots 4.31$$

where

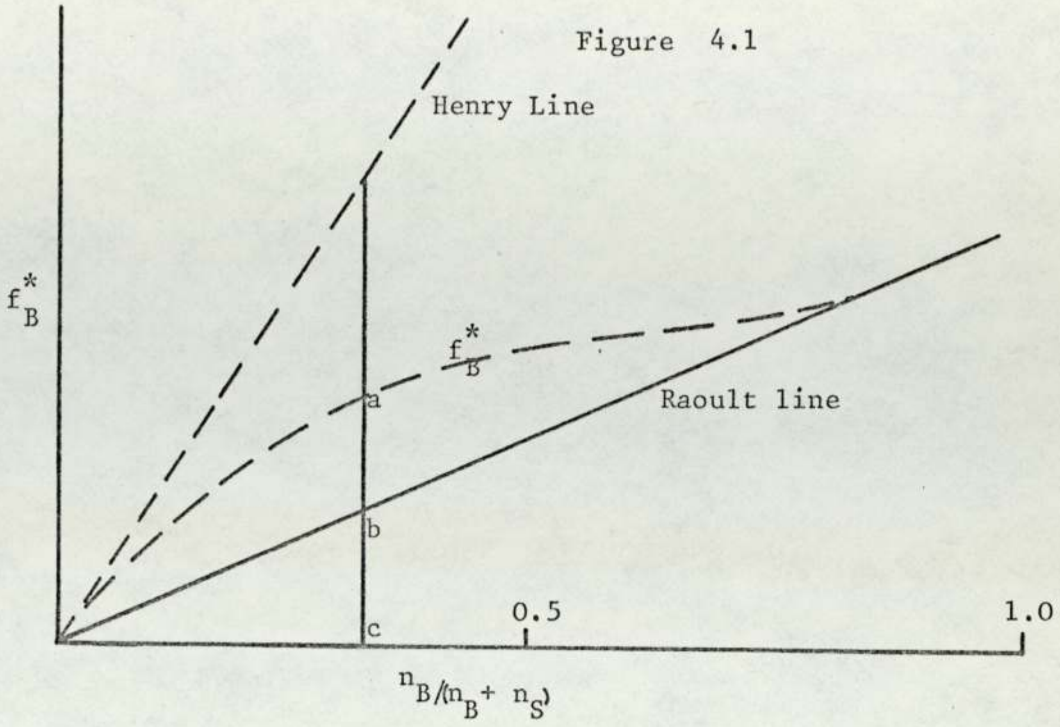


Figure 4.1 and 4.2. Typical plots of the fugacity of B (f_B^*) against the mole ration of B to S ($n_B/(n_B + n_S)$). The Raoult activity co-efficient is given by ac/bc.

$$w_{AB} = E_{AB} - \tfrac{1}{2}\left[E_{AA} + E_{BB}\right] \qquad ...4.32$$

$$w_{AS} = E_{AS} - \tfrac{1}{2}\left[E_{AA} + E_{SS}\right] \qquad ...4.33$$

where E_{ij} is the energy required to bring together one molecule of i and one molecule of j; L is Avogardo's Number. $\mu_A^{\ominus''}$ would be expected to be dependent on the ratio n_B/n_S simply because the ratio b/s would be so dependent. However, in the system studied here the interaction of A and B is very strong in comparison with interaction between A and S and thus, at a high concentration of B, A can be considered to be completely surrounded by B and thus the expression for $\mu_A^{\ominus''}$ reduces to

$$\mu_A^{\ominus''} = \mu_A^{o} + Z\,Lw'_{AB} \qquad ...4.34$$

where Z is the number of molecules of B surrounding a molecule of A. Therefore, it is suggested, but not proven, that the value of $\mu_A^{\ominus''}$ refers to the chemical potential of A when completely surrounded by B and is independent of n_B/n_S. It should be noted that at some lower concentration of B, the assumption of the exclusion of S from the first solvent shell is no longer statistically justified. Expressions for μ_A can be obtained in terms of the molar and molal scales, from equations 4.18 and 4.19, namely:

$$\mu_A = \mu_A^{\ominus''} + RT\ln V_{BS} + RT\ln c_A = \mu_A^{c} + RT\ln c_A \qquad ...4.35$$

and

$$\mu_A = \mu_A^{\ominus''} + RT\ln m_A + RT\ln M_{BS} \qquad ...4.36$$

where V_{BS} is the molar volume of the mixture of B and S and M_{BS} is the mean molar mass of the mixture of B and S. By inspection, therefore, the chemical potential of A, when expressed on the latter two scales, is only independent of n_B/n_S if the molar volumes and molar masses of B and S are equal respectively. Similar expressions and limitations apply to the chemical potential of AB. It is possible that, due to fortuitous cancellation of terms, the molar and molal scale may prove more satisfactory than the mole fraction scale. This can only be judged by results.

If the mole fraction of one component, say B, is extremely close to unity and that of the other extremely small, the equilibrium quotient will thus be given by the expressions 4.37 and 4.38 on the mole fraction and molar scales respectively.

$$RT\ln K_x'' = RT\ln \frac{x_{AB_{eq}}}{x_{A_{eq}}\, x_{B_{eq}}} = \mu_A^{\ominus''} + \mu_B^{o} - \mu_{AB}^{\ominus''} = -\Delta G^{o} \quad \ldots . \; 4.37$$

$$RT\ln K_c'' = RT\ln \frac{c_{AB_{eq}}}{C_{A_{eq}}\, C_{B_{eq}}} = \mu_A^{c''} + \mu_B^{o} - \mu_{AB}^{c''} = -\Delta G^{o} + RT\ln Vm = -\Delta G_c^{o} \quad \ldots . \; 4.38$$

Once again the molar equilibrium quotient shows a concentration dependence via a molar volume term. Before proceeding it must be pointed out that the numerical value of K_x'' given by equation 4.37 will be quite different from that of K_x' given by equation 4.20. There are two reasons for this. Firstly, the values of and the physical significance of the terms $\mu_A^{\ominus}$ and $\mu_{AB}^{\ominus}$ in the two expressions are not the same. Those terms in equation 4.20 represent the chemical potentials A and AB in very dilute solutions in S, so that each molecule A or AB is completely surrounded by molecules of S, whereas in equation 4.37, the terms represent the chemical potential of A and AB, very dilute in B so that each molecule is completely surrounded by B. Secondly, equation 4.20 contains the term $\mu_B^{\ominus}$, the chemical potential of B in very dilute solution in S, whilst equation 4.37 contains the term μ_B^{o}, the chemical potential of pure B. It is also worth pointing out that the quantities $\Delta G^{\ominus}$ and ΔG^{o}, which appear in the two equations, are not the same as the Free Energy change which would result from the formation of one mole of the complex AB from one mole of isolated A and one mole of isolated B. An analogous situation applies to equations 4.21 and 4.38.

It is evident from the arguments given above that in order to obtain rational values for equilibrium quotients (and hence Δ_c) it is only permissible to evaluate data, obtained experimentally, in which (a) both A and B are present in very low concentration in S or (b) both A and S are present in very low concentration in B. Consequently any value obtained for the quotient by processing data obtained over a wide range of concentrations of B will at best be some sort of average between K_x' and K_x'' and the "fictitious" values which would be obtained at points in the intermediate concentration range. The question of average equilibrium quotients for solutions covering a wide range of concentrations of B will be considered in section 4.6.

At present it is difficult, if not impossible, to conduct a complete series of experiments using mixtures in which the concentrations of both A and B are extremely small because of the relative insensitivity of commonly used n.m.r. spectrometers. Consequently, it is necessary to study mixtures which comply with condition (ii) and evaluate the data so obtained using equation 4.11 for which K_x is defined by 4.7 and 4.37. In the literature it is often stated[103] that consistent results can only be obtained from the use of the molar scale when the solvent is changed. It is necessary, therefore, to consider whether the BH equation 4.12 in terms of molar concentrations is perhaps more precise. The relationship between K_x and K_c is defined by equation 4.10 and it would therefore appear that, although K_x may be independent of x_B over a particular concentration range, K_c may be independent only if (other considerations apart) the molar volume of the solution is independent of its composition, a condition which will only be met over a finite range if the two species B and S have the same partial molar volumes. This is also evident from a consideration of equation 4.30. It is, therefore, possible that the increased consistency, resultant from the use of the molar scale over ranges in which K_x is not independent of x_B, may arise simply because the variation in the molar volume, by chance, is in the opposite sense from that in K_x. It is thus fortuitous that the values of K_c have been found to be less critically dependent on the nature of S than the values of K_x. It is to be expected that changing the solvent will change the value of K_x obtained from BH plots over ranges intermediate between $x_B = 0$ and $x_B = 1$, simply because the value of μ_B^Θ and μ_{AB}^Θ would be so dependent. Much the same criticisms can be levelled at the molality scale, for in this case K_m can only be independent of $^{n}B/n_S$ over the appropriate range if the molecular weights of B and S are the same. It is clear that the mole fraction scale only is potentially acceptable for the evaluation of data obtained for reaction (4.1), over a range of compositions, and then only if the range if quite restricted.

4.3.3. The Choice of Concentration Range

The limitations of the n.m.r. technique would appear to restrict the choice of experimental concentration range to that in which A and S are present in dilute solutions of B, as defined by equation 4.37. In order to discover the precise concentrations which are acceptable it is necessary to delve more deeply into some of the points raised earlier. It is convenient to use the well documented chloroform (A) - benzene (B) - cyclohexane (S) system as a model. Much information is available regarding the behaviour of mixtures of benzene and cyclohexane. and the Roault activity co-efficient of benzene in cyclohexane is certainly close to unity over the range $x_B = 0.9$ to $x_B = 1.0$, as can be seen in figure 4.3.

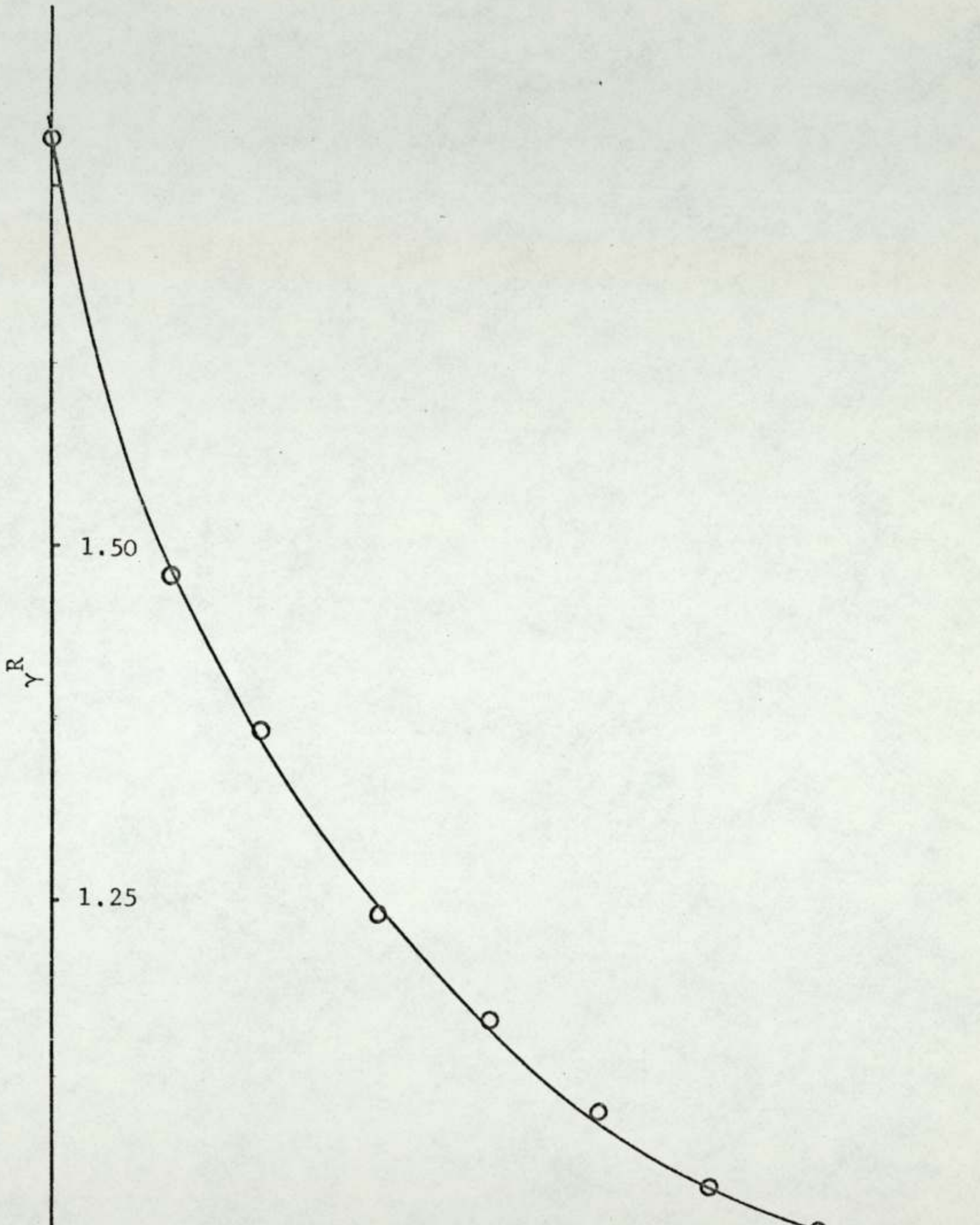


Figure 4.3. The activity co-efficient of benzene in cyclohexane as a function of mole ratio of B to S ($n_B/(n_B + n_S)$)

The data illustrated were deduced by Homer et al[106], from the results of Scatchard et al[107.108]. Consequently, although no information is available regarding the behaviour of benzene in cyclohexane in the presence of a small quantity of chloroform, it would appear reasonable to assume that, as long as the mole fraction of chloroform is very small, to a first approximation the (Roault) activity co-efficient for benzene within this concentration range may be ignored.

For the most part, these studies have been carried out on mixtures in which the mole fraction of chloroform is about 0.005 and the next concern is whether this is sufficiently low. Experimentation shows that very little change occurs in δ_{obs} when the mole fraction of chloroform is changed from 0.005 to 0.01, from which it can be concluded that at these concentrations Henry's law is obeyed. The effect of changing environment (when x_B changes from 0.9 to 1.0) on the chemical potentials of A and AB has to be considered. It has previously been shown on statistical thermodynamic grounds that, it is reasonable to assume that over this narrow concentration range, the activity co-efficients are similar to that in pure benzene and hence should be independent of n_B/n_S.

It would therefore appear that criterion (ii) will be satisfied if x_B is not far removed from unity and x_A is 0.005 or less; K_x as defined by equation 4.37 will be almost independent of the value of x_B and meaningful values for K_x and Δ_c can be obtained by either method (I) or (II). It is the intention to investigate the application of method (I), the Benesi-Hildebrand method, first and hence the machinations of this data processing method will be considered initially.

4.4 Data Evaluation

In the subsequent evaluation of the application of the Benesi-Hildebrand treatment, the results have been obtained by a computer data fitting procedure "BHCURVEFIT". Attempts at obtaining the best fit by first plotting a Δ_{obs} vis. mole fraction correction plot, and then processing the corrected values, introduced anomalies in the computed values of equilibrium quotients and Δ_c's. To eradicate this, the uncorrected data ~~was~~ were processed allowing the computer (an Elliot 1905) to determine the best line fit to the data up to a quadratic, the differential and intercept of the equation at the extrapolated point corresponding to zero inert solvent (S) concentration being evaluated to enable the determination of the equilibrium parameters.

It was found that for all but one of the systems studied, the computer fitted the data to linear equations, inferring that the product term $K\ \Delta_c$ was constant over the concentration range studied. One system, however, was computer fitted to a quadratic equation. A least squares linear fit of this data showed two points to be deviant from the best straight line by 0.03Hz. The computer program being used, therefore, appeared to be curve-fitting even these slight deviations. To maintain a consistent basis, therefore, the data was processed by a linear fitting procedure with the proviso that, if the computer output showed the standard deviation of a shift to be greater than 0.05Hz, the very limit of experimental accuracy, this data point was removed and the remaining data re-evaluated. This procedure removed subjective operator error. As a consequence, all the BH results quoted in this and the subsequent chapter refer to linear evaluations.

4.5 The Limitations of the Benesi-Hilebrand Method

Thermodynamic criteria have defined the relative concentrations of the components of the system, namely that only when x_A is less than 0.005

and x_B in the range 0.9 to 1.0, can plots of Δ_{obs}^{-1} against $(n_B+n_S)/n_B$ be expected to be linear. To check this, the chloroform-benzene-cyclohexane system was studied with respect to both the mole fraction and molar scales initially, the equilibrium quotients and Δ_c values being determined by the procedure stated in section 4.4. From equation 4.10 it is evident that K_c/K_x should be a constant, equal to the molar volume of the mixture which,at the point $(n_B + n_S)/n_B = 1$, is identical to that of benzene. A study of the chloroform-benzene system in various inert solvents should give similar values for K_x or K_c and Δ_c in each case. To test this five solvents which were thought to be inert were chosen as diluents. They were cyclohexane (1), bicyclohexyl (2), cis-decalin(3) tetradecane (4) and hexadecane (5). Solvents (2) and (3) were by analogy with solvent (1) thought to be inert,[86] whilst (4) and (5) were chosen as probably inert. It is to be expected that the electric field and dispersion forces experienced when the solvent is changed will be very similar, as the refractive index and dielectric constant for the five solvents, shown in Table 4.1, which are proportional to electric field and dispersion forces respectively, are almost equal (see Chapter 3.)

Table 4.1

The Di-electic Constants and Refractive Indices[109] of the five solvents used in these studies at 293K (+ at 298K).

Solvent	Refractive Index	Di-electric Constant
cyclohexane	1.4262	2.023[+]
hexadecane	1.4345	2.06[∓]
tetradecane	1.4289	2.04[∓]
cis-decalin	1.4810	2.19[∓]
bicyclohexyl	1.4663	2.15[∓]

[∓] Calculated from the refractive index at 293K

All the reagents were of the best commercial purity available. The purity was checked by n.m.r. and gas-liquid chromatography. The chloroform was dried over calcium chloride and then distilled to remove the ethanol stabiliser. The composition of the samples is given in Table 4.2. The shifts at 306.56K, with benzene as reference, were measured on the R.10 Spectrometer using the conventional modulation side-band technique, the accuracy of the shift measurements being better than 0.1 Hz. These shifts are also shown in Table 4.2. The parameters used in these and subsequent evaluations are shown in Table 4.3. The results of the application of the Benesi-Hildebrand method to those data points in Table 4.3,with x_B in the range 0.9 to 1.0,are given in Table 4.4.

Cont. page 88

Table 4.2

The composition of the mixtures employed in the investigation of the chloroform (A) - benzene (B) reaction in a series of inert solvents (S), together with the effective number of moles of S, the mole fraction of B and the corresponding chemical shifts of chloroform relative to benzene (1) and relative to cyclohexane (2).

No.	$10^4 n_A$/ mol	$10^2 n_B$/ mol	$10^2 n_S$/ mol	$10^3 n_S \frac{V_S}{V_B}$/ mol	x_B	$\delta_{obs}^{(1)}$/ Hz	$\delta_{obs}^{(2)}$/ Hz
S = cyclohexane							
1.1	0.8980	0.2764	25.015	30.435	0.099	16.81	-
1.2	1.1183	0.4160	12.589	15.317	0.246	28.11	-317.16
1.3	0.9307	0.6309	12.456	15.155	0.334	32.66	-311.07
1.4	1.0429	1.0271	12.489	15.195	0.449	39.44	-306.01
1.5	1.5295	1.5259	12.499	15.207	0.547	43.58	-301.43
1.6	1.9223	1.1813	6.2778	7.6382	0.649	47.50	-297.15
1.7	0.7372	1.0956	3.3158	4.0343	0.767	51.44	-293.47
1.8	1.1342	1.0018	1.7697	2.1532	0.842	53.91	-290.84
1.9	0.9214	1.4353	1.2226	1.4875	0.916	55.66	-289.19
1.10	0.8127	1.5673	1.0211	1.2423	0.934	56.06	-288.80
1.11	0.8141	1.9047	1.0121	1.2314	0.945	56.41	-288.43
1.12	0.9206	1.1952	0.5000	0.6083	0.953	56.62	-288.27
1.13	0.9382	1.6172	0.4886	0.5945	0.965	57.05	-288.04
1.14	0.8963	1.6314	0.3462	0.4212	0.974	57.18	-287.71
1.15	0.9298	1.6520	0.2444	0.9831	0.983	57.36	-287.52
1.16	0.8762	1.6585	0.0782	0.0951	0.990	57.53	-287.41
S = cis-decalin							
2.1	1.0395	0.0332	12.014	20.481	0.027	9.74	
2.2	1.7884	0.0739	11.626	19.820	0.058	11.99	
2.3	1.8462	0.1081	10.123	17.257	0.095	14.18	

CONT.

Table 4.2 (Cont.)

No.	$10^4 n_A$/ mol	$10^2 n_B$/ mol	$10^2 n_S$/ mol	$10^3 n_S \frac{V_S}{V_B}$ / mol	x_B	$\delta^{(1)}_{obs}$/ Hz	$\delta^{(2)}_{obs}$/ Hz
2.4	2.3664	0.3329	15.348	26.165	0.176	20.10	
2.5	1.4718	0.8516	15.378	26.216	0.354	30.78	
2.6	1.7492	1.2634	10.789	18.393	0.535	39.91	
2.7	0.9977	1.8207	6.1726	10.523	0.743	48.82	
2.8	2.1193	1.7794	3.1626	5.3916	0.840	52.57	
2.9	1.3386	2.6686	2.8866	4.9213	0.898	54.48	
2.10	1.4911	2.7866	1.4361	2.4481	0.946	56.29	
2.11	1.7181	1.3646	0.1667	0.2842	0.976	57.06	
2.12	1.1316	2.3797	0.1654	0.2819	0.988	57.55	
S = trans-bicyclohexyl							
3.1	1.8571	0.1845	12.2210	25.581	0.125	16.00	
3.2	0.7305	0.2562	9.8884	20.698	0.204	20.54	
3.3	1.2925	1.1188	11.3360	23.791	0.493	36.60	
3.4	1.4495	2.0291	0.0815	16.916	0.711	46.75	
3.5	1.5003	3.4625	8.5583	17.914	0.799	49.73	
3.6	1.8236	4.0791	3.8425	8.0431	0.910	54.71	
3.7	0.9231	2.0955	1.0526	2.2112	0.948	55.99	
3.8	1.0061	5.4165	1.5951	3.3388	0.969	56.85	
3.9	1.9024	4.5961	0.8951	1.8736	0.977	57.31	
3.10	1.6159	4.7219	0.4504	0.9427	0.987	57.43	
S = tetradecane							
4.1	0.7707	0.6291	6.8746	20.039	0.083	10.80	
4.2	0.8687	0.2095	8.0296	23.406	0.205	17.39	
4.3	1.0136	0.5968	5.5071	16.053	0.515	33.21	
4.4	0.9625	1.2073	4.9314	14.375	0.706	43.18	
4.5	1.4333	2.3477	5.5879	16.288	0.803	47.75	
4.6	1.1493	2.1666	2.8296	8.2483	0.880	51.77	

Table 4.2 (Cont.).

No.	$10^4 n_A$/ mol	$10^2 n_B$/ mol	$10^2 n_S$/ mol	$10^3 n_S \overline{V_S / V_B}$/ mol	x_B	$\delta_{obs}^{(1)}$/ Hz	$\delta_{obs}^{(2)}$/ Hz
4.7	0.9767	1.1686	1.4296	4.1673	0.884	52.10	
4.8	0.7849	0.9746	0.9981	2.9095	0.900	52.64	
4.9	1.3721	1.6904	1.0472	3.0536	0.934	54.53	
4.10	0.8695	1.1810	0.4651	1.3558	0.955	55.79	
4.11	0.6274	2.5045	0.4812	1.4027	0.978	56.51	
S = hexadecane							
5.1	1.1510	0.0871	6.0262	19.756	0.124	12.85	
5.2	0.6902	0.2316	4.3887	14.355	0.342	23.02	
5.3	1.8630	0.4359	4.0593	13.308	0.506	31.65	
5.4	1.4349	1.2444	5.3125	17.416	0.695	41.79	
5.5	1.3001	1.7766	4.2607	13.968	0.801	47.36	
5.6	1.9652	3.0950	4.2078	13.795	0.875	51.29	
5.7	0.8486	1.5088	1.5856	5.1982	0.900	52.53	
5.8	1.2063	1.4487	1.1769	3.8583	0.917	53.61	
5.9	0.8670	1.2880	0.7597	2.4899	0.938	56.03	
5.10	0.8921	1.8103	0.6152	2.0168	0.962	56.03	
5.11	0.8435	1.4534	0.3498	1.1467	0.971	56.41	
5.12	1.0245	2.6421	0.3116	1.0215	0.984	57.34	

Table 4.3

Parameters used in the Benesi-Hildebrand computer best fit studies on the mole fraction and molar scales.

No.	$n_B/(n_B+n_S)$	$n_B/(n_B+n_S \frac{V_S}{V_B})$	$10^3 c_B/$ mol m^{-3}	$10^3 c'_B/$ mol m^{-3}	$\Delta_{obs}^{(1)}/$ Hz	$\Delta_{obs}^{(1)}-x_B G/$ Hz	$\Delta_{obs}^{(2)}/$ Hz
S = cyclohexane (α)							
1.1	0.0994	0.0832	0.9194	0.9216	9.52	9.71	
1.2	0.2483	0.2135	2.3523	0.3645	20.71	21.21	
1.3	0. 362	0.2939	3.2416	3.2543	25.26	25.93	
1.4	0.4512	0.4033	4.4485	4.4652	30.04	30.94	
1.5	0.5503	0.5014	5.5263	5.5519	36.18	37.28	
1.6	0.6529	0.6073	6.6945	6.7236	40.10	41.40	
1.7	0.7676	0.7308	8.0555	8.0917	44.04	45.59	
1.8	0.8498	0.8231	8.0362	9.1121	46.51	48.20	
1.9*	0.9215	0.9061	9.9781	10.031	48.26	50.09	50.28
1.10*	0.9388	0.9265	10.213	10.257	48.66	50.52	50.67
1.11*	0.9495	0.9392	10.361	10.392	49.07	50.91	51.04
1.12*	0.9515	0.9515	10.465	10.535	49.22	51.14	51.21
1.13*	0.9706	0.9645	10.624	10.678	49.66	51.59	51.43
1.14*	0.9792	0.9748	10.740	10.792	49.78	51.74	51.76
1.15*	0.9879	0.9854	10.855	10.909	49.96	51.94	51.95
1.16*	0.9953	0.9942	10.955	11.007	50.13	52.13	52.06
S = cis-decalin (α) ‡							
2.1	0.0268	0.0159	0.1736	0.1744	2.44	2.49	
2.2	0.0597	0.0359	0.3902	0.3931	4.59	4.71	
2.3	0.0965	0.0589	0.6393	0.6450	6.78	6.97	
2.4	0.1782	0.1128	1.2275	1.2357	12.70	13.06	
2.5	0.3564	0.2452	2.6798	2.6892	23.38	24.09	

Cont.

Table 4.3 (Cont.).

No.	$n_B/(n_B+n_S)$	$n_B/(n_B+n_S V_S/\overline{V_B})$	$10^3 c_B$/ mol m^{-3}	$10^3 c'_B$/ mol m^{-3}	$\Delta_{obs}^{(1)}$/ Hz	$\Delta_{obs}^{(1)}-x_B G$/ Hz	$\Delta_{obs}^{(2)}$ Hz
2.6	0.5393	0.4072	4.4522	4.4758	32.51	33.59	
2.7	0.7468	0.6337	6.9626	6.9841	41.42	42.91	
2.8*	0.8490	0.7652	8.4021	8.4716	45.17	46.85	
2.9*	0.9023	0.8426	o.2930	9.3281	47.08	48.88	
2.10*	0.9509	0.9183	10.122	10.166	48.89	50.78	
2.11*	0.9878	0.9793	10.723	10.842	49.66	51.61	
2.12*	0.9931	0.9881	10.894	10.939	50.15	52.12	
S = trans-bicyclohexyl (α) ≠							
3.1	0.1311	0.0672	0.7523	0.7569	8.60	8.86	
3.2	0.2057	0.1107	1.2366	1.2394	13.14	13.55	
3.3	0.4967	0.3204	3.5935	3.6056	29.20	30.19	
3.4	0.7151	0.5453	6.1152	6.1367	39.35	40.78	
3.5	0.8018	0.6590	7.3969	7.4159	42.33	43.93	
3.6*	0.9139	0.8353	o.3611	9.3994	47.31	49.13	
3.7*	0.9520	0.9045	10.137	10.178	48.59	50.49	
3.8*	0.9714	0.9419	10.578	10.599	49.45	51.39	
3.9*	0.9808	0.9608	10.769	10.812	49.91	51.87	
3.10*	0.9905	0.9804	10.995	11.032	50.03	52.01	
S = tetradecane (β) ≠							
4.1	0.0838	0.0220	0.3311	0.3425	4.60	4.66	
4.2	0.2069	0.0612	0.9067	0.9909	11.19	11.35	
4.3	0.5200	0.2710	2.9879	3.0000	27.07	27.43	
4.4	0.7099	0.4564	5.0372	5.0536	36.98	37.54	
4.5	0.8077	0.5903	6.5149	6.5361	41.55	42.19	

Table 4.3 (Cont.).

No.	$n_B/(n_B+n_S)$	$n_B/(n_B+n_S\frac{V_S}{V_B})$	$10^3 c_B$/ mol m^{-3}	$10^3 c_B'$/ mol m^{-3}	$\Delta^{(1)}_{obs}$/ Hz	$\Delta^{(1)}_{obs}-x_B G$/ Hz	$\Delta^{(2)}_{obs}$/ Hz
4.6*	0.8844	0.7242	7.9911	8.0183	45.57	46.27	
4.7*	0.8910	0.7371	8.1153	8.1607	45.90	46.61	
4.8*	0.9071	0.7701	8.4781	8.5257	46.44	47.16	
4.9*	0.9416	0.8470	9.3198	9.3775	48.33	49.08	
4.10*	0.9611	0.8970	0.8726	9.9309	49.59	50.35	
4.11*	0.9811	0.9469	10.461	10.4838	50.31	51.09	
S = hexadecane (β)							
5.1	0.1262	0.0422	0.4651	0.4674	6.65	6.78	
5.2	0.3459	0.1389	1.5322	1.5380	16.82	17.09	
5.3	0.5178	0.2467	2.7057	2.7315	25.45	25.86	
5.4	0.7008	0.4167	4.5937	4.6136	35.59	36.15	
5.5	0.8065	0.5593	6.1750	6.1979	41.16	41.86	
5.6	0.8803	0.6916	7.6275	7.6577	45.06	45.76	
5.7*	0.9049	0.7437	8.2032	8.2341	46.33	47.05	
5.8*	0.9249	0.7896	8.6915	8.7426	47.41	48.14	
5.9*	0.9443	0.8379	9.2300	9.2772	48.53	49.28	
5.10*	0.9671	0.8997	9.9216	9.9612	49.83	50.60	
5.11*	0.9765	0.9268	10.212	10.2613	50.21	50.99	
5.12*	0.9883	0.9627	10.623	10.6588	51.14	51.93	

$\frac{n_B}{n_A V_A + n_B V_B + n_S V_S}$ denoted by c_B

$\frac{n_B}{n_B V_B + n_S V_S}$ denoted by c_B'

$\Delta^{(1)}_{obs} = \delta_{obs} - \delta_{free}$ where δ_{free} referenced to benzene is found to be 7.40Hz(α) or 6.20Hz(β) at 60.004MHz and 306.4°K.

$\Delta^{(2)}_{obs} = \delta_{obs} - \delta_{free}$ where δ_{free} referenced to cyclohexane is found to be

Table 4.3 (Cont.).

-339.47Hz at 60.004MHz and 306.4°K.

* samples used in "correct" concentration range studies.

ǂShift measurements by C.J.Jackson.

Table 4.4

Values of K_x and K_c and the associated Δ_c for the chloroform-benzene interaction with various inert materials.

Inert Material	K_x	Δ_c/Hz	10^3K_c/ $m^3 mol^{-1}$	Δ_c/Hz
cyclohexane	1.06	97.7	0.137	83.5
cis-decalin	0.58	136.4	0.158	79.3
bicyclohexyl	0.40	176.4	0.174	76.3
tetradecane	0.02	2452.2	0.180	77.2
hexadecane	-0.14	-312.3	0.163	80.7

The expected consistency on the mole fraction scale is not observed, namely the equilibrium quotient and Δ_c values are solvent dependent. It is noted that the molar scale seemingly gives the more satisfactory results as has been observed in the past. This is not, however, justification for the sole use of the molar scale. It has been found that rational results can be obtained from the application of the mole fraction scale if two modifications are made to the Benesi-Hildebrand equation. These will now be discussed.

4.5.1 Modification I. The Variation of δ_{free} With Mixture Composition.

It is unlikely that the chemical shift of chloroform infinitely dilute in cyclohexane is the same as that of chloroform (A) infinitely dilute and uncomplexed in benzene. Therefore it is to be expected that the use of a single valued δ_c and δ_{free} over a range of concentrations is erroneous. The anticipated variation can be, to an approximation, expected to be a mole fraction function. The total screening of A may be written as

$$\sigma_A^{Tot} = \frac{n_{AB}}{n_A}(\sigma_A + \sigma_c + x_B\sigma_A^B + x_S\sigma_A^S) + \frac{n_A - n_{AB}}{n_A}(\sigma_A + x_B\sigma_A^B + x_S\sigma_A^S) \quad \text{..... 4.39}$$

where σ_A is the screening on isolated A, σ_c is the contribution by B to the complex, and σ_A^B and σ_A^S are the screening effects of A due to B and S, assuming that the screening effects of the mixture affect A, complexed and free, equally. Similarly the shielding experienced by the aromatic (which is acting as the reference) is given by

$$\sigma_B^{Tot} = \sigma_B + x_B\sigma_B^B + x_S\sigma_B^S \quad \text{.... 4.40}$$

It follows from equations 4.39 and 4.40 that δ_{obs} can be expressed as

$$\delta_{obs} = \sigma_A^{Tot} - \sigma_B^{Tot} = \sigma_A - \sigma_B - \frac{n_{AB}}{n_A}\sigma_c + x_B(\sigma_A^B - \sigma_B^B) + x_S(\sigma_A^S - \sigma_B^S) \quad \text{.... 4.41}$$

$$\text{or, } \delta_{obs} = \delta'_{free} + \frac{n_{AB}}{n_A}\Delta_c + x_BE + x_SF \quad \text{.... 4.42}$$

where Δ_c has been equated with σ_c, δ'_{free} is the shift of A with respect to B in the absence of any solvent effects, $E(= \sigma_A^B - \sigma_B^B)$ is the nett effect of the aromatic solvent on δ'_{free} and $F(= \sigma_A^S - \sigma_B^S)$; similarly for the inert solvent. If the solute concentration is ignored, then $x_S = 1 - x_B$, and equation 4.42 may be written as

$$\Delta_{obs} = \delta_{obs} - (\delta'_{free} + F) = \frac{n_{AB}}{n_A}\Delta_c + x_BG \quad \text{.... 4.43}$$

where G is the variation in the solvent shift in changing from pure aromatic to pure inert solvent, i.e. E − F, and $\delta'_{free} + F$ is the measurable shift of A infinitely dilute in S, i.e. δ_{free} in equation 4.2. Rearranging equation 4.43

$$\Delta_{obs} - x_BG = \frac{n_{AB}}{n_A}\Delta_c \quad \text{.... 4.44}$$

Equation 4.44 is compared with equation 4.3 and hence a modified Benesi-

Hildebrand equation can be derived.

$$\frac{1}{\Delta_{obs} - x_B G} = \frac{n_B + n_S}{n_B K_x^a \Delta_c} + \frac{1}{\Delta_c} \qquad \text{.... 4.45}$$

An analogous equation can be derived for the molar scale. The numerical value of $G(=(\sigma_A^B - \sigma_B^B) - (\sigma_A^S - \sigma_B^S))$ cannot be absolutely determined simply because the shift of uncomplexed chloroform infinitely dilute in benzene cannot be evaluated. To a rough approximation G can be determined by measuring the shift between B and S (simulating A) in a series of B - S mixtures of varying mole fraction, the difference between the extrapolated shifts at $n_B/(n_B + n_S) = 1$ and 0 being equated to G. It can be seen from figure 4.4 that for the cyclohexane system G = -2Hz (at 60.004 MHz). It should be noted that the experimental line is a slight curve, but to a first approximation the plot may be taken to be linear with mole fraction. Similar values are noted for G with cis-decalin and bicyclohexyl, whilst for tetradecane and hexadecane. G is found to be -0.8Hz. By a similar extrapolation procedure the δ_{free} values relative to benzene in cyclohexane, cis-decalin and bicyclohexyl were found to be 7.40Hz, the corresponding values in hexadecane and tetradecane being 6.2Hz. These δ_{free} and G values were determined by C.J.Jackson[126]. The evaluation of the terms on the left hand side of equation 4.45 allows new values of $K_x(K_x^a)$, $K_c(K_c^a)$, and Δ_c to be determined. These are shown in Table 4.5.

It can be seen that this modification has very little effect on the resulting values of the equilibrium quotients. It would thus appear that for these systems this correction is of comparatively trivial significance, further modification being necessary.

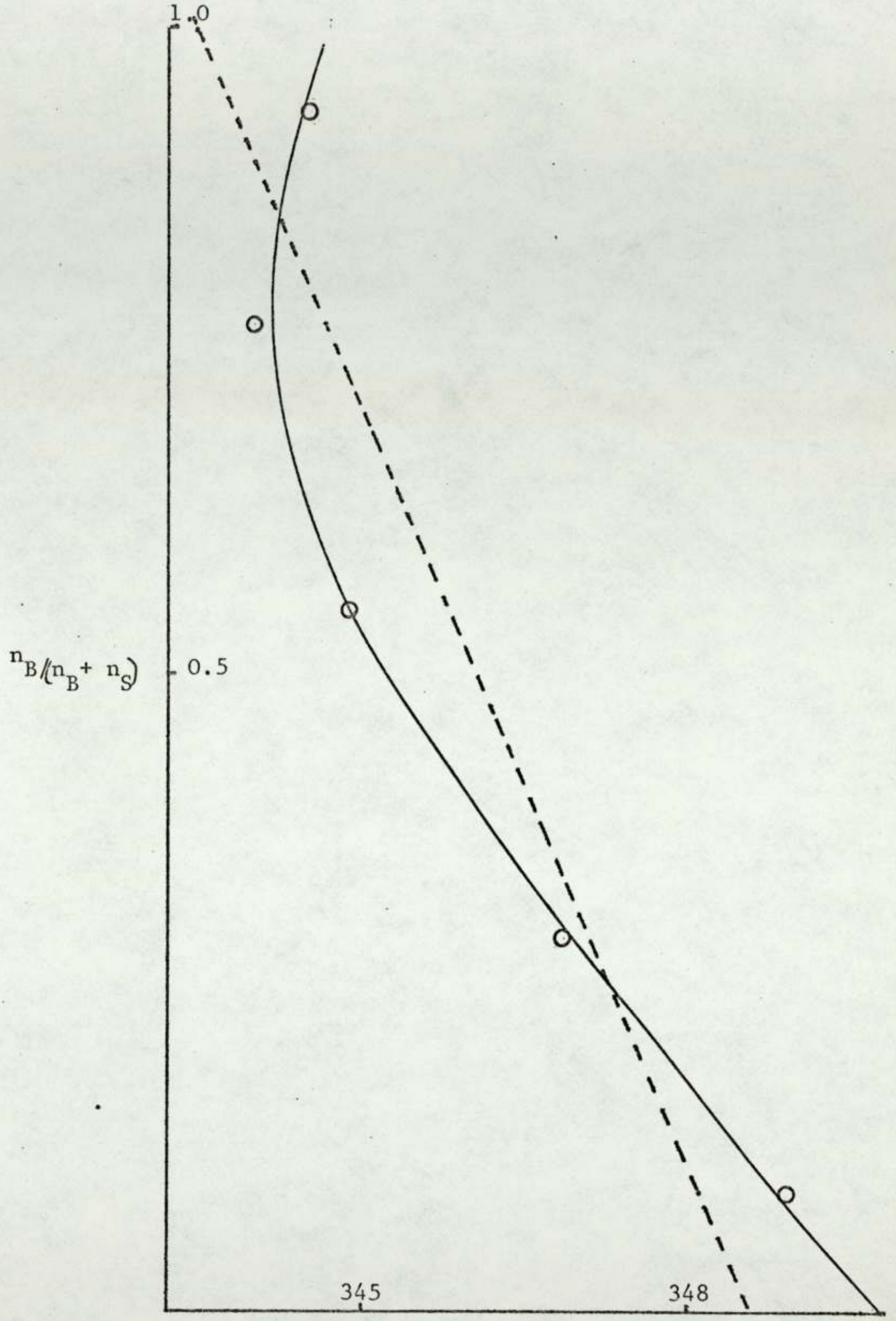


Figure 4.4. The variation of chemical shift of cyclohexane with respect to benzene, as a function of mixture composition.

Table 4.5. Values of K_x and K_c and the associated Δ_c for the chloroform-benzene reaction with various inert materials at 306.6K by the application of the Benesi-Hildebrand equation with the shift correction (equation 4.45).

Inert Material	$K_x^{\,a}$	Δ_c/Hz	$10^3 K_c^{\,a}$/ $m^3 mol^{-1}$	Δ_c/Hz
cyclohexane	1.749	82.0	0.127	89.6
cis-decalin	0.552	146.9	0.153	83.4
bicyclohexyl	0.376	191.7	0.169	80.1
tetradecane	0.021	2517.7	0.180	78.4
hexadecane	-0.178	242.9	0.162	82.0

4.5.2. Modification II. The Effect of the Nature of S.

It can be seen in Tables 4.4 and 4.5 that the values of the equilibrium quotients determined depend on the solvent used. It would seem plausible, therefore, that the assumptions on which the validity of method I rests are not strictly correct; namely $\mu_A^{\Theta''}$, $\mu_{AB}^{\Theta''}$ and γ_B^R are not constant in the range 0.9 to 1.0 but do depend (contrary to assumption) on the nature of S and the extent to which it is present. This dependence must be accounted for and, whilst this is a matter of considerable complexity, it may be done approximately by questioning the necessity of utilising S at all and, moreover, the significance of equations such as 4.2.

In its basic form equation 4.2 should be written as

$$\delta_{obs} = P_I\,\delta_I + P_{II}\,\delta_{II} \qquad \text{.... 4.46}$$

where P_I and P_{II} are generally defined[35] as the fractional populations of states I and II, in which A has shifts δ_I and δ_{II}. One of the several reasons for the anomalies in the currently accepted data processing procedures is a misinterpretation of the significance of P_I and P_{II}. In the context of reaction (4.1) δ_I and δ_{II} are molecular parameters and so P_I and P_{II} may be thought of as fractional times that A spends in each state. If equilibrium quotients are used to characterise P_I and P_{II}, the values obtained for these are in terms of bulk concentrations rather than time fractions. This approach can only be satisfactory if the quotients are suitably defined in accordance with the molecular basis of equation 4.46. The modification this entails may be deduced by considering the implications of the dilution technique. Initially we may consider the reaction proceeding with A almost infinitely dilute in B. In this case, one molecule of A contacts some specific number of molecules of B in the characteristic n.m.r. time. The problem is to determine the fraction of this time that A spends in the free and complexed states. Information about the system is forthcoming by diluting the system with S, and the sole intention in doing this is to change the time fractions that A spends in each state and so change δ_{obs}. Therefore, the compound S should essentially have identical properties to B except the ability to form a complex. Obviously this situation cannot be achieved in practice and data obtained for use with equations 4.11 or 4.12 must depend on the nature of S. To account for the differences in the various inert solvents would be a difficult matter, but it does appear that some correction for this may be achieved to quite a high degree of success. Probably the most important single difference between a real S and a real B molecule is their sizes or more, conveniently, their exclusion volumes. To change δ_{obs}, molecules of a hypothetically ideal S have to be introduced to the A - B system considered initially, so that the introduction of, for example, one molecule of S is required to produce the situation depicted in figure 4.5(a). In practice, the introduction of one real diluent molecule has an effect such as that represented by 4.5(b), from which it can be appreciated that more (or less)

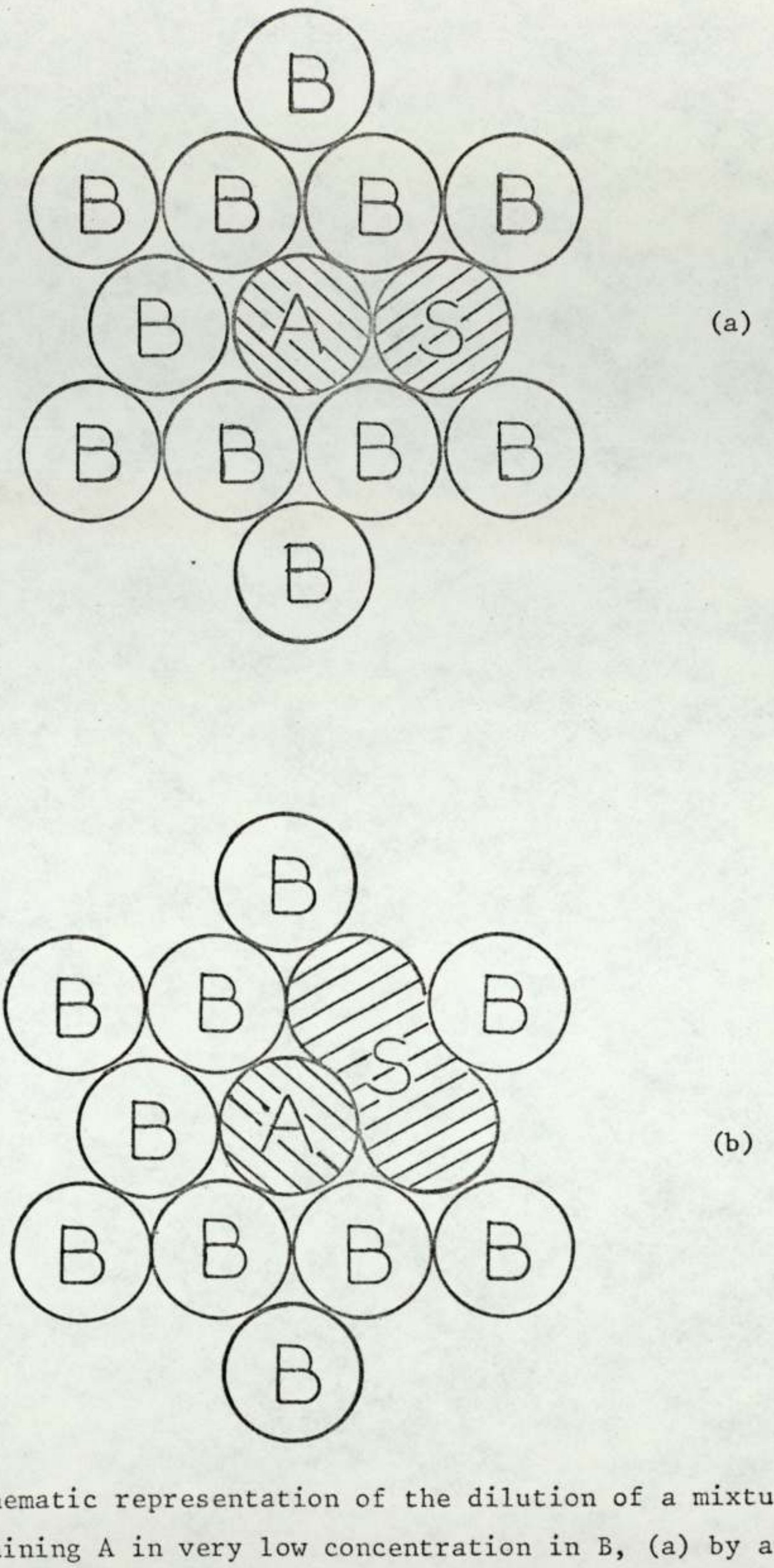


Figure 4.5. A schematic representation of the dilution of a mixture containing A in very low concentration in B, (a) by an ideal inert molecule and (b) by a real molecule of S.

than the required single molecule of B is displaced and the measured value of δ_{obs} cannot reflect the expected effect of dilution. To a reasonable approximation the one molecule of S behaves as $^{V}S/V_B$ (ratio of molar volumes) molecules of <u>inert</u> B. The appropriate molar volumes and $^{V}S/V_B$ ratios at 306K (except for bicyclohexyl for which data is only available at 293K) are shown in Table 4.6. It has been assumed that the trans-isomer of bicyclohexyl has been used and the values of V_S and $^{V}S/V_B$ given in Table 4.6 are therefore relevant to this isomer. The corresponding values of the cis isomer are $V_S = 0.193562 \times 10^3 m^3 mole^{-1}$, $^{V}S/V_B = 2.1414$, these being very similar to those of the trans-isomer. If a mixture of isomers has in fact been used, it is therefore to be expected that only a slight effect on the calculated parameters will be noticed.

<u>Table 4.6</u>. Densities and Molar Volumes (V_B or V_S) and the ratio $^{V}S/V_B$ for the components at 306.6K(*293K).

Compound	10^{-3} density/ Kgm^{-3}	$10^3 (V_S$ or $V_B)$/ $m^3 mol^{-1}$	$^{V}S/V_B$
chloroform	1.4642		
benzene	0.8648	0.090326	
cyclohexane	0.7658	0.109901	1.2162
cis-decalin	0.8865	0.155956	1.7258
bicyclohexyl*	0.8592	0.186508	2.0980
tetradecane	0.7535	0.263298	2.9136
hexadecane	0.7647	0.296128	3.2769

It can be seen that, say, one molecule of tetradecane will replace approximately three molecules of benzene, whilst cyclohexane has only a slightly greater molar volume than benzene. Consideration of Table 4.4 shows that the complex limiting shift value, Δ_c, obtained from the mole fraction scale treatment of the cyclohexane system data is more comparable with the Δ_c values obtained from the molar scale treatment, than that obtained from the tetradecane series. The implication of this is that on a macroscopic basis the amount of S in the equilibrium expressions 4.7, 4.8 and 4.9 has to be quantified in terms of its "effective number" of moles relative to B, so n_S is replaced by $n_S V_S/V_B$. This produces no change in the molar expression, but that for K_x is modified and the final form of equation 4.11, becomes

$$\frac{1}{\Delta_{obs} - x_B G} = \frac{n_B + n_S V_S/V_B}{n_B K_x^{ab} \Delta_c} + \frac{1}{\Delta_c} \qquad \ldots .\ 4.47$$

The results of the application of this equation to the chloroform-benzene reaction in five solvents are shown in Table 4.7. The first column shows the value of $K_x (K_x^{ab})$ and Δ_c obtained by the use of equation 4.47. The Δ_c results are reasonably consistent with the molar results in Table 4.4, considering the approximations made.

Table 4.7. Values of K_x and Δ_c for the chloroform-benzene reaction with various inert materials at 306.6K obtained from the application of equation 4.47, (i) in its complete form (ii) by neglect of the term $x_B G$.

	(i)		(ii)		(iii)
Inert Material	K_x^{ab}	Δ_c/Hz	K_x^b	Δ_c/Hz	$10^3 K_c^*/K_x^b/m^3$
cyclohexane	1.396	89.7	1.506	83.6	0.0907
cis-decalin	1.679	83.4	1.734	79.3	0.0913
bicyclohexyl	1.886	80.3	1.936	76.5	0.0897
tetradecane	1.671	83.3	1.671	82.0	0.1078
hexadecane	1.694	83.8	1.700	82.4	0.0958

* from Table 4.4

It would appear that for this system the shift refinement is of little consequence compared with the correction involving molar volumes. Neglecting the x_BG term enables the second column values to be directly compared with those for K_c and Δ_c given in Table 4.4, for which the simple correction for the size of the molecules is implicitly accommodated. That this latter fact is so may be seen as follows. A mole fraction corrected for the bulk of the inert solvent may be written as $n_B/(n_B + n_SV_S/V_B)$ or $n_BV_B/(n_BV_B + n_SV_S)$ whereas the corresponding concentration in mol m^{-3} is given by $n_B/(n_BV_B + n_SV_SV_B/V_B)$ or $n_B/(n_BV_B + n_SV_S)$; thus the number of moles of inert solvent is always weighted by its molar volume on the molarity concentration scale, and does not require further correction. The expected agreement of Δ_c values is observed in Table 4.7 and in addition the ratio K_c/K_x shown in column (iii) defined by equation 4.10 is in excellent agreement with the theoretical prediction of $0.0903 \times 10^{-3} m^3$, the molar volume of benzene at 306.6K. The results are taken to validate the approach.

It should be noted that the molar concentration of the B component used in the determination of the equilibrium quotients in Table 4.4 and Table 4.5 has been defined as $n_B/(n_AV_A + n_BV_B + n_SV_S)$. However, the basic assumption of the Benesi-Hildebrand equation is that n_A is small and can be neglected. The molar concentration of B should therefore be defined as $n_B/(n_BV_B + n_SV_S)$ to enable a strict comparison of molar and corrected mole fraction scale determined equilibrium parameters. Table 4.8. shows the value of the equilibrium quotients and Δ_c obtained when this molar definition is used, column (i) giving the values when the modified form is used; column (ii) giving values when x_BG is neglected.

Table 4.8. Values of K_c and Δ_c for the chloroform-benzene reaction with various inert materials at 306.6K obtained from the application of the appropriate form of equation 4.47 (i) in its complete form, and (ii) by neglecting the term x_BG, when the molar concentration is defined neglecting n_AV_A.

	(i)		(ii)		(iii)
Inert Material	$10^3/K_c^a/$ $m^3 mol^{-1}$	Δ_c/Hz	$10^3K_c/$ $m^3 mol^{-1}$	Δ_c/Hz	$10^3K_c/$ K_x^{b*}/m^3
cyclohexane	0.126	89.6	0.137	88.5	0.0909
cis-decalin	0.152	83.4	0.157	79.2	0.0905
bicyclohexyl	0.167	80.2	0.171	76.4	0.0884
tetradecane	0.178	78.5	0.178	77.3	0.0106
hexadecane	0.153	83.8	0.153	82.4	0.0900

* K_x^b from Table 4.7 column (ii)

The ratio of K_c/K_x shown in column (iii), where the term x_BG has been neglected in the determination of the respective equilibrium quotients, is once again in good agreement with the predicted value of $0.0903 \times 10^{-3} m^3 mol^{-1}$. It would therefore appear, for the system studied here, that the inclusion or otherwise of the n_AV_A term in the concentration expression is unimportant.

Little mention has so far been made of the molal scale, mainly due to the difficulty envisaged mathematically in deriving an expression for K_m in terms of chemical potentials for, as $x_B \to 1$, $m_B \to \infty$. However, the satisfactory application of the molar scale with its intrinsic volume function encourages the further consideration of the molal scale.

4.5.3. A Molal Scale Benesi-Hildebrand Treatment

It would seem reasonable to expect that, when $x_B \to 1$, equation 4.13 should yield a value of K_m comparable with the values of K_x and K_c, so that values of Δ_c deduced using all three scales should be the same. To test the validity of the use of the molal scale the data for the chloroform-benzene interaction in various inert materials was studied. The limiting linear plots of Δ_{obs}^{-1} vs m_B^{-1} (i.e. $n_B/n_S V_S \rho_S$) were analysed using a modified "BHCURVEFIT" program to give the slope (S) and the intercept (I) at $m_B = \infty$ (∞ was limited to 10^{72} by the computer facilities). The values of I/S (supposedly K_m) and 1/I (supposedly Δ_c) are given in Table 4.9. A comparison of these Δ_c values with the corresponding molar scale values given in Table 4.4 shows them to be completely different. The reason for this is forthcoming if the basic definitions of the molal equilibrium quotients and molality are considered.

Table 4.9. Equilibrium quotient and induced shift (Δ_c) values for the chloroform-benzene interaction in different inert materials.

Inert Material	$({}^{I}/_{S})$/Kgmol^{-1}	$({}^{1}/_{I})$/Hz	$(\rho_S(K_c+V_B))$/ Kgmol^{-1}	$(\frac{K_c}{K_c+V_B})$/Hz
cyclohexane	0.169	50.3	0.174	50.3
cis-decalin	0.219	50.3	0.220	50.4
bicyclohexyl	0.233	50.4	0.233	50.2
tetradecane	0.204	51.4	0.204	51.4
hexadecane	0.205	51.7	0.195	51.9

The molal parameters are derived from the data corresponding to $m_B = \infty$ and whilst the equilibrium quotient conceptually must be finite, equation 4.9 requires that K_m is zero. However, it is an experimental fact that a plot of Δ_{obs}^{-1} vs m_B^{-1} has a finite slope. The only way to rationalise this with equation 4.13 is to express K_m in terms of K_c, defined by equation 4.8 using equation 4.48,

$$K_m = \frac{K_c \rho_s}{V_B m_B \rho_s + 1} \qquad \text{.... 4.48}$$

so that equation 4.13 becomes equation 4.49

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_c \rho_s m_B \Delta_c} + \frac{1}{\Delta_c}\left(1 + \frac{V_B}{K_c}\right) \qquad \text{.... 4.49}$$

Inspection of equation 4.48 shows that if K_c may be assumed to be constant over a range of concentrations of B, then K_m cannot be similarly constant because of the variation of m_B and hence the normal form of equation 4.13 is meaningless.

It is apparent, however, from the redefined Benesi-Hildebrand equation 4.49, that the slope and intercept of a plot of Δ_{obs}^{-1} vs m_B^{-1} have the significance expressed in equations 4.50 and 4.51.

$$\frac{1}{I} = \frac{K_c \Delta_c}{K_c + V_B} \qquad \text{.... 4.50}$$

$$\frac{I}{S} = \rho_s (K_c + V_B) \qquad \text{.... 4.51}$$

Using the molar scale results in Table 4.4, values of $K_c \Delta_c / (K_c + V_B)$ and $\rho_s (K_c + V_B)$ have been calculated for the chloroform-benzene reaction. The values are given in Table 4.9 and can be seen to be in excellent agreement with the experimental values of 1/I and I/S. It must, therefore, be concluded that processing data by plotting Δ_{obs}^{-1} against m_B^{-1} leads to meaningless values of K_m and Δ_c.

Immediately prior to the presentation of this thesis it became evident that the use of the molarity scale could be rationalised if the molality was defined as:-

$$m'_B = \frac{n_B}{n_S V_S \rho_B + n_B V_B \rho_B} \quad .... \; 4.52$$

Utilising this definition, the limiting linear plots of Δ_{obs}^{-1} VS $m_B'^{-1}$ were analysed using the "BHCURVEFIT" program. The results are given in Table 4.9(a). It can be seen that the values obtained for Δ_c are in excellent agreement with those obtained using the corrected mole-fraction or molar scales.

Table 4.9(a). Values of K_m and Δ_c for the chloroform-benzene reaction with various inert materials at 306.6K, using a modified molarity concentration scale.

Inert Material	Δ_c/H_z	K_m/kg mol^{-1}
cyclohexane	84.9	0.114
cis-decalin	79.3	0.135
bicyclohexyl	77.2	0.147
tetradecane	76.9	0.156
hexadecane	78.0	0.153

For a more complete discussion of the use of the molality scale, the reader is referred to the relevant paper in the back of this thesis.

It has been shown that the molal, molar and mole fraction scales may be used for the thermodynamically correct evaluation of data, with the proviso that x_B is in the region of 0.9 to 0.995 and x_A is less than 0.005. The molal parameters should be calculated using the modified definition of molality (equation 4.52). The mole fraction parameters should be obtained from equation 4.47 which is the Benesi-Hildebrand equation with a shift and volume correction, although the shift correction may be neglected in certain circumstances. For the reaction of chloroform with benzene in benzene, the shift correction was found to be unnecessary and to give $K_x = 1.71 \pm 0.21$, $K_m = 0.135 \pm 0.02\,\mathrm{Kg\,mole^{-1}}$, $K_c = 0.162 \pm 0.02 \times 10^{-3}\,\mathrm{m^3\,mole^{-1}}$ and $\Delta_c = 80.1 \pm 3.6\,\mathrm{Hz}$ at 60.004MHz. Further confirmation of the acceptability of these values is forthcoming from the results of the study of the chloroform-benzene interaction in cyclohexane, using cyclohexane as the reference, the corresponding values being $K_x = 1.69$, $K_c = 0.154 \times 10^{3}\,\mathrm{m^3\,mole^{-1}}$ and $\Delta_c = 83.0 \pm 0.03\,\mathrm{Hz}$ (at 60.004 MHz). The relevant shifts are shown in Table 4.2.

The Creswell and Allred data processing method, which is intrinsically more precise must now be considered, with the aim of attempting to justify its use as a means of determining thermodynamically valid parameters.

4.6. The Application of the Creswell and Allred Method

A study of the literature shows that this method of data processing forms the basis of assessing equilibrium parameter values for several spectroscopic methods. Unfortunately very few give the range of concentrations that have been studies but, even if a major part of the concentration range had been considered, seemingly meaningful values have been achieved when the solvent has been changed. This apparent contradiction of thermodynamic dictates may be rationalised by considering equation 4.53.

$$RT\, \ln K_x^{+} = \mu_A^{o} + \mu_B^{o} - \mu_{AB}^{o} + RT \ln \frac{\gamma_A^R\ \gamma_B^R}{\gamma_{AB}^R} \qquad .... \ 4.53$$

Thus K_x^{+} has a different numerical value for each mixture of different composition studied. But x_A and consequently x_{AB} are invariably small and hence $\gamma_A^R | \gamma_{AB}^R$ may remain reasonably constant, say H. Thence equation 4.53 can be expressed as:-

$$\bar{K}_x^{+} = K_x^{o}\ H\ \bar{\gamma}_B^R \qquad .... \ 4.54$$

Where $\bar{K}_x^{+}$ is the best average value of K_x^{+}, and similarly $\bar{\gamma}_B^R$ is the average value of γ_B^R over the range of concentrations studied. K_x^{o} is the true value of the equilibrium constant for the formation of pure AB from pure A and pure B. It is therefore to be expected that the best average value of the equilibrium quotient should be directly proportional to the true value of the equilibrium constant, the proportionality being governed by $H\bar{\gamma}_B^R$. This explains why the most satisfactory correlations have been obtained by the Creswell and Allred method with systems in which B and S are constant and A is varied. It is interesting to note that the determination of ΔH^{o} from $\bar{K}_x^{+}$ will be the same as that calculated from K_x^{o} since a plot of $\ln K_x$ against 1/T is required (see section 3.3.5.3) and it follows from equation 4.54 that

$$\ln \bar{K}_x^{+} = \ln K_x^{o} + \ln H\ \bar{\gamma}_B^R \qquad .... \ 4.55$$

and thence both plots will have the same gradient and value of ΔH^{o} provided that $\bar{\gamma}_B^R$ is not temperature dependent.

It is worth considering whether BH evaluated equilibrium quotients can be related to K_x^{o} and hence give meaningful thermodynamic parameters. It follows from equations 4.34 and 4.37 that

$$RT\ \ln K_x'' = \mu_A^{o} - \mu_B^{o} - \mu_{AB}^{o} + ZL(w'_{AB} - w'_{AB,B}) \qquad .... \ 4.56$$

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

$$\text{Ln}K_x'' = \text{Ln}K_x^o + C \qquad \text{.... 4.57}$$

Thus plots of $\text{Ln}K''$ against 1/T will have the same slope and the value of ΔH^o will be the true value. Furthermore, the values obtained by the Creswell and Allred and BH treatments should be the same. It has, however, been shown that the nature of S has a considerable influence on the value of K_x'' and Δ_c obtained by the BH procedure (i.e. the actual value of Z is solvent dependent). Therefore, it seems reasonable that the nature of S will have a similar effect on the equilibrium quotients and Δ_c values obtained from a CA type treatment.

The application of the Creswell and Allred treatment to the data in the range $x_B = 0.9$ to 0.995, previously used in the BH evaluations, leads to the results in Table 4.10.

Table 4.10. K_x and Δ_c values obtained for the chloroform-benzene interaction in different inert materials, (i) with both the volume and the shift corrections, (ii) with the volume correction only, (iii) with the shift correction only and (iv) without the volume and shift corrections.

	(i)		(ii)		(iii)		(iv)	
Inert Material	K_x^{ab}	Δ_c/Hz	K_x^{b}	Δ_c/Hz	K_x^{a}	Δ_c/Hz	K_x	Δ_c/Hz
cyclohexane	1.416	89.4	1.527	83.3	0.988	105.4	1.079	97.0
cis-decalin	1.678	83.6	1.733	79.5	0.572	144.3	0.603	134.1
bicyclohexyl	1.944	79.7	1.943	78.5	0.000	-	0.000	-
tetradecane	2.008	78.2	2.009	76.9	0.044	1242.2	0.044	1216.3
hexadecane	1.904	80.0	1.954	76.3	0.395	185.6	0.419	171.1

They are in excellent agreement with the corresponding BH results indicating that the assumption of constancy of the activity co-efficient term, γ_B^R, is justified over this narrow range.

To determine the effect of evaluating data over the whole mole fraction range, all the data points in Table 4.2 were used, both with and without the volume correction to the number of moles of S. Surprisingly the results (Table 4.11) obtained using the volume corrected terms were in excellent agreement with the results obtained from the corresponding narrow range studies.

Table 4.11. K_x and Δ_c values obtained by the application of the Creswell and Allred treatment to the chloroform-benzene interaction in different inert solvents over the whole mole fraction concentration range, (i) with the volume correction and (ii) without the volume correction. Both column (i) and (ii) results were obtained by neglecting the shift correction $(-x_B G)$.

	(i)		(ii)	
Inert Material	K_x^D	Δ_c/Hz	K_x	Δ_c/Hz
cyclohexane	1.556	82.8	1.101	96.2
cis-decalin	1.669	80.7	0.563	140.2
bicyclohexyl	1.906	77.0	0.389	180.7
tetradecane	1.948	80.7	0.000	-
hexadecane	2.052	76.6	0.000	-

Processing the whole range data on the BH program led to the results shown in Table 4.12 which are in excellent agreement with the CA results over the same range. However, these results do begin to show an increasingly

Table 4.12. K_x, K_c and their associated Δ_c values obtained by application of the Benesi-Hildebrand treatment to the chloroform-benzene interaction in different inert solvents over the whole concentration range, (i) with the volume correction, (ii) without the volume correction and (iii) on the molar scale. All three columns refer to results obtained by neglecting the shift correction $(-x_BG)$.

	(i)		(ii)		(iii)	
Inert Material	K_x^b	Δ_c/Hz	K_x	Δ_c/Hz	10^3K_c/ $m^3 mol^{-1}$	Δ_c/Hz
cyclohexane	1.592	81.2	1.132	93.74	0.144	81.1
cis-decalin	1.592	82.6	0.520	148.1	0.147	81.7
bicyclohexyl	1.844	77.9	0.358	191.7	0.167	78.0
tetradecane	2.168	74.3	0.086	635.9	0.196	74.3
hexadecane	2.452	70.3	0.058	900.5	0.221	70.3

greater deviation from the BH results obtained over a narrow range. This is no doubt due in part to the data evaluation method. Whilst over the range x_B=0.9 to 0.995 the requisite criterion that $x_B >>> x_A$ is met and it is reasonable to assume that BH plots will be linear, over the whole range this assumption is not valid. The computer program was therefore modified to enable the data points to be fitted up to a quadratic, the equilibrium parameters being obtained from the differential and intercept at the extrapolated point corresponding to zero concentration of inert solvent. The results obtained from this data evaluation procedure are shown in Table 4.13. In some cases the results are identical to the linear-fitting results, indicating that the data is in fact best represented by a linear equation; however, in the other cases, a quadratic seems to produce a better fit.

Table 4.13. K_x, K_c and their associated Δ_c values obtained by the application of a quadratic fitting Benesi-Hildebrand treatment to the chloroform-benzene interaction in different inert solvents over the whole concentration range, (i) with the volume correction, (ii) without the volume correction, (iii) on the molar scale. All three columns refer to results obtained by neglecting the shift correction ($-x_BG$).

	(i)		(ii)		(iii)	
Inert Material	$K_x{}^b$	Δ_c/Hz	K_x	Δ_c/Hz	$10^3K_c/m^3\,mol^{-1}$	Δ_c/Hz
cyclohexane	1.468	84.4	1.032	98.7	0.133	84.4
cis-decalin	1.592	82.6	0.520	148.1	0.147	81.7
bicyclohexyl	1.844	77.9	0.358	191.7	0.164	78.0
tetradecane	2.120	75.0	0.069	790.6	0.191	75.0
hexadecane	1.863	79.9	-0.126	-359.3	0.168	79.9

In conclusion, it would appear that meaningful values for the equilibrium parameters can be obtained for this particular system, by either the CA or BH method, over the whole range or over the "correct" narrow range. This apparent contradiction of all the previously discussed thermodynamic criteria can only be rationalised by assuming that for this system there is fortuitous consistency of the activity co-efficient term $\gamma_{AB}/\gamma_A\gamma_B$, which results in consistent K_x and K_c values being evaluated.

The success of studies over the whole range necessitates the consideration of the validity of processing data obtained from low concentration studies by both methods, even though thermodynamic considerations negate such studies.

Table 4.14. The composition of the mixtures employed in the investigation of the chloroform (A)-benzene (B) interaction in cyclohexane (S) at low mole fractions of benzene, together with the "effective number" of moles of S, the corresponding chemical shifts relative to cyclohexane, and the mole fraction of B.

No.	$10^4 n_A$ /mol	$10^4 n_B$ /mol	$10^2 n_S$ /mol	x_B	δ_{obs}/Hz
1.00	0.8327	0.000	2.5607	0.000	-339.47
1.18	0.8577	2.5181	2.5006	0.009	-338.34
1.19	0.5997	3.2170	2.5009	0.012	-337.63
1.20	0.7874	4.0850	2.5001	0.016	-337.34
1.21	0.6140	5.1795	2.4991	0.020	-336.69
1.22	0.5914	6.7464	2.5014	0.026	-335.96
1.23	0.9943	8.1585	2.5001	0.031	-335.56
1.24	0.7463	10.926	2.4993	0.041	-334.31
1.25	0.7849	16.497	2.4998	0.062	-332.56
1.26	5.4870	54.340	4.992	0.155	-324.45
1.27	1.2222	46.151	2.4994	0.199	-321.13
1.28	1.6251	62.847	2.4997	0.246	-317.16
1.29	1.1183	41.600	1.2589	0.246	-317.16
1.30	7.6231	239.82	5.0306	0.319	-312.95
1.31	8.8295	369.51	4.9965	0.421	-307.28

4.7. The Application of Methods I and II to Low Concentration Studies.

In an attempt to determine the lowest concentration range which would give results comparable to those obtained by whole range studies, the chloroform-benzene interaction in cyclohexane was investigated. The composition and the shifts, referenced to cyclohexane, of the samples are shown in Table 4.14. The benzene referenced shift data given in Table 4.2 were not used as there were insufficient data points in the required concentration range. It was found, using a Creswell and Allred data processing method on both the volume corrected data and the uncorrected data, that anomalously high K_x values were obtained if the concentration range was restricted to between $x_B = 0$ and $x_B = 0.20$, as is shown in Table 4.15. If, however, data points with x_B in excess of 0.20 were introduced to the computer input, the results obtained were comparable with the accepted whole range values of K_x and

Table 4.15. K_x and Δ_c values obtained for the chloroform-benzene interaction in cyclohexane, using a Creswell - Allred data processing method (i) with the volume correction and (ii) without the volume correction, the shift correction ($-x_BG$) being ignored.

Highest Mole	(i)		(ii)	
Fraction (x_B)	$K_x{}^b$	Δ_c/Hz	K_x	Δ_c/Hz
0.062	7.321	25.9	5.838	26.7
0.097	4.543	37.8	3.538	39.8
0.155	2.956	53.1	2.188	58.7
0.195	2.474	61.0	1.593	75.9
0.320	1.699	81.9	1.172	96.4
0.420	1.67_0	82.9	1.147	97.5

K_x^b, namely ca 1.10 and ca 1.70.

The only plausible explanation for this is that over the enlarged concentration range the activity co-efficient terms once again fortuitously remain constant. With reference to figure 4.3, it is evident that the activity co-efficient of benzene undergoes a drastic change in the region $x_B = 0$ to 0.2, but this alone cannot account for these deviations. The effect of changing the environment on the activity co-efficients of A and B have to be considered once more. The equilibrium quotient in this region can be expressed in statistical terms as:-

$$RT\ln K_x^+ = RT\ln K^o + L(bw'_{AB} + sw'_{AB} + s'w'_{AS} - b'w'_{AB,B} - s''w'_{AB,S}) \qquad \ldots.\ 4.58$$

$$= RT\ln K^o + RT\ln \frac{\gamma_A^R\,\gamma_B^R}{\gamma_{AB}^R} \qquad \ldots.\ 4.58$$

where the terms have the same previously defined significance. In the derivation of this expression it is assumed that, the presence of a low concentration of A and AB modifies the chemical potential of each other and of B insignificantly compared with the effects of the major components B and S. It was previously stated that, at low concentrations of the B component, the chemical potentials of A and AB are more or less constant. However, as was stated in section 4.3.1, increasing the concentrations of B modifies their chemical potentials. The number of aromatic molecules surrounding A and AB increases (i.e. b and b' increase) until the first co-ordination shell is complete; correspondingly, S and S'' decrease. ω'_{AB} and $\omega'_{AB,B}$ are expected to be greater than ω'_{AS} and $\omega'_{AB,S}$ respectively, the terms quantifying the interaction of A and AB with B being of the greater importance. As these two terms are of a different magnitude and cannot be expected to undergo identical changes as x_B increases, the term $\gamma A/\gamma_{AB}$ will only slowly tend towards a limiting value corresponding to the completion of the first solvent shells of A and AB. Consequently,over very narrow low concentration ranges, the calculated equilibrium parameters reflect the rapid changes occuring in b, b' and s. Over wider ranges b and b' will reach limiting values,resulting in the activity co-efficient term $\gamma^R_{AB}/\gamma^R_A\gamma^R_B$ becoming less variable and hence more consistent K_x and K_c values being determined.

A problem arises when the component B is insufficiently soluble to satisfy the minimum concentration requirements outlined above. The solubility of butyl substituted benzenes is so limited. It is the intention in the subsequent chapter to detail the reaction of chloroform with alkylated benzenes in cyclohexane and thus the insolubility of the butyl benzenes poses a real problem. The CA treatment of the low concentration tri-butyl benzene system data produced spurious results. The alternative Scott data processing method, based on the Benesi-Hildebrand method, was attempted but produced equally erroneous results. This method and the Foster and Fyfe method have been devised specifically to facilitate the application of the BH method to low concentration studies, the advantage being that the intercept is not as small and does not require extrapolation to pure solvent to determine Δ_c, but extrapolation to infinite dilution. Thermodynamic considerations apart, the application of any method based on Benesi-Hildebrand assumptions to such studies is negated for two reasons, namely (a) the assumption that n_A is small and can be neglected is not valid as n_A may form a not insignificant component and,(b) at low concentrations, the amount of B involved in complexing is no longer insignificant and thus there is no justification for reducing the term $(n_B - n_{AB})$ in the equilibrium expression 4.4 to n_B. The failure to allow for these two factors no doubt, in part, leads to non-linear plots being obtained over this region.[89]

However, it was decided to test the Scott and Foster and Fyfe treatments by their application to a reaction over the "correct range". As the benzene-chloroform-cyclohexane data (referenced to cyclohexane) were readily available this was used, the data being processed by a least squares program. The results obtained by both methods were comparable with those obtained from the BH treatment, as would be expected, as a mathematical consequence of the format of the three equations 4.11, 4.14 and 4.15. It is the appearance of the relevant plots which is of interest. Graphic interpretation of the data can be seen to be difficult from figures 4.6 and 4.7, because of the scatter. It is evident that a visual best line technique would be open to considerable subjective error and therefore a computer line fit is essential to avoid the anomalies previously discussed in section 4.4. It has thus been demonstrated that Foster-Fyfe and Scott plots are not theoretically justified at low concentrations and that there is no advantage to be gained by their application over the "correct" concentration range and therefore, they will not be further considered.

4.8. Conclusions

Within this chapter, an attempt has been made to show the conditions under which reliable equilibrium quotients for reactions of the type

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

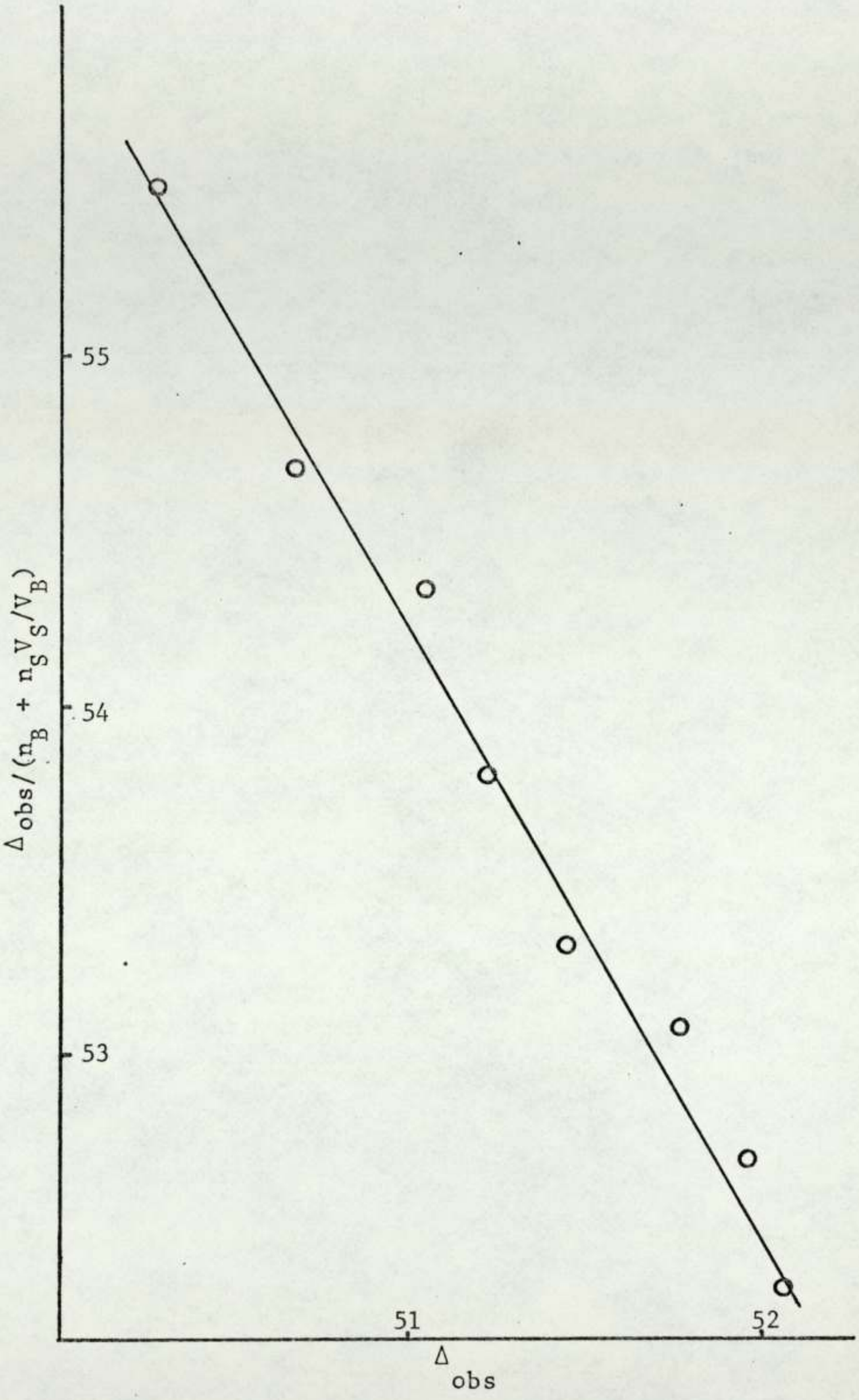


Figure 4.7. Foster and Fyfe plot for the chloroform-benzene interaction in cyclohexane.

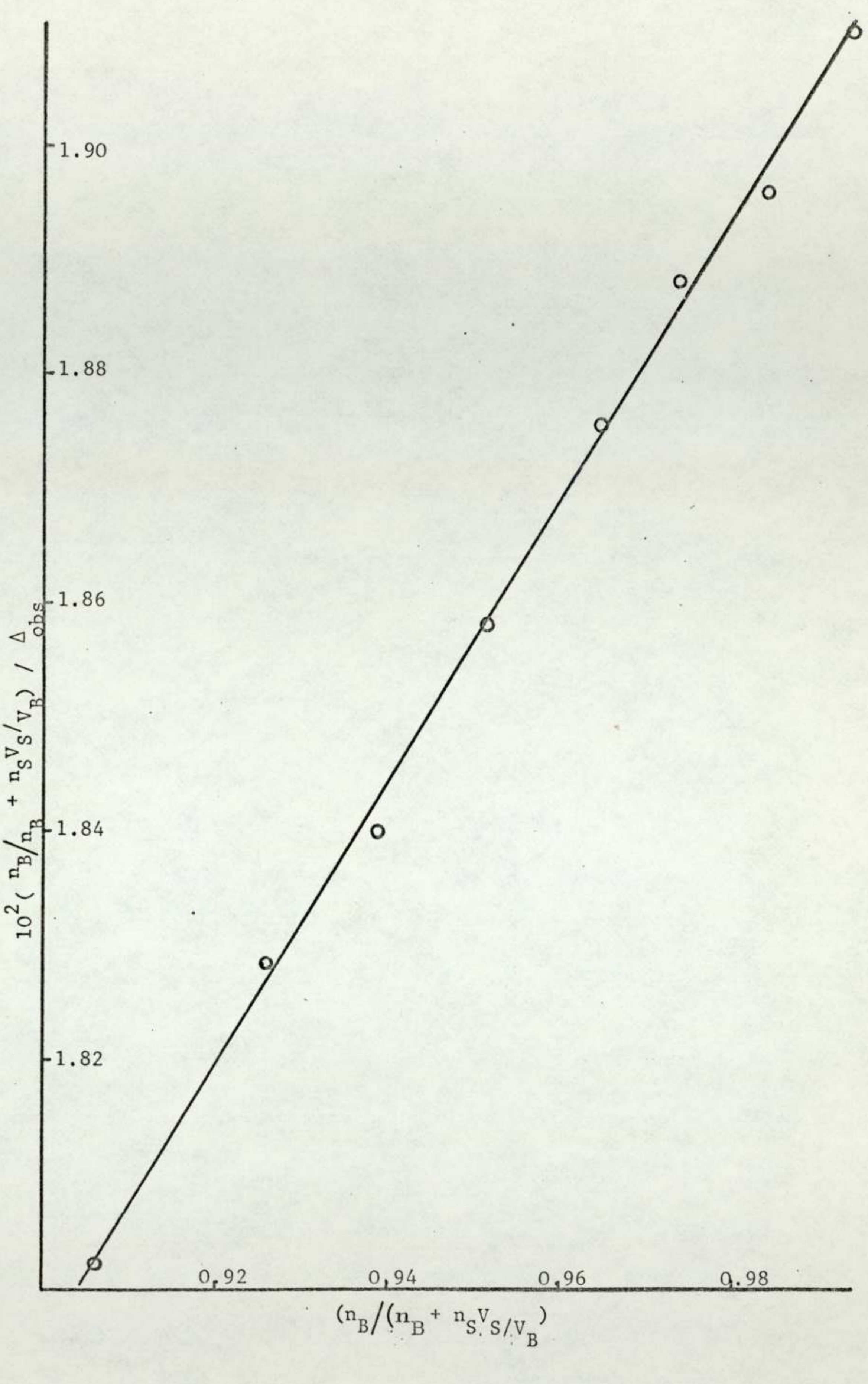


Figure 4.6. Scott plot for the chloroform-benzene interaction in cyclohexane.

can be calculated. The only thermodynamically valid practical concentration range is that in which $x_B = 0.9$ to 0.995 and x_A is less than 0.005, and the only valid concentration scale is the mole fraction scale corrected for the "effective number" of moles of S. The Creswell-Allred treatment over the whole range produces some sort of average equilibrium quotient.

However, for the chloroform-benzene interaction in various inert solvents, both the CA and BH treatments give comparable results over the whole range and within the thermodynamically "correct" range. Studies of this and other systems at low concentration ($x_B < 0.1$) produced spurious values for the equilibrium quotient and the limiting complex shift, Δ_c. The application of the BH based Foster-Fyfe and Scott plots, which were devised specifically for such low concentration studies, also produced equally unacceptable results and was shown to be theoretically unsound; but their application to the high concentration "correct" studies lead to results which were, as expected, comparable with BH results. Experimentally, it was found that results comparable with whole and correct range studies were obtained when x_B was in the region $x_B = 0$ to greater than 0.20, x_A remaining less than 0.005.

It was shown that all three concentration scales have their limitations. The mole fraction scale equilibrium quotients are dependent on the nature of S unless the quantity of inert solvent is modified to allow for the different size between itself and the active aromatic solvent, which it is diluting. As a thermodynamic consequence the equilibrium quotients determined by the use of the molar scale, when expressed in terms of chemical potentials, show a solvent dependence as do the molal scale quotients. With the molar scale this dependence can be obviated by determining the limiting slope of the Δ_{obs}^{-1} against C_B^{-1} plot, when the situation discussed in section 4.5.2 is applicable, namely the limiting value of K_c/K_x should be the molar volume of the aromatic solvent. The solvent dependence of the molal scale may be removed by the adoption of a 'mixed solvent' definition of molality modified,to include a volume correction for the 'effective' number of moles of inert solvent. .

It would appear, therefore, that for the particular systems studied here, meaningful and comparable results can be otained by the use of the BH equation using the molar scale, or the volume corrected mole fraction scale, over two concentration ranges; the Creswell -Allred treatment using the corrected mole fraction scale also produced similar results. In addition a BH treatment using a modified molal scale produced meaningful results. It may, however, be completely unjustified to assume that similarly comparable results may be determined by the use of such ranges and data processing methods for other reactions and thus, in subsequent work, studies will be restricted to the use of the corrected mole-fraction scale over the only thermodynamically practical region. The shift correction appears to be of little consequence and hence will be ignored.

CHAPTER 5. A VARIABLE TEMPERATURE STUDY OF THE INTERACTIONS OF CHLOROFORM WITH BENZENE AND VARIOUS ALKYL SUBSTITUTED BENZENES.

5.1 Introduction

Within this chapter studies of the interaction of a common solute (chloroform) with various alkyl substituted aromatics are reported. The introduction of increasingly bulky substituents to the aromatic nucleus is expected to result in a change in its polarisability and an increasing steric congestion of the six-fold axis of the aromatic to approach by the solute. These two effects are expected to be competing with respect to the strength of the interaction. In the literature, similar investigations have been based on two approaches, namely; the comparison of aromatic solvent induced shifts (ASIS) determined by extrapolation of the measured solute shifts to infinite dilution, or a comparison of equilibrium parameters, particularly equilibrium quotients, determined from the measurement of solute shifts as a function of solution composition and temperature.

In studies of the interactions between a variety of solutes and alkylated benzenes, Brown and Stark[111], and Hatton and Richards[62] noted a decrease in the ASIS in the order benzene $\gg$ toluene > mesitylene. They considered that this was a result of steric hindrance to the approach of the solute. Sandoval and Hanna[112], however, adopting the second approach, stated that with dimethyl formamide as solute, the equilibrium quotients showed the opposite trend. Brown and Stark considered that this was due to an increasingly large dipole-induced dipole interaction. Before continuing it is advisable to consider the basis of ASIS measurements. It is evident that to some extent such correlations must be empirical since, if these solvent shifts are the result of specific complex formation then they are really composite term dependent, not only on the chemical shift of the pure complex, Δ_c, in solution, but also on the fraction of the solute present in the complex state (see section 1.11). For an infinitely dilute solute, the measured shift, Δ_{obs}, will not be equal to Δ_c, unless K, the equilibrium quotient of the solute-solvent complex, is infinite. For[113] finite values of K,

$$\Delta_{obs} = \Delta_c K(1 + K)^{-1} \quad \ldots. \; 5.1$$

As associations of this type are relatively weak, the measured shift will not approach the value of Δ_c. Consequently, unless K and Δ_c vary in a parallel fashion,comparison of a single function of K and Δ_c may not be meaningful, although in a series of closely related compounds some correlation may appear to be obtained. It should be noted that such criticism does not apply to the relative shifts of nuclei in the same molecule, since these will all be a function of the same equilibrium quotient, and consequently the measured shift values for dilute solutions will be proportional to the corresponding Δ_c values.

Critical analysis of the aromatic concentration ranges used in the determination of equilibrium parameters for solute-alkyl benzene interactions, in the literature, reveals that, where quoted, in the majority of cases non-thermodyncamically valid ranges have been used. The equilibrium quotients have been found to increase rapidly for the interaction of a common solute on going from benzene to hexamethyl benzene[102,114,115], but decrease with hexaethyl,[116] n-propyl and ethyl substituted[104] benzenes. Studies in this laboratory have shown the solubility of penta- and hexa-methyl benzenes, in cyclohexane, to be such that it is impossible to satisfy the 'minimum concentration criterion'(x_B must be greater than 0.2) discussed in Chapter 4.It is therefore highly probable that the reported large equilibrium quotients,obtained for the penta-andhexa-methyl benzene systems at least, are a result of unsatisfactory data processing and thus of questionable significance. It should be remembered that the 'minimum concentration criterion' was devised with specific regard to the chloroform-benzene interaction in various inert solvents, and thus it is dubious that the study of dissimilar systems over other than the thermodynamically valid range is justifiable.

It is apparent that no great significance can be placed on the results and conclusions in previous studies of the effect of steric hindrance and changing aromatic polarisability on the formation of transient 1:1 polar solute-aromatic solvent complexes. The application of the newly derived data processing method, which enables thermodynamically valid parameters to be determined, ensures that the results of this present n.m.r. study of such interactions are meaningful. To avoid complications due to permanent dipoles, only non-polar solvents are to be used; these are benzene, p-xylene, mesitylene, p-diethyl benzene, 1.3.5-triethyl benzene, p-diisopropyl benzene, 1.3.5. triisopropyl benzene, p-di(tert)butyl benzene, and 1.3.5.tri-(tert) butyl benzene.

The principal difficulty, once the relevant equilibrium parameters have been determined, will be ascertaining the relative contributions of the polarisabilities and steric effects on complex formation. As the aromatic becomes increasingly substituted, its polarisability increases also. If the interaction is considered to occur by polarisation of the aromatic ring by the electric fields associated with each of the polar bonds in the solute molecule, then the increasing polarisability of the aromatic enhances the interaction energy between the two species. However, the increasing bulk of the substituents may constitute a steric barrier to the approach of the solute to the aromatic, resulting in a weakening of the interaction.

5.2 The Calculation of the Interaction Energy

Homer and Cooke[77] have developed a method of calculating interaction energies, assuming there to be no steric hindrance, which will now be described.

In general, the interaction energy (V) between an induced dipole, in a molecule of polarisability α, and a permanent dipole of moment μ, producing the inducing electric field (E), is twice the potential energy of the system and is given by

$$V = -\alpha E^2 \qquad \text{.... 5.2}$$

If the polarisable aromatic has three different polarisabilities, α_z, α_p and α_u, along three mutually perpendicular axes, z, p and u, the total energy of the interaction due to I different polar bonds is

$$V = -\alpha_z \Sigma_i (E_z)_i^2 - \alpha_p \Sigma_i (E_p)_i^2 - \alpha_u \Sigma (E_u)_i^2 \qquad \text{.... 5.3}$$

For the purpose of these calculations, the z-axis is taken to be co-incident with the aromatic six-fold axis and the origin of the co-ordinate system at the centre of the aromatic molecule. The electric field produced by an isolated polar bond, a distance R_i from the aromatic centre to the electric centre of the bond, can be resolved into two components, $(E_x)_i$ and $(E_y)_i$, along the bond direction and perpendicular to the plane containing E_x and the radius vector respectively. $(E_x)_i$ and $(E_y)_i$ are given classically by

$$(E_x)_i = \frac{\mu_i (3\cos^2\theta - 1)}{R_i^3} \qquad \text{.... 5.3}$$

$$(E_y) = \frac{\mu_i \; 3\cos\Theta_i \sin\Theta_i}{R_i^{\;3}} \qquad \ldots\ldots 5.4$$

where Θ_i is the angle between the radius vector and the direction of the polar bond i. Both components can themselves be resolved along the axes z, p and u in turn, to give E_x, E_p and E_u respectively, the sum of the square of the appropriate contribution being used in equation 5.3. From a knowledge of the structure of the complex, bond lengths and angles, the individual values of the electric field terms can be evaluated. The major inaccuracy with this treatment arises because of the uncertainty in locating the dipole centres of each of the bonds. Good correlation was obtained for halogenated solutes with benzene when the dipole centes were located at 2/3 and 1/2 the bond length measured from carbon for the carbon-chlorine and carbon hydrogen bonds. If the plane containing the polar bond and the radius vector also contains the aromatic six-fold axis, then the $(E_x)_i$ and $(E_y)_i$ components need to be resolved into two components only; namely the z and p directions, as the remaining component will necessarily be zero. As this is the case with the chloroform-benzene complex, if the solute is assumed to be on the six-fold axis, then taking the carbon-chlorine bond dipole moment to be 1.46D, the chloroform proton-aromatic separation to be 3.05Å (Van der Waals contact) and the dipole centres to be as previously specified, then Cooke has calculated that the interaction energy (in J molecule^{-1}) is

$$V = -\alpha_z(1.3270) \times 10^8 - \alpha_p(5.0960) \times 10^6 \qquad \ldots\ldots 5.5$$

The interaction energy therefore provides a measure of the electric effects of substitutients via the polarisability terms α_z and α_p.

In the foregoing theory, the dielectric constant between the solute and the solvent (and intramolecularly) has been assumed to be unity, which must place some doubt on the quantitative validity of the approach. Two further assumptions are necessary if the interaction energies for different aromatics are to be calculated from equation 5.5, namely (a) that possible dipole-dipole interactions between the C-H bonds of any aromatic-substituents and the solute are negligible and (b) that the solute-aromatic separation remains constant at 3.05Å. These assumptions are not unreasonable but will be considered again later.

It is the intention in these studies to compare theoretical interaction energies with those experimentally determined parameters which are thought to reflect complex strength, and any lack of correlation can be taken to reflect the effects of steric hindrance. It is to be expected that if steric effects are operative the lack of correlation will become more marked with increasing substituent bulk.

5.3 Experimental

All the reagents used were of the best commercial quality available and were used without further purification, with the exception of chloroform. The chloroform was washed five times with water, dried over calcium chloride and distilled to remove the 1% ethanol stabiliser. Tri-(tert)butyl benzene was not available commercially and hence was prepared by a Friedel-Craft alkylation method proposed by Barclays and Betts[117], the product being recrystallised five times from ethanol (m.pt.346.2K cf lt.value 347.0-347.2K). The purity of all the reagents was checked by gas-liquid chromatography and n.m.r.spectroscopy.

To investigate the effects of alkyl aromatic substituents on the chloroform-benzene interaction, systems of chloroform with benzene (6), p-xylene (7), mesitylene (8), p-diethyl benzene (9), 1.3.5. tri-ethyl benzene (10), p-di-isopropylbenzene (11), 1.3.5. tri-isopropyl benzene (12), p-di-(tert) butyl benzene (13) and 1.3.5. tri-(tert)butyl benzene (14) were studied. Unfortunately, aromatics (13) and (14) were insufficiently soluble to enable a thermodynamically valid concentration series to be constructed and hence these series will not be further considered. Preliminary measurements were conducted on a Perkin-Elmer R.10 spectrometer but, when the Varian H.A.100 spectrometer became available, all the systems were studied in detail on the latter instrument as the accuracy of the shift measurements was much improved. Each shift measurement was repeated and, in this manner, accuracies better than ± 0.0005 ppm were achieved. All the shifts were measured with respect to the internal cyclohexane (inert diluent); an aromatic signal being used for internal lock in the field sweep mode.

All the series were measured at five or more temperatures in the range 273K - 330K; with the exception of the p-diisopropyl benzene system which, due to a paucity of time, was measured at only three temperatures. The exact temperature was determined accurately by measurement of the shift dependence of the hydroxyl absorption relative to the methyl absorption of methanol. The probe was found to be stable to ± 1.0 K. When small shift differences are being measured a temperature variation of 1 - 2K may well produce an appreciable error in the shift measurements, resulting in significant errors in the values of the highly sensitive equilibrium quotients determined. Shift measurements and data evaluation thus proved very critical and great care was needed. The consistency of the complex limiting shifts (Δ_c) obtained for each series at different temperatures is thought in some way to justify the approach adopted.

The compositions of the samples in each series were such that the thermodynamic dictates of Chapter IV were satisfied, namely that x_A was less than 0.005 and x_B was in the range 0.9 to 1.0; these are shown in Table 5.1. It should be noted that the composition of the chloroform-benzene system documented refers to the series which was used for the shift measurement at ca.320K. The measurement of the benzene system at the other temperatures utilised series 1, whose composition is shown in Table 4.2. Samples in series 1, 7, 8, 9, 10 and 12 were encapsulated in tubes of diameter equal to 0.181", the Varian instrument being modified to enable tubes of this diameter to be used. Unfortunately, before the studies of the benzene series could be completed, the pressure of usage on the instrument necessitated the removal of this modification. Consequently a new benzene series was prepared in 0.195" diameter tubes which enabled the final measurements at ca.320K to be conducted. For the same reason series 11 was prepared in the larger diameter tubes.

The experimentally determined chemical shifts (δ_{obs}) are recorded in Table 5.2, with the exact temperature at which they were measured. The determination of the values of δ_{free}, the shift of uncomplexed chloroform infinitely diluted in cyclohexane, necessitated the use of an external tetramethyl silane reference to provide the lock signal. The values of δ_{free} so determined are also given in Table 5.2. It will be noted that it was not always possible to make measurements on all the samples in a particular series on certain occasions, due to some difficulties encountered with spinning the sample. Nevertheless, all the series contained sufficient

Cont. p.132.

Table 5.1. The composition of the mixtures employed in the investigation of the interaction of chloroform (A) with a series of substituted aromatics (B) in cyclohexane (S) as inert diluent.

No.	$10^5 n_A$/mol	$10^3 n_B$/mol	$10^4 n_S$/mol	x_B
Benzene				
6.1	17.163	38.600	44.064	0.894
6.2	17.951	38.451	40.764	0.900
6.3	18.303	38.824	36.510	0.910
6.4	16.669	38.378	11.968	0.965
6.5	17.457	38.469	8.0782	0.975
6.6	16.937	38.507	5.5335	0.982
6.7	17.013	38.393	1.6771	0.991
p-xylene				
7.1	6.3076	7.0302	6.8130	0.904
7.2	6.5674	8.5695	6.0478	0.927
7.3	6.5841	7.8548	5.0735	0.932
7.4	6.1569	8.0862	3.8128	0.948
7.5	7.0281	9.8930	2.2884	0.971
7.6	9.2144	10.010	0.8899	0.982
7.7	6.6942	9.7792	0.6123	0.987
mesitylene				
8.1	10.303	16.765	17.743	0.899
8.2	7.0860	16.934	17.0883	0.905
8.3	11.174	16.697	16.1413	0.906
8.4	7.6732	16.875	14.356	0.917
8.5	10.487	17.549	12.434	0.928

CONT

Table 5.1 (Cont.)

No.	$10^5 n_A$/mol	$10^3 n_B$/mol	$10^4 n_S$/mol	x_B
8.6	10.940	16.833	8.4645	0.946
8.7	10.010	16.904	6.4506	0.957
8.8	11.752	16.777	2.9443	0.976
8.9	9.1646	18.034	1.3686	0.987
8.10	11.585	16.697	0.8317	0.988
p-diethyl benzene				
9.1	6.3072	6.0271	6.6823	0.892
9.2	6.4082	5.8131	5.0842	0.910
9.3	5.0512	5.7799	5.1329	0.911
9.4	6.4584	6.2946	4.6933	0.922
9.5	6.7349	6.2705	3.8782	0.932
9.6	9.5244	6.8435	3.5455	0.938
9.7	6.8103	6.9007	1.5292	0.969
9.8	8.5526	6.9777	1.2131	0.971
9.9	6.1403	5.8223	0.8709	0.975
9.10	6.1317	6.5959	0.8151	0.978
1.3.5.-triethyl benzene				
10.1	6.6511	4.6002	4.1681	0.905
10.2	6.3077	5.2135	3.6239	0.924
10.3	10.4206	4.9355	2.8088	0.927
10.4	6.6343	5.2103	3.2556	0.930
10.5	6.8019	4.8972	2.8088	0.959
10.6	6.6762	4.3901	0.7889	0.968
10.7	7.4804	4.9686	0.6594	0.972

Table 5.1 (Cont)

No.	$10^5 n_A$/mol	$10^3 n_B$/mol	$10^4 n_S$/mol	x_B
p-diisopropyl benzene				
11.1	9.9592	18.548	18.560	0.904
11.2	9.7000	18.562	16.651	0.915
11.3	9.4741	18.458	13.502	0.927
11.4	9.2816	18.574	10.233	0.933
11.5	10.001	18.470	9.6997	0.945
11.6	10.135	18.528	8.7841	0.949
11.7	8.5356	18.468	7.1825	0.958
11.8	9.4903	18.492	4.0760	0.973
11.9	9.6832	18.658	1.9412	0.985
11.10	9.5320	18.529	1.0868	0.989
1.3.5.-triisopropyl benzene				
12.1	6.3161	4.5062	5.1697	0.886
12.2	6.8270	5.7540	5.0093	0.905
12.3	6.5757	4.5190	2.8468	0.928
12.4	5.9977	4.7552	2.6912	0.935
12.5	7.2710	4.7519	2.5166	0.936
12.6	6.2072	4.3602	2.1018	0.941
12.7	6.0061	4.7995	1.6812	0.955
12.8	6.0647	4.7866	1.2702	0.962
12.9	4.8082	4.8913	0.8127	0.974
12.10	6.3662	4.9542	0.4313	0.977

Table 5.2. Corrected mole-fractions($x_B$corr) and shift values for the interaction of chloroform with alkyl substituted benzenes at various temperatures.

Temp/K	No.	$x_B$corr	δ_{obs}/Hz	Temp/K	$x_B$corr	δ_{obs}/Hz
benzene						
281.84	1.0	0.00000	-567.30	292.29	0.00000	-566.97
	1.8	0.82303	-472.50		0.82340	-
	1.9	0.90604	-469.55		0.90608	-472.86
	1.10	0.92651	-469.05		0.92654	-472.24
	1.11	0.93924	-468.70		0.93927	-471.71
	1.12	0.95154	-468.50		0.95156	-471.65
	1.13	0.96451	-		0.96453	-
	1.14	0.97481	-467.70		0.97482	-470.89
	1.15	0.98541	-467.70		0.98541	-470.56
	1.16	0.99429	-475.50		0.99429	-470.33
302.04	1.0	0.00000	-565.65	309.09	0.00000	-566.55
	1.8	0.82390	-		0.82417	-485.67
	1.9	0.90602	-478.38		0.90614	-483.22
	1.10	0.92657	-477.83		0.92659	-482.36
	1.11	0.93929	-477.44		0.93931	-481.63
	1.12	0.95158	-477.17		0.95159	-481.46
	1.13	0.96455	-476.74		0.96457	-
	1.14	0.97483	-476.44		0.97484	-480.32
	1.15	0.98542	-476.16		0.98542	-480.47
	1.16	0.99429	-475.83		0.99430	-479.94

CONT

Table 5.2 (Cont.)

Temp/K	No.	$x_B$corr	δ_{obs}/Hz	Temp/K	$x_B$corr	δ_{obs}/Hz
	8.6	0.96224	-456.84		0.96218	-461.80
	8.7	0.97069	-456.65		0.97065	-461.47
	8.8	0.98641	-455.97		0.98646	-460.93
	8.9	0.99411	-455.73		0.99410	-460.65
	8.10	0.99612	-455.68		0.99612	-460.54
322.08	8.0	0.00000	-566.04			
	8.1	0.92343	-469.44			
	8.2	0.92673	-469.28			
	8.3	0.92959	-469.16			
	8.4	0.93751	-468.74			
	8.5	0.94741	-468.43			
	8.6	0.96206	-467.80			
	8.7	0.97058	-467.53			
	8.8	0.98643	-466.94			
	8.9	0.99409	-466.71			
	8.10	0.99611	-466.73			
p-diethyl benzene						
276.23	9.0	0.00000	-567.48	288.37	0.00000	-567.10
	9.1	0.92879	-448.48		0.92859	-458.76
	9.2	0.94297	-447.92		0.94281	-457.98
	9.3	0.94219	-447.96		0.94198	-457.88
	9.4	0.95097	-447.59		0.95083	-457.56
	9.5	0.95898	-447.38		0.95887	-457.26
	9.6	0.96541	-446.92		0.96531	-457.00

Table 5.2 (Cont.)

Temp/K	No.	$x_B$corr	δ_{obs}/Hz	Temp/K	$x_B$corr	δ_{obs}/Hz
321.85	7.0	0.00000	-566.05			
	7.1	0.92144	-477.47			
	7.2	0.94154	-476.66			
	7.3	0.94623	-476.54			
	7.4	0.96017	-476.01			
	7.5	0.98005	-475.16			
	7.6	0.99228	-474.84			
	7.7	0.99495	-			
mesitylene						
277.12	8.0	0.00000	-567.15	288.38	0.00000	-567.10
	8.1	0.92413	-438.11		0.92396	-447.38
	8.2	0.92741	-438.38		0.92724	-447.28
	8.3	0.93024	-438.09		0.93008	-447.93
	8.4	0.93809	-437.58		0.93795	-446.78
	8.5	0.94790	-437.21		0.94778	-446.48
	8.6	0.96245	-436.77		0.96237	-445.97
	8.7	0.97086	-436.39		0.97079	-445.51
	8.8	0.98656	-436.15		0.98653	-444.81
	8.9	0.99414	-436.05		0.99411	-
	8.10	0.99615	-435.92		0.99614	-444.50
304.83	8.0	0.00000	-566.30	311.67	0.00000	-566.08
	8.1	0.92372	-458.81		0.92360	-463.45
	8.2	0.92701	-458.60		0.92690	-463.30
	8.3	0.92986	-458.51		0.92975	-463.31
	8.4	0.93775	-458.11		0.93765	-465.85
	8.5	0.94761	-457.64		0.94753	-462.40

Table 5.2 (Cont.)

Temp/K	No.	$x_B$corr	δ_{obs}/Hz	Temp/K	$x_B$corr	δ_{obs}/Hz
319.29	6.0	0.00000	-566.13			
	6.1	0.87816	-487.87			
	6.2	0.88585	-487.52			
	6.3	0.98742	-487.10			
	6.4	0.96348	-484.88			
	6.5	0.97512	-484.43			
	6.6	0.98283	-484.30			
	6.7	0.99471	-483.70			
p-xylene						
286.93	7.0	0.00000	-567.13	292.91	0.00000	-566.96
	7.1	0.92175	-457.92		0.92168	-461.52
	7.2	0.94177	-457.13		0.94172	-460.75
	7.3	0.94645	-456.94		0.94639	-460.75
	7.4	0.96033	-456.38		0.96029	-460.14
	7.5	0.98014	-455.56		0.98012	-459.50
	7.6	0.99231	-455.30		0.99230	-459.12
	7.7	0.99495	-455.20		0.99495	-459.13
302.64	7.0	0.00000	-566.66	311.38	0.00000	-566.38
	7.1	0.92155	-467.53		0.92144	-472.39
	7.2	0.94163	-466.58		0.94154	-471.68
	7.3	0.94631	-466.54		0.94623	-471.66
	7.4	0.96023	-465.93		0.96017	-470.97
	7.5	0.98008	-465.27		0.98005	-470.35
	7.6	0.99229	-464.99		0.99228	-470.09
	7.7	0.99495	-		0.99495	-

Table 5.2 (Cont)

Temp/K	No.	$x_B$corr	δ_{obs}/Hz	Temp/K	$x_B$corr	δ_{obs}/Hz
	9.7	0.98490	-446.32		0.98486	-456.07
	9.8	0.98820	-446.21		0.98817	-455.97
	9.9	0.98976	-446.10		0.98973	-455.82
	9.10	0.99152	-446.07		0.99150	-455.71
294.54	9.0	0.00000	-566.90	303.24	0.00000	-566.63
	9.1	0.92849	-461.37		0.92834	-468.60
	9.2	0.94271	-		0.94261	-468.03
	9.3	0.94170	-460.49		0.94178	-467.85
	9.4	0.95076	-460.39		0.95065	-467.71
	9.5	0.95881	-459.94		0.95872	-467.35
	9.6	0.96526	-459.66		0.96519	-467.28
	9.7	0.98484	-458.81		0.98480	-466.34
	9.8	0.98815	-458.77		0.98812	-466.10
	9.9	0.98970	-		0.98969	-466.20
	9.10	0.99148	-458.50		0.99147	-466.16
311.67	9.0	0.00000	-566.40	322.08	0.00000	-566.04
	9.1	0.92820	-474.26		0.92801	-479.80
	9.2	0.94249	-473.55		0.94234	-479.02
	9.3	0.94166	-473.53		0.94150	-479.12
	9.4	0.95055	-473.13		0.95042	-478.90
	9.5	0.95863	-472.73		0.95852	-478.44
	9.6	0.96511	-472.39		0.96502	-478.14
	9.7	0.98477	-471.70		0.98473	-477.35
	9.8	0.98810	-471.67		0.98807	-477.18
	9.9	0.98967	-471.45		0.98964	-477.16
	9.10	0.99145	-471.30		0.99142	-476.98

Table 5.2 (Cont.)

Temp/K	No.	$x_B$corr	δ_{obs}/Hz	Temp/K	$x_B$corr	δ_{obs}/Hz
p-diisopropyl benzene						
303.78	11.0	0.00000	-566.61	312.57	0.00000	-566.34
	11.1	0.94580	-479.32		0.94567	-484.56
	11.2	0.95250	-478.87		0.95238	-
	11.3	0.95979	-478.72		0.95970	-484.00
	11.4	0.96337	-478.35		0.96328	-483.83
	11.5	0.97081	-478.20		0.97073	-483.61
	11.6	0.97357	-478.20		0.97350	-483.51
	11.7	0.97821	-477.61		0.97816	-483.25
	11.8	0.98753	-477.51		0.98750	-482.93
	11.9	0.99407	-476.98		0.99406	-482.70
	11.10	0.99665	-476.88		0.99665	-482.58
322.00	11.0	0.00000	-566.04			
	11.1	0.94553	-489.63			
	11.2	0.95223	-			
	11.3	0.95959	-488.98			
	11.4	0.96319	-488.58			
	11.5	0.97065	-488.43			
	11.6	0.97343	-488.34			
	11.7	0.97810	-487.96			
	11.8	0.98746	-487.64			
	11.9	0.99407	-487.40			
	11.10	0.99665	-487.18			

Table 5.2 (cont) Corrected mole fractions ($x_B$corr), calculated at 298.2K, and shifts for the chloroform - 1.3.5 triethyl benzene interaction at various temperatures.

No.	$x_B$corr	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz
		277.12K	288.37K	302.16K	311.67K	322.08K
10.0	0.00000	567.45	567.10	566.67	566.40	566.04
10.1	0.95053	437.15	447.12	458.20	465.14	471.84
10.2	0.96161	436.59	446.42	457.61	464.48	471.14
10.3	0.96535	436.40	446.13	457.23	464.36	470.88
10.4	0.96843	436.34	446.11	457.04	464.09	470.73
10.5	0.98001	435.72	445.54	456.47	463.65	470.23
10.6	0.98978	435.44	445.20	456.04	463.28	469.53
10.7	0.99243	435.09	444.82	455.69	464.36	469.53

Table 5.2 (cont) Corrected mole fractions ($x_B$corr), calculated at 293.2K, and shifts for the chloroform - 1,3,5 - triisopropyl benzene interaction at various temperatures.

No.	$x_B$corr	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz	δ_{obs}/Hz
		276.23K	288.23K	304.24K	311.67K	313.96K	322.09K
12.0	0.00000	567.48	567.10	566.60	566.40	566.30	566.04
12.1	0.95073	435.21	449.10	463.07	469.61	470.38	477.26
12.2	0.96219	434.69	448.33	462.25	468.96	469.73	476.44
12.3	0.97233	-	-	461.61	-	469.30	-
12.4	0.97508	434.02	447.68	461.61	468.19	469.81	475.63
12.5	0.97663	433.88	447.63	461.72	468.08	469.83	475.54
12.6	0.97869	433.03	447.31	461.63	467.71	468.87	475.41
12.7	0.98442	433.68	447.28	461.07	467.70	468.94	475.27
12.8	0.98816	433.36	447.02	461.15	467.31	468.84	474.91
12.9	0.99255	433.14	446.56	460.67	467.02	468.19	474.68
12.10	0.99608	433.15	447.63	460.59	467.09	467.95	474.56

data points to enable the data to be processed with confidence.

Values for K_x and Δ_c were obtained by processing the data on an I.C.L.1905 computer using the program 'BHCURVEFIT' (see section 3.4). The mole fraction of the aromatic was modified to account for the effective number of moles of inert solvent (x_{Bcorr}). The determination of the V_s/V_B ratio requires a knowledge of the appropriate densities. The densities at the required temperatures were obtained by a least squares fit of the temperature versus density data[110] shown in Table 5.3. In the case of 1,3,5-tri-ethyl and

Table 5.3. The densities of cyclohexane and alkylated benzenes, at various temperatures, and the molar volumes at 298.2K (*293.2K).

Material	10^{+3}density/kgm^{-3}			10^3(V_s or V_B)/m^{3}mol^{-1}
	293.2K	298.2K	303.2K	
cyclohexane	0.7785	0.7737	0.7693	0.1088
benzene	0.8790	0.8736	0.8685	0.0894
p-xylene	0.8610	0.8567	0.8524	0.1239
mesitylene	0.8652	0.8611	0.8571	0.1396
p-diethyl benzene	0.8619	0.8579	0.8540	0.1564
1,3,5-triethyl benzene	-	0.8568	-	0.1893
p-diisopropyl benzene	0.8567	0.8529	0.8490	0.1898
1,3,5-triisopropyl benzene	0.8545	-	-	0.2391*

1,3,5-triisopropyl benzenes, only the data shown is available. However, in view of the small amount of correction involved, the values corrected at 298.2K and 293.2K respectively were used; this is not expected to invalidate the approach. The values of K_x and Δ_c, obtained by the application

Table 5.4. Equilibrium quotients, K_x, and complex limiting shifts, Δ_c, obtained by the Benesi-Hildebrand and Creswell and Allred data evaluation procedures at various temperatures using volume correction mole fractions, for the reactions of chloroform (A) with various aromatics (B) in cyclohexane(S) as inert diluent.

Material (B)	Temperature /K	Benesi-Hildebrand Results		Creswell and Allred Results	
		K_x	Δ_c/ppm	K_x	Δ_c/ppm
benzene	281.84	3.144	1.314	3.017	1.335
	292.30	2.686	1.328	2.700	1.328
	302.04	2.373	1.277	2.426	1.286
	309.09	2.004	1.298	1.996	1.303
	312.29	1.590	1.343	1.596	1.344
p-xylene	286.93	2.534	1.564	2.2655	1.620
	292.91	2.367	1.538	2.3995	1.535
	302.64	2.016	1.526	1.566	1.505
	311.38	1.899	1.476	1.934	1.471
	321.85	1.563	1.502	1.561	1.506
mesitylene	277.12	3.522	1.691	3.559	1.689
	288.38	2.807	1.661	3.149	1.614
	304.83	2.272	1.595	2.308	1.590
	311.67	2.135	1.551	1.927	1.608
	322.08	1.782	1.554	1.812	1.547

Cont.

Table 5.4 (Cont)

Material (B)	Temperature /K	Benesi-Hildebrand Results K_x	Benesi-Hildebrand Results Δ_c/ppm	Creswell and Allred Results K_x	Creswell and Allred Results Δ_c/ppm
p-diethyl benzene	276.23	2.338	1.737	2.362	1.738
	288.38	2.069	1.652	1.403	1.923
	294.54	1.739	1.711	1.701	1.733
	303.24	1.659	1.616	1.547	1.668
	311.67	1.396	1.637	1.555	1.547
	322.08	1.182	1.649	1.777	1.660
1,3,5-triethyl benzene	277.12	1.979	1.996	2.108	1.963
	288.37	1.532	2.031	1.656	1.975
	302.16	1.355	1.932	1.999	1.671
	311.67	1.205	1.897	1.375	1.801
	322.08	0.989	1.948	0.959	1.992
p-diisopropyl benzene	303.78	1.321	1.573	1.325	1.569
	312.57	1.221	1.523	1.236	1.521
	322.00	0.948	1.621	0.950	1.619
1,3,5 - triisopropyl benzene	276.23	1.496	2.252	1.548	2.277
	288.23	1.248	2.176	1.350	2.113
	304.24	1.083	2.042	1.161	1.988
	313.96	0.912	2.066	0.991	1.992
	322.09	0.675	2.277	0.768	2.125
	311.67	0.736	2.351	0.809	2.243

of the Benesi-Hildebrand and Creswell and Allred treatments to the data in Table 5.2, are given in Table 5.4. It is interesting to see that the BH and CA results are in good agreement.

The values of the thermodynamic parameters ΔS^o, ΔH^o and ΔG^o from the Benesi-Hildebrand evaluated equilibrium quotient values at different temperatures were obtained using the least squares computer program "PARATHERM". PARATHERM is based on equations 3.19 , 3.22 and 3.21. The values so obtained are recorded in Table 5.5. The results obtained for the diisopropyl benzene series from a PARATHERM treatment of the equilibrium quotients should be treated with caution as effectively the program is fitting the best straight line to only three points.

Table 5.5. Thermodynamic parameters at 298.2K for complex formation, calculated using the Benesi-Hildebrand data in Table 5.4, for the interaction of chloroform (A) with various aromatics (B) in cyclohexane as inert diluent.

Material	$-\Delta H^o/\text{KJmole}^{-1}$	$-\Delta G^o/\text{KJmole}^{-1}$	$-\Delta S^o/\text{Jmole}^{-1}\text{K}^{-1}$	K_x^{298K}
benzene	13.363	2.155	37.584	2.388
p-xylene	10.334	1.925	28.196	2.176
mesitylene	10.748	2.263	28.455	2.493
p-diethyl benzene	11.058	1.309	32.689	1.693
1,3,5-triethylbenzene	10.627	0.828	32.852	1.399
p-diisopropylbenzene	13.895	0.999	43.242	1.498
1,3,5-triisopropyl benzene	12.334	0.133	40.980	1.044

A typical plot of $\log_{10}K$ against 1/T is shown in figure 5.1, using the diethyl benzene system data. The linearity of the plot supports the existence of a 1:1 or several 1:1 isomeric complexes only (section 3.3.5.3).

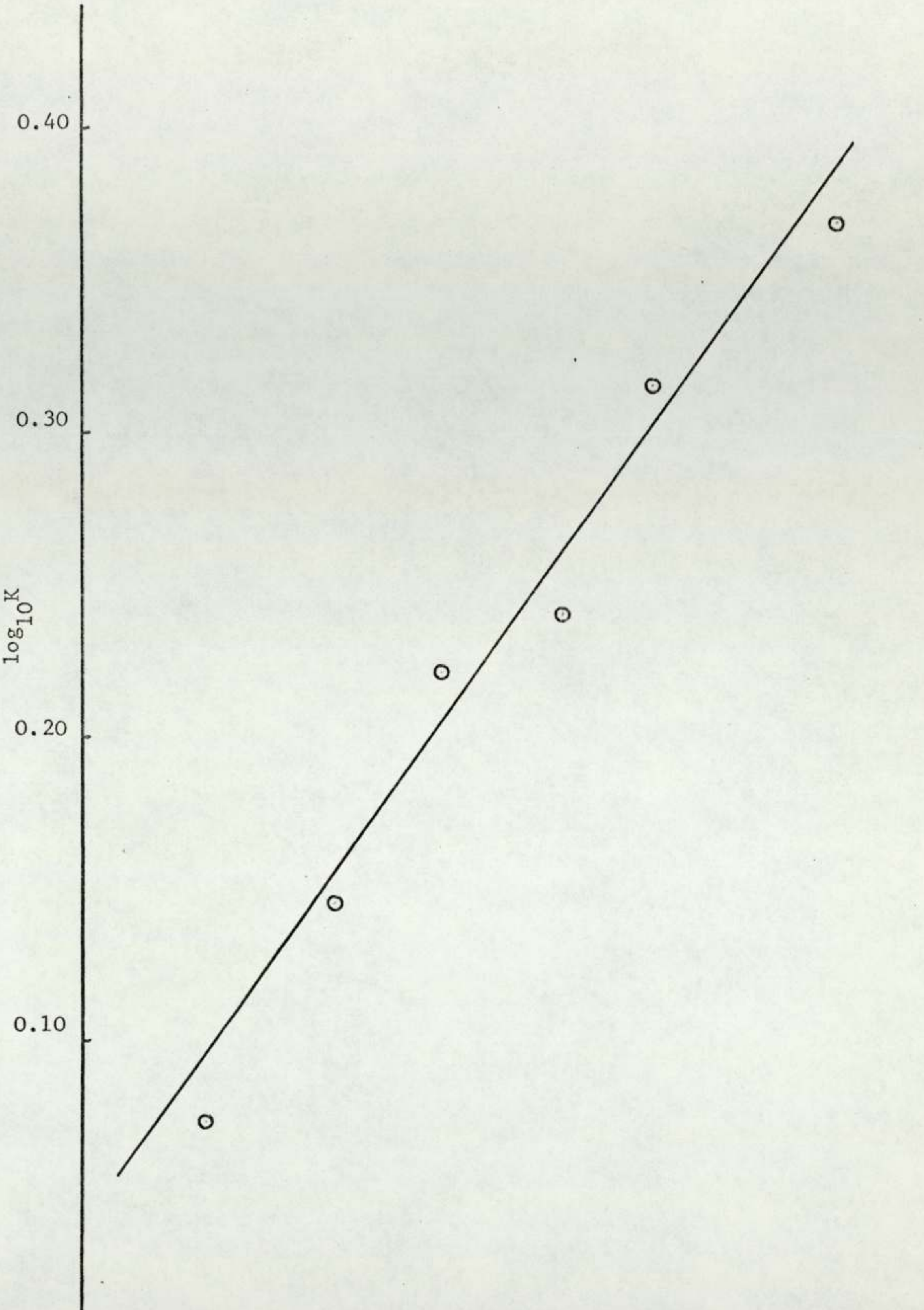


Figure 5.1 van't Hoff plot for the chloroform-p-diethylbenzene-cyclohexane system.

For a considerable time it has been appreciated that, whereas there seems to be little difficulty in evaluating the product term $K_x\Delta_c$, the separation of these factors gives rise to anomalies[118,119,120]. However, it has been shown that, in at least one or two cases[121-124], a reasonable estimate of ΔH^o may be obtained by plotting $\ln K_x\Delta_c$ against T^{-1} instead of using normal van't Hoff plots, provided that it can be assumed that Δ_c is almost temperature independent and hence will only be reflected in the value of the intercept. The ΔH^o values for the systems under consideration here have been evaluated in this manner using the BH evaluated data and are given in Table 5.6. They are in excellent agreement with the values in Table 5.5, which suggest that the separation of the $K_x\Delta_c$ term into two factors by the Benesi-Hildebrand procedure is valid and that Δ_c is in

Table 5.6. Values of ΔH^o for the interaction of chloroform with various alkylated benzenes in an inert solvent, cyclohexane, calculated from the gradient of plots of $\log_{10}K_x\Delta_c$ against T^{-1}, and mean Δ_c values from the BH data in Table 5.4.

Material (B)	$-\Delta H/\text{KJmol}^{-1}$	Δ_c/ppm
benzene	13.271	1.314
p-xylene	11.689	1.521
mesitylene	11.713	1.610
p-di-ethyl benzene	11.949	1.667
1,3,5-triethyl benzene	11.438	1.961
p-diisopropyl benzene	13.472	1.572
1,3,5 -triisopropyl benzene	12.651	2.194

fact almost temperature independent. The respective Δ_c values within any series were averaged to give the mean values shown also in Table 5.6. These will be considered later.

In addition to the BH treatment of the data, the same data points were processed using the Creswell -Allred based computer program "COMPLEXED". The values of K_x and Δ_c so derived are shown in Table 5.4 to allow comparison with the BH results. A perusal of this table shows that in the majority of cases excellent agreement is observed between the two sets of results. The CA results were similarly processed, using the computer program "PARATHERM", to enable the parameters ΔH^o, ΔG^o and ΔS^o to be evaluated. The results are shown in Table 5.7 and they can be seen to be in good agreement with the results given in Table 5.5. It would, therefore, appear that

Table 5.7. Thermodynamic parameters at 298.2K for complex formation, calculated using the Creswell -Allred data in Table 5.4, for the reactions of chloroform (A) with various alkylated benzenes(B) in cyclohexane.

Material	$-\Delta H^o$/KJmol^{-1}	$-\Delta G^o$/KJmol^{-1}	$-\Delta S^o$/Jmol^{-1}K^{-1}	K_x^{298K}
benzene	12.623	2.142	35.135	2.376
p-xylene	8.514	1.732	22.748	2.013
mesitylene	12.091	2.297	32.840	2.529
p-diethyl-benzene	10.455	1.293	30.032	1.684
1,3,5-triethyl-benzene	10.874	1.146	32.635	1.588
p-diisopropyl-benzene	13.941	1.017	43.346	1.507
1,3,5-tri-isopropyl benzene	11.174	0.301	36.484	1.130

over such narrow concentration ranges, the activity co-efficient terms in the equilibrium expression remain almost constant and hence both treatments are applicable. To simplify discussion only the BH results will be further considered.

5.4 Discussion

5.4 1 General

It was previously stated that the experimentally determined parameters pertaining to complex formation were to be compared with the calculated interaction energies. The interaction energies were calculated using the polarisability data in Table 5.8. With aromatics in which the polarisabilities α_u and α_p were not equal the mean value was used. The calculated interaction energies are also given in Table 5.8.

Examination of equation 5.5 shows that the principal contribution to the interaction energy (assuming a six-fold approach of the chloroform) arises from the six-fold axis polarisability (α_z) and hence a direct comparison of the experimentally determined parameters with the corresponding values of α_z may be informative.

Plots of the calculated interaction energy (V) and vertical polarisability (α_z) against the molar volume of the respective alkylated benzenes show that an approximately linear relationship exists between the functions (figure 5.2). Hence plots of ΔH^o, ΔG^o and ΔS^o and K_x values against the molar volumes of the alkylated benzenes at 298K, as shown in figures 5.3 - 5.6, should be of a similar form if the calculated interaction energy or vertical polarisability is used as the abscissa.

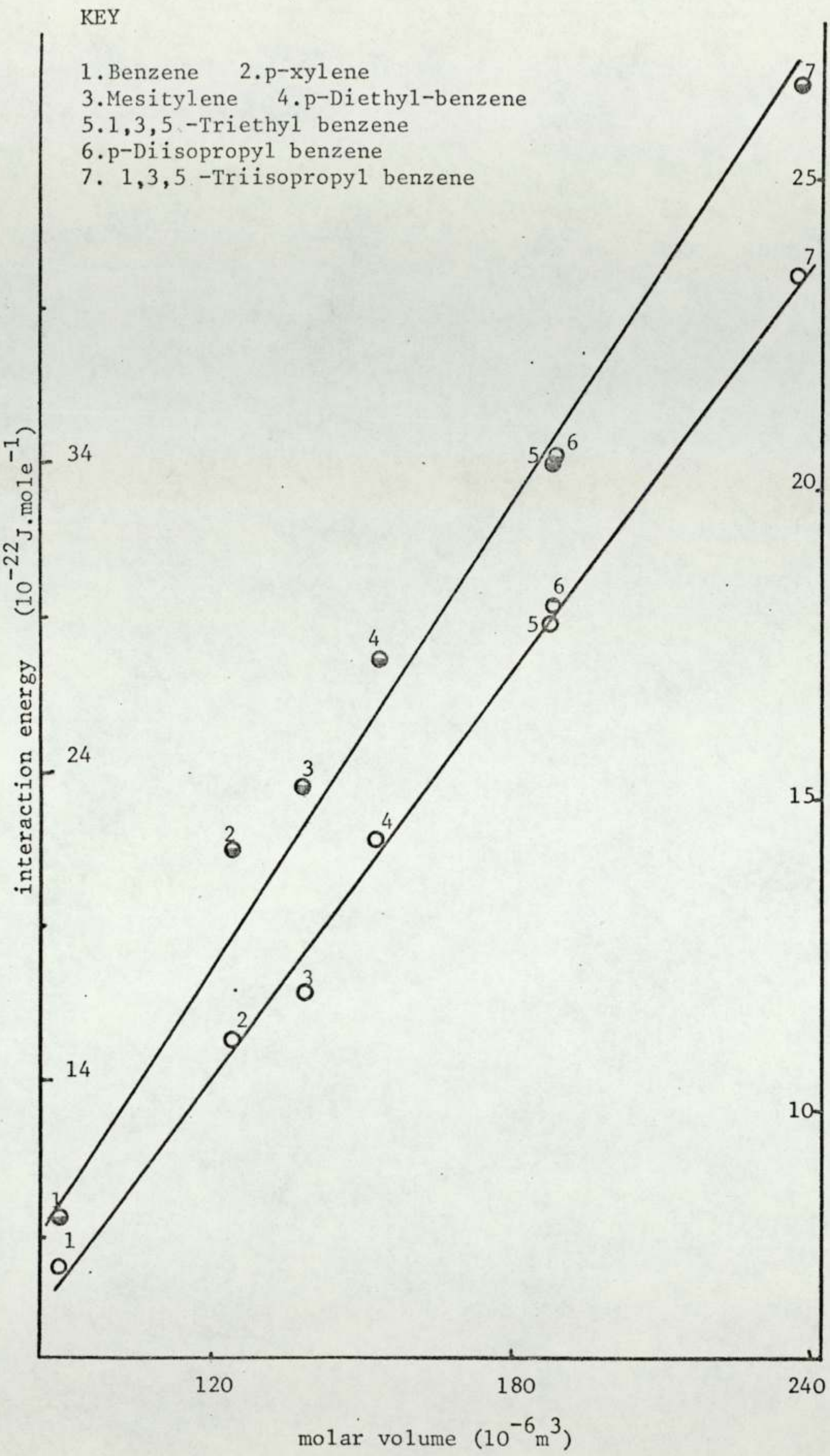


Figure 5.2. The relationship between the calculated interaction energy (●) and six-fold axis polarisability (○) with the molar volume of the aromatic solvents.

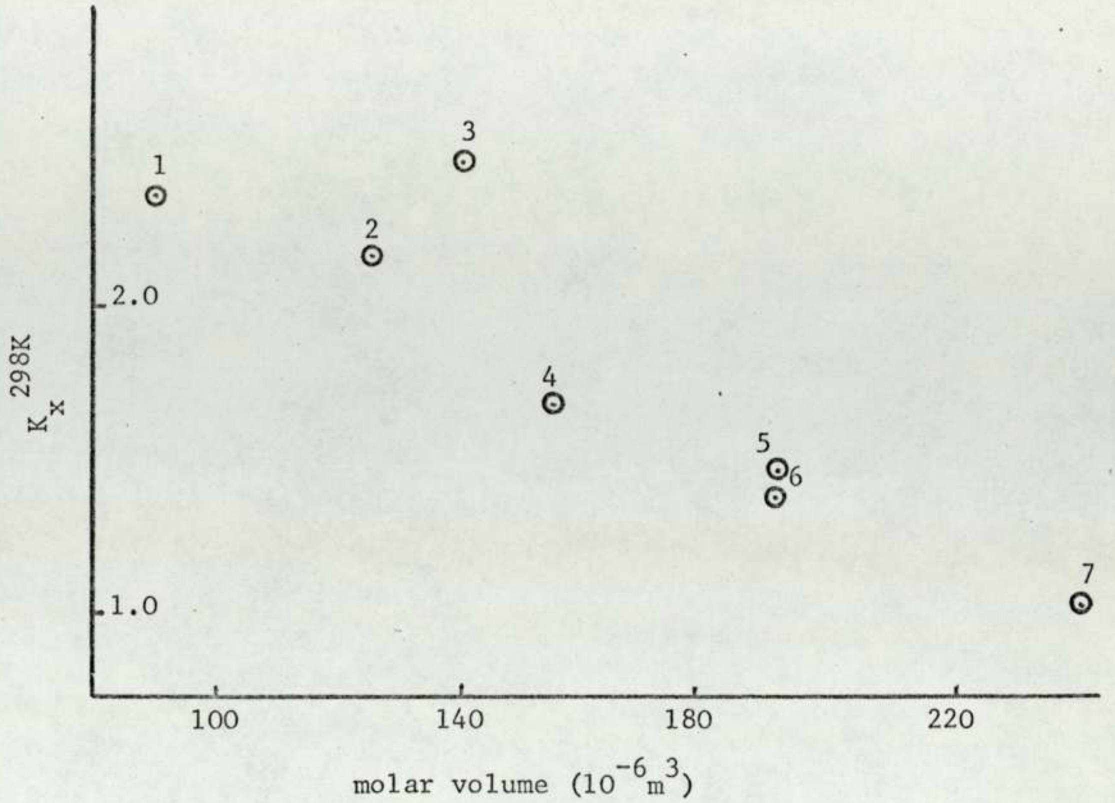


Figure 5.3. The variation of K_x^{298K} for the chloroform-benzene interactions with the molar volume of the aromatic solvents (numbering as in Fig.5.2)

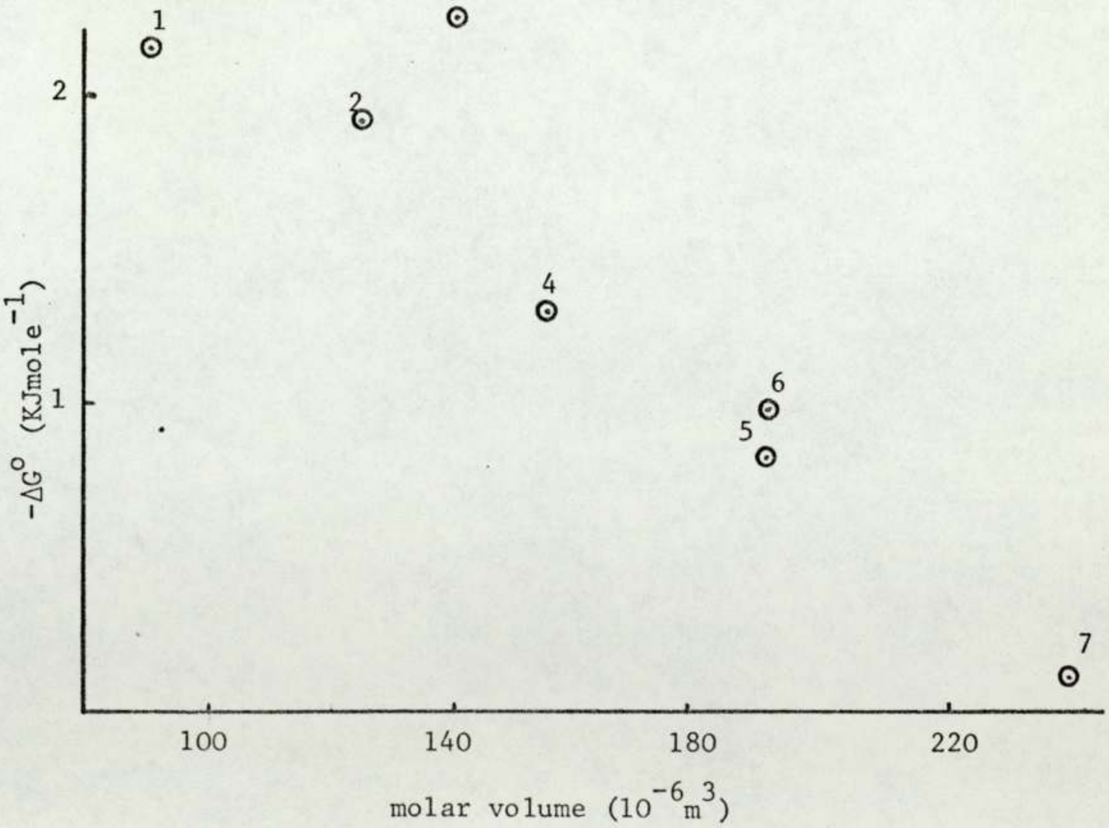


Figure 5.4. The variation of $-\Delta G^o$ for the chloroform-aromatic interactions with the molar volume of the aromatic solvents (numbering as in Fig.5.2)

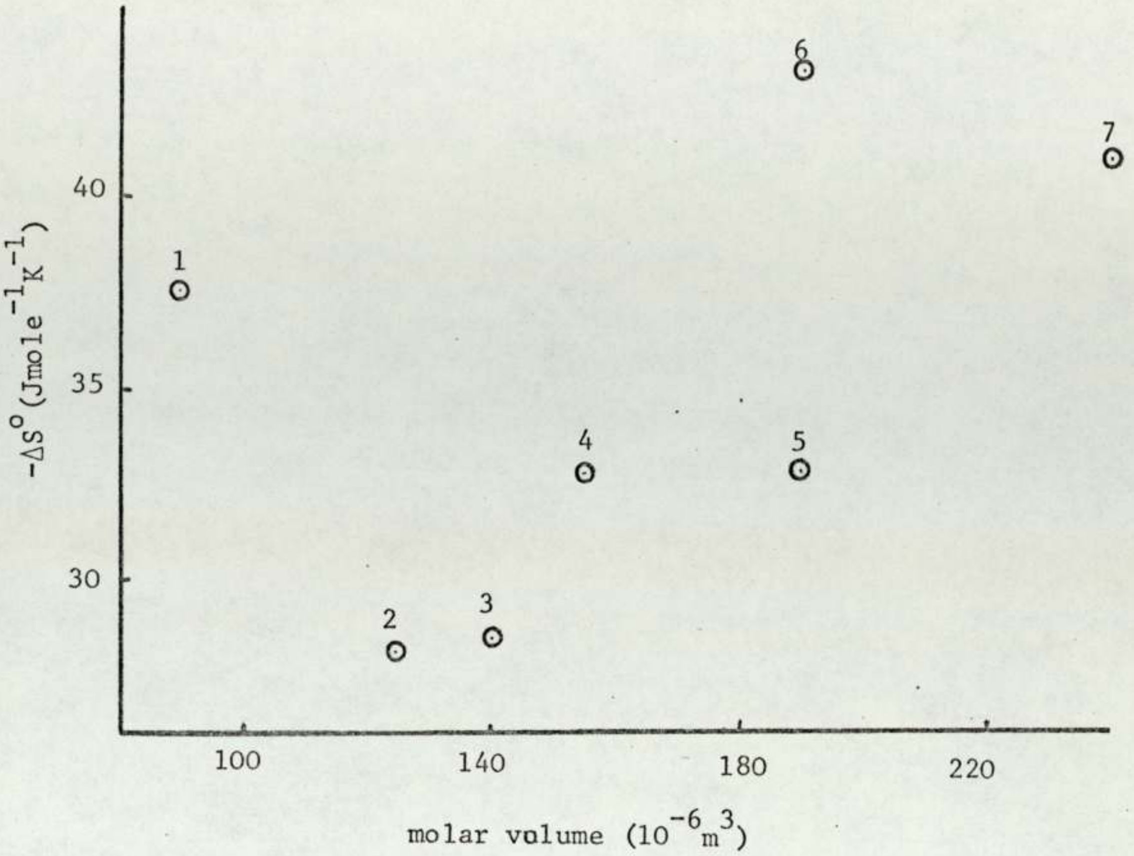


Figure 5.5. The variation of $-\Delta S^o$ for the chloroform-aromatic interactions with the molar volume of the aromatic solvents (numbering as in Fig.5.2).

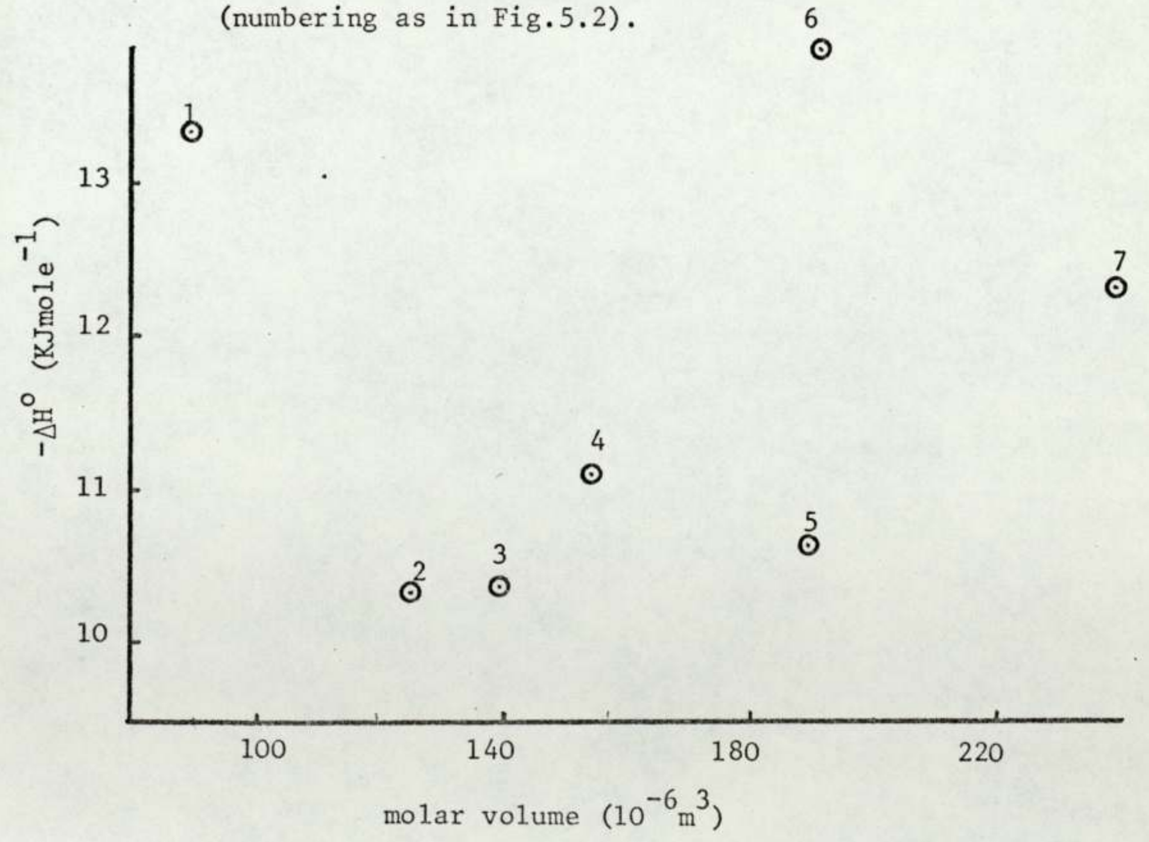


Figure 5.6. The variation of $-\Delta H^o$ for the chloroform-aromatic interactions with the molar volume of the aromatic solvents (numbering as in Fig.5.2).

Table 5.8. Polarisability Ellipsoids[126] of Alkylated Aromatics and the Interaction Energies (V) calculated from them using equation 5.5.

Material	$10^{30}\alpha_u/m^3$	$10^{30}\alpha_p/m^3$	$10^{30}\alpha_z/m^3$	$10^{22}V/Jmol^{-1}$
benzene	11.15	11.15	7.44	10.44
p-xylene	16.6	13.4	11.1	22.37
mesitylene	17.1	17.1	11.85	24.44
1,4-diethyl benzene (planar)	19.0	18.65	13.7	27.77
1,4-diethyl benzene (orthogonal)	19.0	17.4	14.9	29.04
1,3,5-triethyl benzene (planar)	22.6	22.6	16.8	33.81
1,3,5-triethyl benzene (orthogonal)	21.7	21.7	18.7	35.87
p-diisopropyl benzene (i)	22.3	21.2	18.7	35.89
p-diisopropyl benzene (ii)	22.3	22.4	17.5	34.61
1,3,5-triisopropyl benzene (iii)	27.8	26.2	24.3	46.00
1,3,5-triisopropyl benzene (iv)	27.8	28.0	22.5	44.07

(i) the two isopropyl groups have their C-H bonds in planes at $\pi/2$ to the C_6 plane.

(ii) both C-H bonds are in the C_6 plane.

(iii) the three isopropyl groups have their C-H bonds in planes perpendicular to the C_6 plane.

(i) the three C-H bonds are in the C_6 plane.

Within any particular series the equilibrium quotient values increase consistently with decreasing temperature, whilst the corresponding Δ_c values show only a slight temperature variation.

5.4.2 Analysis of the Equilibrium Quotient Values

It was previously stated (section 3.3.5.5) that ΔG^o, and hence K_x, were related to the feasibility of the interaction occurring. Because the interaction can only be thought to result in the formation of a transient time-averaged complex if the approaching solute adopts a position on the cone of possible orientations about the aromatic six-fold axis, the feasibility will depend on a number of factors. In general the polarisability and steric environment of the aromatic, and the dipole moment and steric environment of the solute would be expected to be important factors. However, in these studies a common solute is used and hence the only changing factors relate to the aromatic. An increase in the polarisability of the aromatic may not necessarily result in a greater probability of the complex forming, as the increase in polarisability may have associated with it increasing congestion of the aromatic solvent which hinders the incoming solute. Alternatively, the steric environment of the aromatic may be such that the solute may be held on or near the cone of possible orientations for a longer time.

As a consequence, it would appear that the equilibrium quotient or Gibb's Free Energy values for different solute-substituted aromatic systems may have three principle contributions namely, (a) a polarization term which will be positive, (b) a steric blocking term which will be negative and (c) a trapping term due to the effect of the substituents. A plot of polarisability against molar volume was shown to be linear (figure 5.2) and hence the polarisability term (x) may be weighted by its aromatic molar volume, whilst the blocking term (z) and the trapping term (y) are best weighted by $(V_A - V_B)$, the difference in the molar volumes of the particular aromatic and benzene.

The trapping term is expected to be operative only if the aromatic substituent group (if present) projects appreciably above the benzene ring. Thus the equilibrium quotient for any solute-aromatic solvent system can be expressed in the form,

$$K_x = V_A x + (V_A - V_B)(\delta_i y - z) \qquad \ldots\ldots 5.6$$

where δ_i is equal to +1 if the radius of the substituent group is greater than half the thickness of the aromatic and is zero otherwise.

It is assumed that the steric effect is zero for benzene and hence the corresponding equilibrium quotient expression reduces to

$$K_1 = V_A x = 0.894x \qquad \ldots\ldots 5.7$$

The V_A term in the above equation is in fact $0.894 \times 10^{-4} m^3$ but for the purpose of mathematical simplification the factor 10^{-4} is included in the x term. The same simplification will be applied to the y and z terms.

The trapping factor is expected to be inoperative for p-xylene and mesitylene, as the methyl groups do not project appreciably above the benzene ring, i.e. $\delta_i = 0$, and hence the corresponding equilibrium quotients can be expressed as

$$K_2 = 1.239x + (1.239 - 0.894)z \qquad \ldots\ldots 5.8$$

$$K_3 = 1.396x + (1.396 - 0.894)z \qquad \ldots.\ 5.9$$

No such simplifications can be applied to the remaining aromatics and hence the equilibrium quotients for p-diethyl benzene, 1,3,5-triethyl benzene, p-diisopropyl benzene and 1,3,5-triisopropyl benzene are given respectively by

$$K_4 = 1.564x + (1.564 - 0.894)(y - z) \qquad \ldots.\ 5.10$$

$$K_5 = 1.894x + (1.894 - 0.894)(y - z) \qquad \ldots.\ 5.11$$

$$K_6 = 1.902x + (1.902 - 0.894)(y - z) \qquad \ldots.\ 5.12$$

$$K_7 = 2.392x + (2.392 - 0.894)(y - z) \qquad \ldots.\ 5.13$$

Substitution of the equilibrium quotient values from Table 5.5 leads to

$$2.388 = 0.894x \qquad \ldots.\ 5.14$$

$$2.176 = 1.239x - 0.345z \qquad \ldots.\ 5.15$$

$$2.495 = 1.396x - 0.5022 \qquad \ldots.\ 5.16$$

$$1.690 = 1.564x + 0.670(y - z) \qquad \ldots.\ 5.17$$

$$1.399 = 1.894x + 0.999(y - z) \qquad \ldots.\ 5.18$$

$$1.498 = 1.902x + 1.008(y - z) \qquad \ldots.\ 5.19$$

$$1.048 = 2.392x + 1.498(y - z) \qquad \ldots.\ 5.20$$

Unique values of x, y and z were obtained, by a least squares treatment of equations 5.14 - 5.20, as 2.5864, -0.9727 and 2.4736 respectively. Using these values of x, y and z the three different contributions to the equilibrium quotient values for the interaction of chloroform with various aromatic solvents were calculated and are given in Table 5.9. The data in Table 5.9 is expressed graphically in figure 5.7. The correlation between the experimental and calculated equilibrium values is reasonable.

A similar treatment of the ΔG^o values for the same systems, given in Table 5.5, gave the values of x, y and z as 2.4024, -1.2391 and 2.4562 respectively. The calculated values of the three contributions are shown in Table 5.10.

Table 5.9. The three contributions to the equilibrium quotient values for the interaction of chloroform with various aromatic solvents at 298.2K.

Material	Polarisability factor	'Trap factor'	'Block factor'	Calculated K_x	Experimental K_x
benzene	2.313	0	0	2.313	2.388
p-xylene	3.205	0	-0.853	2.352	2.176
mesitylene	3.610	0	-1.241	2.369	2.493
p-diethylbenzene	4.046	-0.652	-1.658	1.736	1.693
1,3,5-triethyl benzene	4.898	-0.972	-2.473	1.453	1.399
p-diisopropyl benzene	4.920	-0.981	12.494	1.445	1.498
1,3,5-triisopropyl benzene	6.187	-1.457	-3.705	1.025	1.044

Table 5.10. The three contributions to the Gibb's Free Energy values for the interaction of chloroform with various aromatic solvents.

Material	Polarisability factor	'Trap factor'	'Block factor'	Calculated $-\Delta G^{o}/KJmol^{-1}$	Experimental $-\Delta G^{o}/KJmol^{-1}$
benzene	2.1481	0	0	2.148	2.155
p-xylene	2.977	0	-0.847	2.129	1.925
mesitylene	3.353	0	-1.232	2.121	2.263
p-diethylbenzene	3.758	-0.831	-1.646	1.281	1.309
1,3,5-triethyl benzene	4.549	-1.238	-2.456	0.855	0.828
p-diisopropyl benzene	4.570	-1.249	-2.476	0.844	0.999
1,3,5-triisopropyl benzene	5.747	-1.856	-3.679	0.211	0.133

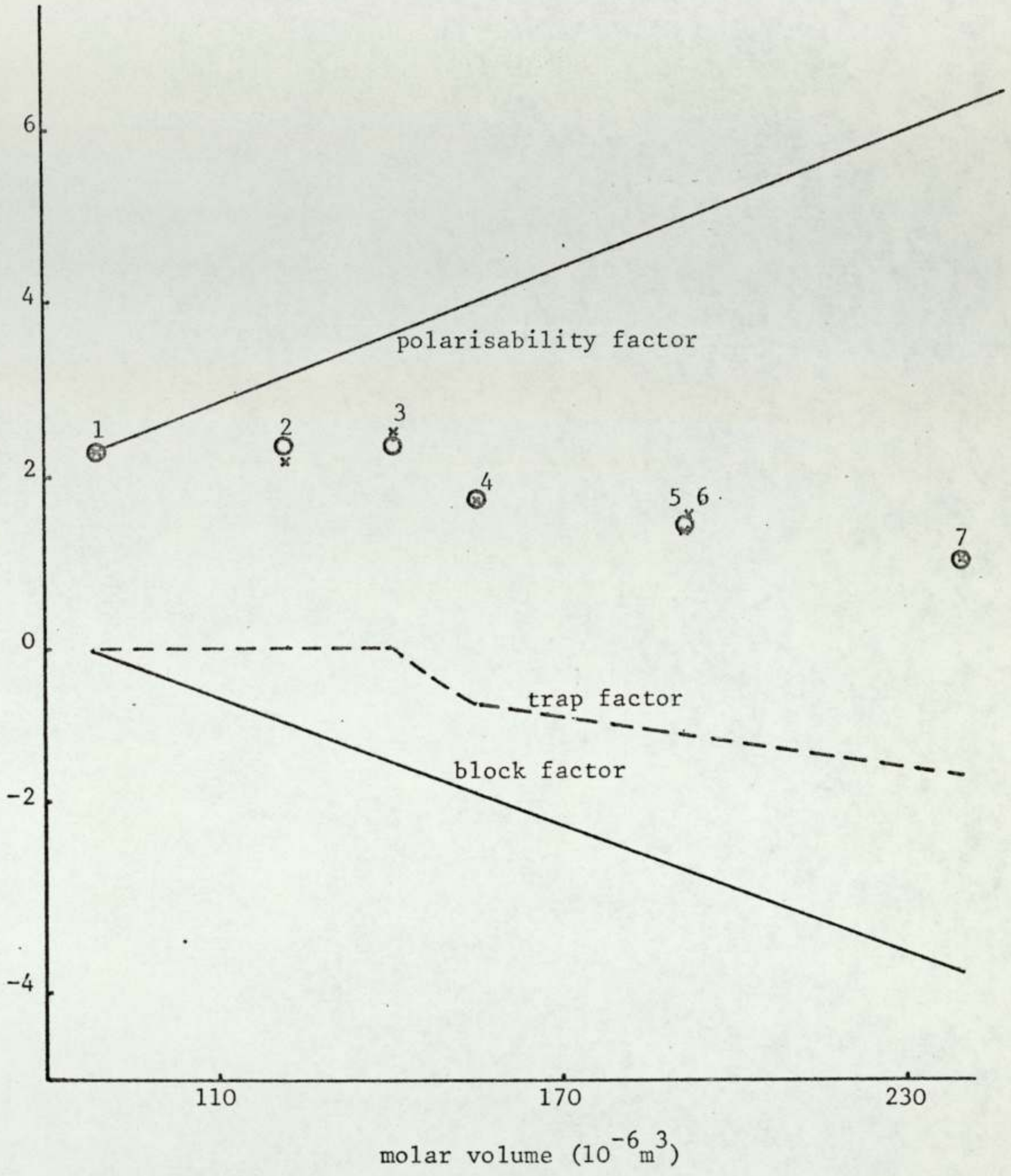


Figure 5.7. The variation of the polarisability, block and trap factors, and the experimental (x) and theoretical (o) mole fraction equilibrium quotients with the molar volume of the aromatic solvents (numbering as in Fig. 5.2).

It is interesting to note that the trapping factor is negative in both of these treatments. This factor is to a large extent a function of the shape and size of the solute. The negative sign leads one to suggest that the aromatic alkyl groups are tending to repel the solute. Chloroform in the complexed state can be regarded as having an inverted cone shape with the proton at the apex. It is possible that increasingly bulky aromatic substituents exert a 'pincer' action on the sides of the solute cone tending to push the solute proton into a less shielded position.

With chloroform as solute, it would appear that the probability of complex formation is greatly reduced when the aromatic substituents are branched, that is of greater steric bulk than three methyl groups.

Further confirmation of the acceptability of this treatment is forthcoming from its application to the equilibrium quotient data of R.R.Yadava[127] for the interaction of acrylonitrile with alkylated benzenes in cyclohexane. The values of x, y and z determined by a least squares treatment of these data were 1.7355, 0.7659 and 3.2723 respectively. Because some doubt existed concerning the validity of the 1,3,5-triisopropyl benzene data set, it was not included in the evaluation of x, y and z. Using these values, the three contributions to the equilibrium quotients for the interactions of acrylonitrile with various aromatic solvents were calculated and are given in Table 5.11. Once again very good agreement between the calculated and experimental results is observed. Yadava[127] has postulated that the solute adopts a time-averaged orientation over the aromatic such that the negative end of the solute dipole is furthest away from the aromatic ring. The

Table 5.11. The three contributions to the equilibrium quotient values for the interactions of acrylonitrile with various aromatic solvents at 298.2K.

Material	Polarisability factor	'Trap factor'	'Block factor'	Calculated K_x	Experimental K_x
benzene	1.567	0	0	1.567	1.521
p-xylene	2.169	0	-1.135	1.034	1.000
mesitylene	2.438	0	-1.643	0.796	0.819
p-diethyl benzene	2.728	0.512	-2.189	1.051	1.217
1,3,5-triethyl benzene	3.266	0.749	-3.203	0.812	0.845
p-diisopropyl benzene	3.320	0.773	-3.305	0.788	0.636

positive trap factor is consistent with this, the acrylonitrile adopting a configuration whereby its two β-hydrogens are transiently trapped in a region of greater shielding by the bulkier aromatic substituents.

5.4.3 Analysis of the Entropy Values

When discussing the stereochemistry of the interaction (section 3.3.5.6) it was postulated that it would appear more realistic to regard the solute as undergoing a wobbling motion about the aromatic perpendicular axis. Such a model will be temperature sensitive owing to changes in the semi-angle (α) of the prescribed cone of motion of the solute. Further evidence for this time-averaged cone model is forthcoming from a consideration of entropy effects with temperature. With increasing temperature, α increases and hence the entropy of the complex (S^o_{AB}) would be expected to increase also. The experimentally determined entropy of formation (ΔS^o) is defined by the equation

$$\Delta S^o = S^o_{AB} - S^o_A - S^o_B \qquad \text{.... 5.21}$$

where S^o_A and S^o_B are the entropies of the free solute and solvent respectively.

Assuming that all entropies will increase at the same rate with increasing temperature, ΔS^o would be expected to become more negative if the complex had a rigid structure. The entropy of the postulated flexible complex would be expected to increase more rapidly than either A or B, and ΔS^o should go negative more slowly or tend to become less negative. Examination of the entropy of formation at different temperatures for the chloroform-benzene complex, given in Table 5.12 (calculated from the data in Tables 5.4 and 5.5), shows that ΔS^o is almost temperature independent, becoming only slightly more negative with increasing temperature. It must be appreciated, however, that only a very narrow temperature range has been studied.

The effect of temperature on the entropy of formation of the chloroform-alkyl benzene complexes has to be considered. Similar behaviour to that shown by the benzene complex is noted for the majority of these systems (Table 5.12), but the range of entropy values within any particular series is so small (less than 2Jmole^{-1}K^{-1}) that no great significance can be placed on any attempted interpretation. In fact, ΔS^o would appear almost temperature independent for all the systems, over the narrow range of temperature considered here.

If sufficiently large alkyl groups are introduced on to the benzene, the cone semi-angle (α) will be reduced and it is reasonable to assume that the entropy of such a complex will be less than that of a complex in which steric hindrance is not evident. In the latter case, not only will there be greater flexibility of the solute about the six-fold axis, but the motion of the aromatic alkyl sustituents (if any) will be unrestricted. Nothwithstanding this, if it is accepted that the formation of a more rigid complex is accompanied by a greater entropy of formation, the examination of figure 5.5, inwhich the entropy of formation at 298.2K for the chloroform-alkylated benzenes complex is given

Table 5.12. The variation of ΔS^o for the complex between chloroform and various aromatics with temperature.

Temperature/K	$-\Delta S^o/Jdeg^{-1}mol^{-1}$	Temperature/K	$-\Delta S^o/Jdeg^{-1}mol^{-1}$
benzene		p-xylene	
281.84	37.877	286.93	28.241
292.29	37.529	292.91	27.970
302.04	37.046	302.64	28.278
309.09	38.819	311.38	27.814
319.29	37.990	321.85	28.352
mesitylene		p-diethyl benzene	
277.12	28.288	276.23	32.956
288.38	28.668	288.38	32.288
304.83	28.480	294.54	32.935
311.67	28.162	303.24	32.242
322.08	28.555	311.67	32.697
		322.09	32.933
1,3,5-triethyl benzene		1,3,5 - triisopropyl benzene	
277.12	32.661	276.23	41.983
288.37	33.364	288.23	41.585
302.16	32.465	304.24	40.647
311.67	32.541	311.67	42.729
322.08	33.080	313.96	40.657
		322.09	39.321
p-diisopropyl benzene			
303.78	43.419		
312.57	42.791		
322.00	43.591		

as a function of the aromatic molar volume, may be informative. The entropy of formation becomes more positive on going from benzene to mesitylene, which is consistent with an increasing degree of flexibility of the resultant complexes, the entropy of the complex (S^o_{AB}) increasing preferentially to that of the uncomplexed aromatic (S^o_B) and solute (S^o_A). However, ΔS^o becomes increasingly negative from mesitylene to triisopropyl benzene, which leads one to suggest that, with substituents of greater bulk than three methyl groups, the semi-angle of the cone (α) of possible orientations becomes increasingly restricted, resulting in a more rigid complex.

5.4.4. Analysis of Δ_c values

Examination of the complex limiting shift values (Δ_c) given in Table 5.4 shows that in general Δ_c decreases, but only slightly, with increasing temperature, which is consistent with the proposed model of complex formation. Some inconsistencies are shown in the variation of Δ_c with temperature, but generally the variation of this parameter within any particular series is of the order of 0.05 - 0.20 ppm, which is acceptably within the limits of the experimental and data processing techniques. To facilitate a comparison of Δ_c values, the values for each individual series were averaged to give the mean values shown in Table 5.6. It is appreciated that, as the temperature ranges of the studies of the various aromatics differ slightly, this is not strictly correct but it is not an unreasonable approximation.

Homer and Cooke[77] have shown the interaction energy of solute-aromatic solvent complex formation to be a function of the aromatic polarisability, and the separation of the solute dipole centres and the aromatic ring centre ($R^{\perp}$). It would appear from a perusal of the mean Δ_c values in Table 5.6 that, with increasingly bulky alkyl substituted benzenes, the solute proton becomes more shielded if a six-fold axis approach by the solute is assumed. A plot of Δ_c against the theoretical interaction energies, calculated assuming $R^{\perp}$ to be 3.05Å to afford some simplification, is shown to be linear in figure 5.8, the value for the diisopropyl benzene system appearing anomalous. This suggests that the increased dipole-induced dipole interaction between the solute and solvent, due to increasing polarisability of the aromatic, is the predominant factor, steric factors being negligible. However, it is to be expected that, as Δ_c is proportional to the relative configuration of the solute and aromatic in the complex state, 'blocking' and 'trapping' factors anologous to those previously discussed will be operative. To elucidate the magnitude of such effects, the Δ_c values were analysed in a manner similar to that adopted for the K_x and ΔG^o values, whereupon the values of x, y and z were calculated as 1.4325, -0.1192 and 0.7622 respectively. The calculated values of the three contributions are shown in Table 5.13. A perusal of the table shows that the

Table 5.13. The three contributions to the mean Δ_c values for the interactions of chloroform with various aromatic solvents.

Material	Polarisability factor	Trap factor	Blocking factor	Calculated Δ_c/ppm	Experimental Δ_c/ppm
benzene	1.3133	0	0	1.313	1.313
p-xylene	1.818	0	-0.297	1.519	1.521
mesitylene	2.043	0	-0.431	1.612	1.610
p-diethyl benzene	2.286	0.018	-0.574	1.729	1.667
1,3,5-triethyl benzene	2.737	0.026	-0.841	1.922	1.961
p-diisopropyl benzene	2.767	0.027	-0.867	1.927	1.572.
1,3,5-triisopropyl benzene	3.478	0.040	-1.279	2.239	2.190

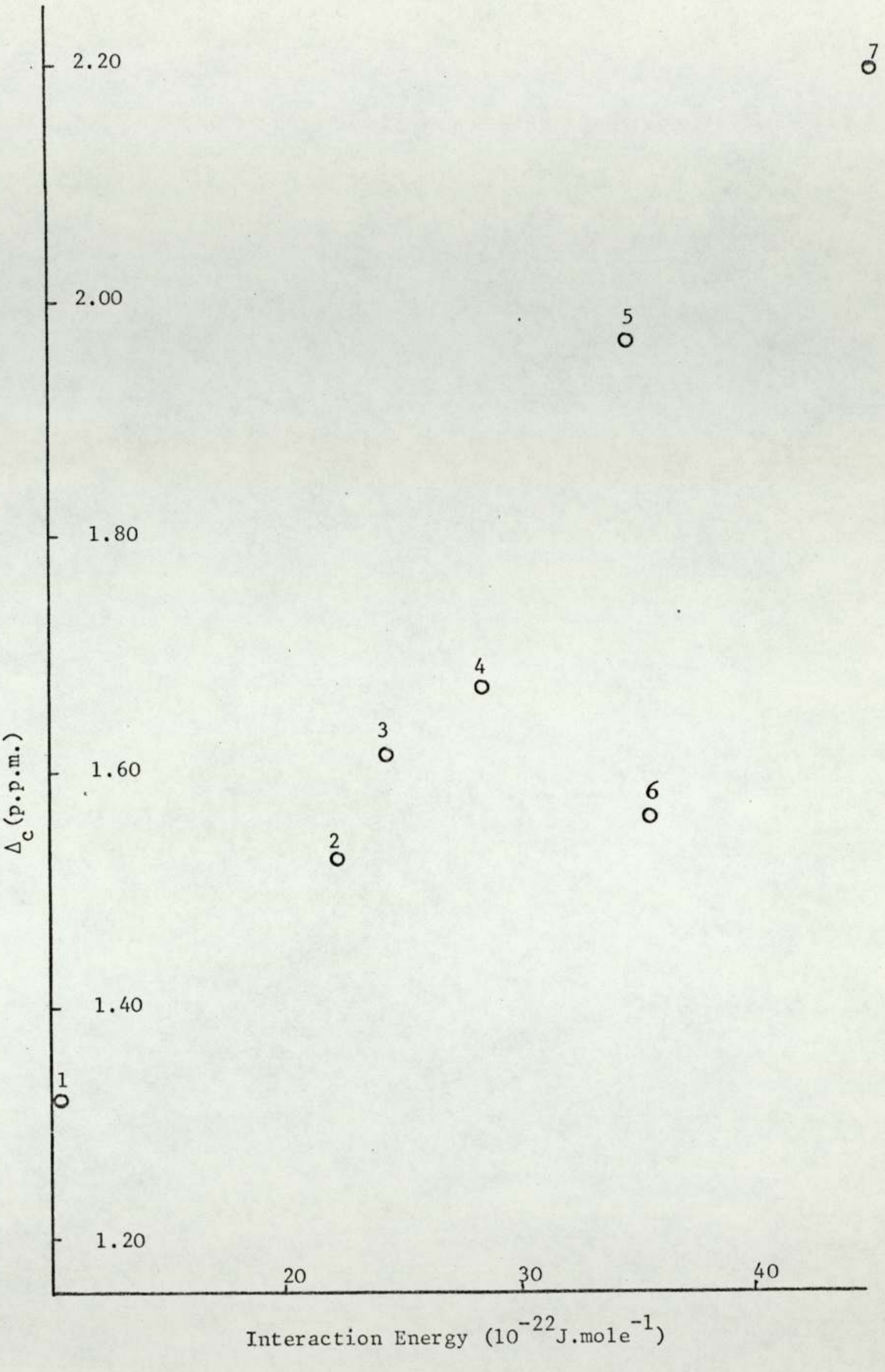


Figure 5.8. The variation of the average limiting shift Δ_c, for the chloroform-aromatic interactions, with the calculated interaction energies (numbering as in Fig. 5.2).

trapping factor is insignificant. The calculated and experimental Δ_c values are in good agreement with the exception of p-diisopropyl benzene but, as was stated earlier, the experimental results for this system are not very satisfactory.

5.4.4.1 The Effect of Alkyl Substituent Anisotropy

Throughout the discussion of the limiting shift (Δ_c) no mention has been made of applying a correction to this for the effects of the anisotropy of magnetic susceptibility of the carbon-carbon and carbon-hydrogen bonds of the alkyl substituents. To facilitate the calculation of such effects, it is necessary to assume that all the carbons are sp^3 hybridised, as the carbon-carbon bond anisotropy is only well documented for this type of bond, and that the secondary field produced at the shielded nucleus can be considered to act from the centre of the carbon-carbon bond. McConnell[43] has formulated an expression for these secondary fields in terms of the magnetic susceptibility of all i neighbouring bonds when they are axially symmetric and this is given as

$$\sigma = \Sigma \frac{\Delta \chi_i (1 - 3\cos^2\Theta_i)}{3R_i^3} \qquad .... \ 5.22$$

The expression is based on the assumption that the electron group is sufficiently distant that the moment induced therein by the applied field may be represented with sufficient accuracy by a point dipole. Equation 5.22 is generally considered valid when R_i, the distance between the induced magnetic dipole of bond i and the nucleus in question, is greater than ca. 3.0A^o. Θ_i is the angle between the direction of R_i and the axis of the bond i. Homer et al[128] have suggested that $\Delta\chi^{C-H}$ and $\Delta\chi^{C-C}$ may be taken as zero and 7.263 x $10^3 cm^3 molecule^{-1}$ respectively. For the purpose of these calculations, the aliphatic carbon-carbon bonds of the ethyl and isopropyl groups are taken to be undergoing free-rotation and R_i is determined from the projection of the aliphatic carbon-carbon bond centres into the plane of the ring. The approximate geometry of the complex is shown in figure 5.9 and the results obtained, assuming the solute and aromatic to be in van der Waal's contact with $R^{\perp} = 3.05A^o$, show that the effects of a methyl, ethyl and isopropyl substituents on the solute proton are 0, 0.016 ppm and 0.032 ppm respectively. Using the experimentally determined Δ_c value for the chloroform-benzene system, the $R^{\perp}$ value was obtained from Johnson and Bovey[65] tables as $3.35A^o$, approach by the solute along the six-fold axis of the aromatic being assumed. With this value of $R^{\perp}$ the recalculated contributions to the shielding are 0.007 ppm for all three substituents. It would appear, therefore, that the alkyl substituent bond anisotropy effects are of little consequence.

5.5 Conclusions

The application of both the Creswell and Allred and Benesi-Hildebrand data evaluation methods to the study of the interactions of chloroform with a variety of alkylated benzenes in cyclohexane has been shown to give meaningful results when the thermodynamically correct concentration range is studied. The use of the mole fraction scale, corrected for the effective number of moles of inert solvent, enables parameters to be obtained which are thermodynamically valid. The parameters obtained from the usual van't Hoff plots have been correlated with both steric (trap and block) and polarisability factors. The effect of introducing increasingly bulky alkyl substituents to the benzene ring would appear to be to block

$R^{\perp}$	R_i	R_j	Θ_i	Θ_j
	Å		rad.	
3.09	3.74	4.41	0.954	0.764
3.36	3.94	4.71	1.021	0.793

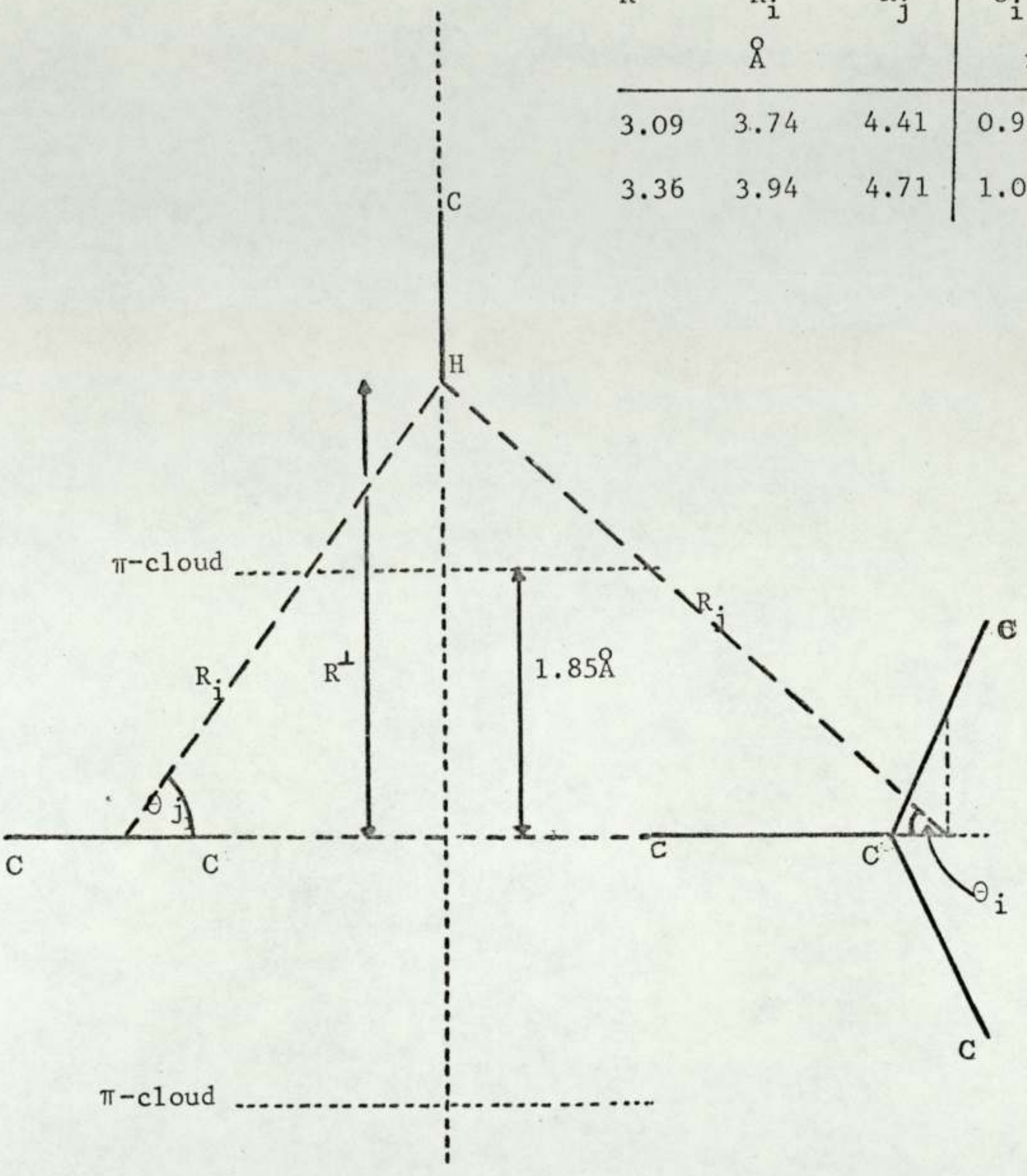


Figure 5.9. The geometry of a representative chloroform-alkyl substituted benzene complex, as used in the calculation of the screening effects of the C-C bond anisotropy.

the approach of the solute proton to the six-fold axis of the aromatic, decreasing the probability of the interaction occurring whilst, at the same instant due to the increasing polarisability of the aromatic, the approaching solute experiences a greater interaction force. The approach of the solute does not appear to be hindered until branched alkyl substituents are introduced. The so called 'trap' effect was found to be negative with chloroform as the solute, indicating that increasingly bulky substituents possibly exert a 'pincer' action on the solute which tends to push the solute proton into a less shielded position.

It should be noted that great care must be taken with shift determination and data evaluation for, with such narrow ranges of shift and concentration, even slight errors result in large changes in the K_x and Δ_c parameters. The composite term $K_x\Delta_c$ is less sensitive. For the systems studied here, van't Hoff and $\ln K_x\Delta_c$ against T^{-1} plots have been shown to produce comparable ΔH^o values and thus the separation of the $K_x\Delta_c$ term, to facilitate the determination of ΔG^o and ΔS^o, has been shown to be adequately achieved by the use of both the BH . and CA data processing methods.

CHAPTER 6. THE APPLICATION OF A REFERENCE-INDEPENDENT SHIFT TECHNIQUE TO EQUILIBRIUM STUDIES.

6.1 Introduction

Becconsall et al[129] have devised a method of determining reference-independent solvent shifts which avoids the uncertainty inherent in the usual procedure of reporting n.m.r. shifts relative to an arbitary internal or external reference. The advantage of the internal reference prodedure is that bulk susceptibility effects do not contribute to the observed shifts. However, as has been emphasised by Laszlo et al[130], it introduces an arbitrary element in the choice of the internal reference which is particularly serious for the study of non-polar solutes where the solvent shifts observed are entirely similar in nature to the degree of screening of the reference proton. Previous studies in this thesis have utilised cyclohexane as an internal reference with a reasonable degree of confidence[86]. It was decided, however, to apply the Becconsall method to a study of the benzene-chloroform interaction in cyclohexane; good correlation with the equilibrium parameters deduced in previously discussed studies would substantiate the acceptability of cyclohexane as an inert reference. The details of the technique will now be discussed.

The main criticism of the external reference procedure, which is overcome by Becconsall's method, is that it requires a knowledge of troublesome magnetic susceptibility differences (section 3.3.1), whose magnitudes are not always well documented. The reference-independent procedure requires that the sample consist of a solute in low concentration in some solvent (y), surrounding a co-axial cylinder containing the same solute at the same concentration in another solvent (x). The solute chemical shift difference is measured in two spectrometers applying the magnetic field perpendicular and parallel to the sample axis respectively. Assuming a perfectly cylindrical sample of effectively infinite length, the bulk susceptibility contribution for the perpendicular (⊥) orientation is

$$\sigma^{\perp} = \frac{2}{3}\pi\chi_v \qquad \ldots\ldots 6.1$$

and for the parallel orientation it is

$$\sigma^{\parallel} = \frac{-4\pi}{3}\chi_v \qquad \ldots\ldots 6.2$$

where χ_v is the volume susceptibility of the solvent. Consequently the solvent screening contribution to the solute (σ_{sol}) by its solvent is given in the two cases by

$$\sigma^{\parallel}_{sol} = \sigma^{\parallel}_{b} + \sigma_{loc} = \frac{-4\pi}{3}\chi_v + \sigma_{loc} \qquad \ldots\ldots 6.3$$

$$\sigma^{\perp}_{sol} = \sigma^{\perp}_{b} + \sigma_{loc} = \frac{2}{3}\pi\chi_v + \sigma_{loc} \qquad \ldots\ldots 6.4$$

for a particular solvent, where σ_{loc} is the sum of the σ_a, σ_w, σ_c and σ_E terms in equation 3.4. From equations 6.3 and 6.4 it is apparent that the total relative shifts are

$$\sigma^{\perp}_{sol(y)} - \sigma^{\perp}_{sol(x)} = \frac{2\pi}{3}\left[\chi_{v(y)} - \chi_{v(x)}\right] + \sigma_{loc(y)} - \sigma_{loc(x)} \qquad \ldots\ldots 6.5$$

$$\sigma^{\parallel}_{sol(y)} - \sigma^{\parallel}_{sol(x)} = \frac{-4\pi}{3}\left[\chi_{v(y)} - \chi_{v(x)}\right] + \sigma_{loc(y)} - \sigma_{loc(x)} \qquad \ldots\ldots 6.6$$

for the perpendicular and parallel orientations respectively. Therefore, combining equations 6.5and 6.6,the required reference-independent shift ($\bar{\Delta}^{x}_{y}$) is

$$\bar{\Delta}^{x}_{y} = \sigma_{loc(x)} - \sigma_{loc(y)} = \frac{1}{3}\left[\sigma^{\parallel}_{sol(y)} - \sigma^{\parallel}_{sol(x)} + 2\left(\sigma^{\perp}_{sol(y)} - \sigma^{\perp}_{sol(x)}\right)\right]$$

$$= \frac{1}{3}\left(\delta^{\parallel}_{(y-x)} + 2\delta^{\perp}_{(y-x)}\right) \qquad \ldots\ldots 6.7$$

The application of this equation should enable the chloroform-benzene reaction in cyclohexane to be fully investigated on a reference-independent basis.

6.2 Experimental Considerations

The application of the reference-independent solvent shifts technique to a study of the chloroform-benzene interaction in cyclohexane requires a series of samples consisting of the solute (chloroform) in low concentration in solutions of benzene and cyclohexane of varied composition (y), surrounding a co-axial cylinder containing the same solute at the same concentration in cyclohexane (x). The measurement of the chloroform chemical shift difference in the two types of spectrometer, mentioned earlier, enables the required shift parameter to be obtained. Unfortunately, as the interaction is to be studied in the thermodynamically correct concentration range (x_B = 0.9 to 0.995 and x_A < 0.005), the relative concentrations of the benzene in the annulus and the chloroform in the capillary are such that is is highly probable that the chloroform proton absorption may be obscured by the benzene absorption itself or one of its spinning side-bands (if present). To overcome this difficulty the interaction of chloroform with fully deuterated benzene (isotopic purity 99.97%) in cyclohexane was investigated, the relative magnitude of the aromatic absorption peak being constantly reduced.

The sensitivity of the less powerful spectrometer (Varian HA.100) is such that, with the 1mm.O.D. capillaries available (supplied by NMR Limited), the minimum detectable concentration of chloroform in solvent (x) was mole fraction equal to 0.015. Work done in this laboratory suggests that no appreciable error will be introduced by the use of such a high concentration, although it is thermodynamically inadvisable. Initially a series of samples was prepared in which individual capillaries, each containing the same concentration of chloroform in cyclohexane, were encapsulated in each sample tube. Preliminary studies showed that, although the annular chloroform-deuterobenzene shifts showed a consistent shift/concentration variation, the chloroform-chloroform shift (the required parameter) did not. This indicated that the capillaries were either not sufficiently uniform for it to be assumed that the shape factors were identical or were tilted with respect to the axis of the sample tubes. The procedure adopted therefore, was to use a single Wilmad precision co-axial capillary for all the measurements, thus ensuring that the shape factor remained constant. The limitation of this procedure is that the samples cannot be permanently sealed and hence, whilst the shifts are being measured, it must be rather dubiously assumed that the tight fit of the capillary in the sample tube is sufficiently adequate to ensure that the composition of the sample in the annulus remains unchanged. The composition of the chloroform-cyclohexane solution in the capillary is less critical and thus it is considered that the plastic cap supplied with the capillary is a sufficiently efficient seal.

The composition of the solutions studied is shown in Table 6.1. The chemical shifts were measured at 306.5 ± 1.0K, in a Varian 220 MHz spectrometer and a conventional Varian HA 100 instrument. The chemical shifts of the chloroform for both field orientations are given in Table 6.2. A plot of $\bar{\Delta}_x^y$ against $\dot{x}_B$corr (figure 7.1) shows some scatter.

The reference-independent shift data in Table 6.2 was processed, using the Benesi-Hildebrand based computer program "BHCURVEFIT", to give the result $K_x = 0.4388$ and $\Delta_c = 4.3865$ ppm. The computer output showed that the standard deviation, from the computer-fitted best line, of two of the data

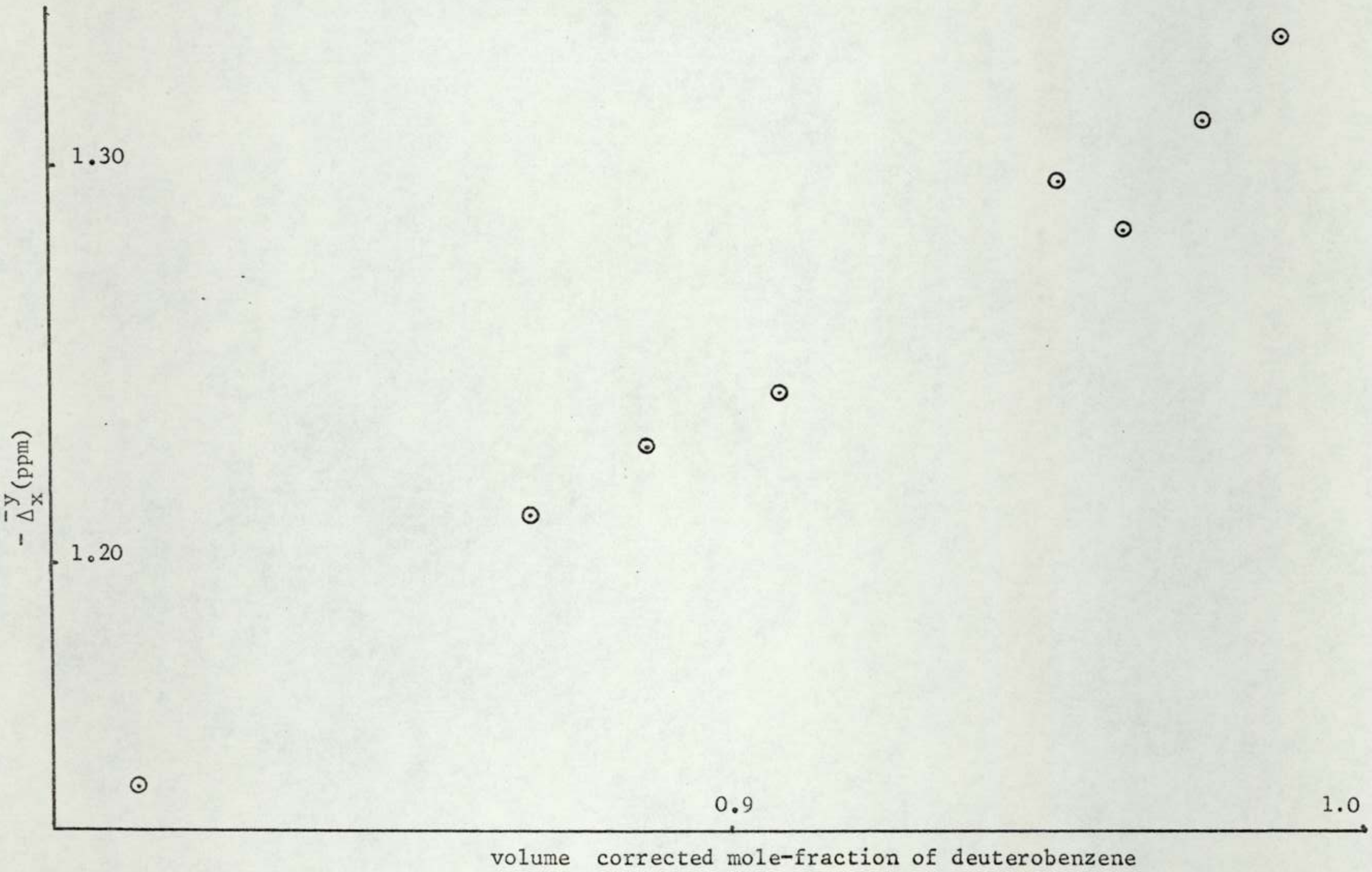


Figure 6.1. The variation of the reference-independent shift with the volume corrected mole fraction of deuterobenzene for the chloroform-deuterobenzene interaction in cyclohexane.

Table 6.1. The composition of the mixtures employed in the investigation of the interaction of chloroform (A) with deuterobenzene (B) in cyclohexane (S), together with the mole fraction of deuterobenzene.

No.	$10^4 n_A$/mol	$10^2 n_B$/mol	$10^3 n_S$/mol	x_B
13.0*	1.0645		10.1691	0.000
13.1	1.2397	1.8196	3.5676	0.831
13.2	1.1869	2.3693	2.9352	0.886
13.3	1.4156	2.3422	2.4533	0.900
13.4	1.2573	2.3644	1.9461	0.919
13.5	1.1836	2.3780	1.0084	0.955
13.6	1.4357	2.4019	0.7853	0.962
13.7	1.1300	2.3843	0. 5101	0.974
13.8	1.1618	2.3801	0.2602	0.984

* capillary sample.

Table 6.2. Solvent induced shifts for chloroform (in ppm) together with the corresponding mole fractions of deuterobenzene corrected for the effective number of moles of S($x_B$corr).

No.	$-\delta^{\perp}$	$-\delta^{11}$	Δ_x^y	$x_B$corr*
13.1	1.1576	1.1736	1.1442	0.8070
13.2	1.2138	1.2173	1.2149	0.8687
13.3	1.2299	1.2286	1.2294	0.8867
13.4	1.2599	1.2564	1.2539	0.9087
13.5	1.2985	1.2941	1.2970	0.9508
13.6	1.2901	1.2755	1.2852	0.9616
13.7	1.3075	1.3186	1.3112	0.9746
13.8	1.3133	1.3341	1.3336	0.9868

* The ratio V_s/V_B at 306.5K was calculated by the extrapolation of density data in Timmermans[110] to be 1.219.

points to be greater than was acceptable (see section 4.4). Reprocessing the data, with these two points excluded, gave the new values $K_x = 0.357$ and $\Delta_c = 5.119$ ppm. These latter results would appear erroneous, for Doyle has calculated K_x and Δ_c to be respectively 2.014 and 1.297 ppm for the same system using an internal reference technique. It must be borne in mind that the Benesi-Hildebrand method is very sensitive to errors in shift determination. Therefore, it is highly probable that the unlikely results obtained originate at least in part from failure to achieve the degree of accuracy required in the shift measurements. The shifts measured on the 220 MHz spectrometer may be suspect as this instrument does not have a field-frequency lock facility. The uncertainty placed on the exact concentrations of the annular samples by the inadequacies of the seal adds to the inaccuracies.

6.3 Conclusions

Although in principle the application of the reference-independent shift method to equilibrium studies appeared very promising, the experimental difficulties, and the sensitivity of the BH data processing method to very small shift errors, negate its use. It is evident that an improved method of sealing the complete sample system would be beneficial. The cost of Wilmad precision tubes precludes the permanent sealing of each sample tube. Due to a paucity of time, therefore, the application of the reference-independent shift technique was not further investigated directly. However, a consideration of the basis of the proposed technique enabled a new method of determining the magnetic susceptibilities to be devised. This method will be discussed in the subsequent chapter.

CHAPTER 7. A NEW NUCLEAR MAGNETIC RESONANCE METHOD FOR DETERMINING MAGNETIC SUSCEPTIBILITIES.

7.1 Introduction

As a result of the consideration of the equations involved in the reference-independent solvent shift studies in Chapter 6, a new method of determining magnetic susceptibilities was devised. This utilises the differences between externally referenced chemical shifts caused by the difference in sample configuration in two spectrometers, one having a conventional magnet which applies the field perpendicular to the sample axis ($\perp$) and the other a superconducting solenoid which applies the field longitudinally (11). For a cylindrical reference vessel co-axial with the main tube, the relative shift for a reference compound at infinite dilution in two solvents x and y in the two regions of the sample cell is, for the perpendicular and parallel field orientations, given by equations 6.5 and 6.6, from which it follows that

$$\delta^{\perp}_{(y-x)} - \delta^{11}_{(y-x)} = 2\pi\,(\chi_{v(y)} - \chi_{v(x)}) \qquad \ldots\ 7.1$$

where $\delta^{\perp}_{(y-x)}$ and $\delta^{11}_{(y-x)}$ are the solute shifts in the two field orientations. The factor 2π corresponds fundamentally to the shape factor for a transversely oriented cylindrical sample as originally evoked by Dickinson.[46] When implementing equation 7.1 to determine magnetic susceptibilities, a value for the shape factor for a chosen reference vessel may be deduced experimentally using a series of solvents x and y of "known" susceptibility, as has been done when using other equations similar to 7.1.[130] The merits of this approach will be further considered later.

Before evaluating the efficacy of the new method of determining susceptibilities it is constructive to consider the accepted n.m.r. methods. There are two principal established techniques which will now be discussed and compared with the proposed method outlined above.

In 1955 Reilly et al[132] devised a method based on the observation of the shape of the resonance arising from a compound contained in the annular region of a cell having a good cylindrical reference vessel precisely co-axial with the main tube containing a second compound. When the sample tube was spun a normal high resolution spectrum was obtained (figure 7.1), whilst if the system was static a broad doublet due to the annular region was observed (figure 7.2), the separation of the doublet lines, $\Delta\nu$, being given by

$$\frac{\Delta\nu}{4\pi\nu_o} = \chi_{v(1)}\frac{a^2}{r^2} - \chi_{v(2)}\frac{(a^2 - b^2)}{r^2} - \chi_{v(3)}\frac{b^2}{r^2} \qquad .... \ 7.2$$

where $\chi_{v(i)}$ are the volume susceptibilities of the material forming the central region (1) reference vessel (2) and annular region (3), a and b are the inner and outer radii of the central tube and r is the mean radius of the annular region. The cell may be calibrated[133] by the use of a constant reference material in the annular region in conjunction with a series of compounds of known magnetic susceptibility in the central region. Equation 7.2 then reduces to

$$\frac{\Delta\nu}{4\pi\nu_o} = C\chi_{v(1)} + C_1 \qquad .... \ 7.3$$

where C_1 and C are constants for the particular cell and reference used.

Equation 7.3 has been shown to be a limiting form of a more general equation[134] and has been theoretically justified[135], but in application it is not without difficulties, of which the most important is that the symmetry and splitting of the broad doublet are affected by the position of the sample tube in

Figure 7.1

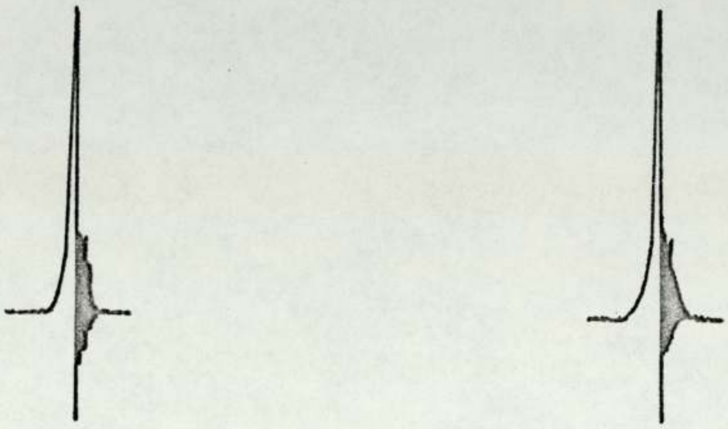


Figure 7.2

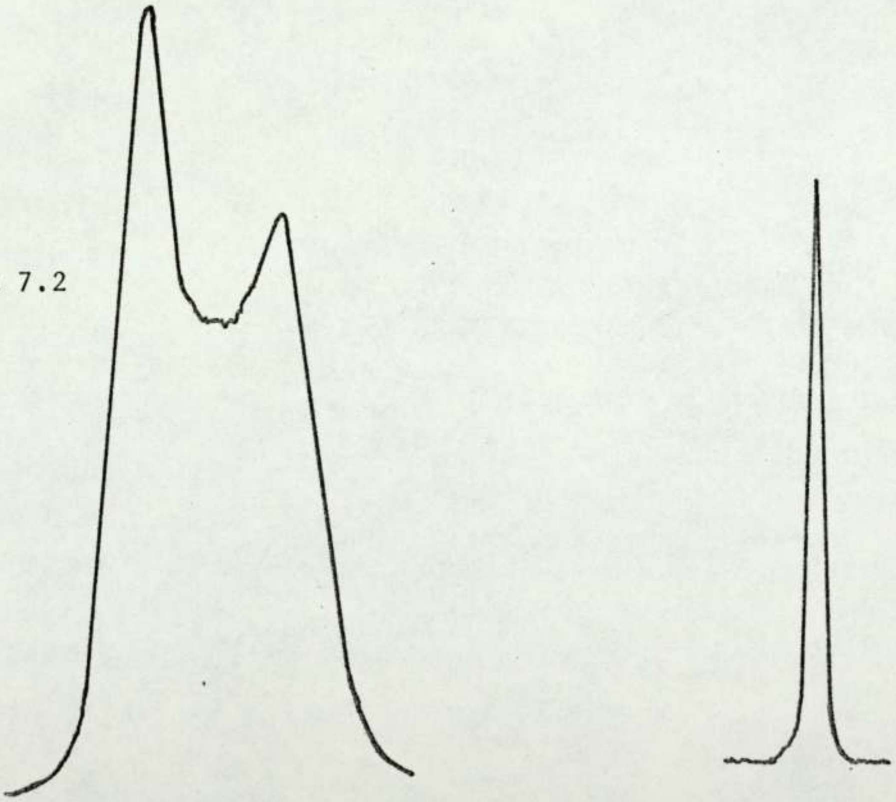


Figure 7.1. The spectrum derived from a spinning cell of co-axial cylinders, with water in the inner and benzene in the outer region.

Figure 7.2. The corresponding spectrum derived from the stationary cell.

the main field.[136,137] To overcome this problem Douglass and Fratiello standardised the position of the tube and the magnetic field homogeneity controls were adjusted to give the sharpest symmetrical doublet which was not affected by manual rotation of the tube. If this procedure, along with the various minor suggestions of Deutsh et al,[138] is adopted the method should be generally applicable and capable of giving volume magnetic susceptibilities to a precision of the order of 1%.

The alternative method[139] utilises spherical and cylindrical reference vessels simultaneously, each containing the same material (i), both being surrounded by a second compound (j), as shown in figure 7.3. The shift difference ($\Delta_{cyl} - \Delta_{sph}$) between the two absorptions from the reference compound (i) in the different vessels is given by

$$\Delta_{cyl} - \Delta_{sph} = (g_{cyl} - g_{sph})(\chi_{v(i)} - \chi_{v(j)}) \quad \ldots. \; 7.4$$

where g_{cyl} and g_{sph} should be $2\pi/3$ and zero respectively in the ideal case. As in the Reilly method, if the cell is calibrated the susceptibilities of unknowns may be determined. It is worthy of comment that this method will be influenced by the degree of tilt of the capillary. Koichi Hatada et al[140] have devised a method based on equation 7.4, the difference in the experimental technique being that, in place of the individual spherical and cylindrical reference vessels, a Flath microcell is used, which is shown in figure 7.4. As both the capillary and sphere are rigidly co-axial the possibility of tilt does not arise. The shift measurement ($\Delta_{cyl} - \Delta_{sph}$) is facilitated by measuring the reference shift when the cell is moved up and down, so that the spherical and cylindrical parts are at the centre of the receiver coil. Results within 1.5% of the literature values have been claimed.

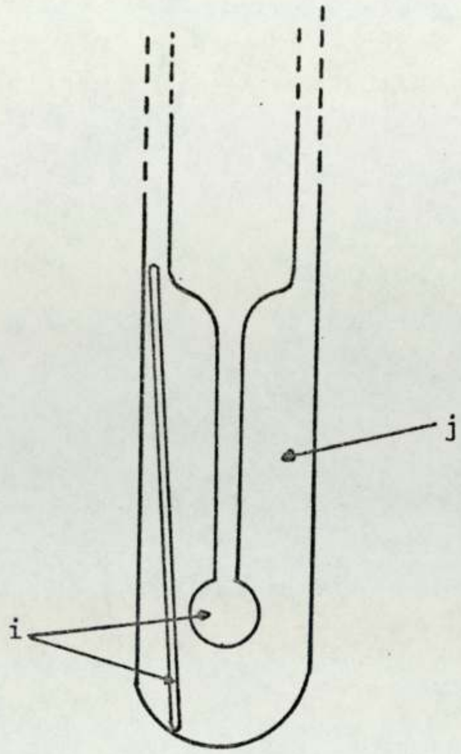


Figure 7.3. Typical sample containing both a cylindrical and spherical reference cell.

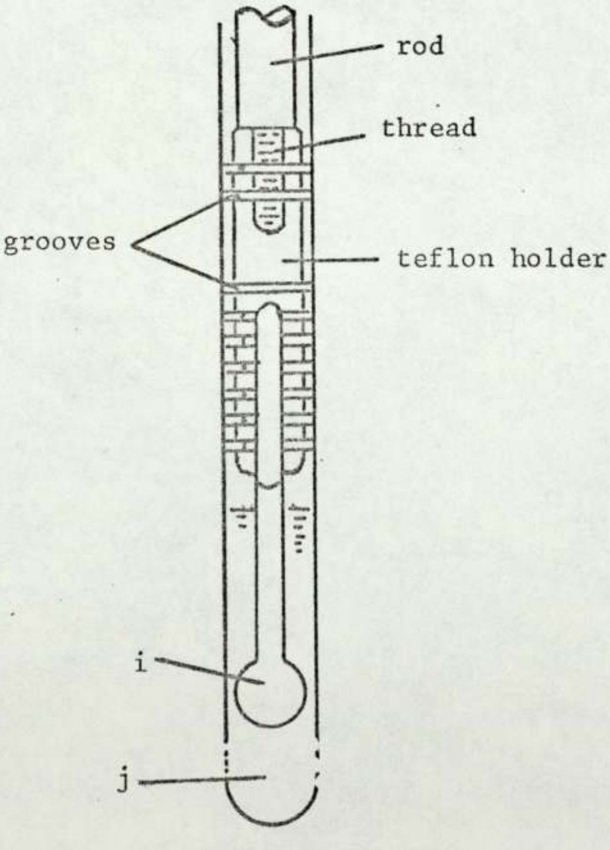


Figure 7.4. Flath microcell.

Both the above methods depend on the value of the parameters describing the physical shape of the reference vessels. Because these values are difficult to determine with certainty, the cells have to be calibrated using compounds of known susceptibilities. However, the value of the shape factor so deduced depends on the collective uncertainty in the classically obtained susceptibilities, and these may be considerable. It is not surprising that when using equation 7.4, for example, values for the cell constant ($g_{cyl} - g_{sph}$) have been found (2.058[136] and 2.245[139]) which are inferior to that expected (2.095). Consequently, when applying equation 7.1 to determine susceptibilities, it would appear that little is to be lost by assuming the validity of the theoretical value for the shape factor for a well-made reference vessel and using a single solvent, whose susceptibility is well documented, as reference.

Comparison of equation 7.4 with equation 7.1 shows that the former is governed by a theoretical shape factor which is one third of that in equation 7.1. Consequently any departure from geometric ideality of the two vessels may lead to higher percentage inaccuracies than pertain to the single vessel situation of the newly proposed method. The method of Reilly et al, although requiring the same single co-axial system, does necessitate careful adjustment of a conventional spectrometer to obtain optimum results. The proposed method requires neither special adjustments to the spectrometer, nor such extensive calibration of the cell as is necessary for the method of Reilly et al. It appears therefore, that this method may afford rapid and accurate determinations of magnetic susceptibilities; this was investigated.

7.2. Experimental Investigation of the Proposed Method for Determining Susceptibilities

The magnetic susceptibility data for benzene is well documented and therefore it was used as the reference solvent, assuming the validity of the theoretical value for the shape factor in equation 7.1, to obtain the magnetic susceptibilities of other materials without experimental evaluation of the shape factor. Cyclohexane was used as the reference solute as it has been shown to be inert in the n.m.r. sense[86]. The composition of the solutions studied is shown in Table 7.1, cyclohexane being present at a mole fraction of ca.0.005.

Table 7.1. Composition of solutions of cyclohexane in various solvents.

Solvent	Moles of Solvent $\times 10^2$	Moles of Cyclohexane $\times 10^4$	Mole Fraction Cyclohexane
Benzene*	5.1211	2.4809	0.0048
toluene	4.3420	2.1244	0.0048
p-xylene	3.7655	1.8595	0.0050
m-xylene	3.7655	1.9462	0.0051
o-xylene	3.7693	1.9557	0.0052
chlorobenzene	3.5538	1.6990	0.0047
1,2-dichloro benzene	2.7277	1.774	0.0042
chloroform	3.3532	1.3295	0.0039
carbon tetrachloride	2.5944	1.2025	0.0046
carbond disulphide	6.8856	3.5562	0.0051

*used as reference sample.

Whilst infinitely dilute solutions should be used theoretically, the effect of the presence of a finite amount of the solute should be negligible because the same concentration was used in both solvents in a particular experiment.

Chemical shift differences of the cyclohexane were measured using a Wilmad precision capillary co-axial with 5mm. O.D. tubes in a Varian 220 MHz instrument and a Perkin-Elmer spectrometer (60 MHz) at 306± 1.0K. The 60 MHz instrument was modified to enable the 5mm. O.D. tubes to be used. The chemical shifts, $\delta^{\perp}$ and δ^{11} as defined by equations 6.5 and 6.6, are recorded in Table 7.2, together with the values of volume susceptibilities deduced therefrom. The literature values are not unambiguously available and so for consistency the values quoted in Table 7.2 are those calculated from the temperature independent specific susceptibilities given by Emsley et al[9], and the densities at 306.5K calculated from those given in Timmermans[110]. To facilitate the calculations, the volume susceptibility of benzene was similarly evaluated as -0.6071×10^{-6} at 306.5K. Comparison of experimental and literature values shows the agreement to be better than 1.0%. Similar agreement can be seen in Table 7.3 which presents the shifts obtained by Becconsall et al, at ambient temperature (taken as 288K for the calculations of the literature values), and the corresponding susceptibility values.

If $\delta^{\perp}$ and δ^{11} are measured at different temperatures equation 7.1 will no longer apply due to the temperature dependence of the screening effects ($\sigma_{loc(i)}$) on the solvent other than its susceptibility. However, if $\sigma_{loc(i)}$ is assumed to be temperature independent, equation 7.1 is still applicable and may be rewritten conveniently in terms of specific susceptibilities, as in equation 7.5.

Table 7.2. Solvent induced shifts (ppm) for cyclohexane, and solvent (y) volume susceptibilities at 306.6K.

Solvent x	Solvent y	$-\delta^{\perp}$	$-\delta^{11}$	$-\chi_v(\mathrm{exp}) \times 10^6$	$-\chi_v(\mathrm{lit}) \times 10^6$
benzene	toluene	0.0632	0.0352	0.6115	0.6132
	p-xylene	0.0965	0.0465	0.6150	0.6143
	m-xylene	0.0976	0.0328	0.6174	0.6149
	o-xylene	0.1462	-0.0511	0.6385	0.6356
	chloro-benzene	0.2452	-0.1900	0.6764	0.6777
	1,2dichloro benzene	0.4632	-0.3300	0.7333	0.7400
	chloroform	0.7723	0.0181	0.7272	0.7277
	carbon tetra-chloride	0.6997	0.2298	0.6819	0.6788
	carbon disulphide	0.8241	0.3507	0.6825	0.6896

Table 7.3. Solvent induced shifts (ppm) for tetramethyl silane and solvent (y) volume susceptibilities at ca.288K.

Solvent x	Solvent y	$\delta^{\perp}$	δ^{11}	$-\chi_v(\mathrm{exp}) \times 10^6$	$-\chi_v(\mathrm{lit}) \times 10^6$
carbon tetra-chloride	benzene	0.67	0.21	0.6213	0.6207
	pyridine	0.80	0.23	0.6033	0.6173
	carbon disulphide	-0.16	-0.12	0.6889	0.6861
cyclohexane	benzene	0.40	0.44	0.6405	0.6207
	pyridine	0.54	0.46	0.6213	0.6173
	carbon disulphide	-0.41	0.11	0.7168	0.6861

$$\delta^{\perp}_{T_2} - \delta^{11}_{T_1} = \frac{2\pi}{3}\{\chi_{(y)}(\rho^{T_2}_{(y)} + 2\rho^{T_1}_{(y)}) - \chi_{(x)}(\rho^{T_2}_{(x)} + 2\rho^{T_1}_{(x)})\} \quad .... \; 7.5$$

where $\chi_{(i)}$ is the specific susceptibility of solvent (i), and $\rho^{T_j}_{(i)}$ is the density of i at temperature j. Departures of the calculated $\chi_{(i)}$ values from the literature values will be symptomatic of the variation of $\sigma_{loc(i)}$ with temperature. To investigate the significance of such possible temperature variation, the specific susceptibilities of a series of solvents were determined with respect to benzene by the application of equation 7.5 to the $\delta^{\perp}$ and δ^{11} values determined at 306.6K and 298K respectively. These are given in Table 7.4. The density data were determined by extrapolation from that given in Timmermans[110].

Table 7.4. Solvent susceptibilities deduced from the induced shifts of cyclohexane at two temperatures.

Solvent x	Solvent y	$-\delta^{11*}$	$-\chi(exp) \times 10^6$	$-\chi(lit) \times 10^6$
benzene	toluene	0.0355	0.7164	0.7176
	p-xylene	0.0453	0.7255	0.7232
	m-xylene	0.0388	0.7243	0.7212
	o-xylene	-0.0335	0.7329	0.7327
	chlorobenzene	-0.1848	0.6192	0.6216
	1,2-dichlorobenzene	-0.4130	0.5790	0.5734
	chloroform	0.6220	0.4951	0.4971
	carbon tetrachloride	0.0233	0.4341	0.4333

* At 293K: $\delta^{\perp}$ as in Table 7.2.

The specific susceptibilities so determined are also given in Table 7.4, together with the literature values. The good agreement between them suggests that over the small temperature range studied here, $\sigma_{loc(i)}$ is temperature independent and therefore may be ignored when obtaining susceptibility data.

7.3 Conclusions

The application of equation 7.1 to shift measurements determined on two spectrometers, one applying the static field perpendicular and the other parallel to the sample axis respectively, enables volume susceptibilities to be determined within 1% of the literature values. The results could no doubt be improved by the determination of $\delta^{\perp}$ at higher spectrometer frequencies. The measurement of δ^{11} and $\delta^{\perp}$ at greatly differing temperatures may help elucidate the temperature dependence of screening effects other than bulk susceptibility.

CHAPTER 8. GENERAL CONCLUSIONS

General Conclusions

From a study of the molecular interaction between chloroform and benzene in several supposedly inert solvents, a new method of data evaluation has been devised which enables thermodynamically valid equilibrium parameters to be obtained. This data processing method was used to study in detail the interaction of chloroform with benzene and alkylated benzenes.

It has been found that thermodynamically valid parameters can only be obtained with certainty if the concentration range is restricted so that the mole-fraction of the aromatic is in the range 0.9 to 1.0 and that of the solute is less than 0.005. To rationalise the processing of n.m.r. data derived from a study of polar solute-aromatic complexes within these concentration constraints, it is necessary to make the bulk parameter concentration scales,which are required to define equilibrium quotients, compatible with n.m.r. measurements. It has been shown that in its simplest form this can be achieved statistically by taking account of the sizes of the aromatic and of the inert diluent. This is implicitly accommodated in the definition of molarity, but necessitates the modification of the definitions of mole fraction and molality. Provided that the above-mentioned conditions are satisfied, both the Creswell and Allred, and Benesi-Hildebrand data evaluation methods may be used. However, from a thermodynamic standpoint the Creswell and Allred method is suspect and hence the Benesi-Hildebrand method is to be preferred.

As a result of the variable temperature study of the interaction of chloroform with various aromatics, the parameters ΔH^o, ΔG^o and ΔS^o for each system were calculated. The temperature independence of ΔH^o is taken to be indicative of the formation of 1:1 complexes only, the solute adopting a time-average orientation on the six-fold axis of the aromatic with the positive end of the solute dipole nearest the aromatic. The magnitude of the equilibrium quotients (and ΔG^o) for the different systems may be rationalised by a treatment which regards the interaction to be dipole-induced dipole in nature and hence greatly influenced by the polarisability of the relevant aromatic. However, in addition, the steric effects of the alkyl substituents on the aromatic play a significant role. The steric effects may affect the equilibrium quotients in two ways, namely they may or may not enhance it,due to a 'trap' effect,as well as reduce it by blocking the approach of the solute to the aromatic. With chloroform as the solute, the 'trap' effect was negative which is indicative of a repulsion of the solute by the alkyl substituents. The Δ_c values increased (relative to the benzene complex) with increasingly polarisable aromatics.

The study of molecular interactions by a reference-independent shift technique was found to be experimentally impractical but,from a consideration of the basis of the technique, a new method for determining susceptibilities was successfully developed, results within 1% of the literature values being obtained.

REFERENCES

1 W.Pauli. Naturwiss. (1924) 12, 741

2 O.Stern. Z. Phys. (1921) 7, 249

3 W.Gerlach and O.Stern. Ann.Phys. Leipzig (1924) 74. 673

4 I.I.Rabi, S.Millman, P.Kusch and J.R.Zacharias. Phys. Rev. (1939) 53, 526

5 N.F.Ramsey.'Molecular Beams' Oxford Univ. Press. Oxford (1956)

6 E.M.Purcell, M.C.Torrey and R.V.Pound. Phys. Rev. (1946) 69, 37

7 F.Bloch, W.W.Hansen and M.Packard. Phys. Rev. (1946) 69, 127

8 J.A.Pople, W.G.Schneider and H.J,Bernstein. "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., N.Y. (1959)

9 J.W.Emsley, J.Feeney and L.H.Sutcliffe. "High Resolution Nuclear Magnetic Resonance Spectroscopy, Vols I and II", Pergamon Press, Oxford (1965)

10 L.M.Jackman."Applications of Nulcear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London (1959)

11 H.S.Gutowsky and D.W.McCall. Phys. Rev. (1951) 82, 748

12 S.G.Starling and A.J.Woodall. 'Physics', 2nd Edition Longmans, London (1957)

13 L.Pauling and E.B.Wilson Jr.. "Introduction to Quantum Mechanics", McGraw-Hill Book Co., N.Y. (1935)

14 E.M.Purcell. Phys. Rev. (1946) 69, 681

15 A.Einstein. Phys. Z (1917) 18, 121

16 W.A.Anderson. Phys. Rev. (1956) 104, 550

17 N.Bloembergen, E.M.Purcell and R.V.Pound. Phys. Rev (1948) 73, 679

18 F.Bloch. Phys. Rev. (1946) 70, 460

19 F.Bloch. Phys. Rev (1956) 102, 104

20 R.K.Wagsness and F.Bloch. Phys. Rev (1953) 89, 728

21 G.V.D.Tiers. J.Phys. Chem (1961) 65, 1916

22 E.R.Andrew. "Nuclear Magnetic Resonance", Cambridge Univ. Press N.Y. (1955)

23 R.V.Pound. Phys. Rev (1950) 79, 685

24 N.Bloembergen. "Nuclear Magnetic Relaxations", W.A.Benjamin N.Y.(1961)

25 W.D.Knight. Phys. Rev (1949) 76, 1259

26 G.V.D.Tiers. J.Phys. Chem (1958) 62, 1151

27 W.G.Proctor and F.C.Yu. Phys. Rev. (1951) 81, 20

28 H.S.Gutowsky and D.W.McCall. Phys. Rev (1951) 82, 748

29 W.E.Quinn and R.M.Brown. J.Chem.Phys. (1953) 21, 1605

30 M.Barfield and D.M.Grant. Adv.Mag.Res. (1965) 1, 149

31 H.S.Gutowsky, D.W.Slichter and D.W.McCall. J.Chem.Phys. (1953) 21,279

32 E.L.Hahn and D.E.Maxwell. Phys. Rev. (1951) 84, 1246

33 N.F.Ramsey and E.M.Purcell. Phys. Rev. (1952) 85, 143

34 H.S.Gutowsky and Saika. J.Chem.Phys. (1948) 71, 2703

35 A.L.Bloom and M.E.Packard. Science (1955) 122, 738

36 J.B.Leane, R.E.Richards and T.D.Schaeffer. J.Sci.Instruments (1959) 36, 230

37 W.E.Lamb. Phys. Rev. (1941) 60, 817

38 N.F.Ramsey. Phys. Rev. (1950) 78, 699

39 N.F.Ramsey. Phys. Rev. (1952) 86, 243

40 J.H.Van Vleck. "Electronic and Magnetic Susceptibilities", Oxford Univ. Press N.Y. (1932)

41 A.Saika and C.P.Slichter. J.Chem.Phys. (1954) 22, 26

42 J.A.Pople. Proc. Roy. Soc. (1957) A239, 541

43 H.M.McConnell. J.Chem.Phys. (1957) 27, 226

44 P.T.Narasinhan and M.T.Rogers. J.Chem.Phys (1959) 31, 1302

45 J.Homer and D.Callaghan. J.Chem.Soc. (A) (1968) 439

46 W.C.Dickinson. Phys. Rev. (1951) 81, 717

47 D.J.Frost and G.E.Hall. Mol.Phys. (1966) 10, 191

48 S.Broersma. J.Chem.Phys. (1949) 17, 873

49 A.D.Buckingham, T.Schaeffer and W.G.Schneider. J.Chem.Soc. (1960) 32, 1227

50 J.Homer and P.J.Huck. J.Chem.Soc (A) (1968) 277

51 A.D.Buckingham. Can.J.Chem. (1960) 38, 300

52 A.A.BothnerBy and R.E.Glick. J.Chem.Phys. (1957) 26, 1651

53 J.Ronayne and D.H.Williams. J.Chem.Soc. (B) (1967) 540

54 F.Hruska, D.W.McBridge and T.Schaeffer. Can.J.Chem. (1967) 45, 1081

55 R.E.Klinck and J.B.Stothers. Can.J.Chem. (1962) 40, 2329

56 R.E.Klinck and J.B.Stothers. Can.J.Chem. (1962) 40, 1071

57 R.E.Klinck and J.B.Stothers. Can.J.Chem. (1966) 44, 37

58 D.H.Williams, J.Ronayne and R.G.Wilson. J.Chem.Soc. (D) (1967) 1089

59 R.G.Wilson and D.H.Williams. J.Chem.Soc (B) (1968) 1163

60 T.Winkler and W.von Phillipsborn. Helv.Chim.Acta. (1968) 51,183

61 K.D.Bartle, D.W.Jones and R.S.Matthews. J.Chem.Soc (A) (1969) 876

62 J.V.Hatton and R.E.Richards. Mol.Phys. (1962) 5, 153

63 L.Pauling. J.Chem.Phys. (1936) 4, 673

64 J.A.Pople. J.Chem.Phys. (1956) 24, 1111

65 C.E.Johnson and R.A.Bovey. J.Chem.Phys. (1958) 29, 1012

66 J.S.Waugh and R.W.Fessenden. J.Amer.Chem.Soc. (1957) 79, 846

67 P.J.Huck, Ph.D. Thesis, University of Aston in Birmingham (1968)

68 J.A.Pople. Proc. Roy. Soc. (1957) A239,541

69 T.K.Wu and B.P.Dailey. J.Amer.Chem.Soc. (1964) 72, 2796

70 L.W.Reeves and W.G.Schneider. Can.J.Chem. (1957) 35, 251

71 P.Polanum. Ph.D. project, University of Aston in Birmingham

72 H.A.Benesi and J.H.Hildebrand. J.Amer.Chem.Soc.(1948) 71, 2703

73 G.D.Johnson and R.E.Bowen. J.Amer.Chem.Soc.(1965) 87, 1655

74 K.M.Baker and R.G.Wilson. J.Chem.Soc.(B) (1970) 236

75 K.E.Orgel and R.S.Mulliken. J.Amer.Chem.Soc.(1957) 79, 483

76 C.J.Creswell and A.L.Allred. J.Phys.Chem.(1962) 66, 1489

77 J.Homer and M.C.Cooke. J.Chem.Soc.(A) (1969) 777

78 W.G.Schneider . J.Phys.Chem. (1962) 66, 2653

79 F.A.Cotton and G.Wilkinson. "Advances in Inorganic Chemistry", Interscience Publishers, Wiley, New York (1962)

80 R.J.Abraham. Mol.Phys.(1961) 4, 369

81 J.V.Hatton and W.G.Schneider. Can.J.Chem.(1962) 40, 1285

82 R.C.Fort and J.R.Lindstrom. Tetrahedron (1967) 23, 3227

83 P.Laszlo and D.H.Williams. J.Amer.Chem.Soc. (1966) 88, 2799

84 J.Ronayne, H.V.Sargeant and D.H.Williams. J.Amer.Chem.Soc.(1966) 88, 5258

85 J.W.Bowie, J.Ronayne and D.H.Williams. J.Chem.Soc.(B) (1966) 846

86 J.Homer, E.J.Hartland and D.J.Jackson. J.Chem.Soc.(A)(1970) 931

87 C.J.Cresswell and A.L.Allred. J.Chem.Soc.(1963) 1723

88 P.J.Berkeley and M.W.Hanna. J.Amer.Chem.Soc.(1963) 67, 846

89 J.E.Anderson. Tetrahedron Letters (1965) 4713

90 D.H.Williams and D.A.Wilson. J.Chem.Soc(B) (1966) 144

91 J.Collin and L.D'Or. J.Chem.Phys.(1955) 23, 397

92 D.Hassel and K.O.Stromme. Acta.Chem.Scand.(1959) 13, 1781

93 J.Homer and M.C.Cooke. J.Chem.Soc.(A) (1969) 773

94 W.T.Huntress Jr. J.Phys.Chem. (1969) 73, 103

95 W.G.Rothschild. J.Chem.Phys. (1971) 55, 1402

96 L.J.Andrews and R.M.Keeter. "Molecular Complexes in Organic Chemistry" Holden-Day Inc., San Francisco 1964

97 C.M.Higgins, G.C.Pimentel and J.N.Shoolery. J.Chem.Phys.(1955) 23, 1244

98 A.D.Cohen and C.Reid. J.Chem.Phys.(1956) 25, 790

99 T.Schaeffer and W.G.Schneider. J.Chem.Phys.(1960) 32, 1218

100 R.L.Scott. Rec.Trav.Chim.(1956) 75, 787

101 R.J.Trotter and M.W.Hanna. J.Amer.Chem.Soc.(1966) 88, 3724

102 M.W.Hanna and A.L.Ashbaugh. J.Phys.Chem.(1964) 68, 811

103 I.D.Kuntz jun., F.P.Gasparro, M.D.Johnston jun., and R.P.Taylor. J.Amer.Chem.Soc.(1968) 90, 4778

104 R.Foster and C.A.Fyfe. Trans.Fara.Soc.(1965) 61, 1626

105 P.D.Groves, P.J.Huck and J.Homer. Chem.and Ind. (1967) 915

106 J.Homer, C.J.Jackson and J.Peters. unpublished work

107 G.Scatchard, S.E.Wood and J.M.Mocher. J.Phys.Chem. (1939) 43,119

108 G.Scatchard, S.E.Wood and J.M.Mochel. J.Amer.Chem.Soc.(1940) 62, 712

109 "Physical Properties of Organic Compounds," Adv. in Chemistry Series, N.15 and N.22 Am.Chem.Soc.Pub., Washington (1955 and 1959)

110 J.Timmermans. "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, Amsterdam 1965

111 T.L.Brown and K.Stark. J.Phys.Chem.(1965) 69, 2679

112 Sandoval and M.W.Hanna. J.Phys.Chem.(1966) 70, 1203

113 T.S.Moore, F.Shephard and F.Goodall. J.Chem.Soc.(1931) 1447

114 S.C.Liao and R.K.Chan. Can.J.Chem.(1971) 49, 2700

115 W.L.Hendron, J.Feur and R.E.Mitchell. J.Chem.Soc.(D)(1971) 435

116 R.Foster, D.L.L.Hammick and B.N.Parsons. J.Chem.Soc.(1956) 555

117 L.R.C.Barclays and E.E.Betts. Can.J.Chem.(1955) 33, 672

118 W.B.Persons. J.Amer.Chem.Soc.(1965) 87, 167

119 S.Carter, J.N.Murrell and E.J.Rosch. J.Chem.Soc.(1965) 2048

120 R.M.Emslie, R.Foster, C.A.Fyfe and I.Horman. Tetrahedron (1965) 21, 2843

121 R.Foster and I.B.C.Matheson. Spectrochim.Acta.(1967) 23A, 2037

122 R.Foster and I.B.C.Matheson. Spectrochim.Acta.(1971) 27A, 1171

123 R.Foster and I.B.C.Matheson. J.Chem.Soc.(B)(1970) 1713

124 J.Grundes and M.Tamres. J.Phys.Chem.(1971) 75, 3682

125 C.J.Jackson. Ph.D.Thesis, University of Aston in Birmingham (1971)

126 C.G.Le fevre. Private communication

127 R.R.Yadava. Ph.D.Thesis, University of Aston in Birmingham (1972)

128 J.Homer and D.Callaghan. J.Chem.Soc.(A) (1968) 518

129 J.K.Becconsall, G.D.Daves jun and W.R.Anderson jun. J.Amer.Chem. Soc. (1970) 72, 430

130 P.Laszlo. "Progress in N.M.R.Spectrosopy", (1967) 3, 231

131 P.Doyle. Private communication

132 C.A.Reilly, H.M.McConnell and R.G.Meisenheimer. Phys.Rev.(1955) 98, 264

133 N.C.Li, R.L.Scruggs and G.D.Becker. J.Amer.Chem.Soc.(1962) 84, 4651

134 M.G.Morin, G.Paillet and M.E.Hobbs. J.Phys.Chem.(1956) 60, 1594

135 J.R.Zimmermans and M.R.Foster. J.Phys.Chem.(1957) 61, 282

136 D.C.Douglass and A.Fratiello. J.Chem.Phys.(1963) 39, 3161

137 H.A.Lanwers and G.P.van der Kelen. Bull.Soc.Chim.Belges (1966) 75, 238

138 J.L.Deutch, A.C.Lanson and S.M.Poling. Anal.Chem.(1968) 40, 839

139 K.Frei and H.J.Bernstein. J.Chem.Phys. (1962) 37, 1891

140 K.Hatada, Y.Terawaki and H.Okuda. Bull.Chem.Soc.Jap.(1969) 42(1),1781

Molecular Complexes. Preliminary Comments on the Rationalization of Procedures for Processing Data Obtained from Nuclear Magnetic Resonance Studies

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Molecular Complexes. Preliminary Comments on the Rationalization of Procedures for Processing Data Obtained from Nuclear Magnetic Resonance Studies

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Summary The procedures which should be used for correctly processing data obtained from n.m.r. studies of molecular complexes are stated, together with the conditions necessary for their use, and the results of the applications of these to studies of the reaction between chloroform and benzene in the presence of various inert materials are given.

NUCLEAR MAGNETIC RESONANCE spectroscopy may be used to study molecular complexes[1] formed in reactions of the type (1)

$$A + B \rightleftarrows A \cdots B \qquad (1)$$

occurring in the presence of an inert material, S. The equilibrium quotient (K) for the reaction and the shift (Δ_c) induced in one of the species, say A, on the formation of a single, or of several isomeric 1:1 complexes,[2] may be deduced by two methods. First, an extrapolation method due to Benesi and Hildebrand,[3] which depends on the use of the familiar equation (2)

$$\frac{1}{\Delta_{obs}} = \frac{1}{K[B]_0\Delta_c} + \frac{1}{\Delta_c} \qquad (2)$$

where $\Delta_{obs} = \delta_{obs} - \delta_{free}$ and $\Delta_c = \delta_c - \delta_{free}$, and δ_{obs}, δ_c, and δ_{free} are the shifts of A, observed, in the fully complexed state, and unassociated states respectively. Secondly, a data-processing method such as that used by Creswell and Allred.[4]

It has been a matter of concern,[5] whichever method is employed for data processing, that (i) when a particular set of data is processed the value of Δ_c obtained is found to depend on the concentration scale used in the processing, and (ii) when a particular reaction is studied in different supposedly inert solvents, different values of Δ_c and the various equilibrium quotients are obtained. Understandably, there is a widespread feeling that there is a major ambiguity in n.m.r. studies of molecular complexes that potentially undermines the utility of this approach. We wish to dispel this belief.

Whilst some workers[5] have claimed that (ii) is not found only if the molar scale is used for data processing, we do not support this claim and now *state* the procedure and related conditions which must be used to process data to avoid both anomalies (i) and (ii); the details of our investigations will be published later.

We have deduced on an entirely theoretical basis that: (A) Meaningful values may be obtained for the equilibrium quotients defined in terms of either mole fractions or molarities. This is only possible when x_B tends towards unity, under which conditions both equilibrium quotients are independent of the concentration of B and activity coefficients of all sorts, these requirements being necessary for the valid use of either of the two methods mentioned above. (B) The Benesi–Hildebrand method must be used for data processing, the parameters $K_{(x \text{ or } c)}$ and Δ_c being obtained from the tangent to the appropriate curve where x_S is zero. (C) For the mole fraction scale, equation (2) must be modified to account for the variation of the shift of "free" species (A and A $\cdots$ B) with the composition of the mixtures, and the normal equilibrium expression must be modified to account for the effect of S (its size) in the mixtures. The operative form of the Benesi–Hildebrand equation then becomes (3)

$$\frac{1}{\Delta_{obs} - [n_B G/(n_B + n_S)]} = \frac{n_B + (V_S n_S/V_B)}{n_B K_x \Delta_c} + \frac{1}{\Delta_c} \qquad (3)$$

where V_B and V_S are the molar volumes of B and S, and $G = (\sigma_A^B - \sigma_B^B) - (\sigma_A^S - \sigma_B^S)$, σ_j^i representing the screening effect of i on j infinitely dilute in i. (D) On the molar scale equation (2) is only modified by the function G since the correction for the size of S is implicit in this scale. (E) Rational values for K_x and Δ_c may only be obtained from the tangent to a plot of $1/[\Delta_{obs} - n_B G/(n_B + n_S)]$ against $(n_B + V_S n_S/V_B)/n_B$ when the latter parameter is unity, and corresponding values for K_c and Δ_c may be obtained from the tangent to a plot of $1/[\Delta_{obs} - n_B G/(n_B + n_S)]$ against $1/c_B$ when $x_S = 0$. For the studies many samples with $n_B/(n_B + n_S)$ varying between 0·9 and 1·0 have to be studied.

TABLE

Values of equilibrium quotients and Δ_c *for the chloroform–benzene reaction, in the presence of various inert materials at* 306·6 K

	(1)		(2)		(3)		(4)
Inert materials	K_x	Δ_c	K_x	Δ_c	K_c[a]	Δ_c	$K_c(3)/K_x(2)$[b]
Cyclohexane	1·4	90	1·5	84	0·14	84	0·091
cis-Decalin	1·7	83	1·7	79	0·16	79	0·091
Bicyclohexyl	1·9	80	1·9	77	0·17	76	0·090
Tetradecane	1·7	83	1·7	82	0·18	77	0·107
Hexadecane	1·7	84	1·7	82	0·16	81	0·095

[a] $\times 10^3$ m^3 mol^{-1}
[b] $\times 10^3$ m^3. These ratios ase based on values of $K_x(2)$ and $K_c(3)$ computed to three significant figures.

We have checked these assertions by investigating, amongst others, the reaction between chloroform and benzene with several compounds S which we are satisfied are sufficiently inert (in the n.m.r. sense). The first set of values for K_X and Δ_c in the Table were deduced by using equation (3), and the second set by omitting the term $n_B G/(n_B + n_S)$ in this equation. It can be seen that for *this reaction* the effect of correcting for G is small and can be neglected, and so the second set can be directly compared with the third set correspondingly deduced on the molar scale. Because of the implicit re-definition of K_X in equation (3), the ratio of K_c/K_X should equal the molar volume of benzene which in this case is $0{\cdot}0903 \times 10^{-3}\,m^3$. The final column of the Table shows that indeed this is so, and validifies the approach. The main consequence of the treatment of the data is that Δ_c can be seen to be a parameter characteristic, within experimental and processing error, of the complex (or isomeric complexes), being independent of the nature of the inert material and the concentration scale adopted for the evaluation. We conclude therefore that for the reaction between chloroform and benzene *in benzene*, $K_X = 1{\cdot}7 \pm 0{\cdot}2$ and $K_c = 0{\cdot}16 \pm 0{\cdot}02 \times 10^{-3}\,m^3\,mol^{-1}$ and $\Delta_c = 80 \pm 4$ Hz (at 60·004 MHz).

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[1] See *e.g.*, L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, **1964**, and R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, **1969**.

[2] I. D. Kuntz, jun. and M. D. Johnston, jun., *J. Amer. Chem. Soc.*, **1967**, **89**, 6008.

[3] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **1949**, **71**, 2703.

[4] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **1962**, **66**, 1469.

[5] I. D. Kuntz, jun., F. P. Gasparro, M. D. Johnston, jun., and R. P. Taylor, *J. Amer. Chem. Soc.*, **1968**, **90**, 4778, and references therein.

The Determination of Magnetic Susceptibilities by a New Nuclear Magnetic Resonance Method

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The Determination of Magnetic Susceptibilities by a New Nuclear Magnetic Resonance Method

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Summary A new n.m.r. technique for the determination of magnetic susceptibilities is described, and the results of its application to several organic compounds are given.

Following the work of Becconsall *et al.*,[1] a method of determining magnetic susceptibilities has been devised which uses the differences between externally referenced chemical shifts caused by the difference in sample configuration in two spectrometers, one having a conventional magnet which applies the field perpendicular to the sample axis (⊥) and the other a superconducting solenoid which applies the field longitudinally (‖).

For a cylindrical reference vessel coaxial with the main sample tube, the relative shift for a reference compound at infinite dilution in two solvents x and y in the two regions of the sample cell are, for the perpendicular and parallel field orientations, given,[1] respectively, by equations (1) and (2). In these equations $\chi_{v(i)}$ is the volume susceptibility

$$\overset{\perp}{\sigma}_{\mathrm{sol(y)}} - \overset{\perp}{\sigma}_{\mathrm{sol(x)}} = \frac{2\pi}{3}\left[\chi_{v(y)} - \chi_{v(x)}\right] + \sigma_{\mathrm{loc(y)}} - \sigma_{\mathrm{loc(x)}} \tag{1}$$

$$\overset{\parallel}{\sigma}_{\mathrm{sol(y)}} - \overset{\parallel}{\sigma}_{\mathrm{sol(x)}} = -\frac{4\pi}{3}\left[\chi_{v(y)} - \chi_{v(x)}\right] + \sigma_{\mathrm{loc(y)}} - \sigma_{\mathrm{loc(x)}} \tag{2}$$

of i and $\sigma_{\mathrm{loc(i)}}$ is the sum of all the screening effects of the solvent, except that of its susceptibility, on the solute. From equations (1) and (2) it follows that the difference between the shifts measured for the solute in the perpendicular ($\delta^{\perp}$) and parallel ($\delta^{\parallel}$) field orientations is given by equation (3).

$$\left[\overset{\perp}{\sigma}_{\mathrm{sol(y)}} - \overset{\perp}{\sigma}_{\mathrm{sol(y)}}\right] - \left[\overset{\parallel}{\sigma}_{\mathrm{sol(y)}} - \overset{\parallel}{\sigma}_{\mathrm{sol(x)}}\right] = (\delta^{\perp} - \delta^{\parallel}) = 2\pi[\chi_{v(y)} - \chi_{v(x)}] \tag{3}$$

The factor of 2π in equation (3) corresponds fundamentally to the shape factor for a transversely oriented cylindrical sample as originally invoked by Dickinson.[2] When implementing equation (3) for the determination of magnetic susceptibilities, a value for the shape factor for the chosen reference vessel may be deduced experimentally using a series of solvents x and y of known susceptibilities, as has been done by other workers when using equations similar to (3).[3] However, the value for the shape factor so deduced must depend on the collective uncertainty in classically obtained susceptibilities, and this may be considerable. It appears, therefore, that little is to be lost by assuming the validity of the theoretical value for the shape factor for a well-made reference vessel and using a single solvent whose susceptibility is well-documented, in order to obtain values for the susceptibilities of other materials. In this work, this latter approach has been adopted initially, using benzene as the reference solvent. The reference solute chosen was cyclohexane because this is believed to be inert (in the n.m.r. sense),[4] and the solutions studied contained this material at a mole fraction of *ca.* 0·005. Whilst infinitely dilute solutions should be used theoretically the effect of the presence of a finite amount of the solute should be negligible because the same concentration was used in both solvents in a particular experiment.

The chemical shifts were measured at 306 K using a Wilmad precision capillary coaxial with 5 mm O.D. tubes on a Varian 220 MHz instrument and a Perkin-Elmer R 10 spectrometer, operating at 60·004 MHz. The chemical shifts of cyclohexane in several solvents are given in Table 1, together with the values of the volume susceptibilities deduced therefrom. It can be seen that the experimental susceptibility values generally agree well within 1% of the literature values. Similar agreement can be seen in Table 2 which presents the shifts obtained by Becconsall *et al.*,[1] at the ambient temperature, and the corresponding susceptibility values.

It is interesting to note that if $\delta^{\perp}$ and $\delta^{\parallel}$ were measured at different temperatures equation (3) would no longer apply due to the temperature dependence of $\sigma_{\mathrm{loc(i)}}$. In order to estimate the significance of this temperature dependent effect we have investigated several systems at 293 and 306·6 K on the 220 and 60 MHz instruments, respectively. If $\sigma_{\mathrm{loc(i)}}$ is assumed to be independent of temperature, equation (3) may be rewritten conveniently in terms of specific susceptibilities as in equation (4).

$$\delta^{\perp}_{T_2} - \delta^{\parallel}_{T_1} = \frac{2\pi}{3}\left\{\chi_{(y)}\left[\overset{T_2}{\rho}_{(y)} + 2\overset{T_1}{\rho}_{(y)}\right] - \chi_{(x)}\left[\overset{T_2}{\rho}_{(x)} + 2\overset{T_1}{\rho}_{(x)}\right]\right\} \tag{4}$$

where $\chi_{(i)}$ is the specific susceptibility of i and $\rho_{(i)}^{T_j}$ is the density of i at temperature T_j. The shifts obtained at two temperatures for several systems are given in Table 3, together with the appropriate values of the specific susceptibilities deduced using equation (4). It can be seen that the approximate experimental values agree quite well with the literature values of the susceptibilities. It appears therefore that over the small temperature range used here, the effect of the temperature dependence of screening effects other than susceptibility is small and may, if necessary, be ignored when obtaining susceptibility data.

The method described here has some advantages over the two main established n.m.r. techniques[5,6] for determining magnetic susceptibilities. The method due to Frei and Bernstein[5] requires the simultaneous use of a spherical and a cylindrical reference vessel with the result that the relevant equation corresponding to (3) is governed by a shape factor whose theoretical value is one third of that given above. Consequently, any experimental departures from geometric ideality of the *two* vessels may lead to higher percentage inaccuracies than that pertaining to the single vessel situation considered here. The method of Reilly *et al.*,[6] although requiring no more than a precision coaxial cylindrical reference vessel, does necessitate careful adjustment of a conventional spectrometer to obtain optimum results. The technique described here requires neither special adjustments to the spectrometer nor such extensive calibration of the cell as is necessary for the method of Reilly *et al.*

It appears that this method may afford rapid and accurate determinations of magnetic susceptibilities. Undoubtedly the results in Tables 1 and 3 can be further improved by the more precise measurement of $\delta^{\perp}$ at higher spectrometer frequencies.

TABLE 1

Solvent induced shifts (p.p.m.) for cyclohexane, and solvent (y) volume magnetic susceptbilities at 306·6 K

Solvent x	Solvent y	$-\delta^{\perp}$	$-\delta^{\parallel}$	$-\chi_v(\text{exp}) \times 10^6$	$-\chi_v(\text{lit}) \times 10^6$[a]
Benzene[b]	Toluene	$0{\cdot}063_2$	$0{\cdot}035_2$	$0{\cdot}611_5$	0·6132
	p-Xylene	$0{\cdot}096_5$	$0{\cdot}046_5$	$0{\cdot}615_0$	0·6143
	m-Xylene	$0{\cdot}097_6$	$0{\cdot}032_8$	$0{\cdot}617_4$	0·6149
	o-Xylene	$0{\cdot}146_2$	$-0{\cdot}051_1$	$0{\cdot}638_5$	0·6356
	Chlorobenzene	$0{\cdot}245_2$	$-0{\cdot}190_0$	$0{\cdot}676_4$	0·6777
	1,2-Dichlorobenzene ..	$0{\cdot}463_2$	$-0{\cdot}330_0$	$0{\cdot}733_3$	0·7400
	Chloroform	$0{\cdot}772_3$	$0{\cdot}018_1$	$0{\cdot}727_2$	0·7277
	Carbon tetrachloride ..	$0{\cdot}699_7$	$0{\cdot}229_8$	$0{\cdot}681_9$	0·6788
	Carbon disulphide ..	$0{\cdot}824_1$	$0{\cdot}350_7$	$0{\cdot}682_5$	0·6896

[a] These data are not available unambiguously, and so for consistency the values quoted are those calculated from the specific susceptibilities given in ref. 7 and the densities at 306.6 K extrapolated from those given in ref. 8. [b] The value of χ_v for benzene has been taken to be $-0{\cdot}6071 \times 10^{-6}$.

TABLE 2

Solvent induced shifts (p.p.m.) for Me_4Si*, and solvent (y) volume magnetic susceptibilities at* ca. 288 K

Solvent x	Solvent y	$\delta^{\perp}$	$\delta^{\parallel}$	$-\chi_v(\text{exp}) \times 10^6$	$-\chi_v(\text{lit}) \times 10^6$[a]
Carbon tetrachloride ..	Benzene	0·67	0·21	$0{\cdot}62_{13}$	0·6207
	Pyridine	0·80	0·23	$0{\cdot}60_{38}$	0·6173
	Carbon disulphide ..	−0·16	−0·12	$0{\cdot}68_{81}$	0·6861
Cyclohexane	Benzene	0·40	0·44	$0{\cdot}64_{05}$	0·6207
	Pyridine	0·54	0·46	$0{\cdot}62_{13}$	0·6173
	Carbon disulphide ..	−0·41	0·11	$0{\cdot}71_{68}$	0·6861

[a] See footnote to Table 1; the relevant temperature is now 288 K.

TABLE 3

Solvent susceptibilities deduced from the induced shifts of cyclohexane at two temperatures

Solvent x	Solvent y	$-\delta^{\parallel}$[a]	$-\chi(\text{exp}) \times 10^6$	$-\chi(\text{lit}) \times 10^6$
Benzene	Toluene	$0{\cdot}035_5$	$0{\cdot}716_4$	0·7176
	p-Xylene	$0{\cdot}045_3$	$0{\cdot}725_5$	0·7232
	m-Xylene	$0{\cdot}038_8$	$0{\cdot}724_3$	0·7212
	o-Xylene	$-0{\cdot}033_5$	$0{\cdot}732_9$	0·7327
	Chlorobenzene	$-0{\cdot}184_8$	$0{\cdot}619_2$	0·6216
	1,2-Dichlorobenzene	$-0{\cdot}413_0$	$0{\cdot}579_0$	0·5734
	Chloroform	$0{\cdot}022_0$	$0{\cdot}495_1$	0·497
	Carbon tetrachloride	$0{\cdot}023_3$	$0{\cdot}434_1$	0·433

[a] At 293 K: $\delta^{\perp}$ as in Table 1.

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[1] J. K. Becconsall, G. D. Daves, jun., and W. R. Anderson, jun., *J. Amer. Chem. Soc.*, 1970, **72**, 430.

[2] W. C. Dickinson, *Phys. Rev.*, 1951, **81**, 717.

[3] See *e.g.* P. Laszlo *Progr. N.M.R. Spectroscopy*, 1967, **3**, 231, and references therein.

[4] J. Homer, E. J. Hartland, and C. J. Jackson, *J. Chem. Soc.* (*A*), 1970, 931.

[5] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, 1962, **37**, 1891.

[6] C. A. Reilly, H. M. McConnell, and R. G. Meisenheimer, *Phys. Rev.*, 1955, **98**, 264.

[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," vol. 1, Pergamon Press, Oxford, 1965.

[8] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1965.

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MOLECULAR COMPLEXES

PART 7.—SOME COMMENTS ON THE PROCESSING OF DATA OBTAINED FROM NUCLEAR MAGNETIC RESONANCE STUDIES

Molecular Complexes

Part 7.[1]—Some Comments on the Processing of Data obtained from Nuclear Magnetic Resonance Studies

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The processing of data obtained by n.m.r. studies of 1 : 1 molecular complexes formed in reactions of the type $A+B \rightleftharpoons A \ldots B$, occurring in the presence of an inert solvent S, is examined in detail. The thermodynamics of the reaction are considered, with particular reference to the Benesi-Hildebrand equation and the iterative procedures which are normally used to obtain the equilibrium quotient and chemical shift differences between the " free " and fully complexed A (Δ_c). It is shown that by the normal use of the processing procedures, Δ_c is expected to be dependent on the concentration scale adopted for its evaluation, and that whichever scale is used the corresponding quotient is expected to depend on the nature of S. It is demonstrated that this anomalous behaviour may be obviated by more critical use of the Benesi-Hildebrand method, and the modifications to it and the conditions for its proper use are explained. The arguments are substantiated by investigations of the chloroform-benzene reaction in a variety of inert materials, and of several reactions of chloroform with aromatic compounds in cyclohexane.

Considerable attention has been directed to n.m.r. studies of short-lived molecular complexes formed in reactions of the type (1)

$$A+B \rightleftharpoons A \ldots B \tag{1}$$

occurring in a supposedly inert solvent S.[2] Two basic procedures are available to process data for the shifts induced in say A by B under different conditions for the initial concentrations of the components. Both of these depend on the familiar eqn (2).[3]

$$\delta_{\text{obs}} = \frac{n_{\text{AB}}}{n_{\text{A}}}(\delta_{\text{c}} - \delta_{\text{free}}) + \delta_{\text{free}} \tag{2}$$

The first is a graphical method due originally to Benesi and Hildebrand [4] (Method I) and the second an iterative procedure such as that used by Creswell and Allred [5] (Method II).

It has been a matter of considerable concern that when any reaction is investigated apparent anomalies concerning the values of $\Delta_c(\delta_c - \delta_{\text{free}})$ and the equilibrium quotients have been found.[6-9] The most significant of these are (*a*) that when a particular set of experimental data is processed the value of Δ_c obtained is found to depend on the concentration scale employed in the processing method, and (*b*) that when a particular reaction is studied in different supposedly inert solvents different values of Δ_c and the various equilibrium quotients are obtained (negative values for the quotients being found in some cases).

Recently we have stated the conditions under which these anomalies can be avoided.[10] We now explain the reasons for our conclusions which depend on the belief that where anomalies have been found they result from the facts that (*c*) eqn (2) is not strictly correct, and (*d*) the concentration ranges over which the experimental data have been obtained are such that the methods by which they are processed are unsound. For convenience we shall develop our arguments by assuming the validity[11] of eqn (2) and attempt to substantiate assertion (*d*) and only subsequently attempt to substantiate assertion (*c*).

METHODS I AND II

Two requirements are necessary when processing data by Method I; (i), that the initial concentration of one component A is very much smaller than that of the second component B, and (ii) that it is possible to construct an equilibrium quotient for reaction (1), all terms in which are known, and which must, therefore, be free from activity coefficients of all sorts, and moreover, *which is independent of the concentration of* B *over an appreciable concentration range*. These apply whichever scale of concentration is used to define the equilibrium quotient.

The general equation on which Method I depends is (3),

$$\frac{1}{\Delta_{\mathrm{obs}}} = \frac{1}{K[\mathrm{B}]_0\Delta_{\mathrm{c}}} + \frac{1}{\Delta_{\mathrm{c}}} \tag{3}$$

which is the n.m.r. analogue of the original Benesi-Hildebrand equation,[4] where $\Delta_{\mathrm{obs}} = \delta_{\mathrm{obs}} - \delta_{\mathrm{free}}$ and $[\mathrm{B}]_0$ is the initial concentration of B. For the mole fraction and molar scales the equilibrium quotients (K) are defined by eqn (4) and (5); V is the volume of the mixture. Eqn (3)-(5) show that a plot of $\Delta_{\mathrm{obs}}^{-1}$ against either $(n_{\mathrm{B}}+n_{\mathrm{S}})/n_{\mathrm{B}}$ or V/n_{B} should give a straight line from which Δ_{c} and either K_x or K_c may be obtained.

$$K_x = \frac{n_{\mathrm{AB}}(n_{\mathrm{A}}+n_{\mathrm{B}}+n_{\mathrm{S}}-n_{\mathrm{AB}})}{(n_{\mathrm{A}}-n_{\mathrm{AB}})(n_{\mathrm{B}}-n_{\mathrm{AB}})} \approx \left(\frac{n_{\mathrm{AB}}(n_{\mathrm{B}}+n_{\mathrm{S}})}{(n_{\mathrm{A}}-n_{\mathrm{AB}})n_{\mathrm{B}}}\right)_{n_{\mathrm{B}} \gg n_{\mathrm{A}}} \tag{4}$$

$$K_c = \frac{n_{\mathrm{AB}}V}{(n_{\mathrm{A}}-n_{\mathrm{AB}})(n_{\mathrm{B}}-n_{\mathrm{AB}})} \approx \left(\frac{n_{\mathrm{AB}}V}{(n_{\mathrm{A}}-n_{\mathrm{AB}})n_{\mathrm{B}}}\right)_{n_{\mathrm{B}} \gg n_{\mathrm{A}}} \tag{5}$$

Method II is somewhat less restrictive than Method I in so far that requirement (i) is unnecessary, but requirement (ii) remains. This method often depends on the premise that a plot of δ_{obs} against $n_{\mathrm{AB}}/n_{\mathrm{A}}$ should be linear (eqn (2)), so by assuming values for K and calculating $n_{\mathrm{AB}}/n_{\mathrm{A}}$ (e.g., using the full form of (4)), it is supposed that the " correct " value for K has been obtained when a straight line results.[5, 12]

Our present thesis rests initially on the belief that the concentration ranges over which the equilibrium quotients have been used are such that requirement (ii) is not satisfied. To substantiate our claim we must consider the thermodynamics of the system in some detail.

THERMODYNAMICS OF THE SYSTEM

CHOICE OF CONCENTRATION SCALES

For convenience we shall consider initially the mole fraction description of the equilibrium quotient. The chemical potential of any component i of a liquid mixture can in all circumstances be represented in terms of its mole fraction by eqn (6),

$$\mu_i = \mu_i^{\circ} + RT \ln \gamma_i^{\mathrm{R}} x_i \tag{6}$$

where μ_i° is the chemical potential of i as a pure liquid at the same temperature and pressure and γ_i^{R} is the (Raoult) activity coefficient, and (7) where μ_i^{θ} is given by eqn (8),

$$\mu_i = \mu_i^{\theta} + RT \ln \gamma_i^{\mathrm{H}} x_i \tag{7}$$

$$\mu_i^{\theta} = \lim_{x_i \to 0} (\mu_i - RT \ln x_i) \tag{8}$$

and so is independent of x_i *but dependent on the nature of the environment*, and γ_i^{H} is the (Henry) activity coefficient. Equations analogous to (6)-(8) apply for the molar and molal scales but then, in the respective cases, include terms in the molar volumes and molecular weights of the appropriate species. All components obey Raoult's law (i.e., $\gamma_i^{\mathrm{R}} \rightarrow 1$) as $x_i \rightarrow 1$ and Henry's law (i.e., $\gamma_i^{\mathrm{H}} \rightarrow 1$) as $x_i \rightarrow 0$. It follows that the value of an equilibrium quotient in terms of mole fractions for reaction (1) will be nearly independent of the values of x_{A} and x_{B} only if (i) the equilibrium quantities x_{ABeq}, x_{Aeq}, and x_{Beq} are all extremely small when, using the reaction isotherm, the appropriate quotient K_x' will be given by the expression (9),

$$RT \ln K_x' = RT \ln \frac{x_{\mathrm{ABeq}}}{x_{\mathrm{Aeq}} x_{\mathrm{Beq}}} = \mu_{\mathrm{A}}^{\theta'} + \mu_{\mathrm{B}}^{\theta'} - \mu_{\mathrm{AB}}^{\theta'} = \Delta G^{\theta'} \tag{9}$$

or (ii) the mole fraction of one component (say B) is close to unity and that of the other extremely small, whereupon the quotient will be given by expression (10).

$$RT \ln K_x = RT \ln \frac{x_{\mathrm{ABeq}}}{x_{\mathrm{Aeq}} x_{\mathrm{Beq}}} = \mu_{\mathrm{A}}^{\theta} + \mu_{\mathrm{B}}^{\circ} - \mu_{\mathrm{AB}}^{\theta} = \Delta G^{\circ} \tag{10}$$

Even then, K_x will be strictly independent of the value of x_{B} (even over a range in which x_{B} is close to unity) only if the values of $\mu_{\mathrm{A}}^{\theta}$ and $\mu_{\mathrm{AB}}^{\theta}$ are similarly independent. It must be pointed out that the numerical value of K_x' will be quite different from that of K_x.

At present it is difficult, if not impossible, to conduct a complete series of experiments by use of mixtures in which the concentrations of both A and B are *extremely* small because of the relative insensitivity of commonly used n.m.r. spectrometers, although this might be possible with the advent of more advanced instrumentation. Consequently, it is necessary to study mixtures which comply with condition (ii) mentioned earlier, and evaluate the data so obtained by use of eqn (3) (Method I) for which K_x is defined by (4) and (10). Because the use of the volume concentration scale has been strongly advocated in the past,[9] we should now question whether the use of K_c defined by eqn (5) and the corresponding form of the Benesi-Hildebrand equation are as potentially acceptable.

Eqn (11),

$$K_c \approx K_x \frac{V}{n_{\mathrm{B}} + n_{\mathrm{S}}} = K_x V_{\mathrm{m}} \tag{11}$$

where V_{m} is the molar volume of the mixture, follows from eqn (4) and (5). Therefore, although K_x may be independent of x_{B} over a particular concentration range, K_c will be independent only if (other considerations apart) the molar volume of the mixture is independent of its composition. For a finite range of x_{B} this condition is only met when the molar volumes (strictly the partial molar volumes in the mixture) of the two species B and S are the same. Similar comments apply to the molality scale, for which K_{m} can only be independent of $n_{\mathrm{B}}/n_{\mathrm{S}}$ in the appropriate range if the molecular weights of B and S are the same.

It is of course true that if the appropriate plot from eqn (3) is made over a concentration range for which K_x is not independent of " x_{B} ", a reasonably straight line may be obtained simply because the variation in V_{m} may, by chance, be in the opposite sense from that in K_x, and so K_c may appear to be more independent of c_{B} than is K_x of x_{B}. This almost certainly explains the observations of other workers[9] which led them to suggest molarity as the best scale for data evaluation. Their suggestions were apparently supported by the observation that the values of K_c so obtained depend less critically on the nature of S than did the values of K_x. This we consider not only fortuitous but misleading, simply because we would expect the value of K_x obtained from a plot of Δ_{obs}^{-1} against $(n_B+n_S)/n_B$ over some range intermediate between $x_B \rightarrow 0$ and $x_B \rightarrow 1$ to be dependent on the nature of S, simply because the values of μ_B^θ and μ_{AB}^θ would be so dependent.

So far as Method II is concerned it is apparent from the preceding arguments that any values obtained for a quotient by processing data determined over a wide range of concentrations of B will at the best be some sort of average between K_x', K_x, and the " fictitious " values which would be obtained at points in the intermediate concentration range. For further discussions of the thermodynamics of reaction (1) it is therefore necessary to base our arguments on eqn (10) and the requirements and restrictions pertaining to this.

CHOICE OF EXPERIMENTAL CONCENTRATIONS

It appears that the only satisfactory range of concentrations for the investigation of reaction (1) at present is that in which both A and S are present in dilute solution in B. In order to discover the precise concentrations which are acceptable we must look more closely at some of the points raised previously. It is convenient to do this by reference to some of the different liquid mixtures studied in this laboratory. Of these the system on which the greatest amount of work has been done consists of mixtures of chloroform (A), benzene (B), and cyclohexane (S).

Much information is available regarding the behaviour of mixtures of benzene and cyclohexane, and the Raoult activity coefficient of benzene in cyclohexane is certainly close to unity over the range $x_B = 0.9$ to $x_B = 1.0$.[13] Consequently, although no information is available regarding the behaviour of benzene in cyclohexane in the presence of small quantities of chloroform, it appears reasonable to assume that as long as the mole fraction of chloroform is very small, we may to a first approximation ignore the Raoult activity coefficient for benzene within this concentration range.

For the most part our studies have been carried out on mixtures in which the mole fraction of benzene varies between 0.9 and *ca.* 1 and that of chloroform is constant at *ca.* 0.005. The next point of concern is whether these conditions are satisfactory. We have some indication that x_A is sufficiently low for Henry's law to be obeyed because little change in δ_{obs} can be observed when the mole fraction of chloroform is changed from 0.005 to 0.01. Whether or not the quantities μ_A^θ and μ_{AB}^θ remain the same when the composition of the B-S environment changes cannot be decided unequivocally, but there is a strong argument that this is the case. By the nature of reaction (1) we known that the forces between A and B are stronger than those between A and S. Therefore, when $n_B \gg n_S$ it is to be expected that molecules of B, rather than S, would cluster around a molecule of A. If this occurs μ_A^θ should be very similar to that in pure B and should be independent of n_B/n_S.

METHOD I, ITS LIMITATIONS AND SOME REFINEMENTS

From the preliminary conclusions drawn from the earlier discussion it is to be expected that for a given reaction a plot of $(n_B+n_S)/n_B$ against Δ_{obs}^{-1} should be linear over the range $x_B = 0.9$ to close to unity, provided that x_A is 0.005 or less. To see if this is so we have investigated the reaction between chloroform (A) and benzene (B) with cyclohexane (S). Critical examination of the data reveals that the plot may change slope at $x_B = ca.\ 0.9$, and since in principle the plots may be curved (we shall refer to them as curves to emphasize this point) the required parameters K_x and Δ_c must *in general* be derived from the tangent to the curve at $(n_B+n_S)/n_B = 1$. Under these circumstances it is evident from eqn (11), that the molar volume of the mixture becomes identical with that of benzene and hence is a constant, so that both the mole fraction and molar scales are expected to yield, *via* Method I, equally meaningful values for K_x and K_c and the same value for Δ_c. Method I has not been used in this critical way in the past. In fact the plots have often been made [14] for mixtures for which x_B barely reaches 0.9 and uncritical examination of these plots indicates approximate linearity in them, so that they have been used wrongly and misleading values for K_x, K_c, and Δ_c have been obtained.

If Method I is used properly, as mentioned above, it might be expected that studies of a particular reaction in different inert solvents should lead to the same, or very similar, values for K_x (or K_c) and Δ_c in each case. We have therefore investigated the

TABLE 1.—THE COMPOSITIONS OF THE MIXTURES EMPLOYED IN THE INVESTIGATION OF THE CHLOROFORM (A)–BENZENE (B) REACTION IN THE PRESENCE OF VARIOUS INERT MATERIALS (S), TOGETHER WITH THE CORRESPONDING CHEMICAL SHIFTS OF CHLOROFORM

$10^4 n_A$/mol	$10^2 n_B$/mol	$10^3 n_S$/mol	δ_{obs}/Hz [a]
S = CYCLOHEXANE (δ_{free} = 7.40 Hz) [b]			
0.9214	1.4353	1.2226	55.66
0.8141	1.9047	1.0121	56.41
0.9206	1.1952	0.5000	56.62
0.8963	1.6314	0.3462	57.19
0.9298	1.6520	0.2009	57.36
0.8762	1.6585	0.0782	57.53
S = *cis*-DECALIN (δ_{free} = 7.40 Hz) [b]			
2.1193	1.7794	3.1626	52.57
1.3386	2.6686	2.8866	54.48
1.4911	2.7866	1.4361	56.29
1.7181	1.3646	0.1667	57.06
1.1316	2.3797	0.1654	57.55
S = BICYCLOHEXYL (δ_{free} = 7.40 Hz) [b]			
1.8236	4.0791	3.8425	54.71
0.9231	2.0955	1.0564	55.99
1.0061	5.4165	1.5951	56.85
1.9024	4.5961	0.8951	57.31
1.6159	4.7219	0.4504	57.43
S = TETRADECANE (δ_{free} = 6.20 Hz) [b]			
1.1493	2.1666	2.8296	51.77
0.9767	1.1686	1.4296	52.10
0.7849	0.9746	0.9981	52.64
1.3721	1.6904	1.0472	54.53
0.8695	1.1810	0.4651	55.79
0.6274	2.5045	0.4812	56.51
S = HEXADECANE (δ_{free} = 6.20 Hz) [b]			
0.8486	1.5088	1.5856	52.53
1.2063	1.4487	1.1769	53.61
0.8670	1.2880	0.7595	54.73
0.8921	1.8103	0.6152	56.03
1.0245	2.6421	0.3116	57.34

[a] measured relative to internal benzene: [b] obtained by graphical extrapolation.

reaction between chloroform and benzene in the presence of various supposedly inert materials. Because cyclohexane alone has been shown with any certainty to be inert [1] (in the n.m.r. sense), this was chosen as the first diluent, then cis-decalin and bicyclohexyl because of their structural and conformational similarities to cyclohexane, and then tetradecane and hexadecane as being probably suitable. The experimental data for the studies are in table 1. If these are processed by Method I under the correct conditions the values for K_x and Δ_c given in table 2 are obtained. These are not as expected, and obviously depend on the nature of S, so apparently demonstrating anomaly (*b*) referred to earlier. The corresponding values for K_c and the associated Δ_c values are also included in table 2 to demonstrate anomaly (*a*). Superficial examination of the two sets of data shows how understandable it would be to suggest that the molar constants are the more satisfactory of the two, as has been done in the past. This would be misleading for two reasons that will now be explained in the context of refinements to Method I.

TABLE 2.—VALUES OF K_x AND K_c AND OF THE ASSOCIATED Δ_c FOR THE CHLOROFORM – BENZENE REACTION WITH VARIOUS INERT MATERIALS AT 306.6 K, OBTAINED BY METHOD I THROUGH EQN (3)-(5)

inert material	K_x	Δ_c/Hz	$10^3 K_c$/m^3 mol^{-1}	Δ_c/Hz
cyclohexane	1.06	97.7	0.137	83.5
cis-decalin	0.58	136.4	0.158	79.3
bicyclohexyl	0.40	176.4	0.174	76.3
tetradecane	0.02	2452.2	0.180	77.2
hexadecane	−0.14	−312.3	0.163	80.7

REFINEMENT 1; THE VARIATION OF δ_{free} WITH MIXTURE COMPOSITION

For most previous work on this subject it has been assumed that δ_{free} (and δ_c) is independent of $n_S/(n_B+n_S)$. This is highly unlikely and a variation is expected which must be accounted for when representing δ_{obs} by an equation of the form (2). To do this completely would be difficult, but it may be done approximately.

If it is assumed that the screening effects of the mixture affects A in the free state and in the complex equally, and that variations in this are functions (in the case of an internal reference) of the mole fractions of B and S present, the total screening of A may be written as eqn (12)

$$\sigma_A^{\text{Tot}} = \frac{n_{AB}}{n_A}(\sigma_A + \sigma_c + x_B\sigma_A^B + x_S\sigma_A^S) + \frac{n_A - n_{AB}}{n_A}(\sigma_A + x_B\sigma_A^B + x_S\sigma_A^S) \qquad (12)$$

where σ_A is the screening of isolated A, σ_c is the contribution by B in the complex, and σ_A^B and σ_A^S are the screening effects on A due to B and S. The total screening of the reference (we have taken this to be B for experimental convenience and have justified its use elsewhere [1]) is given likewise by eqn (13).

$$\sigma_B^{\text{Tot}} = \sigma_B + x_B\sigma_B^B + x_S\sigma_B^S \qquad (13)$$

It follows from eqn (12) and (13) that δ_{obs} should be given by (14)

$$\delta_{\text{obs}} = \frac{n_{AB}}{n_A}\Delta_c + \delta'_{\text{free}} + F + x_B G \qquad (14)$$

where $\delta'_{\text{free}} = \sigma_A - \sigma_B$, $F = \sigma_A^S - \sigma_B^S$, and $G = \sigma_A^B - \sigma_B^B - F$. Because $\delta'_{\text{free}} + F$ is the measurable shift of A infinitely dilute in S [i.e., δ_{free} of eqn (2)] we can rearrange eqn (14) in the style of (3) to give (15).

$$\frac{1}{\Delta_{\text{obs}} - x_B G} = \frac{n_B + n_S}{n_B K_x \Delta_c} + \frac{1}{\Delta_c} \tag{15}$$

The value of G cannot be obtained absolutely because of the " active " nature of A. However, a reasonable estimate of it may be obtained by measuring the shift between B and S (simulating A) in a series of B–S mixtures, and equating the difference between the extrapolated shifts at $n_B/(n_B+n_S) = 1$ and 0 to G. In the case of cyclohexane, G is found to be -2 Hz (at 60.004 MHz); the same value is found for both cis-decalin and bicyclohexyl, but for both tetradecane and hexadecane G is found to be -0.8 Hz. From these values it is now possible to evaluate the appropriate values for the left-hand side of eqn (15) and plot these against $(n_B+n_S)/n_B$ to obtain K_x and Δ_c. This will be deferred until after the following examination of eqn (2) and (4).

REFINEMENT 2; THE EFFECT OF THE NATURE OF S

As explained earlier plots representing eqn (3) may be curved until $(n_B+n_S)/n_B = 1$. The subject of the immediately foregoing discussion may have some small bearing on this, but a more plausible explanation is that the assumptions on which the validity of Method I rests are not strictly correct; namely that μ_A^θ, μ_{AB}^θ, and γ_B^R are not constant in the range $x_B = 0.9$-1.0, but do depend (contrary to assumption) on the nature of S and the extent to which this is present. This dependence must be accounted for, and whilst this is a matter of considerable complexity, it may be done approximately by questioning the necessity of utilizing S at all, and moreover the significance of equations such as (2).

In its basic form eqn (2) should be written as (16)

$$\delta_{\text{obs}} = P_I \delta_I + P_{II} \delta_{II} \tag{16}$$

where P_I and P_{II} are generally defined [3] as the fractional populations of states I and II in which A has shifts δ_I and δ_{II}. In the context of reaction (1), δ_I and δ_{II} are *molecular* parameters and so P_I and P_{II} must be thought of as fractional times that A spends in each state. If equilibrium quotients are used to characterize P_I and P_{II} the values obtained for these are in terms of bulk concentrations rather than time fractions. This approach can be satisfactory only if the quotients are suitably defined in accordance with the molecular basis of eqn (16).

The modifications this entails may be deduced by considering the implications of the dilution technique. Initially we may consider reaction (1) proceeding with A almost infinitely dilute in B. In this case, one molecule of A contacts some specific number of molecules of B in the characteristic n.m.r. time. The problem is to determine the fraction of this time that A spends in the free and in the complexed situations. Information about the system is forthcoming by diluting the system with S, and the sole intention of doing this is to change the time fractions that A spends in each state and so change δ_{obs}. Therefore, the compound S should essentially have identical properties to B except the ability to form a complex. Obviously this situation cannot be achieved in practice and data obtained for use with eqn (3) must depend on the nature of S, and then so must K_x and Δ_c. Probably the most important single difference between a real S and a real molecule is their sizes, or more conveniently their exclusion volumes. To change δ_{obs}, molecules of the hypothetically ideal S have to be introduced to the A-B system considered initially, so that the introduction of, for example, one molecule of S is required to produce the situation depicted in Fig. 1(*a*). In practice the introduction of one real diluent molecule has an effect such as that represented in (*b*), from which it can be appreciated that more (or less) than the required single molecule of B is displaced and the measured value of δ_{obs} cannot reflect the expected effect of dilution. To a reasonable approximation the one molecule of S behaves as V_S/V_B (ratio of molar volumes) molecules of *inert* B. The implication of this is that on a macroscopic basis the amounts of S in the equilibrium expressions (4) and (5) have to be quantified in terms of its " effective number " of moles relative to B, so that n_S is replaced by $V_S n_S/V_B$. This produces no change in the expression for K_c, but that for K_x is modified and the final form of eqn (3) becomes (17).

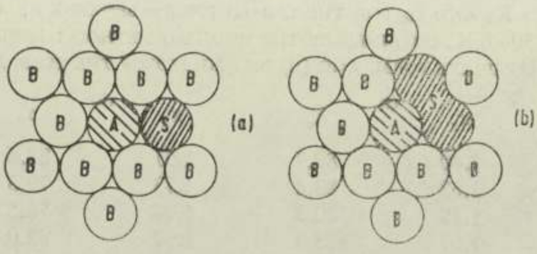

FIG. 1.—A schematic representation of the dilution of a mixture containing A in very low concentration in B, (*a*) by an ideal inert molecule and (*b*) by a real molecule of S.

$$\frac{1}{\Delta_{obs}-x_B G}=\frac{n_B+(V_S n_S/V_B)}{n_B K_x \Delta_c}+\frac{1}{\Delta_c} \tag{17}$$

If data are processed by Method I with the refinements mentioned and use of the limiting tangent procedure, it is to be expected that the same value for Δ_c will be obtained when either the mole fraction or the molar scales are used. Moreover, despite the redefinition of K_x, the ratio K_c/K_x should still be governed by eqn (11) and equal V_B.

TABLE 3.—DENSITIES [a] AT 306.6 K OF THE VARIOUS MATERIALS USED

compound	10^{-3} density/kg m^{-3}
chloroform	1.4642
benzene	0.8648
cyclohexane	0.7658
cis-decalin	0.8865
bicyclohexyl	— [b]
tetradecane	0.7535
hexadecane	0.7647

[a] Deduced from the data given by J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds*, vol. 2 (Elsevier, Amsterdam, 1965).

[b] As a value at 306.6 K is not available from the literature, that (0.8592) at 293.2 K given in *Handbook of Chemistry and Physics*, 45th edn. (The Chemical Rubber Publishing Co., Ohio, 1965), was used.

To test the suggestions made above we have processed the data for the chloroform + benzene reaction, studied with the five diluents referred to earlier, using eqn (17) in the first instance. For this the values of *G* quoted previously were used together with the appropriate ratios of molar volumes which were deduced by use of the densities given in table 3. The values of K_x and Δ_c, obtained from the tangent, at (n_B+

$V_S n_S/V_B)/n_B = 1$, to the computer-fitted curves (in fact these were linear between $x_B = ca.\ 0.9$ and 1.0) for the variation of $1/(\Delta_{obs} - x_B G)$ with $(n_B + V_S n_S/V_B)/n_B$ are the first set in table 4. It can be seen that all five values of K_x and of Δ_c are in close agreement in view of the approximations made in deducing them, and the values of both parameters are quite different from those given in table 2. The greatest contribution to these changes *for the systems studied here* is due to the correction involving molar volumes rather than that due to the variation of the shifts with the composition of the mixtures. This can be seen from the second set of values in table 4 which were deduced by omitting the term $x_B G$ in eqn (17). Because this term can be neglected, the second set of values can be compared directly with those for K_c and Δ_c given in table 2 for which the simple correction for the size of molecules of S is implicitly accommodated. This comparison provides experimental values for the ratio K_c/K_x which can be seen from table 4 to be in excellent agreement with the theoretical prediction of 0.0903×10^{-3} m³ mol⁻¹ for V_B.

TABLE 4.—VALUES OF K_x AND Δ_c FOR THE CHLOROFORM—BENZENE REACTION WITH VARIOUS INERT MATERIALS AT 306.6 K, OBTAINED BY THE MODIFIED METHOD I THROUGH EQN (17), (i) IN ITS COMPLETE FORM, AND (ii) BY NEGLECT OF THE TERM $x_B G$

	(i)		(ii)		
inert material	K_x	Δ_c	K_x	Δ_c	$(10^3 K_c{}^a/K_x{}^{(ii)})/m^3$
cyclohexane	1.40	89.7	1.51	83.6	0.0907
cis-decalin	1.68	83.4	1.73	79.3	0.0913
bicyclohexyl	1.89	80.3	1.94	76.5	0.0897
tetradecane	1.67	83.3	1.67	82.0	0.1078
hexadecane	1.69	83.8	1.70	82.4	0.0959

[a] from table 2.

To test our suggestions further we have investigated several reactions between chloroform and some alkyl-benzenes with molar volumes ranging from 0.125 to 0.239×10^{-3} m³ mol⁻¹. Table 5 gives the K and Δ_c values deduced by use of the procedure suggested above. Once more it can be seen that good agreement is obtained between the experimental ratio K_c/K_x and the literature value for V_B.

TABLE 5.—VALUES OF PARAMETERS CHARACTERISTIC OF THE FORMATION OF SOME 1 : 1 MOLECULAR COMPLEXES *

A	B	S†	K_x	Δ_c	$10^3 K_c$/ m³ mol⁻¹	Δ_c	K_c/K_x	$10^3 V$/ m³ mol⁻¹ (calc)	T/K*
chloroform	*p*-xylene	cyclohexane	1.59	95.9	0.202	95.8	0.127	0.125	306.6
chloroform	1,4-diethylbenzene	cyclohexane	1.19	107.3	0.188	107.6	0.158	0.157	306.6
chloroform	mesitylene	cyclohexane	1.11	123.2	0.148	126.6	0.133	0.140	306.6
chloroform	1,3,5-triethyl-benzene	cyclohexane	1.74	101.2	0.330	101.5	0.190	0.189	298.2
chloroform	1,3,5-tri-isopropyl-benzene	cyclohexane	1.92	93.1	0.517	89.7	0.269	0.239	293.2

* The experimental data were obtained at 306.6 K but the densities used in the processing of these were at the specified temperatures; † internal reference.

Whilst the data in the tables appear to validify our arguments it has to be recognized that several features of the experimental chemical shifts may lead to inaccuracies in the values deduced for K_x, K_c, and Δ_c. First, over the range of concentrations used, the shifts only change by 2-6 Hz at 60 MHz. Whilst we believe these shifts are accurate to 0.1 Hz it is obvious that small variations in them could lead to different values for K and Δ_c from those reported. Secondly, because the range of shifts is small, minor deviations in the screening behaviour of the mixtures from the mole fraction variation described by eqn (12) and (13) could yield additional errors. Despite these possible sources of experimental error, the weight of evidence does favour our arguments which are based on classical principles. Even so, it is intended to obtain further confirmation for the approach described, by making more precise shift measurements at 100 and 220 MHz for similar reactions to those described here.

CONCLUSIONS

It has been shown that for n.m.r. studies of reaction (1) in the presence of inert materials, either the mole fraction or molar scale may be used for the evaluation of data. It is suggested that iterative analysis of data obtained over a range of concentrations of B and S cannot be expected to yield meaningful values for the equilibrium quotients or Δ_c. The only theoretically justifiable approach to obtain these parameters is by using the Benesi-Hildebrand equation, appropriately modified to account for the variation of the chemical shifts of " free " species with the composition of their environment, and for the " effective " amount of the inert material present. By this approach it has been shown that, within the limitations of our experimental technique, values for the equilibrium quotients K_x and K_c and for the induced shift Δ_c can be obtained which are characteristic of the reaction and independent of the nature of the inert materials.

It is noteworthy that many of the arguments invoked herein to rationalize n.m.r. studies of complex formation are applicable to similar studies utilizing other physical techniques. More significant however is the fact that if these arguments are extended to reactions more complex than (1) it is evident that the evaluation of the appropriate equilibrium quotients and induced shifts will be a matter of considerable complexity.

EXPERIMENTAL AND COMPUTATIONS

The ^{1}H n.m.r. chemical shifts were obtained on a Perkin-Elmer R10 spectrometer operating at 60.004 MHz and 306.6 K. The spectra were calibrated by audio-frequency modulation by use of a Muirhead-Wigan D-890-A oscillator, the frequencies of which were determined with a Venner 3336 counter. Owing to difficulties arising from the complexity of the spectra of several of the inert materials, benzene was used as internal reference in preference to these in most cases; this has been shown [1] to be a reliable reference under the conditions employed here, and its use does provide values for K_x and Δ_c comparable with those obtained when cyclohexane is used as internal reference.

The experimental shifts recorded in table 1 are the averages of at least six values obtained for each sample. Whilst these values were used in the relevant computations they should only be regarded to be accurate to 0.1 Hz. Consequently the values for K_x, K_c, and Δ_c, which are recorded for consistency in a similar fashion to those for δ_{obs}, should not be taken to have the accuracy implied. All computations were performed on an I.C.L. 1905 computer.

We thank Professor W. G. S. Parker for facilities, and the S.R.C. for studentships (to C. J. J. and P. M. W.).

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[1] Part 6, J. Homer, E. J. Hartland and C. J. Jackson, *J. Chem. Soc A*, 1970, 931.

[2] see, e.g., L. J. Andrews and R. M. Keefer, *Molecular Complexes in Organic Chemistry* (Holden-Day, Inc., San Francisco 1964), and R. Foster, *Organic Charge-Transfer Complexes* (Academic Press, New York, 1969), and references therein.

[3] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

[4] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1948, **71**, 2703.

[5] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, 1962, **66**, 1469.

[6] R. L. Scott, *Rec. Trav. chim.*, 1956, **75**, 787.

[7] P. J. Trotter and M. W. Hanna, *J. Amer. Chem. Soc.*, 1966, **88**, 3724.

[8] M. W. Hanna and A. L. Ashbough, *J. Phys. Chem.*, 1964, **68**, 811.

[9] I. D. Kuntz, jun., F. P. Gasparro, M. D. Johnston, jun., and R. P. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 4778.

[10] J. Homer, C. J. Jackson, P. M. Whitney, and M. H. Everdell, *Chem. Comm.*, 1971, 956.

[11] It is immaterial to the discussion which follows whether a discrete 1 : 1 complex or isomeric 1 : 1 complexes are formed, the reasons for this having been outlined by I. D. Kuntz, jun., and M. D. Johnston, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 6008.

[12] P. D. Groves, P. J. Huck and J. Homer, *Chem. and Ind.*, 1967, 915.

[13] G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.*, 1939, **43**, 119.

[14] see, e.g., ref. (7).

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MOLECULAR COMPLEXES HC

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Molecular Complexes

Part 8[1].—Rationalization of the Use of the Molal Scale for Processing Nuclear Magnetic Resonance Data

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It is shown that when based on the common definition of molality, the equilibrium quotient K_m for a reaction $A+B \rightleftharpoons A\cdots B$ occurring in an inert solvent S will vary with the concentration of the components and with the nature of S. If this molal scale is employed with the Benesi-Hildebrand equation to process chemical shift data it is shown that the value obtained for Δ_c^m, the chemical shift difference between " free " and fully complexed A, is quite different from that derived using the mole fraction and molar scales. The reasons for this are explained, and a molal based procedure for processing data is described which results in values for $\Delta_c^{m\prime}$ and $K_{m\prime}$, which are compatible with the molar and mole fraction values.

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Data obtained by n.m.r. studies of reactions of the type (1) are frequently processed using the well-known modified Benesi–Hildebrand [2, 3] eqn (2)

$$A+B \rightleftharpoons A\cdots B \tag{1}$$

$$\frac{1}{\Delta_{obs}} = \frac{1}{K[B]_0\Delta_c}+\frac{1}{\Delta_c} \tag{2}$$

to obtain values for the equilibrium quotient K and shift Δ_c induced in A by B for the reaction occurring with $[B]_0 \gg [A]_0$ in the presence of an inert solvent S. It is to be expected that if one set of experimental data is processed using the mole fraction, molar or molal scales to characterize the initial concentrations of B (i.e. $[B]_0$) in a series of samples having $[A]_0$ extremely small and constant, the same value of Δ_c should be obtained using each scale. Recently, by detailed consideration of the thermodynamic and n.m.r. principles underlying such studies the conditions have been deduced under which the mole fraction and molar forms of eqn (2) give equivalent results.[1] We wish to point out now the difficulties that may be encountered when using the molal scale for data processing, and rationalize the use of this scale for n.m.r. purposes.

It has been pointed out elsewhere [1] that the main anomalies that have been found [2-6] when processing n.m.r. chemical shift data using equations such as (2), have arisen because of the failure to describe the bulk quantities of the components in the mixture studied in a manner compatible with the molecular and hence time-based nature of the Gutowsky–Saika equation ① from which (2) is derived. When using the molal concentration scale in studies of three component mixtures there is the additional problem of correctly defining molality. For reactions of the type discussed here the natural tendency is to define the molality of the reacting species A and B relative to the inert solvent S, according to eqn (3), 7

$$m_i = \frac{n_i}{n_s M_s} \tag{3}$$

in which n and M refer respectively to number of moles, and molecular weights of the compounds used. It is constructive to look at the implications of such a definition.

If for reaction (1) the concentration of each of the active species (i) in S is sufficiently low to obey Henry's Law their chemical potentials may be given by eqn (4)

$$\mu_i = \mu_i^m + RT\ln m_i \tag{4}$$

where

$$\mu_i^m = \lim_{x_i\to 0}(\mu_i - RT\ln x_i)+RT\ln M_s \tag{5}$$

and M_s is the molar mass of S; for convenience $\lim_{x_i\to 0}(\mu_i - RT\ln x_i)$ will be written as $\mu_i^{\ominus}$.

Under the conditions $[B]_0 \gg [A]_0 \approx [S]_0$ suggested elsewhere [1] to be the most thermodynamically meaningful for n.m.r. studies of reaction (1), eqn (4) may be rewritten for component B as in eqn (6)

$$\mu_B = \mu_B^\circ + RT \ln x_s M_s + RT \ln m_B + RT \ln \gamma_B^R \tag{6}$$

where μ_B° is the chemical potential of pure B at the same temperature and γ_B^R is the Raoult activity coefficient. Even though the quantities of A and A $\cdots$ B (i) present are small their molalities are high and eqn (4) has to be rewritten as (7),

$$\mu_i = \mu_i^{\theta'} + RT \ln M_s x_s + RT \ln m_i + RT \ln \gamma_i^H \tag{7}$$

where γ_i^H is the Henry activity coefficient and μ_i^θ has been modified to $\mu_i^{\theta'}$ to account for the change in environment of A and A $\cdots$ B from that implicit in eqn (4). From eqns (6) and (7) it is evident that K_m for reaction (1) must be given by eqn (8)

$$RT \ln K_m = \mu_A^{\theta'} + \mu_B^\circ - \mu_{AB}^{\theta'} + RT \ln M_s x_s + RT \ln \frac{\gamma_A^H \gamma_B^R}{\gamma_{AB}^H} \tag{8}$$

and thus even if the activity coefficients tend to unity it must depend both on the concentration of B and on nature of S in which the reaction is carried out, and hence be a variable in eqn (2).

For the mole fraction and molar scales it has been shown [1] that amongst other conditions eqn (2) normally can only be used to deduce values for K and Δ_c when $x_s \rightarrow 0$ and $x_B \rightarrow 1$. Superficially, it might be expected that when $x_B \rightarrow 1$ eqn (2) should yield a value of K_m compatible with the values of K_x and K_c so that the values of Δ_c deduced using all three scales should be the same. To show that the value of Δ_c obtained using the molal scale (as defined above) does not as indicated above equal the correct [1] value deduced using the molar (or mole fraction) scale we have made use of the experimental data recorded in ref. (1) for the chloroform + benzene reaction in the presence of various inert materials. The limiting linear plots of $1/\Delta_{obs}$ against $1/m_B$ (i.e. $n_B/n_s V_s \rho_s$ where V and ρ refer to molar volume and density respectively) were analysed using an ICL 1905 computer to give the slope (S) and intercept (I) at $m = \infty$. The values of I/S (supposedly K_m if the dubious assumption is made that the activity coefficient ratio in eqn (8) tends to unity) and $1/I$ (supposedly Δ_c^m) are given in table 1, together with the corresponding values of K_c and Δ_c^c. It can be seen that the values for Δ_c^c and Δ_c^m are completely different. The reason for this is quite straightforward. The molal parameters are derived from data corresponding to $m_B = \infty$ and whilst the equilibrium quotient conceptually must be finite, eqn (9)

TABLE 1.—VALUES FOR THE EQUILIBRIUM QUOTIENTS AND INDUCED SHIFTS Δ_c (Hz AT 60 MHz) FOR THE CHLOROFORM + BENZENE REACTION IN THE PRESENCE OF VARIOUS INERT MATERIALS AT 306.6 K

inert material	$10^3 K_c/$ $\mathrm{m^3\,mol^{-1}}$	Δ_c^c/Hz	$(I/S)/$ kg mol^{-1}	$(1/I)$/Hz	$(\rho_s(K_c+V_B))/$ kg mol^{-1}	$(K_c\Delta_c^c/(K_c+V_B))/$ Hz
cyclohexane	0.137	83.5	0.169	50.3	0.174	50.3
cis-decalin	0.158	79.3	0.219	50.3	0.220	50.4
bicyclohexyl	0.174	76.3	0.233	50.4	0.233	50.2
tetradecane	0.180	77.2	0.204	51.4	0.204	51.4
hexadecane	0.163	80.7	0.205	51.7	0.195	51.9

$$K_m \approx \frac{n_{AB} n_s V_s \rho_s}{(n_A - n_{AB}) n_B} \tag{9}$$

requires that K_m is zero. However, it is an experimental fact that a plot of Δ_{obs}^{-1} against m_B^{-1} has a finite slope. The only way to rationalise this with the molal form of eqn (2) is to express K_m in terms of K_c, defined by eqn (10),

$$K_c \approx \frac{n_{AB}(n_B V_B + n_s V_s)}{(n_A - n_{AB}) n_B} \tag{10}$$

using eqn (11) so that eqn (2) becomes eqn (12).

$$K_m = \frac{K_c \rho_s}{V_B m_B \rho_s + 1} \tag{11}$$

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_c \rho_s m_B \Delta_c} + \frac{1}{\Delta_c}\left(1 + \frac{V_B}{K_c}\right). \tag{12}$$

Even if K_c is constant over a range of concentrations of B it can be seen from eqn (11) (and (8)) that K_m cannot be similarly constant because of the variation of m_B, and the normal molal form of eqn (2) is meaningless. However, when rewritten as eqn (12) it is evident that the slope and intercept of a plot of Δ_{obs}^{-1} against m_B^{-1} have the significance expressed in eqn (13) and (14) which have been used previously by Kuntz *et al.*[6]

$$1/I = K_c\Delta_c/(K_c+V_B) \tag{13}$$

$$I/S = \rho_s(K_c+V_B). \tag{14}$$

Using the appropriate data given in ref. (1), values for $K_c\,\Delta_c/(K_c+V_B)$ and $\rho_s(K_c+V_s)$ have been calculated for the chloroform + benzene reaction. The values are given in table 1 and can be seen to be in excellent agreement with the experimental values of $1/I$ and I/S. It must be concluded that processing data by plotting Δ_{obs}^{-1} against m_B^{-1} leads to meaningless values for K_m and Δ_c.

The fundamental problem, as with the rationalization [1] of data processing using the mole fraction and molar scales, lies, as mentioned earlier, with the interrelated problems of the definition of molality and the incompatibility of a macroscopic thermodynamic analysis of chemical shifts and the real molecular basis of the latter.

It is convenient to deal first with the definition of molality. Considering the derivation of eqn (8) it is evident that using the normal definitions of molality (eqn (3)) neither γ_A^H or γ_{AB}^H can be considered to tend to unity. One way to achieve this situation, at least conceptually, is to consider B and S to constitute a mixed solvent system so that A and A $\cdots$ B may be considered to obey Henry's Law and eqn (4) may be rewritten as eqn (15)

$$\mu_i = \mu_i^{\theta'} + RT\ln\frac{M_BM_S}{W_BM_S+W_SM_B} + RT\ln m_i \tag{15}$$

in which $W_B+W_S = 1$ kg. The definition of molalities relative to a mixed solvent is not new and has, for example, been proposed by Harned and Owen [8] who suggest in their definition that the (single) solvent molecular weight should be replaced by the average molecular weight of the mixed solvent; other definitions have been used also.[9] It is eminently reasonable, therefore, to pursue these ideas, but in so doing account for the molecular basis of eqn (2).

As explained elsewhere,[1] the use of the mole fraction and molar scales in n.m.r. studies can only be rationalized if S is treated as inert B so that the number of moles of S(n_s) appearing in an equilibrium expression is considered to be n_sV_s/V_B moles of inert B with the same properties as real B except the ability to form a complex A $\cdots$ B. The choice of reference solvent for the molality scale then follows immediately as the "effective" solvent B so that the molality of "active" B (or generally i) is given by eqn (16).

$$m_i' = \frac{n_i}{n_sV_s\rho_B + n_BV_B\rho_B} \tag{16}$$

Bearing in mind that x_i must similarly be defined as $V_Bn_i/(V_Bn_B+n_sV_s)$ eqn (6), (7) and (8) become (17), (18) and (19) respectively. The independence of eqn (19), unlike (8), of x_s is obviously more meaningful.

$$\mu_B = \mu_B^\circ + RT\ln\rho_B + RT\ln m_B' + RT\ln\gamma_B^R \tag{17}$$

$$\mu_i = \mu_i^{\theta'} + RT\ln\rho_B + RT\ln m_i' + RT\ln\gamma_i^H \tag{18}$$

$$RT\ln K_m' = \mu_A^{\theta'} + \mu_B^\circ - \mu_{AB}^{\theta'} + RT\ln\rho_B + RT\ln\frac{\gamma_A^H\gamma_B^R}{\gamma_{AB}^H} \tag{19}$$

Additionally as $x_B \rightarrow 1$ all three activity coefficients in eqn (19) will tend to unity and K_m will be constant and independent of S. The appropriate form of eqn (2) is now (20)

①

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_{m'} m'_B \Delta_c^{m'}} + \frac{1}{\Delta_c^{m'}} \tag{20}$$

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which should provide values of $\Delta_c^{m\prime}$ compatible with those derived using the mole fraction and molar scales.

TABLE 2.—VALUES FOR THE EQUILIBRIUM QUOTIENTS AND INDUCED SHIFTS (Hz AT 60 MHz) DERIVED FOR THE CHLOROFORM+BENZENE REACTION IN THE PRESENCE OF VARIOUS INERT MATERIALS AT 306.6 K, USING A MODIFIED MOLALITY CONCENTRATION SCALE

inert material	$\Delta_c^{m'}$/Hz	$K_{m'}$/kg mol^{-1}	(10^{-3} $K_{m'}/K_c$)/kg m^{-3}
cyclohexane	84.9	0.114	0.8321
cis-decalin	79.3	0.135	0.8544
bicyclohexyl	77.2	0.147	0.8448
tetradecane	76.9	0.156	0.8667
hexadecane	78.0	0.153	0.9386

To test the above proposals we have processed the data recorded in ref. (1) using eqn (16) and (20). The results are given in table 2. It can be seen that the values obtained for $\Delta_c^{m\prime}$ are in excellent agreement with those obtained using the molar and mole fraction scales, thus substantiating our preceding arguments. The latter are further confirmed when it is appreciated that they predict that eqn (21)

$$K_{m'} = K_c \rho_B \tag{21}$$

should apply and that the values for $K_{m'}/K_c$ given in table 2 are similar and compare favourably with the literature value of 0.8648×10^3 kg m^{-3} for the density of benzene; the average experimental value being some 0.29 % different from the accepted figure.

It is evident that chemical shift data derived from studies of molecular complexes can only be expected to yield meaningful values for molal equilibrium quotients and induced shifts if processed using the modified molal scale described by eqn (16).

acknowledgements

[1] Part 7, J. Homer, M. H. Everdell, C. J. Jackson and P. M. Whitney, *J.C.S. Faraday II*, 1972 68, 874.

[2] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1948, **71**, 2703.

[3] R. L. Scott, *Rec. Trav. chim.*, 1956, **75**, 787.

[4] P. J. Trotter and M. W. Hanna, *J. Amer. Chem. Soc.*, 1966, **88**, 3724.

[5] M. W. Hanna and A. L. Ashbough, *J. Phys. Chem.*, 1964, **68**, 811.

[6] I. D. Kuntz, Jr., F. P. Gasparro, M. D. Johnson, Jr. and R. P. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 4778.

[7] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

[8] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold, New York, 3rd Edn., 1958), p. 12.

[9] V. K. La Mer and E. Noonan, *J. Amer. Chem. Soc.*, 1939, **61**, 1487.